RESPONSE TO COMMENTS ON MANUSCRIPT #acp-2021-626

" Measurement report: Molecular characteristics of cloud water in southern China and insights into aqueous-phase processes from Fourier Transform Ion Cyclotron Resonance Mass Spectrometry" by Sun et al.

We are grateful to the editor and three reviewers for their substantial efforts and helpful comments and suggestions, which are of great advantage to the improvement of the manuscript. The manuscript has been revised thoroughly according to the comments from three reviewers. Below, we detail responses and resulting edits to all of the reviewers' comments. We first list the review comments in normal font, then followed by our responses in blue. To make it clear, the contents in the revised manuscript are presented in quotes and in italics. References to line numbers are to the revised manuscript. The revised manuscript with the tracked changes using the blue font was listed after the response.

Responses to comments by Referee 1

General comments: The work by Sun et al., presents the analysis of cloud water from Mt. Tianjing in southern China using Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS). The results are very interesting and provide some insight into in-cloud aqueous-phase chemical composition.

Reply: Thanks for the reviewer's positive comments.

Minor comments:

Considering the emphasis of the paper, I suggest moving sample preparation and analysis procedure into the main text (not the SI). In places it is not clear how the analysis was performed as incorrect referencing to the SI material section was provided. For example, SPE extraction was referred to Text S3, which does not contain this information, but described in the Text S1. Please also see relevant comment below.

Reply: Thanks for the reviewer's suggestion. The contents about sample preparation and analysis procedure have been removed to the main text. Please refer to Lines 106-115 and 124-201. The other references to the Supporting Information have also been carefully checked.

The following sentence is not clear – "The peaks of formulas are intensive within m/z 200-400'', line 139. Please rephrase. What is the impact of these observations?

Reply: Thanks for the comment. The sentence has been revised as "*The most intensive ion peaks are within the range of m/z 200−400.*" Please refer to Line 207. These observations indicated the distribution of molecular weight of assigned formulas, that is, species with molecular weights of ~200-400 Da are abundant in cloud water.

Major comments:

It is not clear whether the authors used a direct infusion or applied a hyphenated technique for their analysis. This needs to be stated in the manuscript. Advantages and limitations of the applied technique need to be stated in the text as well.

Reply: Thanks for the reviewer's helpful suggestion. The direct infusion method was used in this study. The samples were redissolved in 1 mL of methanol and injected into an electrospray ionization (ESI) source at a flow rate of 200 μL/h. We have clarified them in the revised manuscript, please refer to Lines 149-151.

Additionally, we have added the advantages and limitations of the applied technique as follows: "*ESI is a soft ionization technique that offers minimal fragmentation of the analytes (Mazzoleni et al., 2010). $[M\text{-}H]^-$ was detected at the negative ion mode. The coupling of ESI and FT-ICR MS with ultra-high mass resolution makes it possible to characterize the element constitution within molecules. Note that ESI is efficient at ionizing molecules having polar functional groups containing nitrogen and oxygen atoms (Cho et al., 2015).*" , please refer to Lines 145-148, and "*Note that both the recovery of SPE and the selective ionization of negative ESI might cause a bias of mass spectra to certain peaks.*" , please refer to Lines 180-181.

References

Mazzoleni, L. R., B. M. Ehrmann, X. Shen, A. G. Marshall and J. L. Collett Jr (2010). "Water-Soluble Atmospheric Organic Matter in Fog: Exact Masses and Chemical Formula Identification by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." Environ. Sci. Technol. 44: 3690-3697.

Cho, Y., A. Ahmed, A. Islam and S. Km (2015). "Developments in FT-ICR MS instrumentation, ionization techniques, and data interpretation methods for petroleomics." Mass. Spectrom. Rev. 34(2): 248-263.

The information on ESI parameters e.g. source type, nebuliser gas pressure, gas velocity and temperatures, and capillary voltages are missing. These parameters are crucial to understand how the data was acquired and for a comparative analysis with the literature. Major MS parameters have to be provided as well. How was the system calibrated and tuned? Depending on the system optimisation parameters the analyst would see preferentially one or other type of compounds.

Reply: We agree with the reviewer's comments. In this study, a nebulizer gas pressure of 1 bar, a dry gas velocity of 4 L/min and temperature of 200 ℃, and capillary voltages of +4500 V and the end plate offset -500 V were used for ESI source

(Bruker Daltonik GmbH, Bremen, Germany) at negative mode. The optimized mass for quadrupole (Q1) was 170 Da. An argon-filled hexapole collision pool was operated at 2 MHz and 1400 Vp-p RF amplitude. The time of flight was 0.7 ms and the mass range was 150-800 Da and the ion accumulation time was 0.1 s. This information has been added into Section 2.2, please refer to Lines 151-154.

What do the authors mean by the ‘’*mass spectra’’* calibration? ‘*’The mass spectra was calibrated externally using measurements of a known homologous series of N1 (neutral nitrogen compounds) and O2 compounds (acids) with high abundance in a petroleum*’’. Please provide more details on the utilised petroleum type etc. If the system was optimised (tuned) using petroleum on N and O containing ‘’compounds’’ it should not be a surprise that CHON, aliphatic and olefinic species are the major components in the analysed samples. I do not think it is correct to infer that N-containing compounds, aliphatic and olefinic species are the dominating organic species in the analysed water. It might be the case, but if your system is optimised for N-containing compounds then the analysis would be skewed towards these species. There is nothing wrong with this as there are no perfect analytical tools that would cover all compound classes; however, this needs to be acknowledged in the text, so that it is clear for the reader who are not expert in FTIR-MS.

Reply: Thanks for the constructive comments. Followed the methods described by Jiang et al. (2019), we used a known homologous series of $–N_1$ and $-O_2$ formulas (e.g., $C_{16}H_{31}O_2$, $C_{17}H_{33}O_2$, and $C_{18}H_{35}O_2$, etc. that only separated by $–CH_2$ units) frequently detected in a crude oil sample to calibrate the mass spectra before sample detection. The typical peaks (e.g., $-O_4$ species) in our samples were used to internally recalibrate the final spectrum. The calibration was used to improve the mass accuracy of the mass spectra. This information has been clarified in the revised manuscript, please refer to Lines 157-161.

The abundant CHO and CHON in our samples might be related to the bias of the ESI source at negative mode. Thus the acknowledgment of this issue has been added in the revised manuscript: “ *Note that the abundant CHO and CHON cannot directly be related back to the composition of samples since the preferential detection of these molecules in negative ESI. However, the comparison among the samples is still meaningful since they are expected to have the same bias.*” Please refer to Lines 217-219.

Reference

Jiang, B., Z. W. Zhan, Q. Shi, Y. Liao, Y. R. Zou, Y. Tian and P. Peng (2019). "Chemometric Unmixing of Petroleum Mixtures by Negative Ion ESI FT-ICR MS Analysis." Anal. Chem. 91(3): 2209-2215.

In addition, there is a clear evidence that the type of SPE extraction (including Strata X cartridges) and ESI source (e.g. HESI, nano-ESI) can skew the recoveries of specific compound classes. It has been demonstrated that SPE sample pretreatment significantly improves ion recoveries for organic species with nonpolar and moderately polar functional groups, but leads to lower recoveries for highly oxygenated molecules. Therefore, while SPE reduced in-source adduct formation, it also limited the range of compounds identified through a single analysis (Kourtchev et al., 2020). So the observed variation of various molecular groups e.g. CHO, CHON presented in the work by Sun et al. work can be influenced by the applied techniques and thus lead to specific compound classes recoveries. How does this affect the interpretation of their data?

Reply: We agree with the reviewer's comments that both the SPE procedure and ESI source have selectivity for the analytes. The pretreatment of SPE in this study mainly followed the methods in studies that focused on molecular characteristics of cloud water (e.g., Zhao et al., 2013, Cook et al., 2017, Bianco et al., 2018). The operation of SPE was different from Kourtchev et al. (2020), in which the neutral organic compounds were eluted with 0.1% formic acid in methanol. While the mixed solution of acetonitrile/methanol/water (45/45/10, *v*:*v*:*v*) at pH 10.4 was used in this study to elute the analytes. The recovery was not evaluated in our study. However, the Strata-X (Phenomenex) cartridges with both hydrophilic and hydrophobic functional groups are expected a high recovery (Zhao et al., 2013).

As the reviewer mentioned above, selectivity cannot be excluded. However, the high oxygenated molecules ($O/C > 1$), which were demonstrated to have a low recovery (Kourtchev et al., 2020), were not the situation in our study since we have set the selecting criteria of $O/C \leq 1.2$ to exclude formulas undetected frequently in natural materials. Moreover, all the samples were pretreated and detected in the same procedure; thus the same bias was expected. Therefore, the comparison among the samples is still meaningful.

We have clarified the possible selectivity of SPE procedures for analytes in Section 2: "*Note that both the recovery of SPE and the selective ionization of negative ESI might cause a bias of mass spectra to certain peaks.*" Please refer to Lines 180-181. The caveats for the results were also added to the revised manuscript: "*Note that the abundant CHO and CHON cannot be directly related back to the composition of samples since the preferential detection of these molecules in negative ESI. However, the comparison among the samples is still meaningful since they are expected to have the same bias.*" Please refer to Lines 217-219.

References

Zhao, Y., A. G. Hallar and L. R. Mazzoleni (2013). "Atmospheric organic matter in clouds: exact masses and molecular formula identification using ultrahigh-resolution FT-ICR mass spectrometry." Atmos. Chem. Phys. 13(24): 12343-12362.

Cook, R., Y.-H. Lin, Z. Peng, E. Boone, R. K. Chu, J. E. Dukett, M. J. Gunsch, W. Zhang, N. Tolic, A. Laskin and K. A. Pratt (2017). "Biogenic, urban, and wildfire influences on the molecular composition of dissolved organic compounds in cloud water." Atmos. Chem. Phys. 17(24): 15167-15180.

Bianco, A., L. Deguillaume, M. Vaitilingom, E. Nicol, J. L. Baray, N. Chaumerliac and M. Bridoux (2018). "Molecular Characterization of Cloud Water Samples Collected at the Puy de Dome (France) by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." Environ. Sci. Technol. 52(18): 10275-10285.

Kourtchev, I., P. Szeto, I. O'Connor, O. A. M. Popoola, W. Maenhaut, J. Wenger and M. Kalberer (2020). "Comparison of Heated Electrospray Ionization and Nanoelectrospray Ionization Sources Coupled to Ultra-High-Resolution Mass Spectrometry for Analysis of Highly Complex Atmospheric Aerosol Samples." Anal. Chem. 92(12): 8396-8403.

The authors identified and present elemental composition in their work but incorrectly refer (numerous times) to these formulae as compounds. This should be avoided as multiple isomers can be associated with a single molecular formula even at the reported by the author achieved <0.3 ppm mass error especially for *mz* > 319.

Reply: Thanks for the helpful comments. We have replaced the word “compounds” with “molecules” or “formulas” in the revised manuscript.

Responses to comments by Referee 2

General Comments: The manuscript by Sun et al. presents the mass spectral characteristic of cloud water samples throughout a long-lasting cloud event by FT-ICR-MS, and attempts to shed light on the potential influences of in-cloud aqueous phase reactions, which are currently uncertain for the formation of SOA. They show that CHON with aromatic structures are the most abundant type in cloud water, suggesting their enhanced formation in cloud. Their results also indicate distinctly differences between day and night, which is most probably attributed to diurnal differences in aqueous chemistry. Such observation could provide valuable cloud chemistry data for the community, and has the potential to be published after considering my comments. The major weakness is the limited dataset, thus the authors have to clearly indicate in the discussion of the diurnal difference of cloud chemistry between day and night, since there could be other factors contributing to such difference.

Reply: We agree with the reviewer’s comments that the dataset is limited in our study. We took the reviewer’s suggestion and revised Section 3.4.1 by summarizing the diurnal difference of cloud chemistry as follows: “*Previous studies have revealed the differences in atmospheric chemistry between day and night. The daytime chemistry is dominated by photochemical reactions, in which OH radical oxidation and photolysis represent the main processes in the aqueous phase (Ervens et al., 2011). While during the nighttime, NO_3 radical is dominant (Herrmann et al., 2010). The radical nitration of phenols by NO_2 and NO_3 radicals leads to the formation of nitrophenols (Harrison et al., 2005).*” Please refer to Lines 351-355.

Other factors, including liquid water content, pH value of cloud water, and the meteorological condition during sampling, were stable as we described in Supporting Information. Nevertheless, the influences of other factors cannot be excluded. We thus clarified that in Section 4: "*We noted that the database for the diurnal variation analysis is limited in this study, but the results provided novel insights into the diurnal variation of cloud chemistry. Firm conclusions warrant future field studies.*" Please refer to Lines 399-400.

References

Ervens, B., B. J. Turpin and R. J. Weber (2011). "Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies." Atmos. Chem. Phys. 11(21): 11069-11102.

Herrmann, H., D. Hoffmann, T. Schaefer, P. Brauer and A. Tilgner (2010). "Tropospheric aqueous-phase free-radical chemistry: radical sources, spectra, reaction kinetics and prediction tools." Chemphyschem 11(18): 3796-3822.

Harrison, M. A. J., S. Barra, D. Borghesi, D. Vione, C. Arsene and R. Iulian Olariu (2005). "Nitrated phenols in the atmosphere: a review." Atmos. Environ. 39(2): 231-248.

Specific Comments:

-Introduction: Overall it is OK, but it would be better to include the aqueous formation mechanisms related to CHON and CHOS.

Reply: Thanks for the reviewer's helpful suggestion. We included the aqueous-phase formation mechanisms of CHON, mainly including the radical nitration and carbonyls-ammonium/amine reactions, in the original manuscript. Additional information about the aqueous formation of organonitrates was added as follows: "*In addition, the nucleophilic addition of nitrate to the isoprene-derived epoxydiol can effectively form the organonitrates (Darer et al., 2011).*" Please refer to Lines 86-87. The new information about the formation mechanisms of organosulfates was added: "*Several formation mechanisms of organosulfates, such as acid-catalyzed ring-opening of epoxides, sulfate esterification, nucleophilic substitution of alcohols with sulfuric acid, and sulfoxy radical reactions, have been proposed in recent years (Brüggemann et al., 2020).*" Please refer to Lines 88-91.

References

Darer, A. I., N. C. Cole-Filipiak, A. E. O'Connor and M. J. Elrod (2011). "Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates." Environ. Sci. Technol. 45(5): 1895-1902.

Bruggemann, M., R. Xu, A. Tilgner, K. C. Kwong, A. Mutzel, H. Y. Poon, T. Otto, T. Schaefer, L. Poulain, M. N. Chan and H. Herrmann (2020). "Organosulfates in Ambient Aerosol: State of Knowledge and Future Research Directions on Formation, Abundance, Fate, and Importance." Environ. Sci. Technol. 54(7): 3767-3782.

- Lines 172, “the current understanding that aqueous-phase reactions generally increase the degree of oxidation (Ervens et al., 2011).” Please also include the reasons to this understanding. Does such aqueous reactions refer to in cloud processing?

Reply: Thanks for the reviewer’s comments. In the aqueous phase, the precursors and products of aqueous-phase reactions generally exhibit higher water-solubility and polarity than those in the gas phase. The enhanced formation of SOA with a high oxidation degree in the aqueous phase has been observed in many studies (Ge et al., 2012). Here the aqueous phase refers to both aerosol liquid water and cloud droplets. The related sentence has been revised to “*This is not consistent with the current understanding that precursors and products in the aqueous phase have a higher O/C, which generally causes the high water-solubility of molecules (Ervens et al., 2011).*” Please refer to Lines 243-244.

References

Ervens, B., B. J. Turpin and R. J. Weber (2011). "Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies." Atmos. Chem. Phys. 11(21): 11069-11102.

Ge, X., Q. Zhang, Y. Sun, C. R. Ruehl and A. Setyan (2012). "Effect of aqueous-phase processing on aerosol chemistry and size distributions in Fresno, California, during wintertime." Environ. Chem. 9(3): 221-235.

- Lines 182, “The O/C ratios and OSC of CHO collected during the daytime is slightly lower than the nighttime…”. What about the influence of primary emission? Since the samples collected during the daytime and nighttime may originally presents different characteristics without oxidation.

Reply: We agree with the reviewer’s comment that the primary emissions might also affect the differences between daytime and nighttime samples. The sampling site was mainly influenced by long-distance transport rather than local emissions. The wind direction and the air masses origin during sampling did not change dramatically. However, the 72-hour back trajectory of air masses showed that more continental air masses might be included during the daytime than the nighttime (Fig. S1). Thus the influence of air masses origin and the aging processes cannot be excluded. However, being limited by the sample size, the firm conclusion is difficult to draw. Thus the following sentence is added to the revised manuscript: “*The difference of air masses’ origin and the aging processes may also influence the cloud chemistry. However, since the database is limited, the further conclusion cannot be drawn based on them.*” Please refer to Lines 261-262.

- Lines 195, is there any result of aromaticity related to traffic emission or other sources, in addition to coal combustion and biomass burning? Since the present OA molecular does not correspond to these sources, i.e., coal combustion and biomass burning as discussed.

Reply: Thanks for the comments. The fraction of aromatic structures in the WSOC of traffic emission aerosols is also high (> 30% for CHO and CHON, and >20% for CHOS) (Tang et al., 2020). To clarify the question more persuasively, we here additionally compared the results of our study with the reports on urban aerosols, which are mainly influenced by local primary emissions. The related sentences have been revised and the new texts have been added: "*However, it is quite different from the primary emissions, including biomass burning, coal combustion, and traffic emission, of which the fraction of aromatic structures is higher (Song et al., 2018; Tang et al., 2020). The urban aerosols collected in Guangzhou, southern China, which may be mainly influenced by local primary emissions, also have a high fraction of aromatic molecules (> 20%) (Zou et al., 2020), implying the aging processes likely reduce the aromaticity of organics.*" Please refer to Lines 276-280.

References

Tang, J., J. Li, T. Su, Y. Han, Y. Mo, H. Jiang, M. Cui, B. Jiang, Y. Chen, J. Tang, J. Song, P. Peng, and G. Zhang (2020). "Molecular compositions and optical properties of dissolved brown carbon in biomass burning, coal combustion, and vehicle emission aerosols illuminated by excitation-emission matrix spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry analysis." Atmos. Chem. Phys. 20(4): 2513-2532.

Song, J., M. Li, B. Jiang, S. Wei, X. Fan and P. Peng (2018). "Molecular Characterization of Water-Soluble Humic like Substances in Smoke Particles Emitted from Combustion of Biomass Materials and Coal Using Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." Environ. Sci. Technol. 52(5): 2575-2585.

Zou, C., M. Li, T. Cao, M. Zhu, X. Fan, S. Peng, J. Song, B. Jiang, W. Jia, C. Yu, H. Song, Z. Yu, J. Li, G. Zhang and P. a. Peng (2020). "Comparison of solid phase extraction methods for the measurement of humic-like substances (HULIS) in atmospheric particles." Atmos. Environ. 225: 117370.

- Lines 251, It is an interesting result that coal combustion contributes to S-containing formulas in cloud water more significantly compared with CHO and CHON. Is there any other evidence to support the demonstration, such as the correlation between CHOS with the concentration of SO_2 or sulfate?

Reply: Thanks for the constructive comments. We conducted correlation analysis between CHOS with the concentration of SO_2 and sulfate, and found no statistical correlation between CHOS and SO_2 ($p > 0.05$) but significant correlation for CHOS and SO_4^{2-} ($r^2 = 0.72$, $p < 0.05$) in cloud water. However, since the database for the regression analysis was too limited (n = 6), the result might be subject to considerable uncertainty. Thus we did not include the result in the manuscript.

- Lines 278, "For CHO, the most abundant $C_{17}H_{26}O_4$ in cloud water is not detected in the $PM_{2.5}$ samples, suggesting a formation by the in cloud aqueous-phase reactions, although the contribution from BVOCs cannot be ruled out." Reasons should be discussed for such a contradiction.

Reply: Thanks for the comments. The sentences in the original manuscript may be amphibolous. As we discussed in Section 3.3, $C_{17}H_{26}O_4$ was detected in α-pinene ozonolysis SOA. However, $C_{17}H_{26}O_4$ was detected in cloud water but not in $PM_{2.5}$ in this study, indicating that it may mainly form through in-cloud aqueous-phase reactions at this sampling site. We have revised the sentence as follow: "*For CHO, the most abundant $C_{17}H_{26}O_4$ in cloud water was also detected in α-pinene ozonolysis SOA as we discussed in Section 3.3. However, it was not detected in $PM_{2.5}$ in this study, indicating that it may mainly form through in-cloud aqueous-phase reactions.*", please refer to Lines 365-367.

Responses to comments by Referee 3

This work provides a comprehensive analysis of the compounds in cloud water as well as the interstitial PM2.5, and characterize the distribution of different groups of species by using FT-ICR-MS; daytime and nighttime comparison was also made. Based on such analysis, aqueous-phase processing and the reactions involved were inferred to enhance our understanding of the aerosol chemistry. The paper is fairly well written and provide useful information and knowledge regarding the cloud water organics, this reviewer however has a series of comments to be addressed first before its acceptance.

Reply: We would like to thank the reviewer for his/her positive comments.

Line 51: as you stated here, "chromatographic and spectroscopic techniques only determined ~20% of all kinds of organics", then what does the FT-ICR-MS perform? Even though it has a super high mass resolution, is it being able to determine all existing species? If not, organics with what functionalities are preferred to be detected? What is the fraction of determined species to the total? How does this bias affect your interpretation? I think this issue should be clarified in your manuscript.

Reply: Thanks for the reviewer's comments. The detection of ESI FT-ICR MS has a certain selectivity; thus it cannot detect all the existing species. ESI is efficient at ionizing molecules having polar functional groups containing nitrogen and oxygen atoms, but not for molecules lacking nitrogen or oxygen atoms (Cho et al., 2015). Moreover, the reduced nitrogen is not easy to be detected at the negative ion mode. So the related sentence has been revised as "*Ultra-high resolution mass spectrometry such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) has made it possible to provide more comprehensive information of individual molecular formulas in complex mixtures, although the selectivity of detection still exists (Cho et al., 2015; Hockaday et al., 2009).*" Please refer to Line 56. The texts about the selectivity of ESI have been added in Section 2.2: "*ESI is efficient at ionizing molecules having polar functional groups containing nitrogen and oxygen atoms (Cho et al., 2015).*" "*Note that both the recovery of SPE and the selective ionization of negative ESI might cause a bias of mass spectra to certain peaks.*" Please refer to Lines 148-149 and 180-181.

Up to our best knowledge, there are no analytical tools that can cover all compound classes, so the fraction of determined species to the total is challenging to evaluate. Hocladay et al. (2009) estimated that 13% of the dissolved organic matter is either undetected or underrepresented by combined ESI (+,-) and APPI (+) (atmospheric pressure photoionization ionization) sources. Although the ionization of ESI source is selective, which might cause a bias of the distribution of molecular composition to some extent, the same bias was expected since all the samples were pretreated and detected in the same procedure. We have clarified them in the revised manuscript: "*Note that the abundant CHO and CHON cannot directly be related back to the composition of samples since the preferential detection of these molecules in negative ESI. However, the comparison among the samples is still meaningful since they are expected to have the same bias.*" Please refer to Lines 217-219.

References

Cho, Y., A. Ahmed, A. Islam and S. Kim (2015). "Developments in FT-ICR MS instrumentation, ionization techniques, and data interpretation methods for petroleomics." Mass. Spectrom. Rev. 34(2): 248-263.

Hockaday, W. C., J. M. Purcell, A. G. Marshall, J. A. Baldock and P. G. Hatcher (2009). "Electrospray and photoionization mass spectrometry for the characterization of organic matter in natural waters: a qualitative assessment." Limnol. Oceanogr.: Meth. 7: 81-95.

Section 2.2: Even though instrumental details are included in the supplement, I think some key information, for example, the mass resolution, and how to remove background organics, etc can be briefly described here, as well as the IC and TOC/TN analysis.

Reply: Thanks for the reviewer's suggestion. The detailed information about instrument analysis has been removed into the main text, please refer to Lines 106-115 and 124-201.

As described in (2), background organics or impurities during sample storage and treatment, might be detected as FT-ICR-MS is highly sensitive and has ultrahigh resolution. The number of molecules in cloud samples seem to be much higher than those in PM2.5 samples, I am wondering how do these excess compounds come from except from possible aqueous-phase processing?

Reply: Thanks for the comments. In our study, we made blank samples for the high-quality data in order to draw safe conclusions. The results we provided in this study have been corrected by blank samples. Thus the impact of background organics or impurities is considered to be minor. We detected 1264-2767 formulas in cloud water and 1057-1198 formulas in $PM_{2.5}$ samples. The number of assigned formulas may be mainly related to the concentration of organics in extracts of samples. Since the cloud water and $PM_{2.5}$ samples have different concentrations, it is not surprising that the different number of formulas were detected. Therefore, we used the relative fraction (e.g., the fraction of four groups to the total), the statistical results (e.g., average O/C ratios), and some formulas with huge differences in relative abundance between cloud water and $PM_{2.5}$ to do comparison and to indicate the impacts of in-cloud reactions. We have clarified that in the revised manuscript: "*The smaller number of assigned formulas in* $PM_{2.5}$ *may be mainly related to the low concentration of total organics in* $PM_{2.5}$ *extracts.*" Please refer to Lines 221-222.

Line 170-179: This reviewer thinks that cloud cycling might need to be considered, as the interstitial PM2.5 sampled here may contain aqueous oxidation products inside cloud droplets as cloud droplets in reality cycle per few minutes. Therefore a high O/C value might be observed in PM2.5 samples rather than cloud water. Whether or not aqueous processing could enhance the oxidation degree of organics depends on the ageing time. In a short time scale, the organic oxidation degree could increase and the more oxidized species may fragment into low oxygenated ones given enough time.

Reply: We are grateful to the reviewer for providing his/her constructive views. Previous studies using the large-eddy simulation model have shown that the parcel in-cloud residence time is on the scale of a few minutes (Stevens et al., 1996; Feingold et al., 1998). These studies mainly focused on the stratocumulus in the boundary layer with turbulence. However, the sampling site in this study was located at the top of a mountain, and the meteorological conditions at the observation site were stable during sampling. The temperature ranged from 15.2 to 15.9 ℃, and the relative humidity was stable at 100%, which is unfavorable for the droplets' evaporation. Moreover, the wind direction did not change dramatically, which may imply a minor impact of the turbulence. If the interstitial aerosols underwent several cloud cycles during the sampling, the composition of cloud water and interstitial aerosols would tend to be consistent. However, the previous studies have revealed the differences between cloud residues and interstitial aerosols (e.g., Roth et al., 2016; Lin et al., 2017). Thus we infer that the impact of cloud cycling would be limited before the cloud event ending although we cannot completely rule out their influence. The related texts have been added: "*Previous studies using the large-eddy simulation model have shown that the in-cloud residence time of the parcel is on the scale of a few minutes (Stevens et al., 1996; Feingold et al., 1998), thus some masses formed in cloud droplets may remain in aerosols via the evaporation of the droplets, resulting some high oxidation organics entering the interstitial* $PM_{2.5}$*. We cannot completely rule out the influence of cloud cycling, however, this impact may be limited because of the stable meteorological conditions with constant temperature, wind and saturated or supersaturated water vapor during sampling (Fig S2).*" Please refer to Lines 246-251.

References

Stevens, B., Feingold, G., Cotton, W. R., & Walko, R. L. (1996). "Elements of the Microphysical Structure of Numerically Simulated Nonprecipitating Stratocumulus. " J. Atmos. Sci., 53(7): 980-1006.

Feingold, G., Kreidenweis, S. M., and Zhang, Y. (1998). "Stratocumulus processing of gases and cloud condensation nuclei: 1. Trajectory ensemble model. " J. Geophys. Res., 103(D16): 19527-19542.

Roth, A., J. Schneider, T. Klimach, S. Mertes, D. van Pinxteren, H. Herrmann and S. Borrmann (2016). "Aerosol properties, source identification, and cloud processing in orographic clouds measured by single particle mass spectrometry on a central European mountain site during HCCT-2010." Atmos. Chem. Phys. 16(2): 505-524.

Lin, Q., G. Zhang, L. Peng, X. Bi, X. Wang, F. J. Brechtel, M. Li, D. Chen, P. Peng, amp, apos, an, G. Sheng and Z. Zhou (2017). "In situ chemical composition measurement of individual cloud residue particles at a mountain site, southern China." Atmos. Chem. Phys. 17(13): 8473-8488.

Line 286-292: Similar for OS, typically OS can be produced more efficiently in aerosol water rather than liquid water, yet no statistical difference are observed here, as there are repeated cycling between cloud water and interstitial PM2.5.

Reply: Thanks for the reviewer's helpful comments. As we mentioned above, the impact of cloud cycles would be minor before the cloud event ending in the case of this study. However, we clarified that the organosulfates may form in aerosol efficiently: "*For CHOS formulas, the most abundant functions classes are similar between cloud water and* $PM_{2.5}$*. No statistical difference of the fraction of organosulfates is observed between cloud water and* $PM_{2.5}$ *except for a low* f_{RA} *(69.5%) of organosulfates in P2 sample, which may indicate the wide variety of formation mechanisms (e.g., acid-catalyzed particle-phase reactions, nucleophilic substitution reactions in aqueous phase) and/or other common sources of CHOS in cloud water and* $PM_{2.5}$ *(Bruggemann et al., 2020), but possible slightly enhanced formation of that in cloud water.*" please refer to Lines 374-378.

Reference

Bruggemann, M., R. Xu, A. Tilgner, K. C. Kwong, A. Mutzel, H. Y. Poon, T. Otto, T. Schaefer, L. Poulain, M. N. Chan and H. Herrmann (2020). "Organosulfates in Ambient Aerosol: State of Knowledge and Future Research Directions on Formation, Abundance, Fate, and Importance." Environ. Sci. Technol. 54(7): 3767-3782.

Specific comments

Line 25-26, do you mean CHON and CHO-containing species? It is not clear. The last sentence in Line 26 is not a full sentence.

Reply: Yes, CHON and CHO here mean formulas containing C, H, O, N and C, H, O respectively. The sentence has been revised as "*CHON (formulas containing C, H, O, and N elements, the same is true for CHO and CHOS) represents the dominant component (43.6-65.3% of relative abundance), followed by CHO (13.8-52.1%).*" The last sentence has been revised as "*S-containing formulas constitute ~5-20% of all assigned formulas.*" Please refer to Lines 26-28.

Line 28: A recent paper by Wang et al (2021, 118:e2022179118) demonstrates that aqueous-phase oxidation of aromatic species could be a source of SOA, this might be a supporting evidence that "CHON with aromatic structures are abundant in cloud water"

Reply: Thanks for the reviewer's helpful suggestions. The citation has been added in Line 284: "*The aromatic species may provide the precursors of aqueous-phase reactions (Wang et al., 2021).*"

Reference

Wang, J., J. Ye, Q. Zhang, J. Zhao, Y. Wu, J. Li, D. Liu, W. Li, Y. Zhang, C. Wu, C. Xie, Y. Qin, Y. Lei, X. Huang, J. Guo, P. Liu, P. Fu, Y. Li, H. C. Lee, H. Choi, J. Zhang, H. Liao, M. Chen, Y. Sun, X. Ge, S. T. Martin and D. J. Jacob (2021). "Aqueous production of secondary organic aerosol from fossil-fuel emissions in winter Beijing haze." Proc. Natl. Acad. Sci. U.S.A. 118(8): e2022179118.

Line 69: Consider to add citation Ye et al., Atmos Environ 2020;223:117240, which determines the organic acids produced from aqueous-phase oxidation of a certain precursor.

Reply: Thanks for the reviewer's kind suggestion. The citation has been added to the revised manuscript, please refer to Line 72.

Line 144: RA means relative abundance, this reviewer somehow think the authors can directly use "relative abundance", it is easier to understand than RA.

Reply: Thanks for the reviewer’s suggestion. The word “RA” has been replaced by “relative abundance” in the revised manuscript.

Measurement report: Molecular characteristics of cloud water in southern China and insights into aqueous-phase processes from Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Abstract. Characterizing the molecular composition of cloud water could provide unique insight into aqueous chemistry. Field measurement was conducted at Mt. Tianjing in southern China in May, 2018. Thousands of formulas ($C_{5-30}H_{4-55}O_{1-15}N_{0-2}S_{0-2}$) were identified in cloud water by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). CHON (formulas containing C, H, O, and N elements, the same is true for CHO and CHOS) represents the dominant component (43.6-65.3% of relative abundance), followed by CHO (13.8-52.1%). S-containing formulas constitute ~5-20% of all assigned formulas. Cloud water has relative-abundance-weighted average O/C of 0.45-0.56 and the double-bond equivalent of 5.10-5.70. Most of the formulas (> 85%) are assigned as aliphatic and olefinic species. No statistical difference of oxidation state is observed between cloud water and interstitial $PM_{2.5}$. CHON with aromatic structures are abundant in cloud water, suggesting their enhanced in-cloud formation. Other organics in cloud water are mainly from biomass burning and oxidation of biogenic volatile organic compounds. The cloud water contains more abundant CHON and CHOS at night, which are primarily contributed by $–N_2O_5$ function and organosulfates, demonstrating the enhanced formation in dark aqueous or multi-phase reactions. While more abundant CHO is observed during the daytime, likely due to the photochemical oxidation and photolysis of N-/S-containing formulas. The results provide an improved understanding of the in-cloud aqueous-phase reactions.

1 Introduction

On average, approximately 70% of the Earth is covered by clouds (Stubenrauch et al., 2013; Herrmann et al., 2015). Cloud water is an essential sink of organics (Herckes et al., 2013) and provides a medium for the aqueous-phase reactions of dissolved gases and aerosols (Blando and Turpin, 2000), which can substantially modify the characteristics of the organics (McNeill, 2015; Kim et al., 2019). Aqueous-phase secondary organic aerosols (aqSOA) forming in the in-cloud aqueous-phase processes significantly contribute to the total SOA with a negative impact on the visibility, human health, and climate (Ge et al., 2012; Huang et al., 2018; Schurman et al., 2018; Li et al., 2020a; Smith et al., 2014; Paglione et al., 2020; Hallquist et al., 2009). Therefore, understanding the molecular characteristics and aqueous-phase reactions in cloud droplets is crucial to assessing their impact accurately.

Organics in cloud water mainly include organic acids (e.g., formic, acetic, oxalic acids, and other short-chain mono and dicarboxylic acids) (Sun et al., 2016), carbonyls (e.g., formaldehyde, acetaldehyde, glyoxal, and methylglyoxal) (Ervens et al., 2013; Van Pinxteren et al., 2016), as well as some heteroatom-containing compounds such as amino acids (Bianco et al., 2016b), organonitrates, and organosulfates (Zhao et al., 2013). Some less polar organics such as n-alkanes (Herckes et al., 2002), benzene, toluene, ethylbenzene, and xylenes (Wang et al., 2020), polycyclic aromatic hydrocarbons (Herckes et al., 2002; Ehrenhauser et al., 2012), phenols, and nitrophenols (Lüttke et al., 1997; Lüttke et al., 1999) are also observed, though with a much lower fraction of dissolved organic materials (usually < 1%). The organics characterized using chromatographic and spectroscopic techniques only take a proportion of ~20% of all kinds of organics in cloud water (Herckes et al., 2013; Bianco et al., 2018). Ultra-high-resolution mass spectrometry such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) has made it possible to characterize individual molecular formulas in complex mixtures, although the selectivity of detection still exists (Cho et al., 2015; Hockaday et al., 2009). In studies using ultra-high-resolution MS to characterize cloud/fog water, formulas were mainly divided into CHO, CHON, CHOS, and CHONS based on the elemental composition, in which CHO and CHON were usually dominant (Zhao et al., 2013; Cook et al., 2017; Brege et al., 2018; Bianco et al., 2018; Bianco et al., 2019). Boone et al. (2015) observed a high fraction of N-containing formulas in cloud water compared with particles and attributed it to the aqueous-phase formation. However, a more recent study carried out in Po Valley observed more CHO formulas in cloud water, while particle samples contained more N- and S-containing formulas. The authors attribute it to the high possibility of reactions with sulfate and nitrate ions in the concentrated environment of aerosol liquid water (Brege et al., 2018). Thus more observations are needed to provide more convincing evidence of in-cloud aqueous-phase reactions.

Aqueous-phase reactions have been identified as an important source of organics in cloud water in addition to the gas-liquid and particle-liquid partition. Aqueous-phase reactions mainly include radical and non-radical reactions. Under irradiation, hydroxyl radical (OH•) is the primary radical in the atmosphere (Herrmann et al., 2010). In cloud water, the oxidation of precursors can be initiated by the hydrogen abstraction or electron transfer reaction driven by the OH•, resulting in the formation of organic acids and condensed compounds (McNeill, 2015). On the one hand, photolysis causes the fragmentation of high-molecular-weight organic compounds, resulting in the formation of relatively low-molecular-weight compounds such as small acids, including oxalic, glyoxylic, and, in large quantity, formic and acetic acid (Renard et al., 2015; Schurman et al., 2018; Huang et al., 2018; Sun et al., 2010; Li et al., 2014; Löflund et al., 2002; Ye et al., 2020). These compounds are highly oxygenated owing to cloud processing (Brege et al., 2018; Sareen et al., 2016), as indicated by the fact that aqSOA has a higher O/C ratio (~1) than gas-phase SOA (0.3-0.5) in the atmosphere (Ervens et al., 2011). On the other hand, photochemistry also leads to the oligomerization of organics, such as pyruvic acid, phenols, and methyl vinyl ketone under conditions relevant to deliquesced aerosols (Reed Harris et al., 2014; Renard et al., 2015; Yu et al., 2016). The oligomerization of tryptophan was also observed in synthetic cloud water (Bianco et al., 2016a). For the N- and S-containing organics, photochemistry may cause the release of inorganic nitrate and sulfate (Braman et al., 2020; Laskin et al., 2015; Bruggemann et al., 2020). The main radical in the atmosphere at night is NO_3•, which can form from the gas-phase reaction between NO_2 and O_3 and enter cloud droplets. The reactions between NO_3• and organics lead to the oxidation of organics or the addition of functional groups containing N atoms when the aqueous phase is concentrated and acidic (Herrmann et al., 2015; McNeill, 2015; Wang et al., 2008; Szmigielski, 2016; Rudziński and Szmigielski, 2019). Meanwhile, the radical nitration is believed to form dinitroaromatics in the aqueous phase (Kroflic et al., 2015). Non-radical reactions also lead to the formation of N-containing organics. Carbonyls can react with ammonium and amine without illumination, resulting in the generation of imidazoles and N-containing oligomers, especially in aerosol liquid water and evaporating cloud water (De Haan et al., 2009; Kua et al., 2011; De Haan et al., 2011; De Haan et al., 2018). In addition, the nucleophilic addition of nitrate to the isoprene-derived epoxydiol can effectively form organonitrates (Darer et al., 2011). While organosulfates can form through heterogeneous and bulk particle-phase reactions (Brüggemann et al., 2020). Several formation mechanisms of organosulfates, such as acid-catalyzed ring-opening of epoxides, sulfate esterification, nucleophilic substitution of alcohols with sulfuric acid, and sulfoxy radical reactions, have been proposed in recent years (Brüggemann et al., 2020). The non-radical reactions in the aqueous phase also include hydrolysis, hydration, Fenton reaction, and translation metals reactivity with organics, probably ozone reactivity at the gas/liquid interface, and so on (McNeill, 2015; Deguillaume et al., 2005; Herrmann et al., 2015).

To date, only a few studies reported the molecular characteristics of cloud water using ultra-high-resolution MS, hampering our understanding of aqueous-phase reactions on the composition of cloud water. In this study, cloud water and $PM_{2.5}$ samples at a remote mountain site were collected and analyzed by FT-ICR MS. The primary objectives of this study are to investigate the molecular characteristics and composition of the organics in cloud water, and to explore the potential influences of aqueous-phase reactions.

2 Materials and methods

2.1 Sample collection and pretreatment

A sampling campaign was carried out at an atmospheric monitoring station (112°53′56″E, 24°41′56″N, 1690 m above sea level) located in the Tianjing Mountain in southern China (Fig. S1). The site is located in a natural conservation zone far away from anthropogenic activities, which is affected mainly by local biogenic emissions and long-distance transport during the monsoon seasons.

A Caltech Active Strand Cloudwater Collector, *Version 2* (CASCC2), was used for cloud water collection (Demoz et al., 1996). Cloud events were identified using the humidity sensor and the visibility meter in a co-working ground-based counterflow virtual impactor (Model 1205, Brechtel Mfg., Inc., USA) according to the following criteria: visibility ≤ 3 km, relative humidity ≥ 95%, and no precipitation. During sampling, cloud droplets entered the collector powered by a rear fan, and condensed on a bank of Teflon strands at a flow rate of 5.8 m^3 min^{-1} and collection efficiency of 86%. Condensed cloud water flowed into the pre-cleaned sample jar through a Teflon tube equipped at the bottom of the collector. The pH of the cloud water was measured using a pH meter. Samples were refrigerated immediately after sampling and kept until the analysis. The cloud liquid water content (LWC) during the sampling was calculated as follows (Guo et al., 2012):

$$\mathrm{LWC} = \Delta m/(\Delta t \times \eta \times Q)$$

where Δm represents the mass of the sample (g); Δt represents the sampling interval (min). η is the collection efficiency, which is regarded as 86% for cloud droplets larger than 3.5 μm; and Q is the airflow of the CASCC2, i.e., 5.8 m^3 min^{-1}. A total of 24 cloud water samples (Sample ID: CL1-24) were collected in succession during a long-duration cloud event that lasted from May 8 to May 13, 2018. To investigate the molecular characteristics of the organics and the effects of aqueous-phase processes, six samples collected from May 11 to May 12 (CL12-17, Table 1) were selected for FT-ICR MS analysis in detail since these six samples were all collected during the maintenance stage of a cloud event with stable pH and LWC (Table 1), stable meteorological conditions and no dramatic change of air masses origin (Fig. S1, S2). The sampling interval of six samples is presented in Table 1 and Fig. S2. The samples CL12, CL13, and CL14 were collected during the daytime of May 11, while the other three samples (CL15, CL16, and CL17) could be roughly regarded as nighttime samples, although CL15 was partly collected in the evening.

Quartz fiber filters (Whatman, Britain) were used to collected interstitial $PM_{2.5}$ samples at the same site. A $PM_{2.5}$ sampler (PM-PUF-300, Mingye Inc., China) with a cut size of 2.5 μm at a flow rate of 300 L min^{-1} was used for sampling. The sampling interval of $PM_{2.5}$ was roughly 24 hours. Two samples of $PM_{2.5}$ were collected within two days (P1: May 11 10:14-May 12 9:48, P2: May 12 10:15-May 13 10:15, respectively) during the investigated cloud events. The samples were stored at -20 ℃ immediately after sampling. For the laboratory analysis, 60 cm^2 of the sample filters were cut into pieces and soaked in ultra-clean water. Then the water-soluble organic matter in $PM_{2.5}$ was separated into the ultra-clean water by 30 min ultrasonic extraction three times, after that the extract was filtered using 0.22 μm polytetrafluoroethylene filters. The extract was then pretreated and analyzed used the same methods with cloud water samples.

For FT-ICR MS analysis, water-soluble organic compounds in cloud water and $PM_{2.5}$ extract were isolated using solid-phase extraction (SPE) (Zhao et al., 2013; Bianco et al., 2018). The SPE cartridges (Strata-X, Phenomenex, USA) were pre-conditioned sequentially with 3 mL of isopropanol, 6 mL of acetonitrile, 6 mL of methanol containing 0.1% of formic acid, and 6 mL of ultrapure water containing 0.1% formic acid. Then, 40 mL of cloud water without pH adjustment and $PM_{2.5}$ extracts with pH adjusted to 4.5 using formic acid were added to the cartridge at a flow rate of approximately 1 mL min^{-1}. The inorganic salts were removed from the cartridge using 4 mL of ultrapure water containing 0.1% formic acid. Note that some low-weight organic molecules are expected to be lost in this step. The cartridges were then freeze-dried, and the analytes were eluted using 3 mL of acetonitrile/methanol/ultrapure water (45/45/10, *v:v:v*) at pH 10.4, with the pH being adjusted using ammonium hydroxide. All the solvents were HPLC-grade. Blank samples of the cloud water and $PM_{2.5}$ were processed and analyzed following the same procedure as the samples.

2.2 Instrumental analysis and data processing

A solariX XR FT-ICR MS instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 9.4-T refrigerated, actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and a Paracell analyzer cell was used for the analysis in this study. An electrospray ionization (ESI) source (Bruker Daltonik GmbH, Bremen, Germany) at the negative ion mode was used to ionize the organics. ESI is a soft ionization technique that offers minimal fragmentation of the analytes (Mazzoleni et al., 2010). $[M-H]^-$ was detected at the negative ion mode. The coupling of ESI and FT-ICR MS with ultra-high mass resolution makes it possible to characterize the element constitution within molecules. Note that ESI is efficient at ionizing molecules having polar functional groups containing nitrogen and oxygen atoms (Cho et al., 2015). The direct infusion method was used in this study. The samples were redissolved in 1 mL of methanol and injected into an ESI source at a flow rate of 200 µL h^{-1}. A nebulizer gas pressure of 1 bar, a dry gas velocity of 4 L min^{-1} and temperature of 200 ℃, and capillary voltages of +4500 V and the end plate offset -500 V were used for ESI source. The optimized mass for quadrupole (Q1) was 170 Da. An argon-filled hexapole collision pool was operated at 2 MHz and 1400 Vp-p RF amplitude. The time of flight was 0.7 ms and the mass range was 150-800 Da and the ion accumulation time was 0.1 s. A total of 128 continuous 4M data FT-ICR transients were co-added to enhance the signal-to-noise ratio and dynamic range. A typical mass-resolving power ($m/\Delta m50\%$, where Δm50% is the magnitude of the mass spectral peak full width at half-maximum peak height) of more than 450,000 at *m/z* 319 with <0.3 ppm absolute mass error was achieved. The mass spectra were calibrated externally using measurements of a known homologous series of N_1 and O_2 molecules (e.g., $C_{16}H_{31}O_2$, $C_{17}H_{33}O_2$, and $C_{18}H_{35}O_2$, etc. that only separated by $–CH_2$ units) frequently detected in a crude oil sample before sample detection. The final spectrum was internally recalibrated with typical class species peaks in cloud water samples ($-O_4$ species) using quadratic calibration in DataAnalysis 5.0 (Bruker Daltonics) (Jiang et al., 2019). All the mathematically possible formulas for all the ions with a signal-to-noise ratio greater than 10, considering a mass tolerance of ±0.6 ppm were calculated. The maximum numbers of atoms for the formula calculator were set to: 30 ^{12}C, 60 ^{1}H, 20 ^{16}O, 2 ^{14}N, 2 ^{32}S, 1 ^{13}C, 1 ^{18}O, and 1 ^{34}S. Formulas assigned to isotopomers (i.e., ^{13}C, ^{18}O, or ^{34}S) were not discussed in this study. Thus, the chemical formula

$C_cH_hO_oN_nS_s$ was obtained. Future selecting was applied using following criteria to exclude formulas not detected frequently in natural materials: $O/C \leq 1.2$, $0.3 \leq H/C \leq 2.25$, $N/C \leq 0.5$, $S/C \leq 0.2$, $2C + 2 > H$, $C + 2 > O$ and obeying N rule. Finally, only intensities of sample ion peaks enhanced at least 100 times higher than those in the blank were retained for further data analysis in order to avoid possible contamination. The double-bond equivalent (DBE) can be used to evaluate the number of rings and double bonds in a molecule (An et al., 2019). The DBE of each assigned molecular formula ($C_cH_hO_oN_nS_s$) was calculated as follows:

$$\mathrm{DBE} = (2c + 2 - h + n)/2$$

The oxidation state of carbon atoms (OS_C) was calculated as follow based on the approximation described in Kroll et al. (2011) and Brege et al. (2018):

$$OS_C \approx 2*o/c - h/c - 5*n/c - 6*s/c$$

The modified aromaticity index (AI_{mod}) was first proposed by Koch et al. to evaluate the aromaticity of high-resolution mass data (Koch and Dittmar, 2006):

$$AI_{mod} = (1 + c - 0.5*o - s - 0.5*h)/(c - 0.5*o - s - n)$$

$AI_{mod} \geq 0.5$ and 0.67 represent the existence of aromatic and condensed aromatic structures (Koch and Dittmar, 2006).

Relative abundance of each formula was represented by the intensities of each peak after normalization by the maximum intensity in each sample. Note that both the recovery of SPE and the selective ionization of negative ESI might cause a bias of mass spectra to certain peaks. And ESI FT-ICR MS is not a purely quantitative technique, the intensity of the peak for each formula is a product of its concentration and ionization efficiency. However, since all of the samples were pretreated using the same procedure and measured using the same instrumental conditions, each spectrum was biased in an equal fashion, so relative peak intensities within the acquired spectra can be compared to each other, although they cannot be related back to concentrations in the original samples (Sleighter et al., 2010; Wozniak et al., 2014). The relative-abundance-weighted average elemental ratios of oxygen, carbon, and hydrogen (i.e., O/C, H/C, etc.) and other characteristic parameters were calculated following Song et al. (2018):

$$O/C_w = \Sigma(O/C_i \times \mathrm{Int}_i)/\Sigma \mathrm{Int}_i$$

$$H/C_w = \Sigma(H/C_i \times \mathrm{Int}_i)/\Sigma \mathrm{Int}_i$$

$$\mathrm{DBE}_w = \Sigma(\mathrm{DBE}_i \times \mathrm{Int}_i)/\Sigma \mathrm{Int}_i$$

$$OS_{Cw} = \Sigma(OS_{Ci} \times \mathrm{Int}_i)/\Sigma \mathrm{Int}_i$$

where Int_i represents the intensity of the mass spectrum for each individual molecular formula, i. The discussion in this paper is based on the weighted average values unless otherwise specified; thus, the subscript “w” is omitted for brevity in the following texts.

Cloud water samples were also analyzed for ionic species. Descriptions of these analyses are available elsewhere (Guo et al., 2012; Bianco et al., 2018). Briefly, water-soluble inorganic ions and oxalate ($C_2O_4^{2-}$) were detected using an Ion Chromatograph (883 Basic IC plus, Metrohm, Switzerland) with suppressed conductivity detection and a Metrosep C4-150/4.0 column (Metrohm) for cations and a Metrosep A Supp 5-150/4.0 column (Metrohm) for anions.

The 72 h back trajectories were displayed using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (https://ready.arl.noaa.gov) (Stein et al., 2015; Lin et al., 2017). The endpoint of the trajectory in the model was set to a height of 1800 m above sea level. In addition, the meteorological conditions during sampling and water-soluble ions concentrations are provided and discussed in Text S1.

3. Results and Discussion

3.1 Overview of molecular formulas of cloud water and comparison to the interstitial $PM_{2.5}$

A total of 1691, 1546, 1604, 1264, 2364, and 2767 molecular formulas were identified in CL12-17 samples, respectively. According to the elemental compositions, four groups (CHO, CHON, CHOS, and CHONS) were assigned. The reconstructed mass spectrum of a typical sample, CL12, is presented in Fig. 1a. The most intensive ion peaks are within the range of *m/z* 200-400. A similar pattern is also found in cloud (Zhao et al., 2013; Bianco et al., 2018; Cook et al., 2017), fog (Brege et al., 2018), and aerosols (Lin et al., 2012; Mazzoleni et al., 2012).

In cloud water, CHON is the most frequently observed group, representing more than 60% of the total number of assigned formulas. CHO contributes to 16.3-28.3% of the total number of identified formulas, while the proportions of S-containing formulas (CHOS and CHONS) are much lower (3.6-9.4% and 3.7-9.3%, respectively) (Table S2). The relative abundance of each group is evaluated, as shown in Fig. 1b and Table S2. The fraction in relative abundance (f_{RA}) of the CHON group is 43.6-65.3% (54.9% on arithmetic average), and CHO contributes 13.8-52.1% (34.7% on arithmetic average). S-containing formulas constitute the remaining fraction, approximately 5-20% (Table S2). The fractions of four groups in relative abundance and in number are different, which is mainly attributed to some formulas with high intensities contributing much more to relative abundance than to the number. Note that the abundant CHO and CHON cannot be directly related back to the composition of samples since the preferential detection of these molecules in negative ESI. However, the comparison among the samples is still meaningful since they are expected to have the same bias.

The cloud water shows a distinct pattern of molecular composition with the interstitial $PM_{2.5}$. In two $PM_{2.5}$ samples, 1198 and 1057 formulas are identified, in which CHO and CHON are dominant. The smaller number of assigned formulas in $PM_{2.5}$ may be mainly related to the low concentration of total organics in $PM_{2.5}$ extracts. The CHO group contributes to 39.9-49.8%, while the CHON group contributes to 31.8-51.0%. The S-containing formulas constitute the remaining fraction (9.1-18.4%). Similar results can also be obtained by f_{RA} of CHO (44.0-55.5%), CHON (24.3-47.3%), and S-containing formulas (8.7-20.3%) (Table S3). At three sites in Pearl River Delta (PRD), more than half of all detected formulas were assigned as CHO, while CHON only accounted for 8-19% in the aerosols (Lin et al., 2012). The higher fraction of CHON in cloud water compared with $PM_{2.5}$ in PRD and interstitial particles is consistent with the previous finding (Boone et al., 2015), likely indicating the formation of N-containing organics in cloud water.

3.2 Effects of cloud processing on oxidation metrics and aromaticity of the molecular formulas

Oxidation metrics O/C and OS_C are employed to evaluate the oxidation degree of molecules in cloud water. In six cloud water samples, the average O/C values range from 0.45 to 0.56 (Table S4). No significant differences of O/C are observed between cloud water and $PM_{2.5}$, of which average O/C values are 0.45-0.56 (Table S5). In the Van Krevelen (VK) plot, CHON formulas distribute in a wide area (Fig. 2 and Fig. S3). Some of them with O/C exceeding 0.8 distribute in the top-right corner of the plots, which also result in higher O/C of CHON on average (0.51-0.62, Table S4) compared with CHO, of which O/C ratios range from 0.34 to 0.46. On relative-abundance-weighted average, the O/C ratios of CHOS and CHONS range from 0.36 to 0.51 and from 0.65 to 0.88, respectively. This is not unintelligible if we note that the N and S atoms in the CHON and S-containing formulas would probably combine with O (e.g., $-NO_2$, $-NO_3$, or $-SO_3$ function group), leading to the higher average O/C of non-CHO formulas. The OS_C value excludes the influence of oxygen atoms combined with H, N, and S; thus it is a more applicative proxy to evaluate the oxidation state of carbon atoms. The average OS_C values range from -0.91 to -0.72 in cloud water (Table S4), while that in $PM_{2.5}$ ranges from -0.84 to -0.61 (Table S5). Being limited by the sampling size, no statistical difference of OS_C can be identified between cloud water and $PM_{2.5}$. However, a higher OS_C of detected formulas, especially CHO, appears in $PM_{2.5}$ samples (-0.40 in P2 sample). A similar phenomenon is also observed in CHOS. This is not consistent with the current understanding that precursors and products in the aqueous phase have a higher O/C, which generally causes the high water-solubility of molecules (Ervens et al., 2011). However, a previous aircraft sampling also observed a lower O/C in cloud water than below-cloud atmospheric particles (Boone et al., 2015), suggesting that the effects of aqueous-phase reaction may be complex in the actual atmosphere. Previous studies using the large-eddy simulation model have shown that the in-cloud residence time of the parcel is on the scale of a few minutes (Stevens et al., 1996; Feingold et al., 1998), thus some masses formed in cloud droplets may remain in aerosols via the evaporation of the droplets, resulting some high oxidation organics entering the interstitial $PM_{2.5}$. We cannot completely rule out the influence of cloud cycling, however, this impact may be limited because of the stable meteorological conditions with constant temperature, wind and saturated or supersaturated water vapor during sampling (Fig. S2). We note that $PM_{2.5}$ samples were collected during the cloud event; high aerosol liquid water content in $PM_{2.5}$ likely provides a sink containing more concentrated precursors for the aqueous-phase reactions compared with cloud water. However, no formation mechanism of more oxidized organics in aerosol liquid water is proposed in previous studies; thus future researches of aqueous-phase reactions in the atmosphere are needed. In four groups, CHO has the highest OS_C values (-0.80 ~ -0.54) (Table S4), which may be related to the high abundance of carboxyl groups in CHO.

To investigate the diurnal variation of oxidation metrics in cloud water, daytime and nighttime samples are compared. The O/C ratios show no identified diurnal variation except for CHO groups. The O/C ratios and OS_C of CHO collected during the daytime is slightly lower than the nighttime (Table S4), this is not consistent with the high oxidation capacity under the illumination during the daytime, indicating that the oxidation degree of the organics in cloud water is not exclusively affected by the illumination. The difference of air masses' origin and the aging processes may also influence the cloud chemistry. However, since the database is limited, the further conclusion cannot be drawn based on them.

Aromaticity The unsaturation and aromaticity of molecular formulas can be evaluated using the H/C ratios and the DBE, where low H/C and high DBE indicate a high degree of unsaturation, and to some extent, aromatic structure. On relative-abundance-weighted average, H/C ratios in cloud water ranges from 1.44 to 1.49, with no statistical difference than $PM_{2.5}$ (1.40-1.53). In the VK plot, CHOS and CHONS occupy an upper area of the diagram with high H/C ratios, indicating that they may have higher saturation compared with CHO and CHON. On weighted average, DBE values in cloud water range from 5.10 to 5.70 (Table S4), which is generally higher than that in $PM_{2.5}$ (4.74-5.04, Table S5). The weighted average DBE values of CHO, CHON, CHOS, and CHONS are 4.96-6.12, 5.44-6.09, 2.72-4.58, and 3.01-4.29, respectively. DBE values are also projected onto the plots of DBE versus carbon atom numbers (Fig. 3). DBE values generally increase with carbon number, and CHOS and CHONS distribute in a range with low DBE values. The higher unsaturation degree of CHO and CHON is likely corresponding to the high abundance of aromatic functions.

Another commonly used metric of aromaticity is AI_{mod}. In cloud water, most of the formulas (91.1-98.3% of CHO, 79.2-97.5% of CHON, 93.5-98.8% of CHOS, and 95.7-100.0% of CHONS in f_{RA}) are assigned as aliphatic or olefinic molecules (Table S6). The f_{RA} of aliphatic and olefinic molecules in $PM_{2.5}$ also exceeds 90%. The high fraction of aliphatic and olefinic and the low fraction of aromatic structure are also observed in aerosols at a remote site (An et al., 2019). However, it is quite different from the primary emissions, including biomass burning, coal combustion, and traffic emission, of which the fraction of aromatic structures is higher (Song et al., 2018; Tang et al., 2020). The urban aerosols collected in Guangzhou, southern China, which may be mainly influenced by local primary emissions, also have a high fraction of aromatic molecules (> 20%) (Zou et al., 2020), implying the aging processes likely reduce the aromaticity of organics. In four groups of molecules in cloud water, CHON has the most (2.5-20.8% in f_{RA}) aromatic structures, consistent with the high DBE values (unsaturation) of CHON. Previous studies conducted in the Po Valley, Italy (Brege et al., 2018) and Fresno, USA (Leclair et al., 2012) also observed a higher fraction of aromatics in CHON than the S-containing groups in fog water. The aromatic species may provide the precursors of aqueous-phase reactions (Wang et al., 2021). While in this study, the possible dinitrophenols in cloud water contribute to the high f_{RA} of aromatic structures in CHON significantly, which may be related to the aqueous-phase reactions (see the detailed discussion in Section 3.4).

3.3 Molecular composition of cloud water

CHON In cloud water, CHON formulas show no prominent carbon number peaks except sample CL17 (Fig. S4), and one or two nitrogen atoms are assigned to them (Fig. 4). Both the N_1 and N_2 categories contain 1-14 oxygen atoms. The most abundant class of N_1 formulas is $–N_1O_8$ or $–N_1O_7$ (Fig. 4), which include $C_{12}H_{17}NO_8$, $C_{15}H_{19}NO_8$, $C_{17}H_{27}NO_7$, $C_8H_{11}NO_7$, and so on. More than 77.7% of the CHON formulas in f_{RA} in all six samples have O/N ratios exceeding 3, indicating that the N atoms in these molecules may be in the $–NO_3$ functional group (Zhao et al., 2013). Samples CL12-16 show no prominent peak of the function classes in the N_2 category, but a dominant peak of the $–N_2O_5$ class is observed in CL17 (Fig. 4), where

$C_8H_8N_2O_5$ and $C_7H_6N_2O_5$ are the two most abundant formulas. These formulas probably belong to dinitrophenols and their derivatives.

To evaluate the contribution of primary sources, we compared the molecular composition in cloud water with that in particles emitted from the primary sources such as biomass burning (including corn straw, pine branches, and rice straw) and coal combustion using the same analytical instrument (Song et al., 2018). In cloud water, 40.9-51.4%, 21.9-27.1%, and 48.1-59.4% (in terms of number fraction) of CHON molecules appear in the smoke particles of corn straw, pine branches, and rice straw, indicating a non-negligible contribution from biomass burning. While only 7.7-10.5% of molecules in cloud water can be corresponding to the coal combustion emission, suggesting its less contribution to the molecular composition of cloud water. Note that the comparison was only based on the molecular formulas given by FT-ICR MS, the isomeride could not be distinguished; thus the results only represented a possible relationship with the different sources. Additionally, some N-containing molecules are also detected in monoterpene SOA (Park et al., 2017; Zhang et al., 2018), in which the products such as $C_7H_{9,11}NO_{7-8}$, $C_8H_{11}NO_{7-8}$, $C_9H_{13,15}NO_{7-8}$, and $C_{10}H_{15,17,19}NO_{7-8}$ were detected in cloud water, indicating a contribution from monoterpene oxidation.

CHO For CHO formulas in cloud water, a prominent C_{17} peak is observed in all six samples (Fig. S4), in which the most abundant formula is $C_{17}H_{26}O_4$, which also causes a significant peak of O_4 class (Fig. 4). The formula may belong to lipids-like molecule based on the classification in the VK plot (Bianco et al., 2018). Considering the intensive emission of biogenic volatile organic compounds (BVOCs) around the sampling site, the oxidation products of BVOCs may also contribute to the molecular composition. Putman et al. (2012) reported the molecular composition of α-pinene ozonolysis SOA using FT-ICR MS. Including the most abundant $C_{17}H_{26}O_4$, 24.0-39.1% (in term of number fraction) of the CHO formulas in cloud water are corresponding to the yields of α-pinene ozonolysis. In addition, cloud water contains formulas that have been observed in the combustion of coal and biogenic materials. Specifically, 24.2-35.8%, 65.9-77.3%, 50.7-69.3%, and 61.1-76.7% of the CHO formulas in cloud water, by number, were detected in the smoke emitted from the combustion of coal, corn straw, pine branches, and rice straw, respectively (Song et al., 2018), indicating that combustion also potentially contributes to the CHO group in cloud water.

S-containing formulas Most of the CHOS formulas in cloud water have C_{13} or C_{14} peaks (Fig. S4), and $-SO_3$ or $-SO_4$ represent the most abundant classes of CHOS (Fig. 4). We divided the CHOS formulas into two classes according to the O/S ratios: $CHOS_{O/S\geq4}$ and $CHOS_{O/S<4}$. When $O/S \geq 4$, CHOS can be provisionally identified as organosulfates (Lin et al., 2012). The O/S ratios of most of the CHOS formulas (78.9-95.8% in number fraction and 87.5-98.6% in f_{RA}) in cloud water exceed 4. $CHOS_{O/S<4}$ accounts for 1.4-12.5% in f_{RA} of all the CHOS formulas in cloud water, indicating reduced S groups exist in these formulas. Some of them are aliphatic-like, such as $C_{24}H_{42}O_3S$, $C_{29}H_{52}O_3S$. Some are aromatic-like with high DBE values, such as $C_6H_6O_3S$, which may be an aromatic ring bearing a $–SO_3H$ group. Some of them may have more than one aromatic ring, such as $C_{17}H_{16}O_3S$, $C_{20}H_{18}O_3S$. Note that the aromaticity of these formulas cannot be identified accurately using AI_{mod} values since the value is a conservative method to evaluate the aromaticity (Koch and Dittmar, 2006). The presence of aromatic structure in these molecules indicates that they are likely emitted by anthropogenic sources or biomass burning (Ervens et al., 2011). Most of the CHONS formulas clearly peak at C_{10} (Fig. S4) and have more than seven O atoms (Fig. 4), allowing the presence of both sulfate and nitrate functional groups. These species can be nitrooxy organosulfates, which have been widely observed in the cloud/fog water (Zhao et al., 2013; Brege et al., 2018) and aerosols (Wozniak et al., 2014). For the detected S-containing formulas in cloud water, 6.2-23.0%, 15.9-33.6%, and 15.0-34.3% in terms of number fraction are corresponding to the molecules in particles emitted by burning of corn straw, pine branches, and rice straw, respectively, while 21.2-43.1% (37.3% on arithmetic mean) are corresponding to that in coal combustion (Song et al., 2018), indicating coal combustion contributes to S-containing formulas in cloud water more significantly compared with that to CHO and CHON.

3.4 Organic matter formed by in-cloud aqueous-phase reactions

3.4.1 Formation of dinitrophenols

To investigate the formation of molecules in cloud water, we compared the molecular formulas in cloud water with $PM_{2.5}$. For CHON, the $–N_1O_8$ or $–N_1O_7$ formulas are also abundant in $PM_{2.5}$ samples (Fig. S5), suggesting that these formulas may not only form in cloud water. However, the formulas with high intensities, e.g., $C_8H_8N_2O_5$, $C_7H_7N_2O_5$, and $C_6H_4N_2O_5$ in cloud water, are not detected in $PM_{2.5}$ samples. Earlier studies have found that over one-third of the nitrophenols and the majority of the dinitrophenols are contributed by secondary formation (Harrison et al., 2005). The transforming from 2-nitrophenol into 2,4-dinitrophenol was also observed during cloud events (Lüttke et al., 1997; Lüttke et al., 1999). Aqueous-phase radical nitration of mononitroaromatics has been reported to be a potential pathway to form dinitroaromatics (Lüttke et al., 1999; Kroflic et al., 2015; Cook et al., 2017). This implies that in-cloud aqueous-phase reactions represent the main formation pathway of dinitrophenols at the observation site.

Generally, CHON in cloud water has a higher f_{RA} during the nighttime (56.2-65.3%) compared with the daytime (43.6-54.9%) (Table S2), which is consistent with the previous findings for aerosols (O'brien et al., 2014). Particularly, the relative abundance of possible dinitrophenols formulas increases significantly at night. The representative formulas including $C_6H_4N_2O_5$, $C_7H_6N_2O_5$, and $C_8H_8N_2O_5$ account for 0.5%, 0.1%, 0.4%, 0.7%, 2.1%, and 14.8% of CHON in f_{RA} for samples CL12-17, respectively. Previous studies have revealed the differences in atmospheric chemistry between day and night. The daytime chemistry is dominant by photochemical reactions, in which OH radical oxidation and photolysis represent the main processes in the aqueous phase (Ervens et al., 2011). While during the nighttime, NO_3 radical is dominant (Herrmann et al., 2010). The radical nitration of phenols by NO_2 and NO_3 radicals leads to the formation of nitrophenols (Harrison et al., 2005). Thus the high abundance of $–N_2O_5$ formulas may attribute to the aqueous-phase formation of these possible dinitrophenols at night. While during the daytime, the direct photolysis of nitrophenols would release NO_2^- and NO_3^- (Harrison et al., 2005; Chen et al., 2005; Bejan et al., 2006), causing the observed low relative abundance of dinitrophenols. A recent study conducted at the Field Museum Tama Hill, Japan observed that aerosol liquid water accelerated the formation of water-soluble organic nitrogen (WSON), especially at night, and the authors suggested that aqueous-phase reactions between NH_4^+/reactive nitrogen and BVOCs at night contribute significantly to WSON in particles (Xu et al., 2020). While in this study, the elevated abundance of N-containing organics in cloud water at night is mainly contributed by dinitrophenols and their derivatives, which are the products of radical nitration in the aqueous phase, indicating another possible pathway for the generation of WSON.

3.4.2 Formation of oxygenated organic matter and organosulfates

For CHO, the most abundant $C_{17}H_{26}O_4$ in cloud water was also detected in α-pinene ozonolysis SOA as we discussed in Section 3.3. However, it was not detected in $PM_{2.5}$ in this study, indicating that it may mainly form through in-cloud aqueous-phase reactions. Interestingly, CHO formulas in $PM_{2.5}$ samples peak at O_8 (Fig. S5), which is significantly higher than cloud water (Fig. 4). This is consistent with the higher OS_C values appearing in $PM_{2.5}$ samples. Some highly oxidized molecules (HOMs, $O/C \geq 0.6$), e.g., $C_7H_{10}O_5$, $C_8H_{12}O_5$, $C_{13}H_{24}O_{13}$, are identified in cloud water. However, the HOMs in cloud water only account for 12.6-32.2% of the total CHO in terms of f_{RA}. A higher f_{RA} of CHO is observed during the daytime (Fig. 1b), which may result from the photochemical oxidation (e.g., the oxidation of volatile organic compounds) (Ehn et al., 2014; Wang et al., 2017) and photolysis of N- and S-containing formulas in cloud water under the illumination (Brüggemann et al., 2020; Laskin et al., 2015).

For CHOS formulas, the most abundant functions classes are similar between cloud water and $PM_{2.5}$. No statistical difference of the fraction of organosulfates is observed between cloud water and $PM_{2.5}$ except for a low f_{RA} (69.5%) of organosulfates in P2 sample, which may indicate the wide variety of formation mechanisms (e.g., acid-catalyzed particle-phase reactions, nucleophilic substitution reactions in aqueous phase) and/or other common sources of CHOS in cloud water and $PM_{2.5}$ (Brüggemann et al., 2020), but possible slightly enhanced formation of that in cloud water. S-containing formulas in cloud water are abundant at night (8.4-21.0% in f_{RA}) compared with daytime (4.3-10.2% in f_{RA}). We note that the f_{RA} of $CHOS_{O/S\geq4}$ at night (92.9-98.6%) is slightly higher than that during the daytime (87.5-92.2%). Thus the formation of organosulfates likely enhances at night. In contrast, the photochemical oxidation of organosulfates results in the release of inorganic sulfate during the daytime, causing a low fraction of organosulfates.

4 Conclusions and Atmospheric Implications

This study investigated the molecular characteristics of cloud water using ESI FT-ICR MS and highlighted the crucial effects of in-cloud aqueous-phase reactions on the molecular composition and characteristics of cloud water. Thousands of formulas, including CHO, CHON, CHOS, and CHONS, were detected, in which CHON and CHO formulas are dominant. Previous studies expected a higher oxidation state of organics in cloud water. However, no statistical difference between cloud water and $PM_{2.5}$ is observed in this study. While a higher OS_C of detected formulas, especially CHO, appears in $PM_{2.5}$ samples. Most formulas are identified as aliphatic and olefinic species, CHON and their aromatic structures are abundant in cloud water.

Our results showed that N-containing formulas are the most abundant in cloud water, which may mainly relate to the aqueous-phase formation. Dinitrophenols and derivatives exist abundantly in cloud water, especially at night, suggesting the contribution of radical nitration on N-containing organics in cloud water. Meanwhile, organosulfates are also detected in cloud water, and a slightly higher fraction is observed at night, suggesting the dark-reaction formation. Nitroaromatic compounds have been identified as one of the major light absorption components in brown carbon (Li et al., 2020b) and regarded as the phytotoxin as well as suspected carcinogenic materials (Harrison et al., 2005). Organosulfates are thought to affect the physicochemical properties of aerosol, such as hygroscopicity and cloud condensation nuclei formation potential (Brüggemann et al., 2020). Thus the aqueous-phase formation of N-containing organics and organosulfates at night are worth targeting. We noted that the database for the diurnal variation analysis is limited in this study, but the results provided novel insights into the diurnal variation of cloud chemistry. Firm conclusions warrant future field studies.

Supplement. Supporting information includes one text (Text S1), five figures (Fig. S1-S5), and six tables (Table S1-S6) related to the manuscript.

Data availability. The raw data of this study can be obtained by contacting the corresponding author.

Author contributions. XB and GZ designed the research with input from XW, PP and GS. YF, FJ and YY collected samples. WS, BJ carried out the sample pretreatment and instrumental analysis under the guidance of YL. WS processed data when YF and XL gave constructive discussion. WS wrote the manuscript, and XB, GZ and YF interpreted data and edited the manuscript. JC, DC, and JO had an active role in supporting the sampling work. All authors contributed to the discussions of the results and refinement of the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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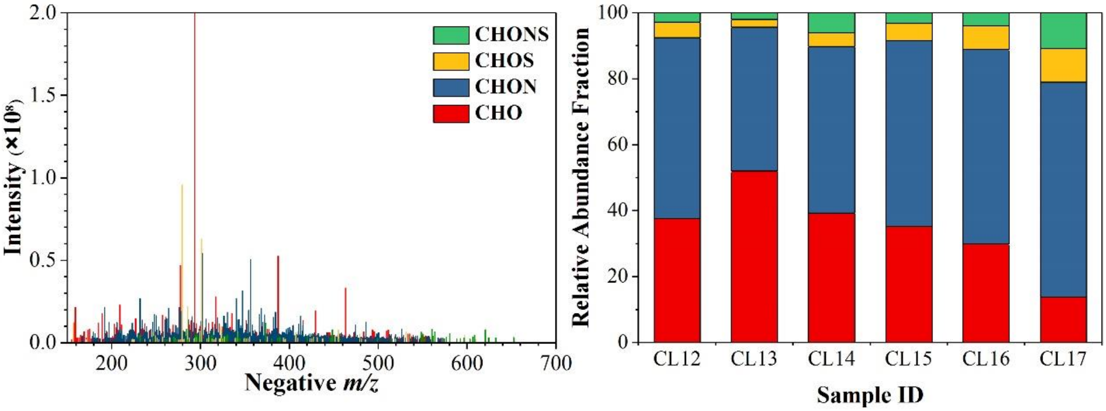

Figure 1. Reconstructed FT-ICR mass spectra of a typical sample, CL12 (a); Relative abundance fraction of the four groups (CHO, CHON, CHOS, and CHONS) in the six cloud water samples (b).

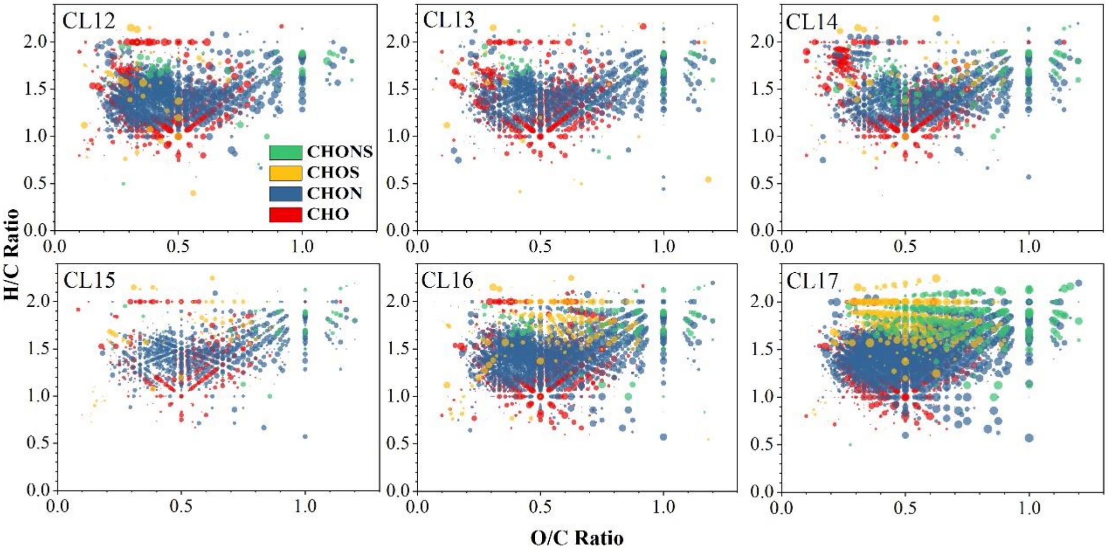

Figure 2. Van Krevelen diagrams as a function of four groups (CHO, CHNO, CHOS, and CHNOS) for the cloud water samples.
665 **The larger point in the diagram represents the higher relative abundance of the formula.**

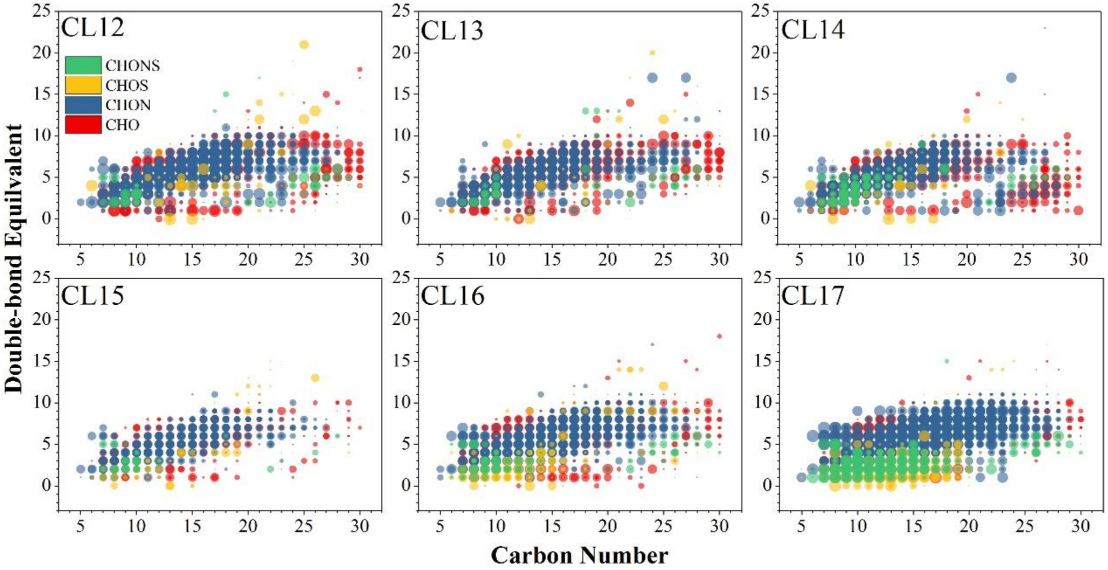

Figure 3. The double bond equivalent (DBE) versus the number of C atoms for unique molecular formulas in cloud water samples. The larger point in the diagram represents the higher relative abundance of the formula.

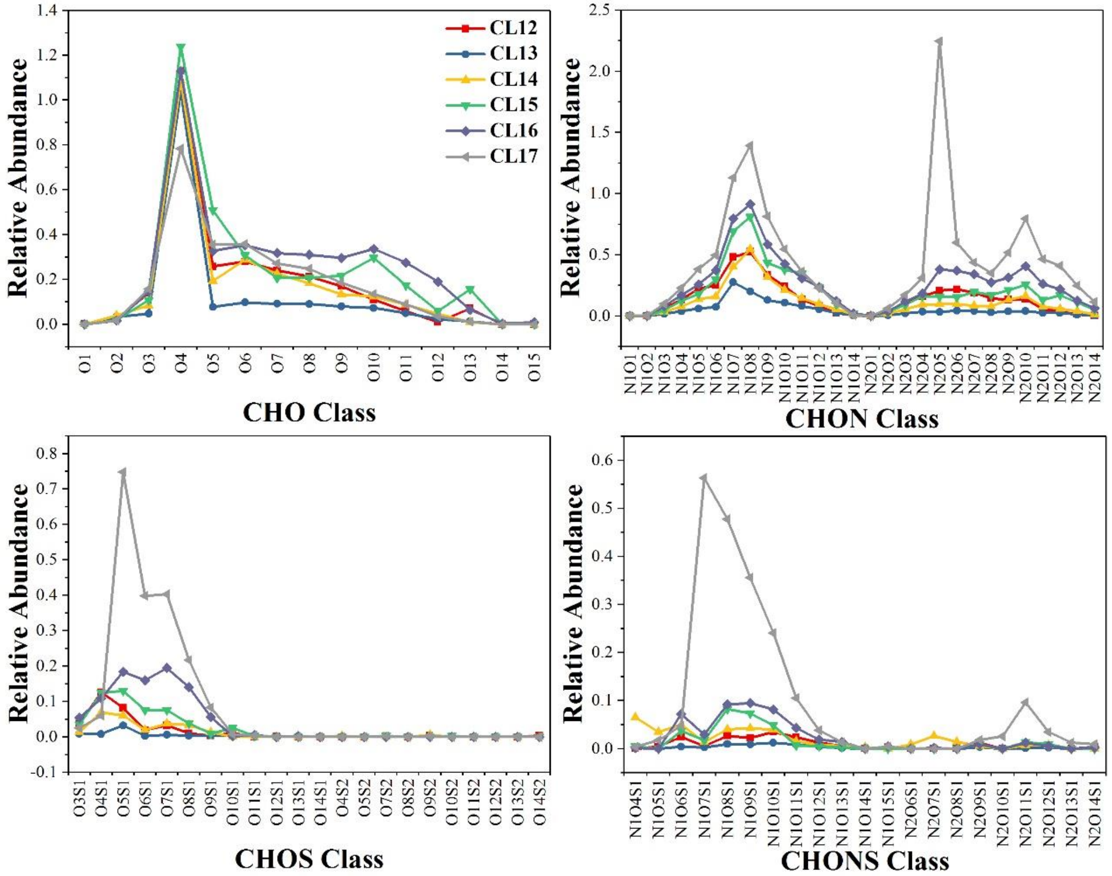

Figure 4. Relative abundance of the categories of CHO, CHON, CHOS, and CHONS formulas according to the characteristic atom groups within the molecular formulas in cloud water.

Table 1. The sampling interval, liquid water content (LWC, g m^{-3}), and pH of each sample.

Time	Sample ID	Sampling Interval	LWC	pH
Daytime	CL12	2018/5/11 10:15-12:40	0.17	4.16
	CL13	2018/5/11 12:40-15:00	0.17	4.22
	CL14	2018/5/11 15:00-18:00	0.19	4.37
Nighttime	CL15	2018/5/11 18:00-21:00	0.17	4.28
	CL16	2018/5/11 21:00-24:00	0.16	4.18
	CL17	2018/5/12 00:00-08:15	0.12	4.13