1 Probing key organic substances driving new particle growth initiated by

2 iodine nucleation in coastal atmosphere

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18 Graphic abstract



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 organic 23 compounds involved in coastal and open ocean NPF. On the coastline of China we 24 observed intense coastal NPF events initiated by iodine nucleation, but particle growth 25 to cloud condensation nuclei (CCN) sizes was dominated by organic compounds. This 26 article revealed a new group of C_{18,30}H_hO₀N_n and C_{20,24,28,33}H_hO₀ compounds with 27 specific double bond equivalents and oxygen atom numbers in sub-20 nm coastal 28 iodine new particles by using ultrahigh resolution Fourier transform-ion cyclotron 29 resonance mass spectrometry (FT-ICR-MS). We proposed these compounds are 30 oxygenated or nitrated products of long chain unsaturated fatty acids, fatty alcohols, non-protein amino acids or amino alcohols emitted mutually with iodine from coastal 31 biota or biological-active sea surface. Group contribution method estimated that the 32 addition of -ONO₂, -OH and -C=O groups to the precursors reduced their volatility of 33 34 by 2~7 orders of magnitude and thus made their products condensable onto iodine new particles in the coastal atmosphere. Non-target MS analysis also provided a list of 440 35

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

39 1. INTRODUCTION

40 Atmospheric new particle formation (NPF) contributes over half of global cloud condensation nuclei (CCN) (Merikanto et al., 2009) and thus influences cloud 41 properties and Earth's radiation budget (Metzger et al., 2010). By deploying high 42 43 resolution Chemical Ionization Mass spectrometer, recent laboratory and field studies 44 have identified a group of highly oxygenated multifunctional organic molecules (HOMs) with high O/C ratios and low volatility from the reactions of volatile organic 45 46 compounds (VOCs) such as monoterpenes (Ehn et al., 2014), Sesquiterpenes (Richters et al., 2016) and alkene (Mentel et al., 2015) with hydroxyl radical (OH), 47 ozone (O_3) , nitrate radicals (NO_3) and chlorine atom (Wang et al., 2020). These 48 49 HOMs play an important role in particle nucleation and growth of continental NPF, as well as in the formation of secondary organic aerosols. 50

51 Unlike the deep understanding of continental HOMs, little is known about the role of 52 organic compounds in the NPF in coastal or open ocean atmosphere. The current state of knowledge is that the photolysis of molecular iodine (I_2) or iodomethane is the 53 source of iodine oxides or oxoacids, the self-clustering of which could initiate NPF 54 events with particle number concentration sometimes exceeding 10⁶ cm⁻³ (O'Dowd et 55 al., 2002; Saiz-Lopez and Plane, 2004; Burkholder et al., 2004; Mahajan et al., 2010, 56 2012; Sipilä et al., 2016; Stevanović et al., 2019; Kumar et al., 2018). But it is unknown 57 if other species are needed to drive the growth of iodine clusters to CCN sizes in coastal 58 or open ocean atmosphere (Saiz-Lopez et al., 2012). Iodine-induced NPF (I-NPF) 59 60 events were mostly reported in European coastlines (Yoon et al., 2006; Mahajan et al., 61 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 62 particle number size distribution and iodine measurements (Yu et al., 2019). The focus 63

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-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 70 71 techniques such as electrospray ionization (ESI) and ambient pressure chemical ionization (APCI) allows characterization of complex organic mixtures at the 72 molecular level due to its ultra-high resolution and mass accuracy (Pratt and Prather, 73 2012). This technique has been used to examine molecular composition of organic 74 aerosols (Schum et al., 2018; An et al., 2019; Zuth et al., 2018; Daellenbach et al., 2018; 75 Xie et al., 2020) and cloud water (Zhao et al., 2013; Bianco et al., 2018). Studies 76 investigating coastal organic aerosols have been rare. Virtually no study reported the 77 78 characterization of organic compounds driving the growth of coastal or open ocean new 79 particles.

80 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 81 (nano-micro orifice uniform deposit impactor) during the intense I-NPF days at a 82 coastal site of China. Relative abundances of HSO4⁻, total iodine and total organic 83 carbon (TOC) in 10-56 nm particles were compared between the I-NPF days and 84 conventional continental NPF (C-NPF) days. In particular, using ultra-high resolution 85 FT-ICR-MS, we conducted a non-target analysis of particle-phase organic compounds 86 87 to explore their molecular identity, formation mechanism and the role in new particle 88 growth in the coastal atmosphere.

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89 2. METHDOLOGY

90 2.1. Sampling collection

The sampling site (29°29' N, 121°46' E) is near a small fishing village without 91 92 permanent residents in the coastline of East China Sea. It can be seen from the aerial photo (Figure S1a) that from the east to the west are the sea, intertidal zone, small 93 paddy fields and the mountain. The sampling site is about 40 and 200 m away from at 94 high tide and low tide, respectively. The classification of I-NPF event, C-NPF event or 95 96 non-NPF 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 97 (SMPS; TSI DMA3081 and CPC3775; scanning range: 40-750 nm) and a neutral 98 cluster air ion spectrometer (NAIS; scanning range: 2-42 nm). A nano-MOUDI 99 100 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 101 second set was collected during overcast non-NPF days from April 16 to 18; a third set 102 was collected during the I-NPF days from May 9 to 11. The PNSD during the 3 periods 103 104 are shown in Figure S2. Each set of nano-MOUDI samples was collected continuously for 72 hours, during which NPF occurred on a daily basis, so that particle chemical 105 composition of different event types can be obtained from offline analyses. Aluminum 106 foil filters were used as sampling substrate to avoid the adsorption of gaseous species. 107 108 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 100 109 nm-18 µm particles (on stages 1-9) separately, in order to reduce potential positive 110 particle-bounce artifacts. Three additional sets of blank samples were collected by 111 112 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). 113

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114 **2.2. Sample preparation and analysis**

Half of each filter was transferred into a 20 mL tapered plastic centrifuge tube, added 115 10 mL mixed solvent (1:1 v/v water and methanol; LCMS grade). The mixture was 116 sonicated for 40 min and filtered by a 0.2 µm PTFE membrane syringe filter. The 117 filtrate was evaporated to almost dryness in a rotary evaporator below 40 $\,$ $\,$ $\,$ and 118 subsequently redissolved in 0.5 mL water. After being centrifuged for 30 min at 12,000 119 120 rpm, the supernatant was collected for total iodine (I) analysis by Agilent 7500a ICP-MS (Agilent Technologies, Santa Clara, CA, USA) and HSO4⁻ analysis by 121 UPLC-ESI-Q-TOF-MS. The measurements of HSO₄⁻ and total I were elaborated in our 122 previous article Yu et al. 2019. Another half of each filter was extracted in the same 123 124 way but used for TOC analysis by a TOC analyzer (Model TOC-5000A, Shimadzu, Japan) and non-target MS analysis of organic compounds (OC) by ESI-FT-ICR-MS 125 (SolariX XR 9.4T instrument, Bruker Daltonics, Coventry, UK). Samples were infused 126 by a syringe pump and analyzed in both positive (ESI+) and negative (ESI-) modes. 127 128 ESI-FT-ICR MS operation conditions are included in Supplement Material. Field blank sample extracts were analyzed following the same procedure. 129

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131 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 132 determination of possible formulas for singly charged molecular ions. Only m/z values 133 between 150-1000 Da that satisfies signal/noise (S/N) ratio > 10 were considered. For 134 each m/z value, several scientific rules were applied to calculate a reasonable elemental 135 formula of natural organic molecule: the general formula is C₁₋₅₀H₁₋₁₀₀O₀₋₅₀N₀₋₁₀I₀₋₃ in 136 the ESI+ mode; elemental ratios H/C, O/C, and N/C are limited to 0.3-3, 0-3 and 0-1.3, 137 138 respectively. The general formula is $C_{1-50}H_{1-100}O_{1-50}N_{0-5}S_{0-2}I_{0-3}$ in the ESI- mode; 139 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, 140 S and I isotopologues were removed from the formula lists. A formula with m/z > 500141

was not reported if it did not belong to any CH₂ homologous series. For a formula 142 $C_cH_hO_oN_nS_sI_x$, double bond equivalents (DBE) defined as $DBE = \frac{2c+2-h+n-x}{2}$ was 143 required to be non-negative. Formula calculation was done following the same 144 procedure for the three field blank samples. All formulas found in the field blank 145 146 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 147 $DBE_{AI} \leq 0$ or $C_{AI} \leq 0$, then AI = 0. A threshold value of $AI \geq 0.5$ provides an 148 unambiguous minimum criterion for the presence of aromatic structure in a 149 molecule(Yassine et al., 2014). 150

151 **3. RESULTS AND DISCUSSION**

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

Although our offline technique did not allow us to probe nucleating cluster 154 composition at ~1.7 nm, four facts from our observation support that the NPF events 155 from May 9 to 11 were initiated by iodine nucleation. First, strong I-NPF events were 156 observed almost every sunny day in April and May, which was the growth and farming 157 season of seaweed. HYSPLIT Back-trajectories analysis (Draxler and Rolph, 2010) 158 shows that air masses moved from East China Sea to the sampling site during the 159 I-NPF days from May 8 to 10, 2018 (Figure S1b). Sea breeze was also expected to 160 flow from the sea to the site in the daytime when the I-NPF events occurred. Second, 161 the evolution of PNSD from May 9 to 11 was not like banana-shape C-NPF observed 162 on the winter days, but was markedly similar to prior reports of iodine-nucleation at 163 164 European coastal sites (M äkel äet al., 2002; Sipil äet al., 2016). Third, the production of 165 2-7 nm particles (N_{2-7}) during the C-NPFs followed a nearly identical variation with solar radiation (Figure S2c), which is an indication that the C-NPFs was initiated by 166 OH and H₂SO₄ production dictated by solar radiation. However, this was not observed 167

during the I-NPF events, instead, N_{2-7} was anti-correlated to tidal height in the daytime (Figure S2a). Fourth, probably the most important, mean total I in 10-56 nm particles during the I-NPF days (13.5 ng m⁻³, Table 1) 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, mean HSO₄⁻ 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).

By assuming nanometer-sized particles are spherical with a density of 1.5 g cm^{-3} , we 174 estimate from the PNSD data that aerosol mass in the 10-56 nm size range was 175 enhanced by 3.0 and 1.3 µg m⁻³ at most by the selected I-NPF and C-NPF events 176 (Figure S2b and S2d). The fraction of organic mass (OM) in the aerosol mass can be 177 further calculated as $(1.5 \times m_{TOC})/(m_{Total I} + m_{HSO4} + 1.5 \times m_{TOC}) \times 100\%$ by assuming an 178 179 OM/TOC ratio of 1.5. The result shows that 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 180 days. Therefore, organic compounds dominate the aerosol mass in the 10-56 nm new 181 particles during the I-NPF days and were critical for I-NPF to contribute to CCN. Our 182 183 result is qualitatively consistent with previous measurements showing that nucleation mode particles initiated by iodine were composed of a remarkable fraction of organic 184 compounds and sulfate (Mäkelä et al., 2002; Vaattovaara et al., 2006). The main 185 purpose of this article is to identify these organic compounds during the I-NPF days. 186 The OC composition during the C-NPF days is beyond the scope of this article. 187

188

189 Table 1. Concentrations of Total iodine (I), HSO₄⁻ and Total Organic Carbon (TOC) in

190 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.

192 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 (µg m ⁻³)	2.3×10 ⁻³	6.2×10 ⁻³	5.0×10 ⁻³	0.20×10 ⁻³	0.37×10-3
HSO4 ⁻ (µg m ⁻³)	2.2×10 ⁻²	3.4×10 ⁻²	14.4×10 ⁻²	50×10-2	BDL
TOC (µg m ⁻³)	3.1×10 ⁻¹	1.8×10 ⁻¹	2.1×10 ⁻¹	2.8×10 ⁻¹	BDL

193 **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 10-18 194 nm, 32-56 nm, 180-560 nm and 3.2-5.6 µm particles during the I-NPF days. Elemental 195 formulas in the 4 size bins can represent OC molecular composition of nucleation mode, 196 Aitken mode, accumulation mode and coarse mode, respectively. OC formulas were 197 divided into two categories: non-iodinated OC and iodinated OC. There are far more 198 199 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 200 non-iodinated OC formulas account for 96.6% of OC total intensity in 10-18 nm 201 particles, while 137 iodinated OC formulas account for the remaining 3.4%. It means 202 that non-iodinated OC dominates new particle growth during the I-NPF events. In this 203 section, we first discuss chemical characteristics of non-iodinated OC, while the 204 205 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 μ m 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 212 groups CHO⁻, CHO⁺, CHON⁻, CHON⁺, CHOS⁻, CHONS⁻ and CHN⁺. The number 213 214 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 215 only once. It should be noted that some formulas were repeatedly detected in ESI+ and 216 ESI- modes. Some formulas detected in one size bin were also detected in another size 217 bin. This is quantitatively shown in the first four rows of Table 2. For instance, 58%, 25% 218 and 4% of the formulas detected in 10-18 nm aerosols were also detected in 32-56 nm, 219 180-560 nm and 3.2-5.6 µm aerosols, respectively. In another word, the particles in 220 neighboring size bins share more similarity in organic composition. An unexpected 221 222 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. 223 Reconstructed mass spectra of the 7 elemental groups in ESI-and ESI+ modes are 224 shown in Figure S3 for the four size bins. 225

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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				1	Total
CHO-	531	565	525	20	892
$\rm CHO^+$	250	501	380	111	857

CHON ⁻	1005	638	347	25	1268	
$\rm CHON^+$	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%

231 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⁺ 232 formulas and 892 CHO⁻ formulas). S-containing formulas are 357 CHOS⁻ and 259 233 CHONS⁻. The formula number of the least common CHN⁺ group is only 46. In terms 234 235 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 236 CHO and CHOS/CHONS increase with particle size. In the ESI+ mode, the fraction of 237 CHON decreases from 88% in 10-18 nm bin to 70% in 180-560 nm bin, being always 238 239 the dominant elemental group of non-iodinated OC (Figure 1b). Low molecular weight (LMW) amines are important stabilizers in acid-base nucleation (Kurt én et al., 240 2008; Jen et al., 2014; Zheng et al., 2000; Yao et al., 2016), but their molecular ions 241 242 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% 243 of total intensity of all ESI+ formulas in the 10-18 nm particles. 244

Previous elemental composition studies using FT-ICR-MS were mostly conducted
on PM_{2.5} or PM₁₀ 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), free 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 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.

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257 **3.2.1.** CHO formulas

There is a total of 531 CHO⁻ formulas and 250 CHO⁺ formulas in 10-18 nm 258 particles. 54 CHO formulas are commonly found in ESI+ and ESI- modes. In terms 259 of relative intensity, CHO⁻ compounds are more abundant than CHO⁺ compounds 260 (Figure 3b, total intensity: 4.14 e+09 vs. 1.24 e+09). However, this is not indicative of 261 absolute concentration of the two groups due to different ionization efficiency 262 between ESI- and ESI+ modes. CHO⁻ is characterized by a series of formulas with 20, 263 264 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 265 CHO⁻ formulas contain at least 1 carboxylic group (-COOH), the rest of their 266 molecules should be saturated (DBE = 0) and contain 2 or 4 O atoms. 267







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

number in the formulas. The size of the circles reflects the relative intensities ofmolecular formulas on a logarithmic scale.

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The above feature is not seen in either CHO⁺ formulas in the 10-18 nm bin or CHO⁻ 275 formulas in the 180-560 nm bin. There are more C_{21} and C_{24} formulas than other C 276 277 subgroups in the CHO⁺ formulas of 10-18 nm bin (Figure S4d), but none of them have exceptionally-high intensity. The prominent formulas in the CHO⁻ group in 180-560 278 279 nm particles have a relatively high unsaturation degree (DBE = 3-7, Figure 2d). The relative intensities of subgroups according to C atom number in the CHO⁻ formulas in 280 281 the 180-560 nm bin are characterized by trimodal distribution with maximum intensity around C₉, C₁₃-C₁₆ and C₂₀ (Figure 3d). The relative intensity of O atom subgroups is 282 mono-modally distributed around O₇ (Figure S5). 283



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Figure 3. Relative intensities of subgroups according to C atom number in CHON, CHO, CHONI and CHOI formulas in 10-18 nm and 180-560 nm particles in ESI+ (in red) and ESI- (in blue). The intensity of the most abundant subgroup in a size bin is defined as 1 and those of other subgroups are normalized by it. The relative intensities of non-iodinated OC formulas (iodinated OC formulas) are plotted in the region above (below) zero line.

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292 **3.2.2.** CHON formulas

As discussed earlier, CHON is the most abundant elemental group observed in the smallest size bin 10-18 nm. There is a total of 1005 CHON⁻ formulas (total intensity

9.96 e+09) and 1139 CHON⁺ formulas (6.45 e+09) in 10-18 nm bin. 355 CHON 295 formulas are commonly found in ESI+ and ESI- modes. A close examination of Figure 296 2a and 3a reveals that CHON⁻ is characterized by a series of C_{18} and C_{30} formulas with 297 low DBE values (1-4). 87 C₁₈ and 26 C₃₀ formulas account for 37% of total intensity of 298 CHON⁻. Such feature is not seen for CHON⁺ formulas that are rather uniformly 299 300 distributed in DBE vs. C diagram (Figure S4a and S4c). Generally speaking, CHONcompounds should contain nitro- (-NO₂) or nitrooxy- (-ONO₂) group and are 301 302 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 C₁₈ as 303 example, 51 out of 87 C₁₈H_hO₀N_n⁻ formulas should contain at least one amine group, 304 either because their O atom numbers are not large enough to allow the assignment of -305 NO₂ for all N atoms, or because some formulas (25 out of 87) were also detected in 306 307 ESI+ mode. In total, 51 $C_{18}H_hO_oN_n^-$ formulas with an amine group account for 54.4% 308 of total intensity of 87 C₁₈H_hO_oN_n⁻ formulas.

The presence of amine group in $C_{18}H_hO_0N_n^-$ formulas in 10-18 nm particles is also 309 310 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 311 around C₁₀ and C₁₅ (Figure 2c). A plot of O atom number vs. N atom number in Figure 312 S6a shows that $C_{10}H_hO_0N_n^-$ in 180-560 nm have O/N ratios ≥ 3 and O atom number is 313 positively correlated with N atom number. It indicates that these C₁₀H_hO₀N_n⁻ formulas 314 are probably nitro- or nitrooxy- oxidation products of monoterpenes from continental 315 316 plant emission. In contrast, O/N ratios of the $C_{18}H_hO_oN_n^-$ formulas in 10-18 nm are 317 mostly small and O atom number do not increase with N atom number (Figure S6b). All 318 collective evidences above reveal that nitrogen-containing organic compounds in 10-18 319 nm particles during the I-NPF days are partly composed of long-chain amino alcohols, amino acids and so on. 320

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

CHON⁻). Monomer-dimer distribution pattern that can arise from particle-phase 325 oligomerisation (Pospisilova et al., 2020) was not observed for these formulas in the 326 327 mass spectra. We also assume that C_{18,30}H_hO₀N_n and C_{20,24,28,33}H_hO₀ are not labile intermediates like ester hydroperoxides that may undergo fast decomposition in the 328 particles or during the sample preparation process (Zhao et al. 2018 a,b). To the best 329 of our knowledge, such CHON⁻ and CHO⁻ formulas have not been reported by 330 previous aerosol studies. The chemical composition of new particles is completely 331 332 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 333 emissions. Fewer O atoms in C_{18,30}H_hO₀N_n and C_{20,24,28,33}H_hO₀ formulas than those in 334 submicron aerosols indicate that these compounds should be more freshly emitted into 335 the atmosphere. The discontinuous chemical composition and PNSD spectrum 336 (Figure S2b) below and above 50 nm particle size reflect the fact that the further 337 growth of new particles beyond 50 nm in local I-NPF events cannot be monitored by 338 our stationary sampling strategy. 339

340 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 341 intensity and are rather uniformly distributed in DBE vs. C diagrams. Like CHON-342 and CHO⁻, those CHO⁺ and CHON⁺ formulas also possess a larger number of C 343 atoms (C > 19) than their counterparts in 180-560 nm submicron aerosols (Figure 3). 344 21 out of 30 most abundant CHON⁺ formulas contain two or more N atoms; this ratio 345 21/30 is higher than those in CHON⁻ formulas. Generally speaking, CHO⁺ and 346 CHON⁺ formulas represent carbonyls/alcohols/epoxides and amino alcohols/amino 347 348 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 349 aerosols (Figure 1c). This indicates that the CHO⁺ and CHON⁺ compounds in new 350 particles during the I-NPF days should possess different basic functional groups 351 352 from those in submicron particles.

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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 355 for a formula with large C atom number (e.g., ≥ 18). Our strategy is to first explore 356 the possible precursors of the newly found $C_{18,30}H_hO_oN_n$ and $C_{20,24,28,33}H_hO_o$ 357 358 formulas. Obviously, C_{18,30}H_hO₀N_n and C_{20,24,28,33}H_hO₀ formulas cannot be attributed to continental terpene emission or anthropogenic aromatic emissions. Sporadic 359 spikes of 10-18 nm particles that can be an indication of cooking and traffic 360 emissions were not seen in the PNSD spectrum, because such human activities were 361 362 rare around the site during the sampling period. We thus also exclude the possibility 363 of cooking and traffic emissions.

Previous field measurements of marine NPF precursor focused on volatile species 364 like iodine (Stevanović et al., 2019), iodomethanes (O'Dowd et al., 2002), dimethyl 365 366 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 367 compounds with C number ≥ 18 in either gas phase or new particles (Cochran et al., 368 369 2017; Bikkina et al., 2019). Therefore, we consulted the literature that reported chemical compounds isolated from biological tissues of algae, plankton or other 370 371 marine organisms. Potential precursors are listed in Table 3.

372 **3.3.1.** Fatty acids

Fatty acids (FAs) are widely found in animals, plants and microbe (Moss et al., 373 1995). Plants have higher content of unsaturated FAs than animals. C₁₄-C₂₄ fatty acids, 374 including both saturated and unsaturated, have long been observed in seaweed 375 376 (Dawczynski et al., 2007). Very long chain FAs (C_{24} - C_{36}) have been isolated from green algae, chlorella kessleri, sponges and marine dinoflagellate (Litchfield et al., 377 378 1976; Řezanka and Podojil, 1984; Mansour et al., 1999). C₁₈ Oleic acid, linoleic acid 379 and linolenic acid are most commonly found unsaturated FAs in macro algae. FAs with carbon chain shorter than C₂₀ were used by atmospheric chemists as organic 380

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% of 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.

388

389 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
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	C20H40O3, C32H64O4	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, C ₂₀₋₂₂ H ₃₉₋₄₁ NO ₅₋₇ mono-unsaturated polyhydroxy amino acids in sphigolipids	Marine fungal metabolites (Ishijima et al., 2016; VanMiddlesworth et al., 1992).	S/N 280 S/N 30-230
Amino alcohols	C16-28H33-53NO1-4 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 ₂ O ₅ polyhydroxy cyclic alkaloid	Moraceae (Tsukamoto et al., 2001)	S/N 800

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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 S7 and S8. 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 O₂ to form a carbonyl (-C=O, pathway 2), reaction with RO₂ radicals to form a hydroxyl (-OH) or a -C=O group (pathway 3) and successive intermolecular H-shift/O₂ addition autoxidation(Crounse et al., 2013; Vereecken et al., 2015) (pathway 4).

404 Pathways 1 and 2 add –ONO₂, –OH and –C=O groups to carbon chain but do not reduce the DBE of FA precursor. We propose that pathway 1 and 2 are preferred for 405 those FAs with higher reactivity with NO (e.g., α -linolenic acid, Figure S7). 406 α -linolenic acid oxidation in the atmosphere via sequential occurrences of pathways 1 407 or 2 yields a series of oxygenated and nitrated organic compounds, among which 408 C18H31NO6, C18H31NO8, C18H31NO10, C18H32N2O10 and C18H33N3O4 are found in 409 10-18 nm particles. These formulas explain the circles with DBE = 4 and C number = 410 18 shown in Figure 2a (DBE vs. C atom number diagram). 411

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. 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 RO₂ (Figure S8). The end products are a series of $C_{28}H_{52}O_{6-8}$, $C_{28}H_{54}O_{4-7}$ and $C_{28}H_{56}O_{6-8}$ 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 C₃₀-C₃₂ mono- and di-unsaturated 418 419 alcohols and diols have been detected in yellow-green algae (Volkman et al., 1992). 420 Although these unsaturated alcohols were not detected in our 10-18 nm particles, we 421 suppose that they or their metabolites in algae may undergo similar reactions like 422 unsaturated FA to generate condensable oxygenated and nitrated fatty alcohols in the atmosphere. Hydroxy fatty acids (HFAs) are important constituents of lipid in 423 424 marine microalgae (Gelin et al., 1997), bacteria (Kim and Oh, 2013), seaweed 425 (Kendel et al., 2013; Blokker et al., 1998) and leaf surface of higher plants (Pollard et al., 2008). Among them, two saturated HFAs C₂₀H₄₀O₃ and C₃₂H₆₄O₄ were found 426

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.

431 **3.3.2.** Nonprotein amino acids and amino alcohols

432 Quantum chemical calculations have showed that amino acids like Glycine, Serine, 433 and Threonine are potential participants in atmospheric nucleation via interaction 434 with sulfuric acid (Elm et al., 2013; Ge et al., 2018; Li et al., 2020). However, we 435 did not observe any of 20 essential amino acids in 10-18 nm in either ESI+ or ESI-436 modes. One reason may be that most of essential amino acids have molecular weight 437 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 438 439 acids or amino alcohols isolated from marine organisms or plant biomembrane (Ishijima et al., 2016; VanMiddlesworth et al., 1992; Jares-Erijman et al., 1993; 440 Tsukamoto et al., 2001). They include saturated dihydroxy amino acid (C₁₈H₃₇NO₄, 441 442 DBE = 1, simplifungin), monounsaturated polyhydroxy amino acids in sphigolipids $(C_{20-22}H_{39-41}NO_{5-7}, DBE = 2-3)$, polyhydroxy amino alcohols $(C_{16-28}H_{33-53}N_{1-2}O_{1-5}, DBE = 2-3)$ 443 DBE = 1-3, sphingosine and its natural metabolites) and polyunsaturated amino 444 445 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 446 compounds that contain at least one amine group and one C=C double bond can be 447 448 precursors of observed CHON formulas containing amine group via the pathways that 449 we showed above. As an example, the oxidation scheme of an amino alcohol 450 $C_{18}H_{31}NO$ with 4 C=C double bonds in carbon chain is illustrated in Figure S9.

Similar to C_{28} FA, $C_{18}H_{31}NO$ undergoes successive intermolecular H-shift/O₂ additions to produce a series of RO₂ 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 457 formula list detected in 10-18 nm particles (Figure S9). These products 458 $C_{18}H_{31}NO_{4-11,13}$, $C_{18}H_{33}NO_{4,6-10}$, $C_{18}H_{35}NO_{5-9}$, $C_{18}H_{37}NO_{7-12}$ and $C_{18}H_{39}NO_{10-11}$ 459 explain perfectly the presence of a series of formulas with C number = 18, DBE = 0-4 460 and a –NH₂ group shown in Figure 2a.

462 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 463 464 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, 23 465 CHON⁺ formulas with peak intensity > 3.00 e+07 and 12 CHO^- formulas (DBE = 1) 466 with peak intensities > 3.00 e+07. Possible combinations of -COOH, $-\text{ONO}_2$, -C=O, 467 C=C double bond, -NH2 and -OH groups are searched for every formula obeying two 468 simple rules: CHON⁻ and CHO⁻ formulas must possess a carboxyl or hydroxyl group; 469 $CHON^+$ formulas must possess an amino group. Saturation concentrations (C*) of the 470 49 formulas were then predicted for all combinations using a simple group 471 472 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 473 alcohols, nonprotein amino acids or amino alcohols, were predicted by the same 474 method. 475

476 As we can see in Table S4, C* of the 49 formulas fall into the range of ELVOC (3 \times 10^{-9} - 3 × 10⁻⁵ µg m⁻³) and even ULVOC (ultra-low volatility organic compound, <3 × 477 10^{-9} µg m⁻³), while C* of their precursors are in the range of SVOC (0.3-300 µg m⁻³) or 478 LVOC $(3 \times 10^{-5}-0.3 \ \mu g \ m^{-3})$. The addition of functional groups reduces the volatility of 479 480 precursors by 2~7 orders of magnitude and thus make their oxidation products 481 condensable onto new particles during the I-NPF event days. According to the definition of Schervish and Donahue, 2019 and Simon et al., 2020, ULVOC can even 482 drive pure biogenic nucleation. Therefore, the analysis of precursor-product volatility 483 484 partly supports our hypothesis about the molecular identity and formation mechanism of the formulas detected in 10-18 nm particles. It should be noted that the volatility of 485 VOC oxidation products can be assessed with numerous existing parameterizations, 486

which require either exact functional groups or only the molecular formula (Per äkyl äet
al., 2019). Their estimation can vary by up to several orders of magnitude. But this will
not change the conclusion drawn here.

490 **3.4. Speciation of iodinated OC**

Organic iodine compounds hold the key to understand aerosol iodine chemistry and 491 its role in regulating the recycling of halogens to the gas phase. We identified 440 492 493 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 494 terms of relative intensity, iodinated OC accounts for 2.6-9.5% of OC in fine particles, 495 496 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⁻, 497 CHONSI⁻, CHOI⁺, CHONI⁺ and CHNI⁺) resembles those of non-iodinated OC groups 498 (Figure 1). If we replace I atom(s) with H atom(s) in a formula, 107 out of 440 499 500 replaced formulas are also found in the non-iodine OC formula list.



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 formulason a logarithmic scale.

508

Iodinated OC with intensity > 1.00 e+07 in the four size bins were shown in Figure 4. 509 The DBE vs. C diagram for 10-18 nm particles is characterized by (1) nine 510 511 $C_{18}H_hO_oN_nI$ 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 512 513 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) 514 diiodo acetic acid C₂H₂O₂I₂, diiodomethane CH₂I₂, (2) iodinated C₂₁ carbonyls 515 $C_{21}H_{39}OI$ and $C_{21}H_{41}OI$, (3) iodinated $C_{21,25,27,29}$ alcohols or ethers with DBE = 0, (4) 516 iodinated C_{10} and C_{15} terpene and sesquiterpene oxidation products and (5) iodinated 517 518 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 519 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 520 521 contribution from seaweed emission to new particles.

In 180-560 nm particles, the majority of iodinated OC are C₆₋₉ aromatic CHOI⁺ 522 compounds with AI > 0.5 and DBE = 5-7. Both C and O atom numbers of these 523 iodinated OC are smaller than those of mono-modally distributed CHO⁺ compounds 524 around C_{15} in the same particle size (Figure 3d and S3b). This implies that iodine has 525 a strong tendency to aromatic compounds in submicron aerosols due to electrophilic 526 substitution on aromatic rings. In 3.2-5.6 µm particles, iodinated OC features C₄-C₆ 527 CHO^+ and $CHON^+$ compounds with DBE = 3-6, which again have fewer C atoms 528 529 than non-iodinated OC. Supporting evidence from AI shows these compounds are not 530 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., 531 2014; Wilson et al., 2015). However, Hao et al. 2017 (Hao et al., 2017) showed that 532 533 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 534

thus apparent that iodinated OC in $3.2-5.6 \mu m$ particles were not directly from iodinated organic compounds in the seawater.

537 **3.5 Atmospheric implications**

Due to the 71% ocean coverage of the earth's surface, marine aerosol generation is 538 important in determining the earth's radiative budget and climate change. Of the 539 limited number of studies reporting coastal NPF, most have focused on iodine 540 541 emission, oxidation and nucleation in the early stage of NPF. In principle, abundant low-volatility condensing vapors other than iodine are required in coastal 542 environments for the growth of iodine clusters to CCN. This article reveals a new 543 544 group of important organic compounds involved in this process. It is most likely that their precursors are emitted mutually with iodine from either direct exposure of 545 coastal biota to the atmosphere or biological-active sea surface. If this is true, we 546 suggest the results in our location can be extrapolated to other iodine-rich coastal 547 548 locations, as long as iodine-NPF can be observed. More fundamental field, laboratory and modeling studies are needed to determine (1) exact emission sources and source 549 rates of these organic precursors, (2) their gas phase intermediates and oxidation 550 mechanisms in the atmosphere and (3) their quantitative contribution to global and 551 552 regional CCN numbers.

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557

558 **Data availability.** All of the datasets related to the chemical formulas detected in

- this work can be accessed in "Global Change Research Data Publishing and
- 560 Repository" via doi:10.3974/geodb.2020.03.26.V1. Any other data used in this

561	publication are	available from	the corres	ponding	author Huan	Yu
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- 563

564	Author contributions.	Huan Yu designed and conducted	chemical analysis. Yibei
		U	2

- 565 Wan and Huan Yu did data analysis and wrote the paper. Xiangpeng Huang conducted
- the field sampling. Bin Jiang and Yuhong Liao did the FT-ICR-MS analysis. Binyu
- 567 Kuang, Manfei Lin, Deming Xia, Jingwen Chen and Jianzhen Yu reviewed and
- 568 revised the manuscript.
- 569

570 Conflict of Interest

- 571 The authors declare that they have no conflict of interest.
- 572

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