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 insights into aqueous chemistry. Field measurements were conducted at Mt. Tianjing in southern China in May, 2018. There are thousands of formulas (C5–30H4–55O1–15N0–2S0–2) identified in cloud water by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). CHON formulas (formulas containing C, H, O, and N elements; the same is true for CHO and CHOS) represent 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 a 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 in the oxidation state is observed between cloud water and interstitial PM2.5. 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 −N2O5 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- or 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 aerosol (aqSOA) forming in the in-cloud aqueous-phase processes significantly contributes to the total secondary organic aerosol (SOA), with a negative impact on the visibility, human health, and climate (Ge et al., 2012; Huang et al., 2018; Schurman et al., 2018; T. Li et al., 2020; 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 monocarboxylic 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 amines (Bianco et al., 2015b), 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 (Lütke et al., 1997, 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 or 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, 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 attributed 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 being 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 quantities, 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; Brüggemann et al., 2020). The main radical in the atmosphere at night is NO3·, which can form from the gas-phase reaction between NO2 and O3 and then enter cloud droplets. The reactions between NO3· 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 (Kroflc et al., 2015). Non-radical reactions also lead to the formation of N-containing organics. Carboxyls 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, 2011, 2018; Kua et al., 2011). In addition, the nucleophilic addition of nitrate to the isoprene-derived epoxydiol can effectively form organonitrates (Darrer 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 the acid-catalyzed ring opening of epoxides, sulfate esterification, nucleophilic substitution of alcohols with sulfuric acid, and sulfoxyl radical reactions, have been proposed in recent years (Brüggemann et al., 2020). The non-
radical reactions in the aqueous phase also include hydrolysis, hydration, the Fenton reaction, translation metals reactivity with organics, probably ozone reactivity at the gas or liquid interface, and so on (McNeill, 2015; Deguillaume et al., 2005; Herrmann et al., 2015).

To date, only a few studies have reported on 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 a.s.l. – above sea level) located at the Tianjing Mountain in southern China (Fig. S1 in the Supplement). 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 Cloud water Collector, version 2 (CASCC2), was used for cloud water collection (Demos 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 Manufacturing 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 a 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):

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

where $\Delta m$ represents the mass of the sample (g), and $\Delta t$ represents the sampling interval (minutes), $\eta$ 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 8 to 13 May 2018. To investigate the molecular characteristics of the organics and the effects of aqueous-phase processes, six samples collected from 11 to 12 May (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 in air masses origin (Figs. 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 11 May, while the other three samples (CL15, CL16, and CL17) could be roughly regarded as nighttime samples, although CL15 was partly collected before sunset.

Quartz fiber filters (Whatman plc, UK) were used to collect interstitial PM$_{2.5}$ samples at the same site. A PM$_{2.5}$ sampler (PM-PUF-300; Mingye Technology Co., Ltd., China) at a flow rate of 300 L min$^{-1}$ was used for sampling. The sampling interval of PM$_{2.5}$ was roughly 24 h. In total, two samples of PM$_{2.5}$ were collected within 2 d (P1 from 11 May at 10:14 LT to 12 May at 09:48 LT; P2 from 12 May at 10:15 LT to 13 May at 10:15 LT) during the investigated cloud events. The samples were stored at −20°C 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 as with cloud water samples.

For FT-ICR MS analysis, water-soluble organic compounds in cloud water and PM$_{2.5}$ extracts were isolated using solid-phase extraction (SPE; Zhao et al., 2013; Bianco et al., 2018). The SPE cartridges (Strata-X; Phenomenex, USA) were preconditioned 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 ace-

| Time      | Sample ID | Sampling interval | LWC  | pH   |
|-----------|-----------|-------------------|------|------|
| Daytime   | CL12      | 2018/5/11 10:15–12:40 | 0.17 | 4.16 |
| Daytime   | CL13      | 2018/5/11 12:40–15:00 | 0.17 | 4.22 |
| Daytime   | 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 |
| Nighttime | CL16      | 2018/5/11 21:00–24:00 | 0.16 | 4.18 |
| Nighttime | CL17      | 2018/5/12 00:00–08:15 | 0.12 | 4.13 |

Table 1. The sampling interval, liquid water content (LWC; grams per cubic meter), and pH of each sample.
tonitriile, methanol, and 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 PM2.5 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 Daltonics GmbH & Co. KG, Bremen, Germany) equipped with a 9.4 T refrigerator, actively shielded superconducting magnet (Bruker France S.A.S., Wissembourg, France) and a ParaCell analyzer cell was used for the analysis in this study. An electrospray ionization (ESI) source (Bruker Daltonics GmbH & Co. KG, 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). \([\text{M-H}]^-\) 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 constiution 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 °C, and capillary voltages of +4500 V and the end plate offset –500 V were used for the ESI source. The optimized mass for quadrupole (Q1) was 170 Da. An argon-filled hexapole collision pool was operated at 2 MHz and 1400 V pp (volts; peak to peak) RF (radio frequency) amplitude. The time of flight was 0.7 ms, the mass range was 150–800 Da, and the ion accumulation time was 0.1 s. A total of 128 continuous 4 mega-data FT-ICR transients were co-added to enhance the signal-to-noise ratio and dynamic range. A typical mass-resolving power \((m/\Delta m \; \text{50%})\), where \(\Delta m \; \text{50%}\) 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 (parts per million) 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., \(C_{16}H_{31}O_2\), \(C_{17}H_{33}O_2\), \(C_{18}H_{35}O_2\), etc., that was only separated by \(-\text{CH}_2\) 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 GmbH & Co. KG, Bremen, Germany; 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 \(C_{6}H_{10}O_9N_6S_3\) was obtained. Future selecting was applied using the following criteria to exclude formulas not detected frequently in natural materials: \(O/C \leq 1.2\), \(0.3 \leq H/C \leq 2.25\), \(N/C \leq 0.5\), \(S/C < 0.2\), \(2C + 2 > H\), \(C + 2 > O\), 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 \((C_{6}H_{10}O_9N_6S_3)\) was calculated as follows:

\[
\text{DBE} = \frac{(2c + 2 - h + n)}{2}.
\]

The oxidation state of carbon atoms (\(O_{\text{SC}}\)) was calculated as follows, based on the approximation described in Kroll et al. (2011) and Brege et al. (2018):

\[
O_{\text{SC}} \approx 2 \times o/c - h/c - 5 \times n/c - 6 \times s/c.
\]

The modified aromaticity index \((\text{AI}_{\text{mod}})\) was first proposed by Koch and Dittmar (2006) to evaluate the aromaticity of high-resolution mass data, as follows:

\[
\text{AI}_{\text{mod}} = \frac{(1 + c - 0.5 \times o - s - 0.5 \times h)}{(c - 0.5 \times o - s - n)}.
\]

The 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. So, 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):

\[
O/C = \frac{\text{O} \times \text{Int}_i}{\sum (\text{O} \times \text{Int}_i)}
\]

\[
H/C = \frac{\text{H} \times \text{Int}_i}{\sum (\text{H} \times \text{Int}_i)}
\]

\[
\text{DBE}_i = \frac{\text{DBE} \times \text{Int}_i}{\sum (\text{DBE} \times \text{Int}_i)}
\]

\[
O_{\text{SC}} = \frac{\text{O}_{\text{SC}} \times \text{Int}_i}{\sum (\text{O}_{\text{SC}} \times \text{Int}_i)}
\]

where \(\text{Int}_i\) 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_2$$O_4^{2−}$) were detected using an ion chromatograph (883 Basic IC plus; Metrohm AG, Switzerland) with suppressed conductivity detection and a Metrosep C 4 – 150/4.0 column (Metrohm AG, Switzerland) for cations and a Metrosep A Supp 5 – 150/4.0 column (Metrohm AG, Switzerland) for anions.

The 72h back trajectories were displayed using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT; https://ready.arl.noaa.gov, last access: 11 November 2021) (Stein et al., 2015; Lin et al., 2017). The endpoint of the trajectory in the model was set to a height of 1800 m a.s.l. 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, 2646, 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 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).

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

3.2.1 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 in 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 (Figs. 2 and 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 a 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 applicable 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) and range $-0.84$ to $-0.61$ in PM$_{2.5}$ (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 the P2 sample). A similar phenomenon is also observed in CHOS. This is not consis-
influence the cloud chemistry. However, since the database in the origin of air masses and the aging processes may also not exclusively affected by the illumination. The difference in the oxidation degree of the organics in cloud water is limited, the further conclusion cannot be drawn based on them.

### 3.2.2 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 a relative-abundance-weighted average, H/C ratios in cloud water range from 1.44 to 1.49, with no statistical difference when compared to 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 (Fig. 2), indicating that they may have higher saturation compared with CHO and CHON. On a weighted average, DBE values in cloud water range from 5.10 to 5.70 (Table S4), which are 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 $A_{\text{mod}}$. 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 $f_{\text{RA}}$) are assigned as aliphatic or olefinic molecules (Table S6). The $f_{\text{RA}}$ 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 structures 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 emissions, 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 that 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 $f_{\text{RA}}$) 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, CA, 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 $f_{\text{RA}}$ of aromatic structures in CHON significantly, which may be related to the aqueous-phase reactions (see the detailed discussion in Sect. 3.4).

3.3 Molecular composition of cloud water

3.3.1 CHON

In cloud water, CHON formulas show no prominent carbon number peaks, except for 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 includes C$_{17}$H$_{17}$NO$_8$, C$_{15}$H$_{19}$NO$_8$, C$_{17}$H$_{27}$NO$_7$, C$_{8}$H$_{11}$NO$_7$, and so on. More than 77.7% of the CHON formulas in $f_{\text{RA}}$ in all six samples have O/N ratios

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exceeding 3, indicating that the N atoms in these molecules may be in the \(-\text{NO}_3\) functional group (Zhao et al., 2013). Samples CL12–16 show no prominent peak of the function classes in the N2 category, but a dominant peak of the \(-\text{N}_2\text{O}_5\) class is observed in CL17 (Fig. 4), where \(\text{C}_7\text{H}_4\text{N}_2\text{O}_5\) and \(\text{C}_7\text{H}_4\text{N}_2\text{O}_3\) 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 to 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 CHON molecules in cloud water correspond to the coal combustion emission, suggesting its smaller contribution to the molecular composition of cloud water. Note that the comparison is only based on the molecular formulas given by FT-ICR MS, and the isomeride can not be distinguished; thus, the results only represent a possible relationship with the different sources. Additionally, some N-containing molecules were also detected in monoterpene SOA (Park et al., 2017; Zhang et al., 2018), in which the products such as C17H16O3S and C20H19O3S are detected in cloud water, indicating a contribution from monoterpene oxidation.

### 3.3.3 S-containing formulas

Most of the CHOS formulas in cloud water have \(\text{C}_{13}\) or \(\text{C}_{14}\) peaks (Fig. S4), and \(-\text{SO}_3\) or \(-\text{SO}_4\) represent the most abundant classes of CHOS (Fig. 4). We divided the CHOS formulas into the following two classes according to the O/S ratios: \(\text{CHOSO}_2\text{S}_{\geq 4}\) and \(\text{CHOSO}_2\text{S}_{<4}\). 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 \(f_{\text{RA}}\)) in cloud water exceed 4. CHOS\text{O}_2\text{S}_{<4} accounts for 1.4\%–12.5\% in \(f_{\text{RA}}\) of all the CHOS formulas in cloud water, indicating that reduced S groups exist in these formulas. Some of them are aliphatic-like, such as \(\text{C}_{24}\text{H}_{12}\text{O}_3\text{S}\) and \(\text{C}_{29}\text{H}_{20}\text{O}_{2}\text{S}\). Some are aromatic-like with high DBE values, such as \(\text{C}_{8}\text{H}_4\text{O}_3\text{S}\), which may be an aromatic ring bearing a \(-\text{SO}_2\text{H}\) group. Some of them may have more than one aromatic ring, such as \(\text{C}_{17}\text{H}_{16}\text{O}_3\text{S}\) and \(\text{C}_{20}\text{H}_{18}\text{O}_3\text{S}\). Note that the aromaticity of these formulas cannot be identified accurately using AImod values, since the value is a conservative method to evaluate the aromaticity (Koch and Dittmar, 2006). The presence of the 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 \(\text{C}_{10}\) (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 average) are corresponding to that in coal combustion (Song et al., 2018), indicating that coal combustion contributes to S-containing formulas in cloud water more significantly compared to that with 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 PM2.5. For CHON, the \(-\text{N}_1\text{O}_6\) or \(-\text{N}_1\text{O}_7\) formulas are also abundant in PM2.5 samples (Fig. S5), suggesting that these formulas may not only form in cloud water. However, the formulas with high intensities, e.g., \(\text{C}_6\text{H}_8\text{N}_2\text{O}_{5}\), \(\text{C}_7\text{H}_7\text{N}_2\text{O}_{5}\), and \(\text{C}_6\text{H}_4\text{N}_2\text{O}_{5}\) in cloud water, are not detected in PM2.5 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
The transformation from 2-nitrophenol into 2,4-dinitrophenol was also observed during cloud events (Lüttke et al., 1997, 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 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 C₆H₄N₂O₅, C₇H₆N₂O₅, and C₈H₈N₂O₅, account for 0.5%, 0.1%, 0.4%, 0.7%, 2.1%, and 14.8% of CHON in RA for samples CL12–17, respectively. Previous studies have revealed the differences in atmospheric chemistry between day and night. The daytime chemistry is dominated by photochemical reactions in which OH• oxidation and photolysis represent the main processes in the aqueous phase (Ervens et al., 2011), while, during the nighttime, the NO₃• is dominant (Herrmann et al., 2010). The radical nitration of phenols by NO₂• and NO₃• leads to the formation of nitrophenols (Harrison et al., 2005). Thus, the high abundance of −N₂O₅ formulas may be attributed to the aqueous-phase formation of these possible dinitrophenols at night, while, during the daytime, the direct photolysis of nitrophenols would release NO₂ and NO₃ (Harrison et al., 2005; Chen et al., 2005; Bejan et al., 2006), causing the observed low relative abundance of dinitrophenols. A recent study conducted in the Field Museum at 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 NH₄+ or reactive nitrogen and BVOCs at night contribute significantly to WSON in particles (Xu et al., 2020). 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 C₁₇H₂₆O₄ in cloud water was also detected in α-pinene ozonolysis SOA, as we discussed in Sect. 3.3. However, it was not detected in PM₂.₅ in this study, indicating that it may mainly form through in-cloud aqueous-phase reactions. Interestingly, CHO formulas in PM₂.₅ samples peak at O₈ (Fig. S5), which is significantly higher than
cloud water (Fig. 4). This is consistent with the higher OSC values appearing in PM$_{2.5}$ samples. Some highly oxidized molecules (HOMs; O/C $\geq$ 0.6), e.g., C$_7$H$_{10}$O$_5$, C$_8$H$_{12}$O$_5$, and C$_{13}$H$_{25}$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 the 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 in the fraction of organosulfates is observed between cloud water and PM$_{2.5}$, except for a low $f_{RA}$ (69.5 %) of organosulfates in the P2 sample, which may indicate the wide variety of formation mechanisms (e.g., acid-catalyzed particle-phase reactions and 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 also the possible slightly enhanced formation of that in cloud water. S-containing formulas in cloud water are abundant at night (8.4 %–21.0 %) compared with daytime (4.3 %–10.2 %) in $f_{RA}$. We note that the $f_{RA}$ of CHOSO$_2$/S$_2$$\geq$4 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 OSC of detected formulas, especially CHO, appears in PM$_{2.5}$ samples. Most formulas are identified as being aliphatic and olefinic species, and 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 be mainly related to the aqueous-phase formation. Dinitrophenols and their 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 being one of the major light absorption components in brown carbon (X. Li et al., 2020) and are regarded as being the phytotoxin and 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 in cloud chemistry. Firm conclusions warrant future field studies.

Data availability. The data set related to this work can be accessed via https://doi.org/10.5281/zenodo.5676489 (Sun, 2021).

Supplement. Supporting information includes one text (Text S1), five figures (Figs. S1–S5), and six tables (Tables S1–S6) related to the paper. The supplement related to this article is available online at: https://doi.org/10.5194/acp-21-16631-2021-supplement.

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