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Probing key organic substances driving new particle growth initiated by iodine nucleation in coastal atmosphere

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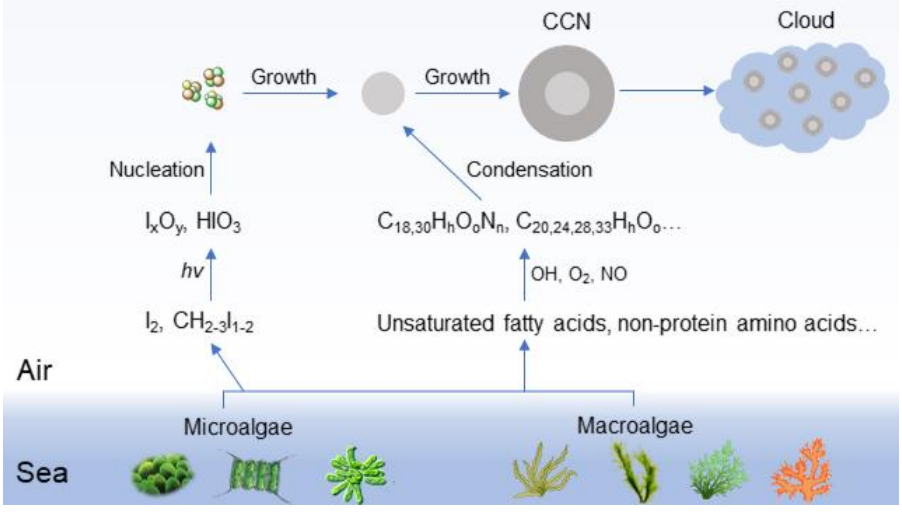
18 **Graphic abstract**

19 

20 **ABSTRACT**

21 Unlike the deep understanding of highly oxygenated organic molecules (HOMs)
22 driving continental new particle formation (NPF), little is known about the organics
23 involved in coastal and open ocean NPF. On the coastline of China we observed intense
24 coastal NPF events initiated by iodine nucleation, but particle growth to cloud
25 condensation nuclei (CCN) sizes was dominated by organic compounds. This article
26 revealed a new group of $C_{18,30}H_hO_oN_n$ and $C_{20,24,28,33}H_hO_o$ compounds with specific
27 double bond equivalents and oxygen atom numbers in sub-20 nm coastal iodine new
28 particles by using ultrahigh resolution Fourier transform-ion cyclotron resonance mass
29 spectrometry (FT-ICR-MS). We proposed these compounds are oxygenated or nitrated
30 products of long chain unsaturated fatty acids, fatty alcohols, non-protein amino acids
31 or amino alcohols emitted mutually with iodine from coastal biota or biological-active
32 sea surface. Group contribution method estimated that the addition of $–ONO_2$, –OH and
33 –C=O groups to the precursors reduced their volatility of by 2~7 orders of magnitude
34 and thus made their products condensable onto iodine new particles in the coastal
35 atmosphere. Non-target MS analysis also provided a list of 440 formulas of iodinated

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organic compounds in size-resolved aerosol samples during the iodine NPF days, which facilitates the understanding of unknown aerosol chemistry of iodine.

1. INTRODUCTION

Atmospheric new particle formation (NPF) contributes over half of global cloud condensation nuclei (CCN) (Merikanto et al., 2009) and thus influences cloud properties and Earth's radiation budget (Metzger et al., 2010). By deploying high resolution Chemical Ionization Mass spectrometer, recent laboratory and field studies have identified a group of highly-oxidized organic molecules (HOMs) with high O/C ratio and extremely low volatility from the reactions of volatile organic compounds (VOCs) such as monoterpenes (Ehn et al., 2014). Sesquiterpenes (Richters et al., 2016) and alkene (Mentel et al., 2015) with hydroxyl radical (OH), ozone (O_3) and nitrate radicals (NO_3). These HOMs play an important role in particle nucleation and growth of continental NPF, as well as in the formation of secondary organic aerosols.

Unlike the deep understanding of continental HOMs, little is known about the role of organics in the NPF in coastal or open ocean atmosphere. The current state of knowledge is that the self-clustering of biogenic iodine oxides or oxoacids could initiate NPF events with particle number concentration sometimes exceeding 10^6 cm^{-3} (O'Dowd et al., 2002; Burkholder et al., 2004; Sipilä et al., 2016; Stevanović et al., 2019; Kumar et al., 2018). But it is unknown if other species are needed to drive the growth of iodine clusters to CCN sizes in coastal or open ocean atmosphere (Saiz-Lopez et al., 2012). Iodine-induced NPF (I-NPF) events were mostly reported in European coastlines (Yoon et al., 2006; Mahajan et al., 2010) and polar regions (Allan et al., 2015; Roscoe et al., 2015; Dall´Osto et al., 2018). In 2019 we provided evidences of I-NPF in the southeast coastline of China, based on particle number size distribution and iodine measurements (Yu et al., 2019). The focus of that paper (Yu et al., 2019) is, however, the speciation of organic iodine compounds in size-segregated aerosol samples. Moreover, the use of relatively low resolution Time-of-Flight (TOF) mass analyzer and *in vitro* signal amplification approach in that paper did not allow the detection of the majority of non-

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aromatic organic iodine compounds. Organic iodine remains to be the most significant unknown in aerosol iodine chemistry at present (Saiz-Lopez et al., 2012).

Fourier Transform Ion Cyclotron Resonance (FT-ICR) coupled with soft ionization techniques such as electrospray ionization (ESI) and ambient pressure chemical ionization (APCI) allows characterization of complex organic mixtures at the molecular level due to its ultra-high resolution and mass accuracy (Pratt and Prather, 2012). This technique has been used to examine molecular composition of organic aerosols (Schum et al., 2018; An et al., 2019; Zuth et al., 2018; Daellenbach et al., 2018; Xie et al., 2020) and cloud water (Zhao et al., 2013; Bianco et al., 2018). Studies investigating coastal organic aerosols have been rarely. Virtually no study reported the characterization of organic compounds driving the growth of coastal or open ocean new particles.

In this study, comprehensive chemical composition analyses were conducted on the size-segregated aerosol samples down to 10 nm, collected by 13-stage nano-MOUDI (nano-micro orifice uniform deposit impactor) during the intense I-NPF days at a coastal site of China. Relative abundances of HSO_4^-, total iodine and total organic carbon (TOC) in 10-56 nm particles were compared between the I-NPF days and conventional continental NPF days. In particular, using ultra-high resolution FT-ICR MS, we conducted a non-target analysis of particle-phase organic compounds to explore their molecular identity, formation mechanism and the role in new particle growth in the coastal atmosphere.

2. METHDOLOGY

2.1. Sampling collection

The sampling site (29°29′ N, 121°46′ E) is in a building about 40 and 200m away from the coastline of East China Sea (Zhejiang Province) at high tide and low tide, respectively. The classification of I-NPF event and continental regional NPF (C-NPF) event was based on particle number size distributions (PNSD) between 2 and 750 nm monitored from January to May 2018 by a scanning mobility particle spectrometer

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(SMPS; TSI DMA3081 and CPC3775; scanning range: 40-750 nm) and a neutral cluster air ion spectrometer (NAIS; scanning range: 2-42 nm). Strong I-NPF events were observed almost every day in April and May, which was the growth and farming season of seaweed. A nano-MOUDI sampling scheme was implemented according to the PNSD measurement. One set of nano-MOUDI samples was collected during the C-NPF days from February 11 to 13; a second set was collected during the non-NPF days from April 16 to 18; a third set was collected during the I-NPF days from May 9 to 11. The PNSD during the 3 periods are shown in Figure S1. Each set of nano-MOUDI samples was collected continuously for 72 hours, during which NPF occurred on a daily basis, so that particle chemical composition of different event types can be obtained from offline analyses. Aluminum foil filters were used as sampling substrate to avoid the adsorption of gaseous species. For each set of nano-MOUDI samples, two nano-MOUDIs were placed side by side to collect 10-100 nm particles (on stages 10-13; other stages were silicon greased) and 100 nm-18 μm particles (on stages 1-9) separately, in order to reduce potential positive particle-bounce artifacts. Three additional sets of blank samples were collected by placing a high efficiency particulate air (HEPA) filter at the gas inlet of nano-MOUDI. Detailed information on aerosol sample collection could be found in Yu et al. (2019).

2.2. Sample preparation and analysis

Half of each filter was transferred into a 20 mL tapered plastic centrifuge tube, added 10 mL mixed solvent (1:1 v/v water and methanol; LCMS grade). The mixture was sonicated for 40 min and filtered by a 0.2 μm PTFE membrane syringe filter. The filtrate was evaporated to almost dryness in a rotary evaporator below 40 °C and subsequently redissolved in 0.5 mL water. After being centrifuged for 30 min at 12,000 rpm, the supernatant was collected for total iodine (I) analysis by Agilent 7500a ICP-MS (Agilent Technologies, Santa Clara, CA, USA) and HSO_4^- analysis by UPLC-ESI-Q-TOF-MS. The measurements of HSO_4^- and total I were elaborated in our previous article Yu et al. 2019. Another half of each filter was extracted in the same way but used for TOC analysis by a TOC analyzer (Model TOC-5000A, Shimadzu, Japan) and

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non-target MS analysis of organic compounds (OC) by ESI-FT-ICR-MS (SolariX XR 9.4T instrument, Bruker Daltonics, Coventry, UK). Samples were infused by a syringe pump and analyzed in both positive (ESI+) and negative (ESI-) modes. ESI-FT-ICR MS operation conditions are included in Supplement Material. Field blank sample extracts were analyzed following the same procedure.

2.3. FT-ICR MS data processing

A resolving power ($m/\Delta m_{50\%}$) 550,000 at m/z 300 of our FT-ICR-MS allows the determination of possible formulas for singly charged molecular ions. Only m/z values between 150-1000 Da that satisfies signal/noise (S/N) ratio > 10 were considered. For each m/z value, several scientific rules were applied to calculate a reasonable elemental formula of natural organic molecule: the general formula is $C_{1\text{-}50}H_{1\text{-}100}O_{0\text{-}50}N_{0\text{-}10}I_{0\text{-}3}$ in the ESI+ mode; elemental ratios H/C, O/C, and N/C are limited to 0.3-3, 0-3 and 0-1.3, respectively. The general formula is $C_{1\text{-}50}H_{1\text{-}100}O_{1\text{-}50}N_{0\text{-}5}S_{0\text{-}2}I_{0\text{-}3}$ in the ESI- mode; elemental ratios H/C, O/C, N/C and S/C are limited to 0.3-3, 0-3, 0-0.5 and 0-0.2, respectively. Mass error must be smaller than 0.5 ppm. Formula containing C, H, O, N, S and I isotopologues were removed from the formula lists. A formula with m/z > 500 was not reported if it did not belong to any CH_2 homologous series. For a formula $C_cH_hO_oN_nS_sI_x$, double bond equivalents (DBE) defined as $DBE = \frac{2c+2-h+n-x}{2}$ was required to be non-negative. Formula calculation was done following the same procedure for the three field blank samples. All formulas found in the field blank samples, regardless of peak intensity, were excluded from the formula lists of real samples. Aromaticity index (AI) is calculated from $AI = \frac{DBE_{AI}}{C_{AI}} = \frac{1+c-o-s-0.5h}{c-o-s-n}$. If $DBE_{AI} \leqslant 0$ or $C_{AI} \leqslant 0$, then AI = 0. A threshold value of $AI \geqslant 0.5$ provides an unambiguous minimum criterion for the presence of aromatic structure in a molecule(Yassine et al., 2014).

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3. RESULTS AND DISCUSSION

3.1. Organics dominate the growth of new particles initiated by iodine nucleation

We first compare relative concentrations of major aerosol components, that is, total I, HSO_4^- and TOC, in nano-meter new particles during different event days. Total I (13.5 ng m^{-3}, Table 1) in 10-56 nm particles during the I-NPF days was 67 and 36 times higher than those during the C-NPF days (0.2 ng m^{-3}) and non-event days (0.37 ng m^{-3}). In the same size range, HSO_4^- concentration (0.2 μg m^{-3}) during the I-NPF days was lower than that during the C-NPF days (0.5 μg m^{-3}). This clearly indicates that the NPF events from May 9 to 11 was linked to iodine nucleation. Even so, aerosol mass in 10-56 nm new particles during the I-NPF days was dominated by organics. We define the mass fraction of organic mass (OM) in the particles as $(1.5m_{TOC})/(m_{Total\ I} + m_{HSO4}^- + 1.5m_{TOC}) \times 100\%$ by assuming a OM/TOC ratio of 1.5. Mass fractions of OM are 95%, 87% and 68%, respectively, in the size bins 10-18 nm, 18-32 nm and 32-56 nm during the I-NPF days. Therefore, organic compounds are critical for I-NPF to contribute to CCN. The main purpose of this article is to identify these organic compounds during the I-NPF days. The OC composition during the C-NPF days is beyond the scope of this article.

Table 1. Concentrations of Total iodine (I), HSO_4^- and Total Organic Carbon (TOC) in 3 size bins between 10-56 nm during the I-NPF, C-NPF and non-NPF days. For simplicity, only the sum of three size bins are shown for the C-NPF and non-NPF days. BDL=below detection limit.

	I-NPF			C-NPF	non-NPF
	10-18 nm	18-32 nm	32-56 nm	10-56 nm	10-56 nm
Total I (ng m^{-3})	2.3	6.2	5.0	0.20	0.37
HSO_4^- (μg m^{-3})	0.022	0.034	0.144	0.50	BDL
TOC (μg m^{-3})	0.31	0.18	0.21	0.28	BDL

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3.2. Elemental composition of non-iodinated OC on the I-NPF days

Non-target analysis of OC elemental composition was performed in detail on 10-18 nm, 32-56 nm, 180-560 nm and 3.2-5.6 μm particles during the I-NPF days. Elemental formulas in the 4 size bins can represent OC molecular composition of nucleation mode, Aitken mode, accumulation mode and coarse mode, respectively. OC formulas were divided into two categories: non-iodinated OC and iodinated OC. There are far more non-iodinated OC formulas than iodinated OC formulas in <1 μm particles in terms of both formula number (Table 2) and relative intensity (Figure 1). For example, 2831 non-iodinated OC formulas account for 96.6% of OC total intensity in 10-18 nm particles, while 137 iodinated OC formulas account for the remaining 3.4%. It means that non-iodinated OC dominates new particle growth during the I-NPF events. In this section, we first discuss chemical characteristics of non-iodinated OC, while the speciation of iodinated OC will be discussed in Section 3.4.

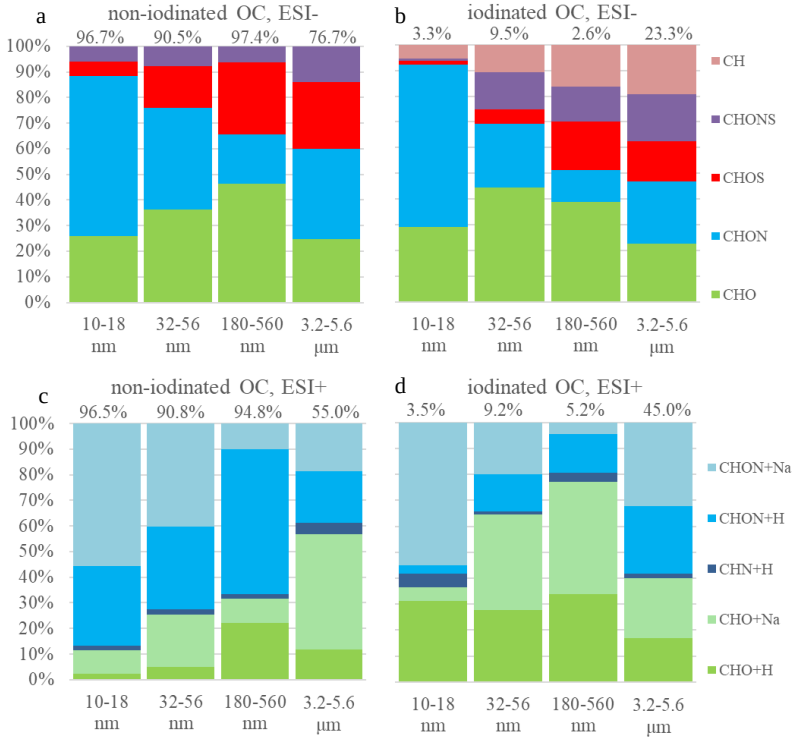

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Figure 1. Relative intensity distributions of elemental groups observed in 10-18 nm, 32-56 nm, 180-560 nm and 3.2-5.6 μm size bins in ESI+ and ESI- modes. The percentage above a column denote the percent of non-iodinated OC (or iodinated OC) intensity in total OC intensity in a size bin. +Na and +H denote $[M+Na]^+$ and $[M+H]^+$ adduct in ESI+ mode, respectively.

The molecular formulas of non-iodinated OC were divided into seven elemental groups CHO^-, CHO^+, $CHON^-$, $CHON^+$, $CHOS^-$, $CHONS^-$ and CHN^+. The number distribution of 7 elemental groups for the 4 size bins is listed in Table 2. If both $[M+Na]^+$ and $[M+H]^+$ adducts of a formula were detected, the formula was counted only once. It should be noted that some formulas were repeatedly detected in ESI+ and ESI- modes. Some formulas detected in one size bin were also detected in another size bin. This is quantitatively shown in the first four rows of Table 2. For instance, 58%, 25% and 4% of the formulas detected in 10-18 nm aerosols were also detected in 32-56 nm, 180-560 nm and 3.2-5.6 μm aerosols, respectively. In another word, the particles in neighboring size bins share more similarity in organic composition. An unexpected finding is that the number of non-iodinated OC formulas detected in 3.2-5.6 μm coarse particles (n = 266) is one order of magnitude lower than those of other bins. Reconstructed mass spectra of the 7 elemental groups in ESI-and ESI+ modes are shown in Figure S2 for the four size bins.

Table 2. The numbers of assigned formulas of elemental groups of organic compounds in 10-18 nm, 32-56 nm, 180-560 nm and 3.2-5.6 μm size bins. The first 4 rows show the percent of formula repeatability between two size bins. 1I-OC: molecular formula containing one iodine atom.

Repeatability	10-18 nm	32-56 nm	180-560 nm	3.2-5.6 μm	
10-18 nm		58%	25%	4%	
32-56 nm	57%		38%	4%	
180-560 nm	34%	51%		6%	
3.2-5.6 μm	35%	35%	34%		
Non-iodinated OC					Total
CHO^-	531	565	525	20	892
CHO^+	250	501	380	111	857

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$CHON^-$	1005	638	347	25	1268	
$CHON^+$	1139	1055	828	72	2121	
$CHOS^-$	147	216	256	22	357	
$CHONS^-$	134	131	93	10	259	
CHN^+	34	26	7	7	46	
Total	2831	2770	2151	266	4979	
Iodinated OC					Total	1I-OC (%)
$CHOI^-$	32	53	11	5	80	64%
$CHOI^+$	17	85	31	31	136	93%
$CHONI^-$	52	29	7	7	77	88%
$CHONI^+$	34	57	18	52	132	81%
$CHOSI^-$	3	8	7	3	18	72%
$CHONSI^-$	2	7	3	2	13	62%
$CHNI^+$	6	4	4	3	16	56%
CHI^-	4	2	1	4	9	67%
Total	137	228	76	100	440	80%

CHON is the most commonly assigned elemental group in both ESI+ (2121 $CHON^+$) and ESI- (1268 $CHON^-$) modes, followed by the CHO group (857 CHO^+ formulas and 892 CHO^- formulas). S-containing formulas are 357 $CHOS^-$ and 259 $CHONS^-$. The formula number of the least common CHN^+ group is only 46. In terms of relative intensity, CHON fraction in the ESI- mode decreases from 61% of OC in the 10-18 nm bin to 20% in the 180-560 nm bin (Figure 1a), while the fractions of CHO and CHOS/CHONS increase with particle size. In the ESI+ mode, the fraction of CHON decreases from 88% in 10-18 nm bin to 70% in 180-560 nm bin, being always the dominant elemental group of non-iodinated OC (Figure 1b). Low molecular weight (LMW) amines are important stabilizers in acid-base nucleation (Kurtén et al., 2008; Jen et al., 2014; Zheng et al., 2000; Yao et al., 2016), but their molecular ions are out of the mass range of our FT-ICR-MS. The CHN^+ formulas that we observed contained 9-50 C atoms and 1-7 N atoms, accounting for a negligible fraction 1.7% of total intensity of all ESI+ formulas in the 10-18 nm particles.

Previous elemental composition studies using FT-ICR-MS were mostly conducted on $PM_{2.5}$ or PM_{10} collected from marine (Schmitt-Kopplin et al., 2012; Bao et al., 2018; Ning et al., 2019), urban (Wu et al., 2019; Jiang et al., 2016), troposphere (Schum et al., 2018; Mazzoleni et al., 2012) and forest sites (Kourtchev et al., 2013). In general, these studies showed that the numbers of CHO compounds were comparable with or more

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than those of CHON compounds. Our study shows clearly that elemental composition of aerosol OC is highly size dependent. New particle growth in the size range of 10-18 nm during the I-NPF event is dominated by CHON elemental group, followed by CHO. The focus of this article narrows on the identity and source of the CHON and CHO formulas in 10-18 nm particles, by comparing with those in the 180-560 nm size bin.

3.2.1. CHO formulas

There is a total of 531 CHO^- formulas and 250 CHO^+ formulas in 10-18 nm particles. 54 CHO formulas are commonly found in ESI+ and ESI- modes. In terms of relative intensity, CHO^- compounds are more abundant than CHO^+ compounds (Figure 3b, total intensity: 4.14 e+09 *vs.* 1.24 e+09). However, this is not indicative of absolute concentration of the two groups due to different ionization efficiency between ESI- and ESI+ modes. CHO^- is characterized by a series of formulas with 20, 24, 28, and 33 C atoms, 4 or 6 O atoms and 1 equivalent double bond (Figure 2b). The total intensity of top 10 formulas accounts for 30% of all 531 formulas. Assuming CHO^- formulas contain at least 1 carboxylic group (–COOH), the rest of their molecules should be saturated (DBE = 0) and contain 2 or 4 O atoms.

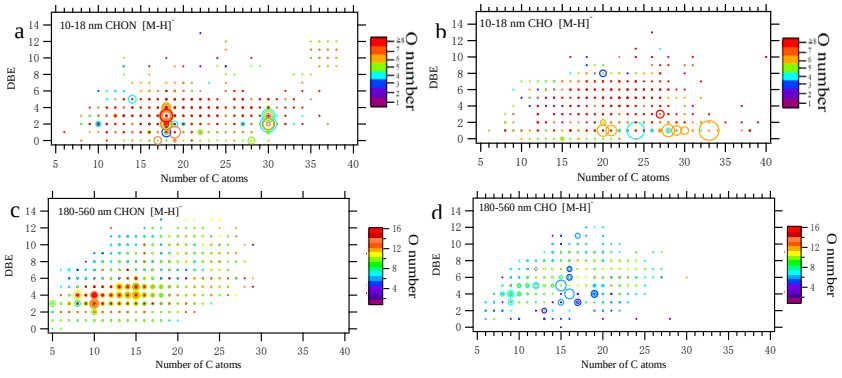

Figure 2. DBE *vs.* C atom number diagrams of all CHON and CHO formulas detected in 10-18 nm and 180-560 nm particles in ESI- mode. The color bar denotes O atom

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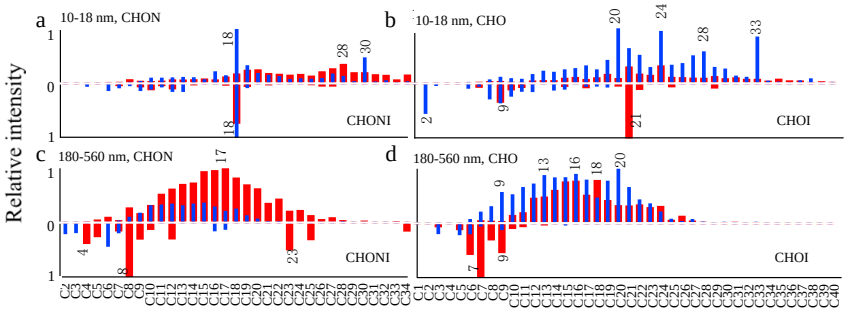
246 number in the formulas. The size of the circles reflects the relative intensities of
247 molecular formulas on a logarithmic scale.
248
249 The above feature is not seen in either CHO^+ formulas in the 10-18 nm bin or CHO^-
250 formulas in the 180-560 nm bin. There are more C_{21} and C_{24} formulas than other C
251 subgroups in the CHO^+ formulas of 10-18 nm bin (Figure S3d), but none of them have
252 exceptionally-high intensity. The prominent formulas in the CHO^- group in 180-560
253 nm particles have relatively high unsaturation degree (DBE = 3-7, Figure 2d). The
254 relative intensities of subgroups according to C atom number in the CHO^- formulas in
255 the 180-560 nm bin are characterized by bimodal distribution with maximum intensity
256 around C_{15}-C_{16} and C_{20} (Figure 3d). The relative intensity of O atom subgroups is
257 mono-modally distributed around O_7 (Figure S4).



258
259 Figure 3. Relative intensities of subgroups according to C atom number in CHON, CHO,
260 CHONI and CHOI formulas in 10-18 nm and 180-560 nm particles in ESI+ (in red) and
261 ESI- (in blue). The intensity of the most abundant subgroup in a size bin is defined as
262 1 and those of other subgroups are normalized by it. The relative intensities of non-
263 iodinated OC formulas (iodinated OC formulas) are plotted in the region above (below)
264 zero line.
265
266 ***3.2.2. CHON formulas***
267 As discussed earlier, CHON is the most abundant elemental group observed in the
268 smallest size bin 10-18 nm. There is a total of 1005 $CHON^-$ formulas (total intensity

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9.96 e+09) and 1139 $CHON^+$ formulas (6.45 e+09) in 10-18 nm bin. 355 CHON formulas are commonly found in ESI+ and ESI- modes. A close examination of Figure 2a and 3a reveals that $CHON^-$ is characterized by a series of C_{18} and C_{30} formulas with low DBE values (1-4). 87 C_{18} and 26 C_{30} formulas account for 37% of total intensity of $CHON^-$. Such feature is not seen for $CHON^+$ formulas that are rather uniformly distributed in DBE vs. C diagram (Figure S3a and S3c). Generally speaking, $CHON^-$ compounds should contain nitro- ($–NO_2$) or nitrooxy- ($–ONO_2$) group and are ionizable due to the presence of –COOH or hydroxy (–OH) (Lin et al., 2012). However, the presence of amine group in $CHON^-$ formulas cannot be excluded. Take C_{18} as example, 51 out of 87 $C_{18}H_hO_oN_n^-$ formulas should contain at least one amine group, either because their O atom numbers are not large enough to allow the assignment of $–NO_2$ for all N atoms, or because some formulas (25 out of 87) were also detected in ESI+ mode. In total, 51 $C_{18}H_hO_oN_n^-$ formulas with an amine group account for 54.4% of total intensity of 87 $C_{18}H_hO_oN_n^-$ formulas.

The presence of amine group in $C_{18}H_hO_oN_n^-$ formulas in 10-18 nm particles is also supported by the comparison with $CHON^-$ in 180-560 nm submicron aerosols. $CHON^-$ in 180-560 nm is characterized by a number of formulas with maximum intensity around C_{10} and C_{15} (Figure 2c). A plot of O atom number *vs.* N atom number in Figure S5a shows that $C_{10}H_hO_oN_n^-$ in 180-560 nm have O/N ratios ≥ 3 and O atom number is positively correlated with N atom number. It indicates that these $C_{10}H_hO_oN_n^-$ formulas are probably nitro- or nitrooxy- oxidation products of monoterpenes from continental plant emission. In contrast, O/N ratios of the $C_{18}H_hO_oN_n^-$ formulas in 10-18 nm are mostly small and O atom number do not increase with N atom number (Figure S5b). All collective evidences above reveal that nitrogen-containing organic compounds in 10-18 nm particles during the I-NPF days are partly composed of long-chain amino alcohols, amino acids and so on.

In summary, a series of very distinctive $CHON^-$ and CHO^- formulas was observed in 10-18 nm new particles during the I-NPF days. These formulas are characterized by some specific numbers of C atoms (i.e. $C_{18}H_hO_oN_n$, $C_{30}H_hO_oN_n$, $C_{20}H_hO_o$, $C_{24}H_hO_o$, $C_{28}H_hO_o$ and $C_{33}H_hO_o$) and equivalent double bonds (DBE = 1 for CHO^- and 1-4 for

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CHON$^-$). To the best of our knowledge, such CHON$^-$ and CHO$^-$ formulas have not been reported by previous aerosol studies. The chemical composition of new particles is completely decoupled with the CHO$^-$ and CHON$^-$ formulas around C_{10}, C_{15} and C_{20} in 180-560 nm submicron particles, which might be originated from continental terpene emissions. Fewer O atoms in $C_{18,30}H_hO_oN_n$ and $C_{20,24,28,33}H_hO_o$ formulas than those in submicron aerosols indicate that these compounds should be more freshly emitted into the atmosphere. The discontinuous chemical composition and PNSD spectrum (Figure S1a) below and above 50 nm particle size reflect the fact that the further growth of new particles beyond 50 nm in local I-NPF events cannot be monitored by our stationary sampling strategy.

On the other hand, we observed more complicated distributions of CHO$^+$ and CHON$^+$ formulas in 10-18 nm new particles that are of relatively small individual intensity and are rather uniformly distributed in DBE vs. C diagrams. Like CHON$^-$ and CHO$^-$, those CHO$^+$ and CHON$^+$ formulas also possess a larger number of C atoms (C > 19) than their counterparts in 180-560 nm submicron aerosols (Figure 3). 21 out of 30 most abundant CHON$^+$ formulas contain two or more N atoms; this ratio 21/30 is higher than those in CHON$^-$ formulas. Generally speaking, CHO$^+$ and CHON$^+$ formulas represent carbonyls/alcohols/epoxides and amino alcohols/amino acids, respectively. One interesting finding about CHO$^+$ and CHON$^+$ is that they tend to form $[M+Na]^+$ adducts in small aerosols and $[M+H]^+$ adducts in large aerosols (Figure 1c). This indicates that the CHO$^+$ and CHON$^+$ compounds in new particles during the I-NPF days should possess different basic functional groups from those in submicron particles.

3.3. Possible precursors and formation mechanism of organic compounds detected in 10-18 nm new particles during the I-NPF days

It is unrealistic to simply propose one out of a large number of possible structures for a formula with large C atom number (e.g., ≥ 18). Our strategy is to first explore the possible precursors of the newly found CHON and CHO formulas. It is obvious that these $C_{18,30}H_hO_oN_n$ and $C_{20,24,28,33}H_hO_o$ formulas cannot be attributed to continental

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terpene emission or anthropogenic aromatic emissions. Previous field measurements of marine NPF precursor focused on volatile species like iodine (Stevanović et al., 2019), iodomethanes (O'Dowd et al., 2002), dimethyl sulfonic acid (Yvon et al., 1996; Barone et al., 1996; Barnes et al., 2006) and LMW amines (Ning et al., 2019; Ge et al., 2011). So far there is no report about aliphatic compounds with C number ≥ 18 in either gas phase or new particles (Cochran et al., 2017; Bikkina et al., 2019). Therefore, we consulted the literature that reported chemical compounds isolated from biological tissues of algae, plankton or other marine organisms. Potential precursors are listed in Table 3.

3.3.1. Fatty acids

Fatty acids (FAs) are widely found in animals, plants and microbe (Moss et al., 1995). Plants have higher content of unsaturated FAs than animals. C_{14}-C_{24} fatty acids, including both saturated and unsaturated, have long been observed in seaweed (Dawczynski et al., 2007) and very long chain FAs (C_{24}-C_{36}) have been isolated from green algae, chlorella kessleri, sponges and marine dinoflagellate (Litchfield et al., 1976; Řezanka and Podojil, 1984; Mansour et al., 1999). C_{18} Oleic acid, linoleic acid and linolenic acid are most commonly found unsaturated FAs in macro algae. FAs with carbon chain shorter than C_{20} were used by atmospheric chemists as organic tracers of atmospheric aerosols from microbe or kitchen emission (Simoneit and Mazurek, 1982; Zheng et al., 2000; Guo et al., 2003; Rogge et al., 1991; DeMott et al., 2018; Willoughby et al., 2016). In our study, no saturated FAs were detected in 10-18 nm particles. Only 1.5% CHO^- formulas can be assigned to unsaturated FAs (that is, include 2 O atoms, 14-28 C atoms and DBE = 3-6). Other CHO compounds observed in 10-18 nm particles contain > 2 O atoms and thus can be assigned as the oxidized derivatives of FAs.

Table 3 Possible precursors and their presence in marine biological sources and our aerosol samples. ND: not detected.

Potential precursors	Presence in marine sources	Presence in aerosol particles

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Unsaturated fatty acid	C_{14}-C_{24} fatty acids	Seaweed (Dawczynski et al., 2007)	1.5% of CHO^- in terms of relative intensity
	C_{25}--C_{36} very long chain fatty acids	Green algae, chlorella kessleri, sponges, marine dinoflagellate (Litchfield et al., 1976; Řezanka and Podojil, 1984; Mansour et al., 1999).	ND
fatty alcohols	C_{30}-C_{32} mono- and diunsaturated alcohols and diols	Yellow-green algae (Volkman et al., 1992)(eustigmatophytes)	ND
Saturated hydroxyl fatty acids	$C_{20}H_{40}O_3$, $C_{32}H_{64}O_4$	Nannochloropsis, cutins and suberins of higher plants (Gelin et al., 1997).	S/N 15 and 28
Nonprotein amino acid	$C_{18}H_{37}NO_4$ saturated dihydroxy amino acid (simplifungin,	Marine fungal metabolites (Ishijima et al., 2016; VanMiddlesworth et al., 1992).	S/N 280
	$C_{20\text{-}22}H_{39\text{-}41}NO_{5\text{-}7}$ mono-unsaturated polyhydroxy amino acids in sphigolipids		S/N 30-230
Amino alcohols	$C_{16\text{-}28}H_{33\text{-}53}NO_{1\text{-}4}$ polyhydroxy amino alcohols	Plant biomembrane, secondary metabolites in marine organisms (Jares-Erijman et al., 1993).	S/N 23-640
	$C_{18}H_{31}NO$ and $C_{18}H_{29}NO$ polyunsaturated amino alcohols	Mediterranean tunicate (Jares-Erijman et al., 1993)	S/N 10-60
	$C_{18}H_{36}N_2O_5$ polyhydroxy cyclic alkaloid	Moraceae (Tsukamoto et al., 2001)	S/N 800

Possible oxidation schemes of two typical C_{18} ($C_{18}H_{30}O_2$, α-linolenic acid, three C=C double bonds in carbon chain) and C_{28} unsaturated FAs ($C_{28}H_{52}O_2$, two C=C double bonds), for instance, are proposed in Figure S6 and S7. The reaction of an unsaturated FA after the emission into the atmosphere is initiated by OH addition to C=C double bond and subsequent O_2 addition to form a peroxy radical (Atkinson et al., 1995; Calvert et al., 2000). Depending on the level of NO and reactivity, four competitive pathways are available for peroxy radicals to produce CHO or CHON formulas observed in our study: reaction with NO to form a $–ONO_2$ group (pathway 1) or an alkoxy radical that further reacts with O_2 to form a carbonyl (–C=O, pathway 2), reaction with RO_2 radicals to form a hydroxyl (–OH) or a –C=O group (pathway 3) and successive intermolecular H-shift/O_2 addition autoxidation(Crounse et al., 2013; Vereecken et al., 2015) (pathway 4).

We propose that pathway 1 and 2 are preferred for those FAs (e.g., α-linolenic acid) with higher reactivity with NO (Figure S6). Pathways 1 and 2 add $–ONO_2$, –OH and –C=O groups to carbon chain but do not reduce the DBE of FA precursor. α-linolenic acid oxidation in the atmosphere via sequential occurrences of pathways 1 or 2 yields

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a series of oxygenated and nitrated organic compounds, among which $C_{18}H_{31}NO_6$, $C_{18}H_{31}NO_8$, $C_{18}H_{31}NO_{10}$, $C_{18}H_{32}N_2O_{10}$ and $C_{18}H_{33}N_3O_4$ are found in 10-18 nm particles. These formulas explain the circles with DBE = 4 and C number = 18 shown in Figure 2a DBE *vs.* C atom number diagram.

We propose that pathway 3 and 4 are preferred for those FAs (e.g. C_{28} FA $C_{28}H_{52}O_2$) with higher reactivity with RO_2 (Figure S7). The net outcome of sequential pathway 3 and 4 reactions is to add –OH and –C=O groups and reduce the DBE of FA precursor. The end products are a series of $C_{28}H_{52}O_{6\text{-}8}$, $C_{28}H_{54}O_{4\text{-}7}$ and $C_{28}H_{56}O_{6\text{-}8}$ compounds, which can explain the circles with C number = 28 and DBE = 1-3 in Figure 2b.

In addition to fatty acids, fatty alcohols such as C_{30}-C_{32} mono- and di-unsaturated alcohols and diols have been detected in yellow-green algae (Volkman et al., 1992). Although these unsaturated alcohols were not detected in our 10-18 nm particles, we suppose that they or their metabolites in algae may undergo similar reactions like unsaturated FA to generate condensable oxygenated and nitrated fatty alcohols in the atmosphere. Hydroxy fatty acids (HFAs) are important constituents of lipid in marine microalgae (Gelin et al., 1997), bacteria (Kim and Oh, 2013),seaweed (Kendel et al., 2013; Blokker et al., 1998) and leaf surface of higher plants (Pollard et al., 2008). Among them, two saturated HFAs $C_{20}H_{40}O_3$ and $C_{32}H_{64}O_4$ were found in our 10-18 nm aerosol sample with S/N ratios 15 and 28. However, because saturated hydroxy fatty acids are not oxidizable via the pathways proposed in our study, they are assumed unlikely to be precursors of other formulas observed in 10-18 nm particles.

3.3.2. Nonprotein amino acids and amino alcohols

Quantum chemical calculations have showed that amino acids like Glycine, Serine, and Threonine are potential participants in atmospheric nucleation via interaction with sulfuric acid (Elm et al., 2013; Ge et al., 2018; Li et al., 2020). However, we did not observe any of 20 essential amino acids in 10-18 nm in either ESI+ or ESI- modes. One reason may be that most of essential amino acids have molecular weight less than 150 that is below mass scan range of our FT-ICR-MS.

There are a number of records in the literature about long chain non-protein amino acids or amino alcohols isolated from marine organisms or plant biomembrane

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(Ishijima et al., 2016; VanMiddlesworth et al., 1992; Jares-Erijman et al., 1993; Tsukamoto et al., 2001). They include saturated dihydroxy amino acid ($C_{18}H_{37}NO_4$, DBE = 1, simplifungin), monounsaturated polyhydroxy amino acids in sphigolipids ($C_{20\text{-}22}H_{39\text{-}41}NO_{5\text{-}7}$, DBE = 2-3), polyhydroxy amino alcohols ($C_{16\text{-}28}H_{33\text{-}53}N_{1\text{-}2}O_{1\text{-}5}$, DBE = 1-3, sphingosine and its natural metabolites) and polyunsaturated amino alcohols ($C_{18}H_{31}NO$ and $C_{18}H_{29}NO$, DBE = 4-5). All of these formulas were detected in 10-18 nm aerosols with S/N in the range of 10-800. More importantly, all those compounds that contain at least one amine group and one C=C double bond can be precursors of observed CHON formulas containing amine group via the pathways that we showed above. As an example, the oxidation scheme of an amino alcohol $C_{18}H_{31}NO$ with 4 C=C double bonds in carbon chain is illustrated in Figure S8.

Similar to C_{28} FA, $C_{18}H_{31}NO$ undergoes successive intermolecular H-shift/O_2 additions to produce a series of RO_2 radicals with hydroperoxyl group (–OOH) in its carbon chain. The subsequent pathway 3 reactions, as well as the decomposition of –OOH groups, add –OH and –C=O groups in the carbon chain. Because $C_{18}H_{31}NO$ possesses as many as 4 C=C double bonds, sequential pathway 3 and 4 reactions produce a large number of oxidation products, among which 57 are found in the formula list detected in 10-18 nm particles (Figure S8). These products $C_{18}H_{31}NO_{4\text{-}11,13}$, $C_{18}H_{33}NO_{4,6\text{-}10}$, $C_{18}H_{35}NO_{5\text{-}9}$, $C_{18}H_{37}NO_{7\text{-}12}$ and $C_{18}H_{39}NO_{10\text{-}11}$ explain perfectly the presence of a series of formulas with C number = 18, DBE = 0-4 and a $–NH_2$ group shown in Figure 2a.

3.3.3. Volatility estimation

Based on the reaction mechanisms proposed above, it is possible to estimate the volatility change from potential precursors to their oxidation products. First, from the list of elemental formulas detected in 10-18 nm particles, we select 49 formulas with high intensities, including 14 $CHON^-$ formulas with peak intensity > 1.00 e+08, 23 $CHON^+$ formulas with peak intensity > 3.00 e+07 and 12 CHO^- formulas (DBE = 1) with peak intensities > 3.00 e+07. Possible combinations of –COOH, $–ONO_2$, –C=O, C=C double bond, $–NH_2$ and –OH groups are searched for every formula obeying two simple rules: $CHON^-$ and CHO^- formulas must possess a carboxyl or hydroxyl group;

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CHON$^+$ formulas must possess an amino group. Saturation concentrations (C*) of the 49 formulas were then predicted for all combinations using a simple group contribution method developed by Pankow and Asher (Pankow and Asher, 2008). On the other hand, the C*of their possible precursors, including unsaturated FAs, fatty alcohols, nonprotein amino acids or amino alcohols, were predicted by the same method.

As we can see in Table S4, C* of the 49 formulas fall into the range of ELVOC (< 3 × 10^{-5} μg m^{-3}), while C* of their precursors are in the range of SVOC (0.3-300 μg m^{-3}) or LVOC (3 × 10^{-5}-0.3 μg m^{-3}). The addition of functional groups reduces the volatility of precursors by 2~7 orders of magnitude and thus make their oxidation products condensable onto new particles during the I-NPF event days. Therefore, the analysis of precursor-product volatility partly supports our hypothesis about the molecular identity and formation mechanism of the formulas detected in 10-18 nm particles.

3.4. Speciation of iodinated OC

Organic iodine compounds hold the key to understand aerosol iodine chemistry and its role in regulating the recycling of halogens to the gas phase. We identified 440 iodinated OC formulas from the 4 size bins during the I-NPF days (Table 2). 80% of the 440 formulas contain one I atom and the rest of them contain two I atoms. In terms of relative intensity, iodinated OC accounts for 2.6-9.5% of OC in fine particles, but its fraction in coarse particles increases to 23.3% in ESI- mode and 45% in ESI+ mode. The size distribution of 7 iodinated OC groups (i.e., CHOI$^-$, CHONI$^-$, CHOSI$^-$, CHONSI$^-$, CHOI$^+$, CHONI$^+$ and CHNI$^+$) resembles those of non-iodinated OC groups (Figure 1). If we replace I atom(s) with H atom(s) in a formula, 107 out of 440 replaced formulas are also found in the non-iodine OC formula list.

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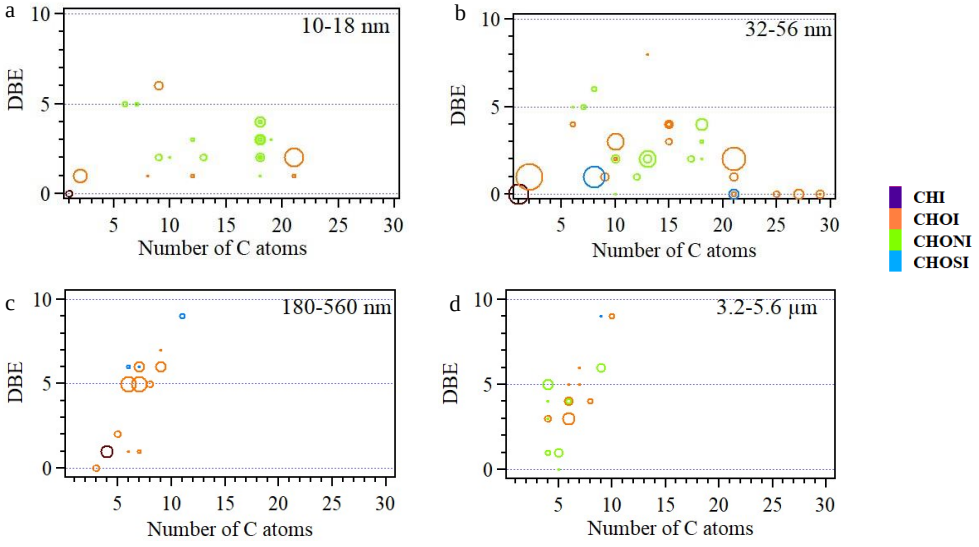

Figure 4. DBE vs. C atom number diagrams of iodinated OC formulas with intensity > 1.00 e+07 in the four size bins. The color bar denotes the elemental groups of assigned formulas. The size of the circles reflects the relative intensities of molecular formulas on a logarithmic scale.

Iodinated OC with intensity > 1.00 e+07 in the four size bins were shown in Figure 4. The DBE vs. C diagram for 10-18 nm particles is characterized by (1) nine $C_{18}H_hO_oN_nI$ formulas with DBE = 1-4 and (2) $C_9H_{16}NO_3I$ and its C_{10}-C_{13} homologues. Because these formulas were detected in ESI+ mode, they are most likely iodinated amino acids. 32-56 nm particles accommodate most abundant iodinated OC formulas, in terms of both formula number and relative intensity. Prominent formulas include (1) diiodo acetic acid $C_2H_2O_2I_2$, diiodomethane CH_2I_2, (2) iodinated C_{21} carbonyls $C_{21}H_{39}OI$ and $C_{21}H_{41}OI$, (3) iodinated $C_{21,25,27,29}$ alcohols or ethers with DBE = 0, (4) iodinated C_{10} and C_{15} terpene and sesquiterpene oxidation products and (5) iodinated organic sulfate $C_8H_{17}N_2SO_8I$ and $C_{21}H_{43}SO_4I$. In addition, $C_9H_{10}NO_3I$ detected in this size bin (S/N ratio: 35) can be tentatively assigned to an iodinated amino acid iodotyrosine that has been observed in seaweed(Yang et al., 2016), implying direct contribution from seaweed emission to new particles.

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In 180-560 nm particles, the majority of iodinated OC are C_{6-9} aromatic $CHOI^+$ compounds with AI > 0.5 and DBE = 5-7. Both C and O atom numbers of these iodinated OC are smaller than those of mono-modally distributed CHO^+ compounds around C_{15} in the same particle size (Figure 3d and S3b). This implies that iodine has a strong tendency to aromatic compounds in submicron aerosols due to electrophilic substitution on aromatic rings. In 3.2-5.6 μm particles, iodinated OC features C_4-C_6 CHO^+ and $CHON^+$ compounds with DBE = 3-6, which again have fewer C atoms than non-iodinated OC. Supporting evidence from AI shows these compounds are not aromatic. Coastal 3.2-5.6 μm particles can be sea salt particles formed during bubble bursting of sea water (Russell et al., 2010; Schmitt-Kopplin et al., 2012; Quinn et al., 2014; Wilson et al., 2015). However, Hao et al. 2017 (Hao et al., 2017) showed that iodinated OC products from the reaction between iodine and seawater are highly unsaturated carboxylic-rich polyphenols with DBE = 4-14 and C atoms = 10-30. It is thus apparent that iodinated OC in 3.2-5.6 μm particles were not directly from iodinated organic compounds in the seawater.

3.5 Atmosphere implications

Due to the 71% ocean coverage of the earth's surface, marine aerosol generation is important in determining the earth's radiative budget and climate change. Of the limited number of studies reporting coastal NPF, most have focused on iodine emission, oxidation and nucleation in the early stage of NPF. In principle, abundant low-volatility condensing vapors other than iodine are required in coastal environments for the growth of iodine clusters to CCN. This article reveals a new group of important organics involved in this process. It is most likely that their precursors are emitted mutually with iodine from either direct exposure of coastal biota to the atmosphere or biological-active sea surface. More fundamental field, laboratory and modeling studies are needed to determine (1) exact emission sources and source rates of these organic precursors, (2) their gas phase intermediates and oxidation mechanisms in the atmosphere and (3) their quantitative contribution to global and regional CCN numbers.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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