

Size-dependent Molecular Characteristics and Possible Sources of Organic Aerosols at a Coastal New Particle Formation Hotspot of East China

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Abstract

We investigated size-dependent molecular characteristics of coastal organic aerosols from $< 0.032 \mu\text{m}$ to $3.2 \mu\text{m}$ at a new particle formation (NPF) hotspot of east China by using Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR-MS). Strong connection between $\text{C}_{20-33}\text{H}_h\text{O}_o/\text{C}_{18,30}\text{H}_h\text{O}_o\text{N}_n$ compounds in particles smaller than $0.10 \mu\text{m}$ and the VOCs emitted from local intertidal macroalgae suggests that the organic compounds (OC) in ultrafine particles are formed probably via the gas-phase oxidation of long-chain fatty aldehydes or acids, followed by particle-phase accretion reactions or imine formation during the coastal NPF events. In $0.18\text{-}0.56 \mu\text{m}$ particles, dominant $\text{C}_8\text{-C}_{20}$ CHO, CHON, CHOS and CHONS compounds (maximum: C_{10} or C_{15}) are suggested most likely to be terpene oxidation products. Highly oxygenated compounds with 0.6 $[\text{?}] \text{ H/C } [\text{?}] \text{ 1.5}$ and 0.67 $[\text{?}] \text{ O/C } [\text{?}] \text{ 1.2}$ reside mostly in $0.18\text{-}0.56 \mu\text{m}$ particles, accounting for 5% of the OC formulas in this size range. Iodinated OC are subsequently formed via electrophilic substitution of non-iodinated OC by iodine cations in iodine-rich particles. CHN and Cl/Br-containing OC account altogether for only 1-4% of total OC intensity. As a result of the above compound distribution, the intensity weighted unsaturation degree and carbon oxidation state of OC increase with particle size. The distribution of aromatic compounds (i.e. Aromaticity Index > 0.5) is bimodal with peaks in $0.056\text{-}0.18 \mu\text{m}$ and $1.0\text{-}3.2 \mu\text{m}$. In addition, our study observed higher unsaturation degree, carbon oxidation state and aromaticity of OC in coastal $\text{PM}_{2.5}$ than inland urban $\text{PM}_{2.5}$ in the same region.

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Key Points:

- Size-dependent organic molecular characteristics was revealed by FT-ICR-MS measurement at a coastal new particle formation hotspot.
- SPME-GC-MS analysis linked coastal ultrafine organic aerosols with VOC emission from local intertidal macroalgae.
- We conducted a systematical comparison of PM_{2.5} chemical composition between the coastal NPF hotspot and a typical inland urban site.

Abstract

We investigated size-dependent molecular characteristics of coastal organic aerosols from $< 0.032 \mu\text{m}$ to $3.2 \mu\text{m}$ at a new particle formation (NPF) hotspot of east China by using Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR-MS). Strong connection between $\text{C}_{20-33}\text{H}_h\text{O}_o/\text{C}_{18,30}\text{H}_h\text{O}_o\text{N}_n$ compounds in particles smaller than $0.10 \mu\text{m}$ and the VOCs emitted from local intertidal macroalgae suggests that the organic compounds (OC) in ultrafine particles are formed probably via the gas-phase oxidation of long-chain fatty aldehydes or acids, followed by particle-phase accretion reactions or imine formation during the coastal NPF events. In $0.18\text{--}0.56 \mu\text{m}$ particles, dominant $\text{C}_8\text{--C}_{20}$ CHO, CHON, CHOS and CHONS compounds (maximum: C_{10} or C_{15}) are suggested most likely to be terpene oxidation products. Highly oxygenated compounds with $0.6 \leq \text{H/C} \leq 1.5$ and $0.67 \leq \text{O/C} \leq 1.2$ reside mostly in $0.18\text{--}0.56 \mu\text{m}$ particles, accounting for 5% of the OC formulas in this size range. Iodinated OC are subsequently formed via electrophilic substitution of non-iodinated OC by iodine cations in iodine-rich particles. CHN and Cl/Br-containing OC account altogether for only 1–4% of total OC intensity. As a result of the above compound distribution, the intensity weighted unsaturation degree and carbon oxidation state of OC increase with particle size. The distribution of aromatic compounds (i.e. Aromaticity Index > 0.5) is bimodal with peaks in $0.056\text{--}0.18 \mu\text{m}$ and $1.0\text{--}3.2 \mu\text{m}$. In addition, our study observed higher unsaturation degree, carbon oxidation state and aromaticity of OC in coastal $\text{PM}_{2.5}$ than inland urban $\text{PM}_{2.5}$ in the same region.

1 Introduction

Organic aerosols (OA) contributes 20%–90% of submicron aerosol mass in the troposphere (Jimenez et al., 2009; Zhang et al., 2007). The OA in coastal atmosphere is expected to be more diverse than continental OA due to the contributions from both continental and marine sources. Unlike the deeper understanding of continental OA, the OA from marine sources is less investigated and thus poorly quantified in aerosol-cloud-climate models. The seawater contains a complex mixture of dissolved organic matter (DOM) including amino acids, proteins, fatty acids, carbohydrates and humic-type components etc. (Garrett, 1967; Hansell & Carlson, 2014; Liss & Duce, 1997). They are exported to marine aerosols primarily via the formation of sea spray aerosol (SSA) (Lapina et al., 2011; Prather et al., 2013). Direct marine volatile organic compound (VOC) emissions include biological vapor emissions from marine biota (Gašparović et al., 1998; Žutić et al., 1981) and abiotic production of functionalized VOCs from sea surface microlayer (Brüggemann et al., 2018; Carpenter & Nightingale, 2015; Chiu et al., 2016). Subsequent photochemistry of these VOCs may lead to marine and coastal secondary OA (SOA) formation.

Halogen (Cl, Br and I) is a group of non-negligible atmospheric constituents in both gas and aerosol phases. Their sources include sea salt aerosols (Finlayson-Pitts, 2003; Rossi, 2003), halogenated methane emission from the ocean (Gribble, 1992; Mosher et al., 1993), biomass burning (Rahn et al., 2006) and fossil fuel combustion (Maenhaut et al., 1993; Xu et al., 2005). There have been many studies of halogen

chemistry in the stratosphere and the troposphere, however, mainly focusing on their atmospheric sources, cycle mechanisms, the reactivity of halogen atoms towards VOC and ozone depletion mechanism (Farman et al., 1985; Peter, 1996; Riva et al., 2015; Tham et al., 2016; Thornton et al., 2010; Wang et al., 2017a; Wennberg et al., 1994). , So far, Cl/Br/I-containing organic compounds (OC) in aerosol particles are seldom reported (Wang & Ruiz, 2017; Wang et al., 2020), although they may play an important role in regulating the recycling of active halogens from particles to gas phase.

Traditionally, Gas Chromatography or Liquid Chromatography-Mass Spectrometry (GC-MS or LC-MS) were widely used in the offline molecular characterization of OA. Electron ionization instruments like Aerosol Mass Spectrometry (SP-AMS) and Aerosol Chemical Speciation Monitor (ACSM) have also been widely used to provide fragment ion information of both inorganic and organic components in complex aerosol samples (Canagaratna et al., 2007; DeCarlo et al., 2006). Soft ionization techniques like Chemical Ionization (CI), Electrospray Ionization (ESI) and EESI (Extractive ESI) interfaced with High Resolution (HR)-MS such as Time-of-Flight (ToF)-MS, Orbitrap-MS, Fourier transform-ion cyclotron resonance MS (FT-ICR-MS) (Laskin et al., 2018) make it possible to examine molecular ions of OA, either online or offline, in laboratory experiments (Kundu et al., 2012; Putman et al., 2012), field campaigns (Lin et al., 2012; Mazzoleni et al., 2012; O'Brien et al., 2014; Wang et al., 2016; Willoughby et al., 2016) or specific emission sources (Cui et al., 2019; Fleming et al., 2017; Laskin et al., 2009). One of the recent hot topics arising from the application of online CI-API-TOF is the investigation of highly oxygenated organic molecules (HOM), which are believed to play an important role in SOA formation and new particle formation (NPF) (Bianchi et al., 2019).

Herein, we reported size-resolved molecular characteristics of OA collected at a coastal NPF hotspot in east China coastline. We presented a comprehensive analysis of elemental composition, carbon number distribution, oxidation degree, unsaturation degree, aromaticity and the content of highly oxygenated compounds (HOC) of organic elemental groups with a high size resolution. VOC emission from local coastal macroalgae was measured with Solid Phase Micro-Extraction (SPME)-GC-MS technique to assist in interpreting the sources and formation mechanism of OA. Chemical composition of bulk aerosol particles was also compared between coastal and urban PM_{2.5} in the region to obtain a better understanding of OA in the context of severe PM pollution in China.

2 Materials and Methods

2.1 Sample collection

Size-resolved coastal aerosol particles were collected at Xiangshan gulf (29°29' N, 121°46' E) of east China, a coastal NPF hotspot where iodine-induced NPF (I-NPF) occurred regularly from spring to summer (Yu et al., 2019). The sampling site is about 40 and 200 m away from at high tide and low tide, respectively. 13-stage nano Micro-Orifice Uniform Deposit Impactor (nano-MOUDI, MSP Corp, Shoreview, MN) was used with 50% aerodynamic cutoff sizes 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10,

0.056, 0.032, 0.018, and 0.010 μm . Pre-baked Aluminum foil filters were used as sampling substrate to reduce the adsorption of gaseous species. In order to reduce potential particle-bounce artifacts, two nano-MOUDI were placed side by side to collect 0.010-0.10 μm particles (on stages 10-13; other stages were silicon greased) and 0.10-18 μm particles (on stages 1-9) separately. The sampling lasted continuously for 72 hours from 9-11 May 2018 when NPF occurred daily, so that particle chemical composition of the NPF events can be obtained from offline analyses. Afterwards one set of field blank samples was collected alike, but with a high efficiency particulate air (HEPA) filter being placed at the gas inlet of nano-MOUDI. Particle number size distribution during the period is shown in Figure S1. Detailed information of PNSD measurement could be found in Yu et al. (2019).

A 23-hour $\text{PM}_{2.5}$ sample was collected onto 90 mm diameter pre-baked quartz fiber filter in another I-NPF day from 27-28 April 2018 at the same site. To make comparison, a 23-hour $\text{PM}_{2.5}$ sample was collected simultaneously at an inland urban site (32°20' N, 118°71' E) in Nanjing, a megacity in the same region (Yangtze River Delta region). The urban sampling site is located at the third floor (15m above the ground level) of an academic building on the Nanjing University of Information Science and Technology (NUIST) campus. $\text{PM}_{2.5}$ samples were collected using a median-volume aerosol sampler (TH-150C, Wuhan Tianhong Ltd., China) at a flow rate of 100 L min^{-1} . Field blank filters were collected at both sites. All samples were stored at -20°C in a refrigerator until chemical analysis.

2.2 ESI-FT-ICR-MS

Half of a MOUDI filter or one quarter of a $\text{PM}_{2.5}$ filter was extracted by ultrasonication in an ice-water bath for 40 min with 10 mL mixed solvent (1:1 v/v water and methanol; LCMS grade) and was filtered through a 0.2 μm PTFE membrane syringe filter. The extract was dried using a rotary evaporator below 40°C and redissolved in 0.5 mL water. Sample solution was directly infused into an ESI-FT-ICR-MS (SolariX XR 9.4T instrument, Bruker Daltonics, Coventry, UK) at a flow rate of $180 \mu\text{L h}^{-1}$. ESI source conditions were as follows: nebulizer gas pressure 1 bar; dry gas pressure 4 bar and its temperature 200°C ; capillary voltage 4.5 kV. Ion accumulation time in argon-filled hexapole collision pool with 1.5 V of direct current voltage and 1400 Vp-p of radio frequency (RF) amplitude was 0.05 s, followed by transporting ions through a hexapole ion guide to the ICR cell for 0.7 ms. 4 M words of data were recorded over the mass range of 150-1000 for each run. A total of 128 scans were collected to enhance signal/noise (S/N) ratio and dynamic range. The OC analysis was conducted only for aerosol particles smaller than 3.2 μm . The extracts of 10-18 nm sample and 18-32 nm sample were combined to enhance the sensitivity of OC detection in small particle sizes. Field blank samples were treated following the same procedure.

A resolving power ($m/\Delta m_{50\%}$) 550,000 at m/z 300 of the FT-ICR-MS allows the determination of possible formulas for singly charged molecular ions. Only m/z values between 150-1000 Th that satisfies $S/N > 10$ were considered. Formula assignment fulfils the following criteria (Fuller et al., 2012; Mazzoleni et al., 2012): molecular

formulas are restricted to $C_{1-50}H_{1-100}X_{0-3}N_{0-5}O_{1-50}S_{0-2}$ in ESI- mode and $C_{1-50}H_{1-100}X_{0-3}N_{0-50}O_{0-50}$ in ESI+ mode ($X = Cl/Br/I$); mass tolerance is ± 0.5 ppm. H/C, O/C, and N/C ratios are limited to 0.3-3, 0-3 and 0-1.3 in the ESI+ mode. H/C, O/C, N/C and S/C ratios are limited to 0.3-3, 0-3, 0-0.5 and 0-0.2 in the ESI- mode. Isotopologue-containing formulas are removed from the formula lists. A formula with $m/z > 500$ is not reported if it did not belong to any CH_2 homologous series. S, Cl and Br containing formulas are assigned only if their isotope patterns match with the theoretical ones. Formula calculation was done following the same procedure for the field blank samples. All formulas found in the field blank samples, regardless of peak intensity, were excluded from the formula lists of real samples.

To evaluate the degree of unsaturation and oxidation state of a molecular formula $C_cH_hX_xN_nO_oS_s$, double bond equivalent (DBE) and carbon oxidation state (OSC) are calculated as follows (Kroll et al., 2011; Mazzoleni et al., 2012; Minerath & Elrod, 2009):

$$DBE = 1 + 0.5 \times (2c - h + n - x) \quad (1)$$

$$OSC = 2 \times \frac{o}{c} - \frac{h}{c} \quad (2)$$

DBE was required to be non-negative. To evaluate the degree of unsaturation or oxidation state of a group of molecular formulas in a sample, relative intensity (RI) weighted $(DBE/C)_w$ and OSC_w are calculated as:

$$(DBE/C)_w = \sum RI_i \times (DBE/C)_i / \sum RI_i \quad (3)$$

$$OSC_w = \sum RI_i \times OSC_i / \sum RI_i \quad (4)$$

where RI_i , $(DBE/C)_i$ and OSC_i are the RI, DBE/C and OSC of an individual molecular formula i in a sample.

Aromaticity index (AI) of a molecular formula is calculated as

$$AI = \frac{DBE_{AI}}{C_{AI}} = \frac{1+c-o-s-0.5h}{c-o-s-n} \quad (5)$$

For the formulas detected in the ESI- mode, half of the oxygen (O) atoms are assumed to be associated with σ -bond. Equation (5) is then modified to $AI = \frac{DBE_{AI}}{C_{AI}} =$

$\frac{1+c-0.5o-s-0.5h}{c-0.5o-s-n}$. If $DBE_{AI} \leq 0$ or $C_{AI} \leq 0$, then $AI = 0$. Threshold value of $AI \geq 0.5$

provides unambiguous minimum criteria for the presence of aromatic structure in a molecule (Koch & Dittmar, 2006; Yassine et al., 2014).

We define highly oxygenated compound (HOC) as a compound with $0.6 < H/C \leq 1.5, 0.67 \leq O/C \leq 1.2$ according to its position in a Van Krevelen diagram (Ning et al., 2019; Wozniak et al., 2008; Wu et al., 2019). Apparently, HOC is not equivalent to HOMs, which is defined by Bianchi et al. (2019) as high O/C molecules formed via gas phase autoxidation reaction. Nevertheless, HOC can be used as a proxy to show the intensity and size distribution of HOMs in aerosol particles.

2.3 SP-AMS

Half of each quartz fiber filter was extracted, dried and redissolved in 20 mL water, as above, for PM_{2.5} bulk chemical composition analysis by using a Soot Particle-AMS (Aerodyne Research Inc., Massachusetts, USA). The aliquot of PM_{2.5} sample solution was atomized by an aerosol atomizer (TSI Model 3076) and dehumidified to RH less than 10% through a diffusion dryer filled with silica-gel before entering the SP-AMS. The aerosols in the sample flow were thermally vaporized at 600 °C using a resistively heated tungsten vaporizer. The resulting vapor was ionized in an EI source (70eV). The SP-AMS was switched between a high sensitive V-mode and a high mass resolution W-mode. The m/z range was ~1000 for V-mode and ~450 for W-mode, respectively. In this study, we used only W-mode data for characterization of non-refractory components in the PM_{2.5} samples. The relative ionization efficiencies (RIE) of sulfate, nitrate, organics, ammonium and chloride were 1.2, 1.1, 1.4, 3.8 and 1.0, respectively. Field blank samples were treated alike. Detailed procedures for offline analysis of PM chemical composition using SP-AMS can be found in Ge et al. (2017) and Sun et al. (2010).

2.4 SPME-GC-MS

Fresh macroalgae (*Undaria pinnatifida*) was collected from intertidal zone at Xiangshan gulf and stored at -20 °C until the SPME-GC-MS analysis of the VOCs emitted by the algae. About 0.5 g algae was capped in a 20 mL headspace vial, where the emitted VOCs were extracted onto 100 µm polydimethylsiloxane (PDMS) coated fiber (Supelco, Bellefonte, PA, USA) at 60 °C and an agitation speed of 500 rpm for 40 min equilibration time on an automatic injection platform (MPS, Gerstel, Germany). The fiber was then removed from the headspace vial and inserted into the injection port of a GC-MS apparatus (GCMS-QP2010 Plus, Shimadzu). The compounds on the fiber were desorbed for 2 min at 280 °C in the injection port operated in splitless mode. Carrier gas was He with a flow rate of 1.5 mL min⁻¹. The analytes were separated in a Rtx-5MS capillary column (30 m, 0.25 mm i.d. 0.25 µm film of 5% diphenyl-polysiloxane and 95% dimethyl-polysiloxane). Oven temperature program was held at 50 °C for 2 min, ramped to 230 °C at the rate of 20 °C min⁻¹, ramped to 280 °C at 2.5 °C min⁻¹ and held for 2 min. MS conditions were as follows: EI 70 eV, interface temperature 240 °C, ion source 220 °C, solvent delay time 1 min. MS detector was operated in full scan mode, by scanning a mass range of m/z 10-450. The most probable identities of the analytes were obtained based on the best matching score by comparing with the reference mass spectra in the NIST library.

3 Results and Discussion

3.1 PM_{2.5} bulk chemical composition

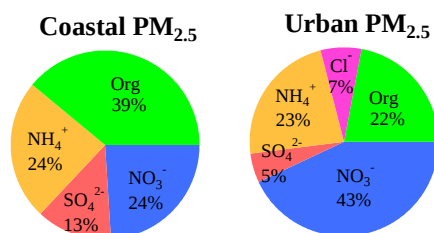


Figure 1. Mass contributions of organics (Org), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+) and chloride (Cl^-) in coastal PM_{2.5} (left) and urban PM_{2.5} (right).

Figure 1 shows a comparison of PM_{2.5} bulk chemical composition between the coastal site and the urban site measured by offline SP-AMS. Coastal PM_{2.5} contains a higher OA and SO_4^{2-} mass fraction than urban PM_{2.5}, probably due to stronger primary emission or high conversion ratio of precursor vapors (like SO_2 , dimethyl sulfide and other VOCs) at the coast site (Andreae, 1990; Kettle et al., 1999). On the contrary, urban PM_{2.5} contains more NO_3^- (43% vs. 24%) and Cl^- (7% vs. 0%) than coastal PM_{2.5}. Nitrate is the end product of NO_x photochemistry that is expected to be more active in urban atmosphere (Liao et al., 2004). The higher mass fraction of Cl^- in urban PM_{2.5} is probably a result of primary Cl^- emission from fossil fuel combustion. The absence of Cl^- in coastal PM_{2.5} indicates that Cl^- is probably abundant in coarse-mode sea salt aerosols (SSA), but not in fine particles.

3.2 Molecular formula assignments

The formulas detected as deprotonated species in the ESI⁻ mode are grouped into 7 subgroups based on their elemental composition: CHO^- , CHON^- , CHOS^- , CHONS^- , iodine containing OC (I-OC^-), chloride containing OC (Cl-OC^-) and bromine containing OC (Br-OC^-). The subgroups in the ESI⁺ mode include 6 subgroups (CHO^+ , CHON^+ , CHN^+ , I-OC^+ , Cl-OC^+ and Br-OC^+) detected as protonated species and 2 subgroups ($\text{CHO}+\text{Na}$ and $\text{CHON}+\text{Na}$) detected as sodium adducts. We show the formula numbers of each OC subgroup in Table 1, as well as their relative contributions to total OC intensity in the PM_{2.5} samples and size-resolved coastal samples in Figure 2b and 2c.

Size-dependent OC formula number and total intensity show a bimodal distribution in coastal aerosols (Figure 2a). Surprisingly high formula number and total intensity in < 56 nm particles are obviously attributed to intense NPF events during the sampling period. Another peak of OC number and total intensity is in 0.32-0.56 μm particles, after which OC decreases rapidly with particle size. Organic composition of coastal aerosols is highly size-dependent and high similarities are only seen in neighboring size bins (e.g., 0.18-0.32 μm and 0.32-0.56 μm , < 32 nm and 32-56 nm). This can be seen in Table S1 showing the repeatability of molecular formulas in any two of nine size bins. One exception is the OC in 0.56-1.0 μm particles.

261 **Table 1.** Formula numbers of subgroups for size-resolved coastal aerosols, coastal PM_{2.5} and urban PM_{2.5} in both ESI+ and ESI- modes.

	< 0.032 μm	0.032-0.056 μm	0.056-0.10 μm	0.10-0.18 μm	0.18-0.32 μm	0.32-0.56 μm	0.56-1.0 μm	1.0-1.8 μm	1.8-3.2 μm	Coastal PM _{2.5}	Urban PM _{2.5}
ESI- mode											
CHO ⁻	518	561	146	370	505	473	241	37	18	937	1023
CHON ⁻	929	620	216	271	329	344	106	23	25	754	2176
CHOS ⁻	162	208	59	211	230	369	110	38	22	657	628
CHONS ⁻	126	107	34	93	79	118	21	11	10	217	555
I-OC ⁻	89	93	22	56	17	15	12	8	17	625	36
Cl-OC ⁻	24	5	7	7	0	0	0	1	0	2	35
Br-OC ⁻	0	0	0	0	0	1	0	0	0	3	0
Total	1850	1594	484	1008	1160	1320	490	118	92	3195	4453
ESI+ mode											
CHO ⁺	43	101	20	109	239	338	92	3	10	611	316
CHO+Na	165	284	310	181	118	21	67	103	96	523	1116
CHON ⁺	437	467	225	372	717	713	178	36	27	2162	1544
CHON+Na	782	681	635	210	118	25	48	58	36	445	1315
CHN ⁺	15	14	17	18	3	2	3	2	5	17	24
I-OC ⁺	48	127	47	77	27	15	26	48	58	682	21
Cl-OC ⁺	1	3	2	2	2	0	0	1	1	8	11
Br-OC ⁺	1	0	0	0	0	0	0	0	1	0	4
Total	1335	1542	1196	920	1150	1104	402	247	229	4055	3828
Summary											
Non-halogen	2629	2549	1535	1640	2003	2163	804	307	248	5052	6847
OC											
I-OC	124	200	68	123	39	28	34	53	68	1203	56
Cl-OC	25	8	9	9	2	0	0	2	1	10	46
Br-OC	1	0	0	0	0	1	0	0	1	3	4

36-87% of the formulas in 0.56-1.0 μm particles are also present in $< 0.56 \mu\text{m}$ particles. The results imply that the OC in 0.56-1.0 μm particles, to some extent, originated from smaller particles.

Among 6953 formulas in coastal $\text{PM}_{2.5}$ and 6271 formulas in urban $\text{PM}_{2.5}$, nearly half of them (3526) were commonly found in both samples. Coastal $\text{PM}_{2.5}$ sample and size-resolved MOUDI samples were both collected during I-NPF days at the same site and are thus expected to have similar composition. However, only 3009 formulas are commonly present in $\text{PM}_{2.5}$ (6953 formulas in total) and size-resolved samples (6013 formulas in total). More specifically, 83-89% of OC formulas in 0.18-1.0 μm particles are also present in coastal $\text{PM}_{2.5}$, but only 43-57 % of OC formulas in $< 0.1 \mu\text{m}$ particles and 35-38% in $> 1.0 \mu\text{m}$ particles are present in coastal $\text{PM}_{2.5}$ (Table S1). This suggests that the $\text{PM}_{2.5}$ sampling offers an approach to assess the chemical composition of only submicron particles (0.18-1.0 μm), not ultrafine ($< 0.1 \mu\text{m}$) or supermicron ($> 1.0 \mu\text{m}$) particles.

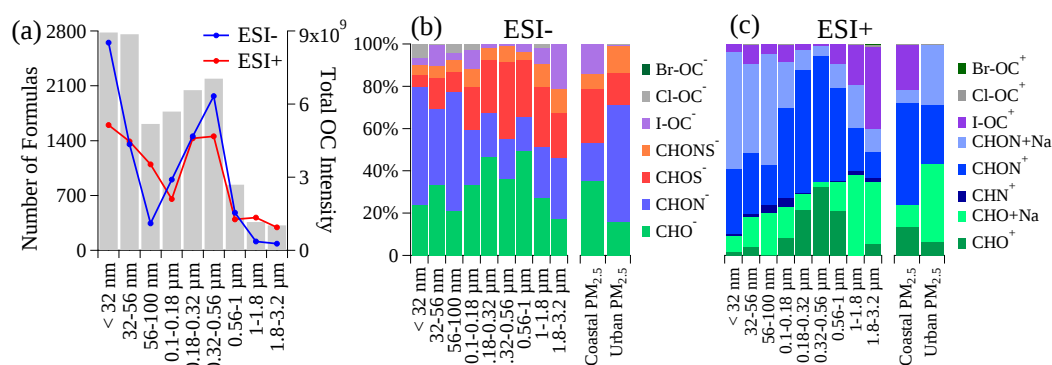


Figure 2. (a) The number (grey bars) and total intensity (blue and red lines for ESI- and ESI+ modes, respectively) of OC in size-resolved coastal aerosols. (b) Intensity fraction of 7 subgroups in ESI- mode. (c) Intensity fraction of 8 subgroups in ESI+ mode.

3.3 Size-dependent molecular characteristics and sources of OC subgroups

Size-dependent carbon number distribution, OSC_w , $(\text{DBE}/\text{C})_w$ and aromaticity are shown in Figure 3 for all OC subgroups in size-resolved coastal aerosols. The comparison of these parameters between coastal $\text{PM}_{2.5}$ and urban $\text{PM}_{2.5}$ is shown in Figure 4.

3.3.1 CHO compounds

CHO subgroup is the second largest contributor of OC in coastal ultrafine particles. In general, the fraction of CHO in total OC intensity increases with particle size (Figure 2). The intensity distribution of CHO⁻ compounds is bimodal in terms of particle size (Figure 3a), being dominated by $\text{C}_{20,24,28,32}$ and $\text{C}_{21,25,29,33}$ in $< 56 \text{ nm}$ particles and C_{10-20} in 0.18-0.56 μm particles. The intensity distribution of CHO⁺ compounds is unimodal dominated by C_{12-18} species in 0.18-0.56 μm particles (Figure 3a). The $(\text{DBE}/\text{C})_w$ and OSC_w values of CHO compounds are higher in submicron particles than those in ultrafine particles (Figure 3b). The percentage of aromatic compounds (i.e. $\text{AI} > 0.5$) in CHO subgroup is below 10% and increases with particle size.

The intensity fraction of CHO compounds in urban PM_{2.5} (16%) is lower than that in coastal PM_{2.5} (35%) in the ESI- mode, but the opposite is observed in the ESI+ mode (urban vs. coastal: 43% vs. 25%). The carbon numbers of CHO compounds in urban PM_{2.5} are higher than (or close to) those of coastal PM_{2.5} (Figure 4a): C₁₅₋₂₂ (maximum: C₂₀) and C₂₀₋₃₃ (maximum: C₂₆) subclasses are prominent in CHO⁻ and CHO+Na compounds of urban PM_{2.5}, while C₉₋₂₀ (maximum: C₁₀) and C₁₃₋₁₆ (maximum: C₁₅) subclasses are prominent in CHO⁻ and CHO⁺ compounds of coastal PM_{2.5}. Unsaturation degree, carbon oxidation state and the percentage of aromatic compounds are lower in urban PM_{2.5} than in coastal PM_{2.5} (Figure 4b).

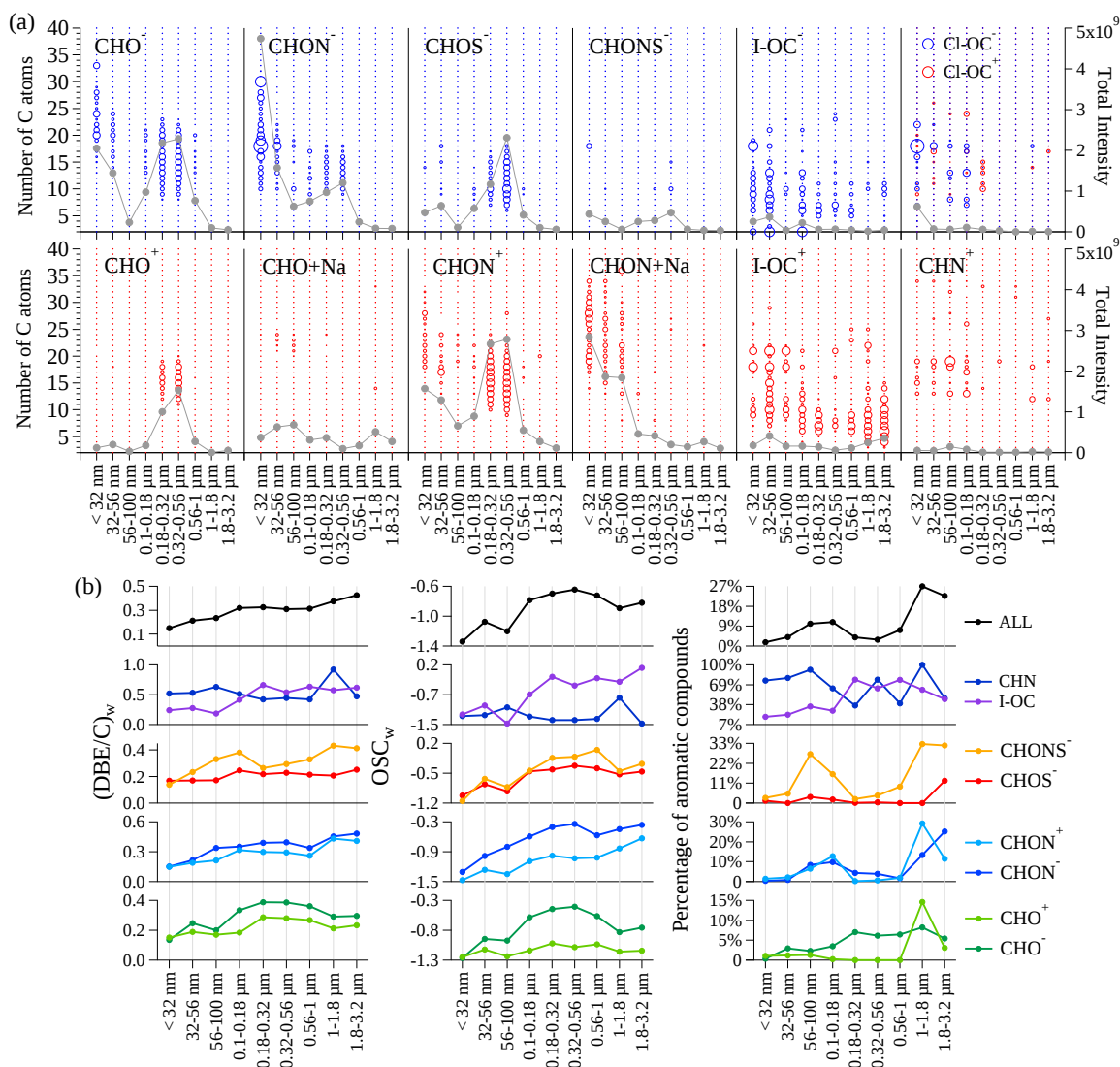


Figure 3. (a) Carbon number distributions (circles) and total intensity (gray lines) for each OC subgroup in size-resolved coastal aerosols. Circle size is proportional to the relative intensities of molecular formulas on a logarithmic scale. Note that the circle sizes of CHN⁺, I-OC⁻, I-OC⁺, Cl-OC⁺ and Cl-OC⁻ subgroups are not scaled proportionally with other subgroups, due to their

autoxidation of icosanal and subsequent reaction with RO_2 produce C_{20} hydroxyaldehydes. Second, low-volatility C_{20} hydroxyaldehydes condense onto nano-particles to form particle-phase C_{20} hydroxyaldehydes, their hydrolysis products, as well as C_{24} α,β -unsaturated aldehydes via the aldol condensation with butyraldehyde. Third, $\text{C}_{28,32}$ acetal or hemiacetal formation between all above aldehyde products and butane-2,3-diol.

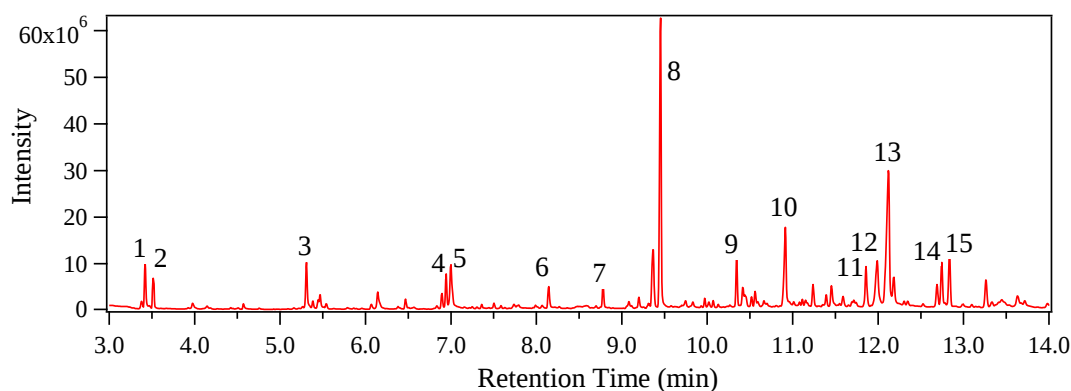


Figure 5. Total ion chromatogram of macroalgae (*Undaria pinnatifida*) emission: 1. Butyraldehyde, 2. Butane-2,3-diol, 3. Amyl vinyl carbinol, 4. 2-Nonenal, 5. 2-Nonen-1-ol, 6. Undecanal, 7. Dodecanal, 8. Icosanal, 9. Henicosanal, 10. Tetradecanoic acid, 11. Petroselinic acid, 12. Stearic acid, 13. Linolenic acid, 14. Eicosapentaenoic acid, 15. Docosahexaenoic acid.

The end products of Scheme I are the eight most abundant $\text{C}_{20,24,28,32}$ polyhydroxy alcohols with one $\text{C}=\text{C}$ or $\text{C}=\text{O}$ bond and 4 or 6 O atoms. The formation of other similar products with 3, 5, 7 and 8 O atoms are also possible if the number of added O atoms is varying in the gas phase oxidation intermediates. $\text{C}_{21,25,29,33} \text{H}_{44}\text{O}_{4-8}$ can be formed similarly from their precursor C_{21} henicosanal. In our previous study, we have confirmed that the NPF events at this coastal NPF hotspot were induced by iodine species (Yu et al., 2019). In this work, we further establish the relationship between the OC in ultrafine particles and the VOCs emitted from local intertidal macroalgae. These VOCs are thus most likely emitted mutually with iodine or iodomethanes from the macroalgae, although iodine or iodomethanes were not observed by the SPME-GC-MS technique.

3.3.2 CHON compounds

CHON is the most abundant subgroup in ultrafine particles, accounting for 53 % and 80% of total OC intensity in the ESI- and ESI+ modes respectively (Figure 2). The fraction of CHON in total OC intensity decreases with particle size. CHON^- and CHON^+Na are characterized by significant peaks around $\text{C}_{18,30}$, and $\text{C}_{20,28}$ in < 32 nm particles, respectively. CHON^+ is dominated by C_{10-20} peaks (maximum: C_{15}) in $0.18\text{-}0.56 \mu\text{m}$ particles (Figure 3a). The $(\text{DBE}/\text{C})_{\text{w}}$ and OSC_{w} of CHON compounds increase generally with particle size. The percentage of aromatic compounds exhibits a bimodal size distribution with peaks in $0.056\text{-}0.18 \mu\text{m}$ ($\sim 10\%$) and $1.0\text{-}3.2 \mu\text{m}$ ($\sim 30\%$) (Figure 3b).

Table 2. Number (*n*) and carbon number distribution of identical OC formulas detected both in size-resolved coastal aerosols and potential sources. Also shown is the percentage of total OC intensity that can be attributed to those identical molecular formulas. The last column shows the MS techniques used to detect the OC formulas from potential sources.

Potential source	Ultrafine	submicron	Supermicron	MS technique
CHO				
Isoprene ozonolysis ^a	n=139 (15%), C _{8,15,20}	n=408 (48%), C _{9,15,20}	n=31 (12%), C _{11,16,21}	LTQ-Orbitrap MS
α-pinene ozonolysis ^b	n=136 (15%), C _{9,15,20,23}	n=354 (44%), C _{9,15,20,24}	n=21 (7%), C _{8,15,19}	FT-ICRMS
Limonene ozonolysis ^c	n=145 (16%), C _{9,15,20}	n=361 (45%), C _{9,15,19}	n=20 (7%), C _{8,15,19}	
β-caryophyllene ozonolysis ^d	n=235 (27%), C _{9,14,19,24}	n=497 (62%), C _{9,15,19,24}	n=43 (16%), C _{11,16}	
Food cooking emission ^e	n=9, C _{8,9,12,16-18,20,21}	n=33, C _{6,8-14,16-18,21}	n=5, C _{9,11,12,17,21}	FIGAERO–ToF-CIMS
Brushwood burning emission ^f	n=5, C _{12,13,18}	n=12, C _{10-14,18}	n=3, C ₁₀₋₁₃	LTQ-Orbitrap MS
CHON				
α-pinene ozonolysis (NO _x) ^g	n=8, C ₁₀	n=28, C ₇₋₁₀	n=3, C ₁₀	FIGAERO ToF-CIMS
Brushwood burning emission ^f	n=10, C ₁₀₋₁₄	n=21, C _{7,10-15}	n=1, C ₁₃	LTQ-Orbitrap MS
S-containing formulas				
Nine monoterpenes SOA ^h	n=6, C ₉₋₁₀	n=19, C ₇₋₁₀	n=9, C ₇₋₁₀	UPLC/ESI-TOF MS
β-caryophyllene SOA	n=9, C _{9,14-16}	n=14, C _{9,14-16}	n=1, C ₉	
CHN				
Brushwood burning emission ^f	n=3, C ₁₃₋₁₄	n=3, C ₁₃	ND	LTQ-Orbitrap MS
Crop biomass burning emission ^j	n=2, C ₁₃	n=3, C ₁₃	ND	
Formulas tentatively attributed to algae emission				
The reaction of C ₁₈ fatty acid and C _{20,21} fatty aldehydes in macroalgae emission	C _{20,24,28,32} H _h O _o , C _{21,25,29,33} H _h O _o , DBE=1: n=26 (32%)	C _{20,24,28,32} H _h O _o , C _{21,25,29,33} H _h O _o , DBE=1: n=7 (0.4%)	C _{20,24,28,32} H _h O _o , DBE=1: n=2 (7%)	SPME-GC-MS
	C _{18,30} H _h O _o N _n , DBE=1-4: n=78 (36%)	C _{18,30} H _h O _o N _n , DBE=1-4: n=22 (6%)	C _{18,30} H _h O _o N _n , DBE=1-4: n=3 (8%)	

Note. a. Nguyen et al. (2010), b. Putman et al. (2012), c. Kundu et al. (2012), d. Kundu et al. (2017), e. Reyes-Villegas et al. (2018), f. Fleming et al. (2017), g. Lee et al. (2016), h. Surratt et al. (2008), i. Chan et al. (2010), j. Wang et al. (2017b).

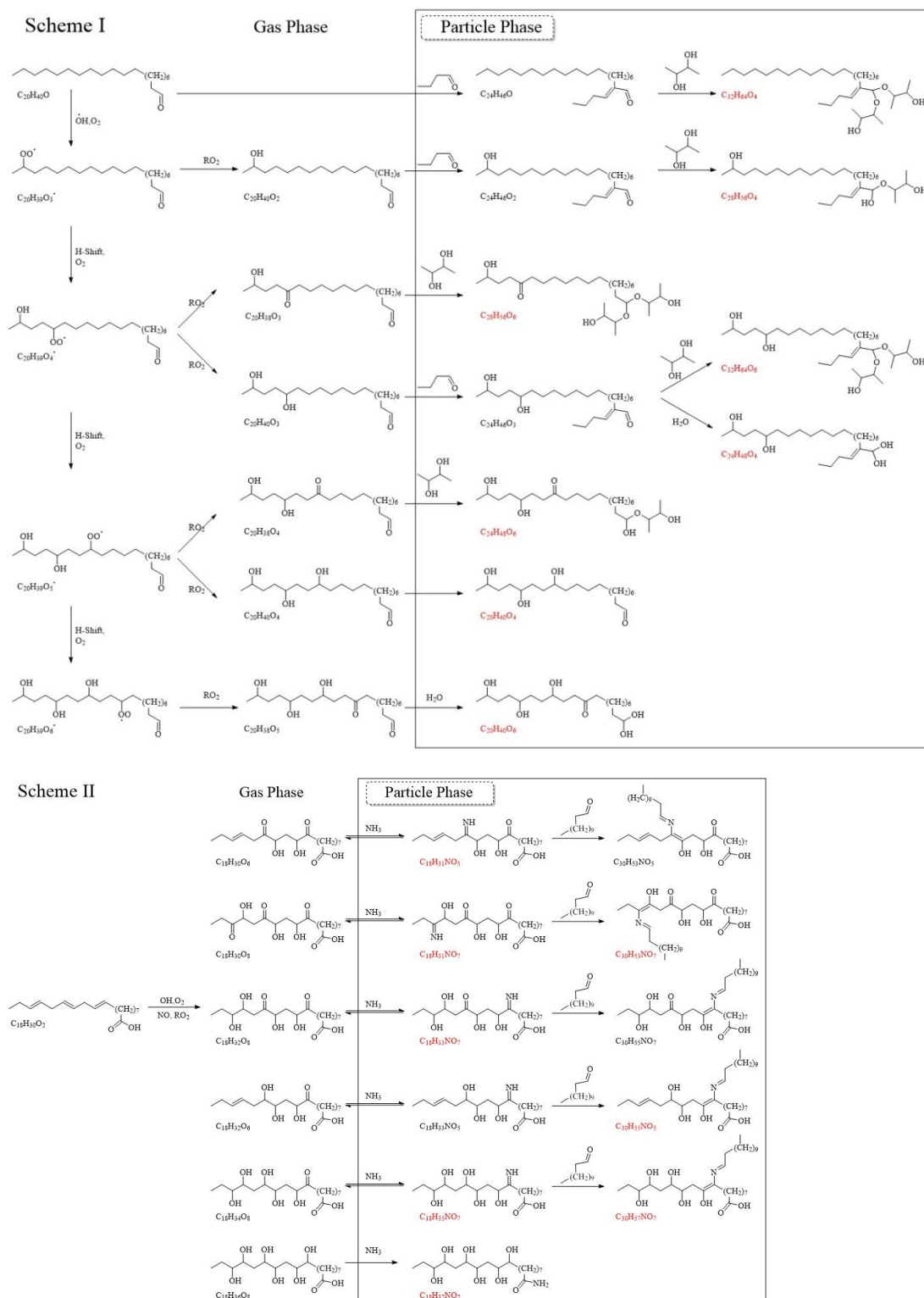
CHON compounds in urban PM_{2.5} contain more carbon atoms than those in coastal PM_{2.5} (Figure 4a). The most abundant C number subclasses of CHON⁻, CHON⁺ and CHON+Na formulas are C₁₅\C₁₅\C₁₉ and C₁₀\C₁₅\C₁₅ in urban and coastal PM_{2.5}, respectively. The (DBE/C)_w, OSC_w and the percentage of aromatic compounds in urban PM_{2.5} are lower than those in coastal PM_{2.5}, which are consistent with CHO compounds (Figure 4b).

Nitrogen atoms in CHON compounds could exist as either oxidized form (-NO₂ or -ONO₂) or reduced form (e.g. amine and imine). The average O/N ratios of CHON formulas in size-resolved aerosols are shown in Figure S2. No matter in ESI⁺ or ESI⁻ mode, CHON formulas in the submicron particles have higher average O/N ratios (2.3-5.7) than ultrafine particles (3.2-6.8)

and supermicron particles (2.4-5.3). This implies there are more amine or imine-containing CHON compounds in the ultrafine and supermicron particles than in the submicron particles. 78 $C_{18,30}H_hO_oN_n$ formulas with DBE=1-4 contribute 36% of the total intensity of CHON⁻ formulas in ultrafine particles. $C_{18,30}H_hO_oN_n$ are also the most abundant formulas among all OC formulas detected in the coastal aerosols (Figure 3a). Among them, at least 47 formulas should contain at least one amine or imine group, because their O atom numbers or DBE values are not large enough to allow the assignment of -NO₂ for all N atoms. On the other hand, we note that there is no N-containing compound in the VOCs emitted from the macroalgae sample (Figure 5). This leads to the conclusion that the reduced-N atoms in $C_{18,30}H_hO_oN_n$ compounds must be from atmospheric reactions.

The most plausible formation mechanism of $C_{18,30}H_hO_oN_n$ with DBE=1-4 is proposed to stem from linolenic acid (the highest abundant organic acid in the algae emission), ammonia and C₁₂ fatty aldehyde in a 3-step Scheme II (Figure 6): first, OH and O₂ addition to C=C double bonds of linolenic acid and subsequent reaction with RO₂ form oxygenated C₁₈ fatty acids containing hydroxyl or carbonyl group. Second, those low-volatility C₁₈ products then condense onto aerosol particles and $C_{18}H_hO_oN_n$ compounds are formed via imine formation reactions with NH₃ or ammonolysis. Third, C₁₈ imine products react with another carbonyl-containing C₁₂ fatty aldehyde to form $C_{30}H_hO_oN_n$. It should be noted that the products in Scheme II include merely some of the most abundant formulas detected in the ultrafine particles. Other C₁₈ and C₃₀ products with 3-8 O atoms are possible, given the unsaturation degree of C₁₈ fatty acid precursors and the extent of oxygen addition in the gas phase are varying. In addition, $C_{20,28}H_hO_oN_n$ compounds detected in the ESI⁺ mode might be formed similarly via imine formation reactions between NH₃ and the carbonyl-containing $C_{20,28}H_hO_o$ products formed in Scheme I.

As shown in Table 2, 33 CHON formulas are commonly found in field and α-pinene chamber experiments by Lee et al. (2016). They are supposed to be organic nitrate products initiated by nitrate radical (NO₃) or by O₃ or OH in the presence of NO_x. Among them, we find 28 C₇₋₁₀ compounds in submicron particles, but only 8 and 3 C₁₀ compounds in ultrafine and supermicron particles, respectively. Fleming et al. (2017) reported 150 CHON formulas in aerosol particles collected from brushwood burning smokes. Among them, 10, 21 and 1 formulas are observed in the ultrafine, submicron and supermicron particles at our coastal site, respectively. These results indicate that being compared to ultrafine aerosol particles, the CHON compounds in submicron particles are largely attributed to terpene SOA products in the high NO_x condition or biomass burning smokes.



3.3.3 S-containing compounds (CHOS and CHONS)

The total intensity of CHOS formulas is 2.6 times on average that of CHONS formulas in size-resolved coastal aerosols. The size distribution of S-containing compounds is unimodal dominated by C₈₋₁₈ species (maximum: C₁₀) in 0.18-0.56 μm particles (Figure 3a). More than 90% of CHOS or CHONS formulas in size-resolved aerosol particles have O/S ratios greater than 4. 50%, 83% and 57% of CHONS compounds have O/S ratios greater than 7 in ultrafine, submicron and supermicron particles, respectively, implying the existence of nitrooxy-organosulfates. In general, the (DBE/C)_w and OSC_w of S-containing compounds increase with particle size. Similar to CHON, the percentage of aromatic compounds in CHOS and CHONS subgroups exhibits a bimodal size distribution with peaks in 0.056-0.10 μm and 1.0-3.2 μm (Figure 3b).

S-containing compounds accounted for 33% and 28% of total OC intensity (ESI- mode, Figure 2b) in coastal and urban PM_{2.5}, respectively. The most abundant C number subclass of S-containing compounds are C₁₀ in coastal PM_{2.5}, while carbon number shift more to C₁₅ in urban PM_{2.5} (Figure 4a). (DBE/C)_w, OSC_w and the percentage of aromatic compounds in S-containing compounds in urban PM_{2.5} are again lower than those in coastal PM_{2.5} (Figure 4b).

Surratt et al. (2008) and Chan et al. (2010) conducted a series of photooxidation experiments on 9 monoterpenes and β -caryophyllene in the presence of acidified sulfate seed aerosols, respectively (Table 2). They identified 36 CHOS and 16 CHONS formulas in the products (Chan et al., 2010; Surratt et al., 2008). Among them, 14, 32 and 9 formulas are observed in our coastal ultrafine, submicron and supermicron particles, respectively. 35 and 34 of them are observed in coastal PM_{2.5} and urban PM_{2.5}, respectively, including two most abundant compounds C₁₀H₁₇NO₁₀S and C₁₀H₁₇NO₉S. This suggests that S-containing compounds in our sites were probably formed via the reactions of CHO and CHON compounds with sulfate in the aerosol particles.

3.3.4 CHN compounds

A total of 42 CHN formulas are observed in size-resolved coastal aerosols, accounted for less than 4% of the total OC intensity in each size bin. CHN formulas are dominated by C₁₃₋₂₀ species in ultrafine particles (Figure 3a), among which C₁₉H₂₃N₃, C₁₅H₁₃N₃ and C₁₈H₂₀N₆ are the most abundant formulas. 17 and 24 CHN formulas accounted for less than 0.5% of the total OC intensity in coastal PM_{2.5} and urban PM_{2.5}, respectively. The most abundant formulas in coastal PM_{2.5} are C₂₀H_{11,13}N₇ and C₂₉H₂₉N₃, while the most abundant one in urban PM_{2.5} is C₂₇H_{25,27,29}N₃. All these high-intensity formulas had AI values > 0.5, indicating the possible presence of benzene rings or heterocyclic amines in their molecular structures (Song et al., 2018; Sun et al., 2010).

(DBE/C)_w and OSC_w of CHN formulas show relatively small variation with particle size (Figure 3b), except for 1.0-1.8 μm particles. On the other hand, a strong variation with particle size is seen for the percentage of aromatic compounds. Among all the subgroups in the coastal aerosols, CHN formulas possess relatively high (DBE/C)_w, low OSC_w and high percentage of aromatic compounds. These three parameters in urban PM_{2.5} are again lower than those in coastal PM_{2.5} (Figure 4b).

CHN compounds, also known as alkaloids, have been proved as the main composition of BBOA by the previous studies (Laskin et al., 2009; Lin et al., 2012; Magda et al., 2012; Samy et al., 2013). Fleming et al. (2017) and Wang et al. (2017b) identified 101 and 74 CHN formulas, respectively, in the burning emissions of brushwood, straw, corn and wheat. However, only 5 of

them ($C_{13}H_{10,24}N_2$, $C_{14}H_{18}N$ and $C_{13}H_{11,19}N_3$) are found in ultrafine and submicron particles at the coastal site. Another five formulas $C_{10}H_{14}N_2$, $C_{11,15}H_{20}N_2$, $C_{14}H_{18,20}N_2$ and $C_{10}H_{14}N_2$ are found in the $PM_{2.5}$ samples. This indicates that the burning emissions of these biomass materials play a minor role in the formation of OC in coastal and urban aerosol particles.

3.3.5 Halogen-containing organic compounds

There are 1216 and 106 halogen-containing formulas in coastal $PM_{2.5}$ and urban $PM_{2.5}$, respectively. The vast difference of halogen-containing formula numbers between coastal $PM_{2.5}$ and urban $PM_{2.5}$ is due to the different numbers of I-OC formulas.

I-OC There are 450 I-OC formulas in total detected in size-resolved coastal aerosols, less than 1203 I-OC formulas in coastal $PM_{2.5}$, indicating positive artifacts are formed via chemical reactions between iodine and OC in coastal $PM_{2.5}$. The size distribution of I-OC is bimodal (Figure 3a). Those in ultrafine particles include (1) nine $C_{18}H_hO_nN_nI$ formulas with DBE = 1-4, (2) $C_9H_{16}NO_3I$ and its C_{10} - C_{13} homologues, (3) diiodo acetic acid $C_2H_2O_2I_2$, diiodomethane CH_2I_2 , (4) iodinated C_{21} carbonyls $C_{21}H_{39}OI$ and $C_{21}H_{41}OI$, (5) iodinated $C_{21,25,27,29}$ alcohols or ethers with DBE = 0, (6) iodinated C_{10} and C_{15} terpene and sesquiterpene oxidation products and (7) iodinated organic sulfate $C_8H_{17}N_2SO_8I$ and $C_{21}H_{43}SO_4I$. The I-OC in supermicron particles are dominated by C_{4-10} species, the most abundant of which are iodinated C_4 - C_6 CHO and CHON compounds with DBE = 3-6. Therefore, I-OC is most likely formed in iodine-rich particles via electrophilic substitution of aromatic hydrogen or α -H of carbonyl and carboxyl groups in non-iodine compounds by iodine cations (probably from HOI or I_2).

The 1203 I-OC formulas in coastal $PM_{2.5}$ accounted for 14% and 21% of total OC intensity in the ESI- and ESI+ modes, respectively. On the contrary, 56 I-OC formulas in urban $PM_{2.5}$ accounted for only 0.2% and 0.1% of total OC intensity in the two ESI modes. These results indicate that the coastal site is an emission hotspot of aerosol particles rich in organic iodine compounds.

Cl/Br-OC 10 and 46 Cl-OC formulas are detected in coastal $PM_{2.5}$ and urban $PM_{2.5}$, respectively, account for less than 0.5% of the total OC intensity in both samples. More Cl-OC formulas in urban is consistent with the higher Cl^- content observed by using SP-AMS. These Cl species arose probably from the combustion of fossil fuels or biomass in the urban areas. A total of 50 Cl-OC formulas (S/N: 10.7-1164) is observed in the size-resolved coastal samples. 25 Cl-OC formulas are detected in $< 0.032 \mu m$ particles, among which $C_{18}H_{36}ClNO_2$ is the most abundant one. The number of Cl-OC formulas decreases with increasing particle size. Wang et al. (2020) studied chlorine-initiated oxidation of alpha-pinene in the presence of NO_x in chamber experiments. $C_{10}H_{15}ClO_{5-6}$ detected in urban $PM_{2.5}$ fits well to the reaction mechanism proposed by Wang et al. (2020).

Virtually no prior studies have reported Br-OC in aerosol particles. Only 3, 3 and 4 Br-OC formulas are found in the MOUDI samples, coastal $PM_{2.5}$ and urban $PM_{2.5}$, respectively. The total intensity of Br-OC is one order of magnitude lower than that of Cl-OC. The 10 Br-OC formulas (S/N: 10.7-27.4), as well as the Cl-OC with S/N over 100, are listed in Table S2. Br-OC can be either from primary emission in aerosol particles or the reaction of reactive bromine species towards organic compounds in the atmosphere. It thus seems that both pathways are not effective for the formation of Br-OC.

3.4 Highly Oxygenated Compounds (HOC)

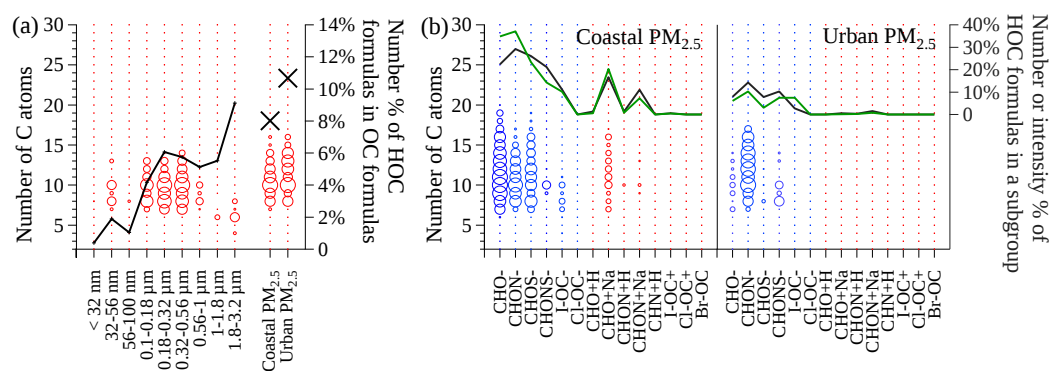


Figure 7. (a) Carbon number distribution of HOC formulas (circles) and the number percentage of HOC formulas in OC formulas of a sample. (b) The number percentage (green lines), intensity percentage (black lines) and carbon number distributions (red and blue circles) of HOC formulas in a subgroup of coastal PM_{2.5} and urban PM_{2.5} sample.

HOC are dominated by C₇₋₁₃ species (maximum: C₁₀) in submicron particles from 0.1 μm to 0.56 μm (Figure 7a). 69, 170 and 34 formulas are assigned to HOC in ultrafine, submicron and supermicron particles, respectively, contributing < 2%, 5% and 5-8% of the formulas in the three size ranges. Our data lead to the conclusion that organic compounds in aged submicron particles are more oxygenated than those in fresh ultrafine particles.

742 and 502 HOC formulas are observed in coastal PM_{2.5} and urban PM_{2.5}, contributing 8% and 11% of total formulas in the two samples, respectively (Figure 7a). The total intensity of HOC in coastal PM_{2.5} is higher than urban PM_{2.5} (Figure 7b). This indicates a higher oxidation degree of OC in coastal PM_{2.5} than urban PM_{2.5}. In terms of elemental subgroup, 20% to 37% of CHO⁻, CHON⁻, CHOS⁻ and CHO+Na formulas are HOC in coastal PM_{2.5}, while only 10% of CHON⁻ formulas are HOC in urban PM_{2.5}. HOC in coastal PM_{2.5} and urban PM_{2.5} have similar carbon number distribution that is dominated by C₈₋₁₅ species (maximum: C₁₀).

4 Conclusions

We conducted a comprehensive analysis of elemental composition, unsaturation degree, carbon oxidation state and aromaticity of coastal OA with a high size resolution. A systematical comparison of bulk PM_{2.5} chemical composition between a coastal NPF hotspot and a typical inland urban site was shown in the context of severe PM pollution in the Yangtze River Delta region of China. Our analysis shows that the molecular composition of organic aerosols is highly size-dependent at the coastal NPF hotspot, including the OC in ultrafine particles generated in NPF events, secondary products of terpene oxidation in aged submicron particles and the OC in sea salt particles. The analysis based on size-resolving sampling technique and ultrahigh resolution MS helps to understand the molecular characteristics and sources of organic aerosols. On the contrary, PM_{2.5} sampling is subject to both the loss of ultrafine particle components due to lower collection efficiency and positive artifacts formed via post-sampling reactions among aerosol components (e.g. I-OC).

Based on the measurement of VOC emission from local intertidal macroalgae, dominant C₂₀₋₃₃H_hO_o and C_{18,30}H_hO_oN_n compounds in particles < 0.10 μm are proposed to form via gas-

phase oxidation of C_{20,21} fatty aldehydes and C₁₈ fatty acids, followed by organic accretion reaction with small aldehyde/alcohol in aerosol particles. The presence of abundant reduced-N atoms in the OC of this size range suggests the involvement of ammonia via imine formation reaction. On the other hand, CHO, CHON, CHOS and CHONS compounds in 0.18-0.56 μm submicron particles are dominated by C₈-C₂₀ peaks (maximum: C₁₀ or C₁₅). They can be most likely attributed to terpene SOA products by comparing with previous chamber experiment studies. Submicron particles also accommodate most of highly oxygenated compounds. Organic iodine compounds are suggested to form via electrophilic substitution of all above compounds by iodine cations in iodine-rich particles. In total, CHN and Cl/Br-containing OC only accounted for 1-4% of total OC intensity of organic aerosols at this coastal NPF hotspot site.

Acknowledgments and Data

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Data availability: datasets for this research are available in the in-text data citation reference Yu et al. (2020)

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