Molecular characterisation of ambient aerosols by sequential solvent extractions and high-resolution mass spectrometry

Jingyi Zhang\textsuperscript{A,B}, Bin Jiang\textsuperscript{A,C}, Zhiheng Wang\textsuperscript{A}, Yongmei Liang\textsuperscript{A,D}, Yahe Zhang\textsuperscript{A}, Chunming Xu\textsuperscript{A} and Quan Shi\textsuperscript{A,D}

\textsuperscript{A}State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China.
\textsuperscript{B}Patent Examination Cooperation Centre of the Patent Office, State Intellectual Property Office (SIPO), Guangzhou 510530, China.
\textsuperscript{C}State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China.
\textsuperscript{D}Corresponding authors. Email: ymliang@cup.edu.cn; sq@cup.edu.cn

Environmental context. Organic compounds generally make a large contribution to ambient aerosol fine particles, and can influence atmospheric chemistry. Solvent extraction before mass spectrometry is widely used for the determination of organic compounds in aerosols, but the molecular selectivity of different solvents is unclear. We extracted an aerosol sample with various solvents and show how the organic compound profile obtained by mass spectrometry changes depending on the extracting solvent.

Abstract. For a comprehensive characterisation of organic compounds in aerosols, samples collected on a hazy day from Beijing were sequentially extracted with various solvents and analysed by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Electrospray ionisation (ESI) was used for the MS analysis. Aerosol samples were extracted in an apolar-to-polar solvent order of \textit{n}-hexane (\textit{n}-C\textsubscript{6}), dichloromethane (DCM), acetonitrile (ACN) and water, and also extracted in reverse sequence. The separated fractions were defined as non-polar, low-polarity, mid-polarity and high-polarity organic compounds respectively. Approximately 70\% of the total organic carbon (TOC) was extractable, of which the water-soluble organic carbon (WSOC) and non-polar organic carbon accounted for 30 and 25\% of the TOC respectively. Non-polar and low-polarity compounds with a high degree of molecular condensation such as oxidised polycyclic aromatic hydrocarbons (PAHs) and nitrogen-containing compounds (CHN) were extracted by \textit{n}-C\textsubscript{6} and DCM. Water-soluble organic matter (WSOM) was predominant with aliphatic and aromatic organosulfates (CHOS) and nitrooxy-organosulfates (CHONS). Most oxygen-containing compounds (CHO) and oxygen- and nitrogen-containing compounds (CHON) with high double-bond equivalents (DBEs) and long carbon chains tended to be extracted into organic solvents.

Additional keywords: molecular sensitivity, organic compounds, organosulfates.

Introduction
Organic aerosols are an important part of ambient aerosols. Approximately 10–90\% of total aerosol mass comprises organic material (Kanakidou et al. 2005; Jimenez et al. 2009). In addition to producing poor health effects and affecting atmospheric visibility (Chameides et al. 1999; Okada et al. 2001; Schichtel et al. 2001; Yadav et al. 2003), organic aerosols also have a significant impact on climate and biogeochemical cycling (Crutzen and Andreae 1990; Andreae and Crutzen 1997; Jacobson 2000; Ramanathan et al. 2001; Andreae and Gelencser 2006; Booth et al. 2012; Bond et al. 2013). The composition of organic aerosols is very complex, with tens of thousands of molecular species (Hildemann et al. 1991; Rogge et al. 1993; Nolte et al. 1999; Tolocka et al. 2004; Inuma et al. 2007b; Surratt et al. 2007). Volatile organic compounds (VOCs) in aerosols such as alkanes, aromatics and monooxacylic acids have been widely analysed so far (Rogge et al. 1998; Rudich 2003; Falkovich et al. 2005; Hoffer et al. 2006; Rudich et al. 2007), but for most semi-volatile and non-volatile species, the detailed molecular composition is still unclear. Recently, ultrahigh-resolution mass spectrometers, such as Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and Orbitrap MS, have enabled molecular characterisation of semi-volatile and non-volatile organic macromolecules in aerosols by their high resolution and mass accuracy (Reentsma et al. 2006; Reinhardt et al. 2007; Muller et al. 2009; Schmitt-Kopplin et al. 2010; Lin et al. 2012a, 2012b; Putman et al. 2012; Jiang et al. 2014).

Organic compounds on fine particles in aerosols should be extracted with solvents for MS characterisation. However, the solvents used for the extraction can differ. Most studies relevant to organic aerosols analysis by high-resolution MS have focussed on water-soluble organic matter (WSOM). These
substances, owing to their resemblance to aquatic and terrestrial fulvic and humic acids, are often called humic-like substances (HULIs). HULIs have attracted much attention and have been analysed because they have good hygroscopic properties and can act as cloud condensation nuclei (CCN), which affect global climate (Lin et al. 2010a; Fan et al. 2012; Song et al. 2012; Zheng et al. 2013; Cheng et al. 2016; Voliotis et al. 2017). Meanwhile, fewer studies have focussed on the detailed molecular composition of water-insoluble matter, which accounts for 10–70 wt-% (Zappoli et al. 1999; Kleefeld et al. 2002; Sullivan et al. 2004; Decesari et al. 2007) of aerosol organic matter. Soluble organic compounds of the PM$_{2.5}$ (particles with aerodynamic diameter of ≤2.5 μm) samples collected from the campus of Tsinghua University in Beijing account for 55% of the aerosol organic matter extracted with a mixture of n-hexane, dichloromethane and acetonitrile (1:1:1 by volume) (Cheng et al. 2012). Compared with water or acetonitrile, pyridine can extract a molecularly unique fraction of the organic matter. The fraction was less polar, more aliphatic, and contained sulfur in the elemental formulae (Willoughby et al. 2014). Some low-volatility polycyclic aromatic hydrocarbons (PAHs) and heteroatomic PAHs with high molecular weight were identified in aerosols extracted with dichloromethane (DCM) (Jiang et al. 2014). These PAHs contain a large number of double bonds, have low H/C ratios and have UV light-absorbing properties, and may contribute to the brown carbon in aerosols (Jiang et al. 2014).

In the present study, sequential solvent extracts of a typical aerosol sample in Beijing collected on a hazy day were characterised by FT-ICR MS coupled with negative-ion electrospray ionisation (ESI⁻) and positive-ion ESI (ESI⁺). The purpose of this study is to obtain a greater understanding of the chemical composition and molecular characteristic of different compounds in aerosols and also to provide guidance for the selection of extraction methods in future work.

**Experimental**

**Sample collection**

The sampling was carried out on the roof of a five-storey building on the campus of China University of Petroleum Beijing (CUPB). The building is ~18 m above ground and the campus is located in a northern suburb of Beijing that is primarily a residential and commercial area without major industrial sources. A high-volume aerosol sampler (TH-1000 series, Tianhong Corp., Wuhan, China) was used to collect PM$_{2.5}$ particles on prebaked microquartz fibre filters. The studied ambient sample was collected on 9 December 2014 for 24 h at a flow rate of 1.05 m$^3$ min$^{-1}$. The filter was weighed before and after sample collection of PM$_{2.5}$. The filter sample was stored at −20 °C before analysis.

**Solvent extraction**

Single-step solvent extractions were carried out with n-hexane (n-C$_6$), DCM, acetonitrile (ACN) and water separately. Analytical-grade n-C$_6$, DCM and ACN were purified by distillation using a rotating band distillation apparatus before use. Ultra-purified water was purchased from Fisher Scientific (USA). Sequential solvent extractions were carried out by forward (apolar-to-polar) and reverse sequential extraction (polar-to-apolar). For the forward sequential extraction, the process was as follows: a 10-cm$^2$ filter (cut from the whole sample filter, corresponding to 36 m$^3$ sampled air) was extracted twice with 10 mL n-C$_6$ for 15 min in an ultrasonic bath, followed by filtration using a 0.45-μm Teflon syringe filter to remove the insoluble suspension. The extract was dried with a stream of nitrogen to obtain the n-C$_6$ extract. The insoluble suspension on the filter was then extracted twice with 10 mL DCM for 15 min in an ultrasonic bath followed by filtration using a 0.45-μm Teflon syringe filter to remove the insoluble suspension. The extract was dried with nitrogen to obtain the DCM extract. The same process was repeated with ACN and water to obtain the ACN extract and the water extract respectively. The reverse sequential extractions used the solvent sequence: water, ACN, DCM and n-C$_6$. Organic solvent extracts were blown dry with nitrogen and stored at −20 °C before analysis.

**Organic carbon analysis**

Organic carbon (OC) was analysed using a 2001A-type aerosol OC/EC analyser (US Desert Research Institute). The solid fraction was dissolved in 1 mL of the appropriate solvent, 40 μL of the mixture was sprayed onto a quartz film, blown dry with nitrogen and then analysed. Determination of the OC content of water-soluble organic carbon (WSOC) on a filter was carried out as follows: the 3-cm$^2$ filter was extracted for 15 min in an ultrasonic bath with 4 mL ultrapure water followed by filtration using a 0.45-μm Teflon syringe filter (Macherey-Nagel) to remove insoluble suspensions. A total of 80 μL of the mixture was sprayed onto the quartz film, and then analysed. The OC detection method follows the ACE-Asia warming procedure (Wu et al. 2012). OC blank samples associated with the solvent residue were also analysed. No OC was detected in the blank samples.

**FT-ICR MS analysis**

All of the extracts of the aerosol samples were analysed using a Bruker Apex-Ultra FT-ICR mass spectrometer equipped with a 9.4-T superconducting magnet. Before analysis, each organic solvent extract was re-dissolved in 1 mL of the corresponding extraction solvent. Then, 20 μL of each organic solvent extract was dissolved in 1 mL of extraction solvent/methanol (1:3) for analysis. The water extracts were acidified to pH 2 and then loaded on to a preconditioned solid-phase extraction (SPE) cartridge (Oasis HLB, Waters, Milford, USA) for desalting. The majority of inorganic ions and low-molecular-weight organic molecules such as some isoprene-derived organosulfates and sugars should not be retained by the cartridge (Lin et al. 2010b). The organic compounds retained on the cartridge were eluted using 12 mL methanol. The eluate was immediately evaporated to dryness under a gentle nitrogen stream. A 20-μL aliquot of the extracts was dissolved in 1 mL methanol before ESI FT-ICR MS analysis.

Sample solutions were infused via an Apollo II electrospray source at a flow rate of 180 mL h$^{-1}$ with a syringe pump. Operating conditions for the ESI⁻ FT-ICR MS were 3.5-kV spray shield voltage, 4.0-kV capillary voltage and ~320-V capillary column end voltage. Ions accumulated for 0.001 s in a hexapole with 3-V direct current (DC) voltage and 350-V peak-to-peak (Vp-p) radio frequency (RF) amplitude. The optimised mass for quadrupole (Q1) was 180 Da. An argon-filled hexapole collision pool was operated at 5 MHz and 700 Vp-p RF amplitude, in which ions accumulated for 0.5 s. The extraction period for ions from the hexapole to the ICR cell was 1.1 ms. The RF excitation was attenuated at 14.25 dB and used to excite ions over the range 100–800 Da. A total of 128 continuous 4 MB data FT-ICR transients were added to enhance the signal-to-noise ratio and dynamic range. Operating conditions for ESI⁺ FT-ICR MS were −4.0-kV spray shield voltage, −4.5-kV capillary voltage...
and 320-V capillary column end voltage. Ions accumulated for 0.001 s in a hexapole with −1.5 V DC voltage and 350 Vp-p RF amplitude. The optimised mass for quadrupole (Q1) was 170 Da. An argon-filled hexapole collision pool was operated at 5 MHz and 700 Vp-p RF amplitude, in which ions accumulated for 0.3 s. The extraction period for ions from the hexapole to the ICR cell was 1.0 ms. The RF excitation was attenuated at 14 dB and used to excite ions over the range 150–1000 Da. A total of 128 continuous 4M data FT-ICR transients were added to enhance the signal-to-noise ratio and dynamic range.

The mass spectrometer was internally calibrated using a known and highly abundant homologous series of nitrogen-containing compounds in a petroleum mixture, and then recalibrated with the O2 and O7S1 mass series from the mass spectra of the extracts from PM2.5. The molecular composition of weak polar compounds such as water, methanol and ACN, can extract polar compounds whereas polar solvents, such as DCM, can extract weakly polar compounds, whereas polar solvents, such as water, methanol and ACN, can extract polar compounds. It is known that the molecular compositions of different solvent extracts from PM2.5 are significantly different. Weak polar solvents extracted 25 % of TOC, and water extracted 30 % of TOC. From the results of sequential extractions soluble OC accounted for 70–70 % of TOC. In these extractions, non-polar OC accounted for 25 % of TOC, WSOC accounted for 30 %, and 40 % of OC was extracted by organic solvent.

**Molecular composition of extracts from single-step solvent extractions**

It is known that the molecular compositions of different solvent extracts from PM2.5 are significantly different. Weak polar solvents can extract weakly polar compounds, whereas polar solvents, such as water, methanol and ACN, can extract polar compounds in PM2.5. The molecular composition of weak polar compounds has generally not been well characterised so far. Fig. 1 shows the reconstructed ESI– mass spectra of the extracts from PM2.5 from n-C6, DCM, ACN and water separately. The pie charts show the number and the proportion of assigned compounds in the samples. It can be seen that the proportion of CHO class species in the organic solvent extracts decreased with increasing solvent polarity, while the CHOS increased, indicating that the CHOS class species have a stronger molecular polarity. There are significant differences in molecular number and proportion of CHOS class species in ACN and water extracts, which implies that there are different molecular compositions of CHOS class species in these extracts. The comparative analysis of molecular composition is discussed in the sections below.

**Molecular composition of extracts from sequential solvent extractions**

**Class species detected in various extracts**

Fig. 2 shows the relative abundance of various class species of different solvent extracts assigned from ESI–.
Solvent selectivity of PM$_{2.5}$ extraction

FT-ICR mass spectra that represent the composition of molecules with acidic functional groups or neutral nitrogen compounds. The $n$-$C_6$ extracts have abundant O$_x$ (or CHO$_x$, $x=1$–10) class species and a small amount of N$_1$O$_2$ class species. The relative abundance of N$_1$O$_3$, N$_2$O$_4$, and N$_1$O$_3$S$_1$ increased with increasing of solvent polarity, indicating that N$_1$O$_3$, N$_2$O$_4$, and N$_1$O$_3$S$_1$ compounds were more polar, and O$_x$ compounds with more oxygen atoms could be extracted by polar solvents. The O$_x$S$_1$ compounds were only observed from the extracts with polar solvents. With increasing solvent polarity, the double-bond equivalent (DBE) values and the number of oxygen atoms in O$_x$S$_1$ compound increased. The O$_x$S$_1$ compounds with a higher O/C ratio were more easily extracted by water.
Fig. 3. Van Krevelen diagrams of the compounds from different solvent extracts. Compound type classification is according to reference (Hockaday et al. 2009).

Fig. 4. Relative abundance of various class species assigned from positive-ion electrospray ionisation Fourier-transform ion cyclotron resonance (ESI FT-ICR) mass spectra of different solvent extracts.

Fig. 3 presents Van Krevelen diagrams of the compounds detected from different solvent extracts with negative ion ESI (Kim et al. 2003; Wu et al. 2004; Hockaday et al. 2009; Antony et al. 2014). The compounds with a low H/C ratio with a high degree of molecular condensation such as oxygenated PAHs, which are considered as possible components contributing to brown carbon, are extracted mainly by organic solvents, and carbohydrate and tannic acid are almost completely extracted by water.

Fig. 4 shows the relative abundance of various class species of different solvent extracts assigned from ESI+ FT-ICR mass spectra. As expected, nitrogen-containing compounds were predominant, and should be basic nitrogen compounds. Oxygen-containing compounds without nitrogen atoms were also detected; these compounds should have ketone functional groups, which also could be ionised by positive ESI. N-containing species are generated in the ionisation source by Na+ ion addition. In general, with increasing organic solvent polarity, the compounds containing more oxygen were extracted. N1 and N2 compounds were soluble in organic solvents with low polarity, whereas N1O and N1O2 compounds tended to be soluble in polar organic solvents (like DCM and ACN), and were particularly abundant in the ACN extracts. Oxygen-containing compounds tended to form Na+ ion adducts (O1Na1 class species) and the relative abundance of compounds with a high number of oxygen atoms increased with increasing solvent polarity.
Solvent selectivity of PM$_{2.5}$ extraction

Fig. 5. Double-bond equivalent (DBE) versus carbon number distribution for O$_6$S$_1$ class species of different solvent extracts (forward sequential extraction) assigned from negative-ion electrospray ionisation Fourier-transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS).

Fig. 6. Double-bond equivalent (DBE) versus carbon number distribution for O$_5$ class species of different solvent extracts by forward sequential extraction assigned from negative-ion electrospray ionisation Fourier-transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS). Note: the proposed structures are representative possibilities, not determined.
Molecular composition of oxygen- and sulfur-containing (OS) class species

OS class species were present in the negative ion ESI, while absent in positive ion ESI analysis. This indicates the OS compounds have acidic oxygen functional groups instead of sulfones or sulfoxides, which generally have a strong response in positive ion ESI analysis. These compounds include CHOS (O\textsubscript{1}S\textsubscript{1}) and CHONS (N\textsubscript{1}O\textsubscript{1}S\textsubscript{1}) class species. As we know, OS class species are considered organosulfates and nitrooxy-organosulfates, typical secondary pollutants both from anthropogenic and natural sources (Liggio and Li. 2006; Iinuma et al. 2007a; Surratt et al. 2007; Surratt et al. 2008; Schmitt-Kopplin et al. 2010; Darer et al. 2011; Lin et al. 2012b; Tao et al. 2014; Jiang et al. 2016). Recent research reported that more organosulfates with different molecular structures were found on hazy days than on clear days (Jiang et al. 2016). The OS class species can be divided into three categories: aliphatic OS having a low degree of molecular condensation and oxidation (DBE = 0, 1 for OS and DBE = 1, 2 for nitrooxy OS), biogenic OS (DBE = 2, 3 for OS and DBE = 3, 4 for nitrooxy OS), and PAH-derived OS (DBE ≥ 4 for OS and DBE ≥ 5 for nitrooxy OS).

As shown in Fig. 2, O\textsubscript{1}S\textsubscript{1} class species had an x-value starting from 3 and O\textsubscript{2}S\textsubscript{1} class species had a DBE value of 4, corresponding to alkane sulfonates, which are known to exist widely in the atmosphere. The abundant O\textsubscript{2}S\textsubscript{1} class species, which had a high relative abundance, should be organosulfates. To compare the molecular composition of different solvent extracts, DBE versus carbon number distributions for O\textsubscript{2}S\textsubscript{1} class species of different solvent extracts from the forward sequential extraction are shown in Fig. 5. The area of each circle is positively correlated with the relative abundance of each molecule. The O\textsubscript{3}S\textsubscript{1} class species were absent in the n-C\textsubscript{6} extract, confirming the speculation that these compounds are organosulfates (R–SO\textsubscript{4}–R’). Compared with water, the organic solvents DCM and ACN mainly extract aliphatic OS with longer carbon chains. More O\textsubscript{4}S\textsubscript{1} class species with high DBE values (DBE ≥ 6) were observed in DCM and ACN extracts than in water extracts. The O\textsubscript{4}S\textsubscript{1} class species dissolved in water had a lower number of carbon atoms and lower DBE values; for example, the abundance of O\textsubscript{4}S\textsubscript{1} with 8–10 carbon atoms and 1–3 DBEs is high in water. The results show that the O\textsubscript{2}S\textsubscript{1} class species in different solvents had different molecular compositions, so OS class species cannot be extracted completely by a single solvent.

Molecular composition of O class species

O class species (O\textsubscript{x}) are commonly found in organic aerosols, and have carboxyl and/or hydroxyl functional groups. Numerous O class species were assigned from the negative-ion ESI FT-ICR mass spectra. As the polarity of the solvent increased, O\textsubscript{x} class species with higher oxygen numbers were extracted (shown in Fig. 2). Different O class species can be extracted by different solvents. Fig. 6 shows DBE versus carbon number distribution for the O\textsubscript{x} class species of different solvent extracts from forward sequential extraction. It was shown that n-C\textsubscript{6} and DCM extracted O\textsubscript{2} class species with higher DBE values (DBE ≥ 10) and larger carbon numbers. These compounds could be derived from the oxidation of PAHs. The O\textsubscript{3} class species extracted by ACN and water have lower DBE values and
shorter carbon chains. Some proposed structures of highly abundant molecules are also shown in Fig. 6.

**Molecular composition of N class species**

N class species (N1 and N2) were mainly ionised in ESI$^+$ and are usually considered as basic nitrogen-containing compounds. N1 class species (DBE ≥ 4) may be six-membered heterocyclic compounds containing one nitrogen heteroatom, like pyridine, which may derive from fossil fuels (Zhu et al. 2011). N2 class species may be alkaloids, which are usually found in biogenic aerosols (Zhang et al. 2016). As shown in Fig. 4, most N class species were extracted into organic solvents. Fig. 7 shows DBE versus carbon number distribution for N1 class species of different solvent extracts from forward sequential extraction assigned from ESI$^+$ analysis. N1 class species were mainly extracted by organic solvents, especially n-C6 and DCM. In n-C6 and DCM extracts, the abundance of N1 compounds with DBE values lower than 12 was higher, whereas DBE values of N1 compounds from ACN extracts were predominantly above 12.

**Molecular composition of NO class species**

NO class species represent organic nitrogen compounds (N1Ox and N2Ox) that have been observed in fog and continental precipitation (Altieri et al. 2009; Mazzoleni et al. 2010). The high O/N ratios (≥3) of these compounds allow an assignment of one nitro (–NO2) or nitrooxy (–ONO2) group, making nitro-substituted compounds and organonitrates candidate compounds. NO class species extracted by different solvents have similar characteristics to O class species. From Figs 2 and 4, the NO class species were the highest in the water extract, both in the forward and the reverse extraction by negative ion ESI, and had high relative abundance in forward extraction by positive-ion ESI. Fig. 8 shows DBE versus carbon number distribution for N1O6 class species of different solvent extracts from forward sequential extraction assigned from ESI$^-$ mass spectra. DCM extracted N1O6 class species with high DBE values (mainly ≥10), whereas ACN and water extracted compounds with relatively low DBE values.

**Deductions from different extraction strategies**

**Comparison of molecular compositions of DCM extracts and ACN extracts**

According to Table 1, both DCM and ACN extracted ~50 % of the TOC, but their composition appeared to be different. From Fig. 1, it is seen that DCM extracted more CHO compounds, whereas ACN extracted more polar compounds such as CHOS and CHONS class species. Studying carefully the extracts from different extraction strategies is a good way to comprehensively understand the different molecular composition of DCM extracts and ACN extracts. Comparing the molecular compositions of the ACN extracts from the forward sequential extraction and the DCM extracts from the reverse sequential extraction can help us determine the unique compounds extracted into ACN and DCM respectively. Fig. 9 shows DBE versus carbon number distribution for O5, N1O4 and O5S1 class species of the ACN extracts from the forward sequential extraction and the DCM.
extracts from the reverse sequential extraction from negative-ion ESI FT-ICR MS. It was shown that ACN could extract more unique O₅ and N₁O₄ class species with lower DBE values and many O₅S₁ compounds, whereas DCM could extract more unique O₅ and N₁O₄ class species with higher DBEs (DBE ≥ 10), but not extract unique O₅S₁ class species.

Unique molecular composition of extracts soluble in water and insoluble in conventional organic solvents

Comparing the composition of the water extracts from the forward sequential extraction and from the reverse sequential extraction (same as single-solvent water extracts) was useful to help us determine the unique composition of the most polar compounds in the water extracts after the apolar–polar organic solvent extractions. From Figs 2 and 4, it can be seen that the water extracts from the forward sequential extraction contained a higher abundance of compounds with a higher oxygen number (usually O ≥ 6) than the water extracts from the reverse sequential extraction, including the O₅ compounds and O₅S₁ compounds from negative-ion ESI FT-ICR MS, and O₅Na₁ class species and N₁O₅ compounds from positive ion ESI FT-ICR MS. Fig. 10 shows DBE versus carbon number distribution for O₅, N₁O₄ and O₅S₁ class species of the water extracts from the forward sequential extraction and the water extracts from the reverse sequential extraction with negative-ion ESI FT-ICR MS. It was shown that the water extracts from the forward sequential extraction contained fewer compounds and presented a narrower molecular range, including a high abundance of O₅, N₁O₄ class species and O₅S₁ class species with low DBEs and carbon number (DBE ≤ 10 and C ≤ 20 for O₅, DBE ≤ 10 and C ≤ 20 for N₁O₄ class species and DBE ≤ 4 and C ≤ 13 for O₅S₁ class species), compared with those from the reverse sequential extraction.
Conclusions

Aerosol samples were extracted sequentially or in reverse order with \( n-C_6 \), DCM, ACN and water to separate non-polar, low-polarity, mid-polarity and high-polarity organic compounds. Approximately 70% of the TOC was extractable by solvent. Approximately 30% of the TOC was WSOC and 25% of the TOC was non-polar OC. A total of 50% of the TOC was DCM-soluble organic carbon and 53% of the TOC was ACN-soluble organic carbon. The total of 59 class species, including \( N_1O_6 \), \( N_2O_1–N_2O_{10} \), \( O_1–O_{10} \), \( O_3S_1–O_{9S_1} \), \( O_1Na_1–O_{10Na_1} \) and \( N_1O_1Na_1–N_1O_{10Na_1} \) were assigned from the positive- and negative-ion ESI FT-ICR mass spectra. The results revealed the molecular selectivity of different solvents for organic compound extraction from aerosol samples. Non-polar and low-polarity compounds with a high degree of molecular condensation such as oxidised PAHs and nitrogen-containing compounds (CHN) were extracted into \( n-C_6 \) and DCM. WSOM was predominant with aliphatic and aromatic organosulfates (CHOS) and nitrooxy-organosulfates (CHONS). Most oxygen-containing compounds (CHO) and oxygen- and nitrogen-containing compounds (CHON) with high DBEs and long carbon chains tended to be extracted into organic solvents. The results are valuable for understanding the molecular composition of aerosol-derived organic compounds and instructive for sample preparation of aerosol samples as well as other environmental samples for molecular characterisation.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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