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# Chemical characterization of organic compounds involved in iodine-initiated new particle formation from coastal macro-algal emission

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5 Yibei Wan<sup>1</sup>, Xiangpeng Huang<sup>2</sup>, Chong Xing<sup>1</sup>, Qiongqiong Wang<sup>1</sup>, Xinlei Ge<sup>2</sup>, Huan Yu<sup>1,\*</sup>

<sup>6</sup> <sup>1</sup> School of Environmental Studies, China University of Geosciences, Wuhan, 430074, China

<sup>2</sup> Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control,
 Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, School
 of Environmental Science and Engineering, Nanjing University of Information Science and
 Technology, Nanjing 210044, China

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12 \* To whom correspondence should be addressed: yuhuan@cug.edu.cn

# 13 Abstract

14 Iodine-initiated new particle formation (I-NPF) has long been recognized in coastal hotspot regions. However, no prior work has studied the exact chemical composition of organic compounds 15 and their role in the coastal I-NPF. Here we present an important complementary study to the 16 ongoing laboratory and field researches of iodine nucleation in coastal atmosphere. Oxidation and 17 NPF experiments with vapor emissions from real-world coastal macroalgae were simulated in a bag 18 reactor. On the basis of comprehensive mass spectrometry measurements, we reported for the first 19 20 time a variety of volatile precursors and their oxidation products in gas and particle phases in such a 21 highly complex system. Organic compounds overwhelmingly dominated over iodine in the new 22 particle growth initiated by iodine species. The identity and transformation mechanisms of organic 23 compounds were proposed in this study to provide a more complete story of coastal NPF from 24 low-tide macroalgal emission.

# 25 **1. Introduction**

Coastal new particle formation (NPF) may be driven by daytime low-tide emission of iodine species from macroalgae fully or partially exposed to the air. The phenomenon was reported in hotspot locations of west Europe, Australia and polar regions (O'dowd et al., 2002; Heard et al., 2006; Mcfiggans et al., 2010; Whitehead et al., 2009; Sipil äet al., 2016; Allan et al., 2015; Baccarini et al., 2020; Beck et al., 2021). In the southeast coastline of China, we reported intense iodine-initiated NPF based on particle number size distribution and iodine measurements (Yu et al., 2019).

To simulate iodine-initiated NPF (I-NPF) in controlled laboratory conditions, I2 or CH2I2 vapor 32 33 was usually photolyzed in the presence of ozone to provide nucleation precursors (Burkholder et al., 2004; Jimenez et al., 2003; Monahan et al., 2012; Saunders and Plane, 2005; O'dowd et al., 2004; 34 35 Gómez Mart n et al., 2020; He et al., 2021; Huang et al., 2022; Gómez Mart n et al., 2022). Ashu-Ayem et al. (2012); Monahan et al. (2012); Mcfiggans et al. (2004); Sellegri et al. (2005) and 36 Sellegri et al. (2016) also investigated the NPF from the vapors emitted by real-world macroalgal 37 38 specimens or seawater in laboratory chamber or apparatus. However, the focus of all above studies 39 are emission rate, oxidation mechanisms or nucleation pathways of iodine species. For example, 40 positive correlations between particle concentrations and I<sub>2</sub> or CH<sub>2</sub>I<sub>2</sub> mixing ratios were usually 41 observed (Burkholder et al., 2004; Jimenez et al., 2003; Sellegri et al., 2005; Monahan et al., 2012). 42 Kinetic studies in flow tube or CERN CLOUD chamber proposed the clustering of iodine oxides  $(I_xO_y)$  or iodine oxoacids (HIO<sub>3</sub>, HIO<sub>2</sub>) as nucleation mechanisms on the basis of photoionization 43 TOF-MS (Gómez Mart n et al., 2020), Api-TOF and nitrate-Chemical Ionization Mass Spectrometer 44 45 (CIMS) measurements (He et al., 2021; Gómez Mart ń et al., 2022).

46 Organic compounds have also been suggested to be involved in coastal NPF (Vaattovaara et al., 2006; Yu et al., 2019). Huang et al. (2022) and Saunders et al. (2010) investigated the effect of 47 48 uptake of meso-erythritol, glyoxal, dimethylamine and oxalic acid on the growth of iodine oxide 49 nanoparticles. However, no prior work has investigated the exact chemical identity of organic 50 compounds (other than iodomethane) and their role in I-NPF. The role of biogenic terpenes and anthropogenic aromatics in continental NPF has been recognized for a long time (Donahue et al., 51 52 2013). Their ozonolysis or photochemistry products have been investigated in depth by using 53 Electrospray Ionization Mass Spectrometry (ESI-MS) and more recently, CIMS (Nguyen et al., 2010; 54 Kundu et al., 2017; Kundu et al., 2012; Faxon et al., 2018; Wang et al., 2020; Riva et al., 2017; Yan 55 et al., 2020; Ehn et al., 2014). It is very likely that certain volatile organic compounds (VOCs) emitted mutually with iodine or iodinated methane from coastal biota or biologically active sea 56 57 surface may also be involved in coastal I-NPF process and promote the growth of iodine particles.

To test this hypothesis, we conducted oxidation and NPF experiments with vapor emissions from real-world coastal macroalgae in a bag reactor. A suite of mass spectrometric methods including Inductively Coupled Plasma-MS (ICP-MS), Gas Chromatography-MS (GC-MS), iodide-CIMS and ESI-orbitrap MS were applied to measure vapor precursors, gaseous products and particulate products during the NPF process. Mass concentrations of total organic carbon (TOC) and total iodine (TI) of new particles were compared to evaluate the relative importance of organics and iodine in new particle growth. The identity and transformation mechanisms of organic compounds were identified to provide a more complete story of coastal NPF from low-tide macroalgal emission. Our
study is thus complementary to prior laboratory and field studies of I-NPF, but has an emphasis on
organics.

# 68 **2. Experiments**

# 69 2.1 Experimental apparatus and sample collection

Similar to Potential Aerosol Mass (PAM) Oxidation Flow Reactor, a bag reactor was designed to provide an oxidizing environment for simulating atmospheric oxidation processes of algae-emitted VOCs. The bag reactor was made from 75  $\mu$ m-thick fluorinated ethylene propylene (FEP) Teflon (1.2 m×1.5 m, flat dimension). The volume of the bag at full inflation was determined experimentally to be about 200 L. The bag was suspended vertically (Figure 1) and kept in the dark or directly exposed to room light of fluorescent lamp. Before each experiment, the bag was purged for several hours to reduce background particle concentrations to below 1 cm<sup>-3</sup>.

*Undaria pinnatifida*, a common brown seaweed species at Xiangshan gulf of east China coast,
was collected from local intertidal zone and stored at -10 °C until the experiments. 2 kg macroalgae
was put in a 20 L Pyrex glass bottle that was filled with ~1 L natural seawater. The specimens was
partially exposed to the air to simulate tidal emersion of macroalgae. A flow of particle-free ultra
high purity (UHP) air blew algae-emitted VOCs out of the bottle and merged with a diluting air flow
before entering the bag reactor.

83 Two types of experiments were conducted. In the three ozonolysis experiments, ozone  $(O_3)$  was generated by flowing an UHP air flow through a 5 Watt 185 nm UV lamp. The O<sub>3</sub> flow was fed just 84 before the bag reactor was fully inflated. Final O<sub>3</sub> concentration in the bag reactor was measured to 85 86 be ~500 ppbv using an ozone analyzer (Model 49i, Thermo-Fisher Scientific Inc.). RH was estimated to be 10% in the bag reactor assuming 0.3 lpm water-saturated VOC flow was diluted by 2.7 lpm dry 87 air flow. In an additional OH-enhanced experiment, the O<sub>3</sub>/VOC mixture flow was directed through a 88 254 nm UV light before entering the bag reactor. OH radicals were produced via the reaction 89  $O_3+hv \rightarrow O_2+O(^1D)$  and  $O(^1D)+H_2O \rightarrow 2OH$ . Integrated OH exposure time was determined by SO<sub>2</sub> 90 decay experiment to be 2.4 days in the experimental apparatus assuming ambient average OH 91 concentration  $1.5 \times 10^6$  molecules cm<sup>-3</sup> (see Supporting Material S1). Other oxidants may include 92  $O(^{3}P)$  resulted from the quenching of  $O(^{1}D)$  (Li et al., 2015). Because the purpose of this study is to 93 94 identify gas and particle products of algae-emitted VOCs in the simulated NPF event, significantly higher oxidation level in the bag reactor than atmosphere should not change the conclusions in the 95

96 article. Wall loss, aerosol yield, reaction rate and other kinetic factors in the bag reactor were also not97 evaluated.

The bag reactor was first operated in a static mode to monitor the time evolution of gaseous products and particle size. In the static mode, the bag was first filled to full inflation with the VOCs/O<sub>3</sub> flows. The flows were then shut down; a Scanning Mobility Particle Sizer (SMPS, model 3936, TSI Inc., Shoreview, MN, USA) and an Aerodyne iodide-CIMS pulled two flows of 0.3 liters per minute (lpm) and 1.8 lpm out of the bag, respectively. The SMPS measured the particle number size distribution from 14 to 600 nm.

104 The bag reactor was then operated in a dynamic mode for a few hours to collect enough particles 105 for offline chemical analysis. In the dynamic mode, the VOCs/O<sub>3</sub> flow of 3 lpm was fed to the bag 106 continuously, while the SMPS and a vacuum pump (GAST Group Ltd.) pulled sample flows of 0.3 107 and 2.7 lpm, respectively, out of the bag reactor. This resulted in an overall residential time of 67 108 minutes for the O<sub>3</sub>/VOC mixture in the fully inflated bag. The particles in the 2.7 lpm sample flow 109 were collected onto a Zefluor® PTFE membrane filter mounted in a filter inlet for gases and aerosols (FIGAERO) for iodide-CIMS analysis, or alternatively, onto 47 mm diameter double quartz fiber 110 111 filter pack mounted in a filter holder for ESI-orbitrap MS, ICP-MS and TOC analysis. The front filter 112 of the double filter pack collected the particles and also adsorbed some volatile species as positive 113 artifact, while the back filter placed downstream of the front filter was supposed to adsorb the same 114 amount of volatile species as the front filter.

# 115 **2.2 Chemical analysis**

116 Before the ozonolysis experiments, the algae-emitted VOCs in the bag reactor were collected by a 6-liter pre-evacuated stainless-steel canisters (Entech Instruments, Inc., Simi Valley, CA, USA) and 117 analyzed using a quadrupole GC-MS system (model TH-300B, Wuhan Tianhong Instruments Co. 118 Ltd., Wuhan, China). The algae-emitted VOCs, as well as their gaseous and particulate products, 119 120 were also measured by the FIGAERO-iodide-CIMS. Iodide-adduct chemical ionization is well suited 121 for measuring oxygenated or acidic compounds with minimal fragmentation. More details of the 122 GC-MS and FIGAERO-iodide-CIMS measurements can be found in Supporting Material S2. The 123 theory and design of the two instruments were described by Wang et al. (2014) and Lopez-Hilfiker et 124 al. (2014).

125 The particles collected on quartz fiber filters were sent for offline quantification of TOC and TI, 126 as well as non-target analysis of organic compounds using ESI-orbitrap MS. The front and back 127 filters were treated, separately, following the procedure as below: the filter was ultrasonicated twice 128 with 10-mL water and acetone nitrile solvent mixture (v:v=1:1). Ultrasonication time and power 129 were 20 minutes and 150 Watt. The extract was filtered by a 0.2 µm PTFE syringe filter and 130 evaporated in a rotary evaporator to 0.5 mL. After being centrifuged for 30 min at 12000 rpm, the 131 supernatant was collected for TI analysis by Agilent 1100 HPLC-7900 ICP-MS (Agilent 132 Technologies, Santa Clara, CA, USA) and TOC analysis by a TOC analyzer (Model TOC-5000A, 133 Shimadzu, Japan). TI or TOC in the particles was obtained by subtracting the amount on the back filter from that on the front filter. Nontarget analysis of organic compounds in the supernatant was 134 135 conducted using a Q Exactive hybrid Quadrupole-Orbitrap mass spectrometer (Thermo Scientific, 136 Bremen, Germany). The supernatant was directly infused by a syringe pump and ionized in negative 137 ESI source. All the ions in the m/z range from 50 to 500 Th were scanned with a mass resolution of 138 70000. The chemically sound CHO molecular formulas were computed with a mass tolerance of  $\pm 2$ 139 ppm for these ions. Only the compounds that existed solely in the front filter or with ion intensity in 140 the front filter higher than that in the back filter by a factor of 3 were regarded as the organic 141 compounds in the particle phase (Wang et al., 2017).

### 142 **3. Results and discussion**

No particles formed in the absence of room light or  $O_3$ . Therefore, light was on throughout the experiments reported in the article. In the static mode experiments, we could not observe gas-phase products until 48 minutes after  $O_3$  injection. New particles larger than 14 nm were observed only 58 minutes after  $O_3$  injection. Afterwards, new particles begun to grow to form a typical banana-shape particle size spectrum (Figure 2a). This relatively long waiting time was likely due to the build-up of  $O_3$  and oxidation products. Time zero of Figure 2 was thus set as the time when gaseous products first appeared.

# 150 **3.1 Macroalgal emission**

It is of particular interest to know what VOCs are emitted from coastal macroalgae. They are potential precursors of iodine particle nucleation and growth. The canister sampling followed by GC-MS analysis showed that the top 9 non-CHO compounds with highest TIC peak areas (Table 1) are  $C_5$  alkanes,  $C_{10}$  alpha-pinene and halogenated  $C_1$ ,  $C_3$  and  $C_5$  alkanes. The top 10 CHO compounds are  $C_2$ - $C_6$  alcohols and carbonyls with saturated or unsaturated carbon chain.

Iodide-CIMS is more sensitive to more oxygenated or acidic compounds and thus complementaryto the GC-MS measurement. The 76 organic precursors detected by iodide-CIMS before ozone

addition were characterized by  $C_{1,2,3,6}$  and  $O_{2-3}$  formulas (Figure 3a). The top 7 compounds with highest ion intensities were  $CH_2O_2$ ,  $C_2H_4O_2$ ,  $C_3H_6O_3$ ,  $C_6H_{10}O_3$ ,  $C_2H_6O_2$ ,  $C_4H_8O_2$  and  $C_6H_{12}O_3$ , which accounted for 82.5% of total ion intensity. They are  $C_1$ - $C_6$  mono-carboxylic acids, hydroxyl carboxylic acids or oxo-carboxylic acids with 2 to 3 oxygen atoms (Table 1). Their carbon atom numbers are in general consistent with the VOCs detected by GC-MS.

Relatively high signals of  $NO_3^-$  and  $HNO_3\Gamma$  were observed before the addition of ozone to the bag reactor. They were likely  $HNO_3$  or nitrate vaporized from algal specimens or natural seawater. Because  $NO_3^-$  and  $HNO_3\Gamma$  were also observed in the particle phase during the NPF (Figure 4), we assume  $HNO_3$  was also an important precursor of particle formation.

### 167 **3.2 Gaseous products**

# 168 **3.2.1 Gaseous inorganic molecules and radicals**

Being different from nitrate-CIMS, our iodide-CIMS did not detect nucleating clusters of iodine oxides or oxyacids after the addition of ozone. Instead, dozens of new inorganic molecules or radicals were observed as clusters with  $\Gamma$ , NO<sub>3</sub><sup>-</sup> or deprotonated ions in the gas or particle phase (Figure 4). We grouped these species by elemental composition and investigated their role in the NPF by observing how their gaseous ion intensities evolved during the NPF event in the bag reactor (Figure 2b-2f).

175 1. Cl, I, Cl<sub>2</sub> and ClI in gas phase: the intensities of I and Cl increased ca. 10 minutes before 14 nm 176 particles appeared and decreased as the particles grew up (Figure 2b). Based on prior work of Burkholder et al. (2004); Jimenez et al. (2003); O'dowd et al. (2004), we suggested the photolysis of 177 178 CH<sub>2</sub>Cl<sub>2</sub>, CHBrCl, CH<sub>3</sub>I and C<sub>3</sub>H<sub>7</sub>I was the source of halogen atoms (e.g., CH<sub>3</sub>I+hv $\rightarrow$  CH<sub>3</sub>+I), although we could not exclude the photolysis of other precursors like I2 and HOI that are invisible to 179 180 GC-MS and iodide-CIMS. There was a time lag of 20-25 minutes between the appearances of Cl and I and those of CII and Cl<sub>2</sub>, which were probably resulted from anion exchange reactions of Cl I and 181 182 I I with Cl atoms.

2. IO<sub>2</sub>, IO and CIIO in gas phase: these species showed a similar time evolution to I and Cl atoms
(Figure 2c). They could be from the reactions between I, CII and O<sub>3</sub> (Saiz-Lopez et al., 2014).
Sequential oxidation and aggregation reactions might have formed other halogen oxides (Gómez
Mart ń et al., 2013), but they might not be detectable by iodide-CIMS.

187 3.  $INO_2$ ,  $CINO_2$  and  $INO_3$ :  $INO_2$  and  $CINO_2$  were detected in gas phase with similar time

188 evolution with halogen atoms and halogen oxides (Figure 2d). INO<sub>3</sub> was found in both gas and particle phases. INO<sub>2</sub> and INO<sub>3</sub> were usually thought to form upon the reactions 189 I+NO<sub>2</sub>+M $\rightarrow$ IONO+M and IO+NO<sub>2</sub>+M $\rightarrow$ IONO<sub>2</sub>+M in the atmosphere (Saiz-Lopez et al., 2012), 190 191 which seems to be unlikely in our bag reactor because  $NO_2$  was not added. Considering  $NO_3^-$  was 192 ubiquitous in the bag reactor of our experiment, it is likely that INO<sub>2</sub> and INO<sub>3</sub> formed via  $I_2O_2+NO_3 \rightarrow IO_3 + IONO$  and  $I_2O_3+NO_3 \rightarrow IO_3 + IONO_2$ . These reaction pathways have been 193 194 supported by theoretical calculation and flow tube mass spectrometry experiments (Gómez Mart n et al., 2022; G ómez Mart n et al., 2020). ClNO<sub>2</sub> was likely to form upon similar reaction between Cl<sub>2</sub>O<sub>2</sub> 195 196 and  $NO_3^-$  in the bag reactor.

197 3. HIO, HIO<sub>2</sub> and HIO<sub>3</sub>: HIO<sub>3</sub> seems to be the end product of above intermediates, because its 198 gas-phase ion intensity kept on increasing during new particle growth (Figure 2e). Based on this fact, we assume that HIO<sub>3</sub> could be from  $I_2O_5+H_2O\rightarrow 2HIO_3$  or  $I_2O_y+NO_3\rightarrow IO_3+INO_y$ . On the other 199 hand, HIO<sub>3</sub> was not detected in particle phase by iodide-CIMS, which is contrary to the offline 200 201 analysis of quartz filter by HPLC-ICP-MS showing that total iodine was mostly dominated by IO<sub>3</sub><sup>-</sup> 202 peak. We speculate that HIO<sub>3</sub> might have been dehydrated to I<sub>2</sub>O<sub>5</sub> under thermal desorption temperature up to 180 °C in FIGAERO. The signals of IO<sup>-</sup>, IO<sub>2</sub><sup>-</sup> and HIONO<sub>3</sub><sup>-</sup> (corresponding to HIO 203 204 and HIO<sub>2</sub>) were found in particle phase, but not in gas phase. He et al. (2021) proposed HIO<sub>2</sub> formation via  $I+H_2O+O_3 \rightarrow HIO_2$  or  $I_2O_2+H_2O \rightarrow HIO+HIO_2$ . With limit experimental evidence of 205 206 our work, the exact formation pathways of HIO<sub>x</sub> remains to be explored in future.

4.  $CH_3SO_3H$ ,  $S_2^-$ ,  $S_3^-$ ,  $SO_3^-$ : We observed methane sulfonic acid ( $CH_3SO_3H$ , MSA) in both gas and particle phases. Gaseous MSA increased in the beginning, but decreased after new particles appeared (Figure 2f). Apparently, our measurement suggested MSA contributed to the growth of new particles, but it is unknown if it also participated in nucleation. We suggested  $S_2^-$ ,  $S_3^-$ ,  $SO_3^-$  ions observed in the particle phase were thermal decomposition products of MSA.

212 We noticed that CH<sub>3</sub>I vapor was added as ion source reagent to the ion molecule reactor (IMR) of 213 iodide-CIMS. It is likely that this extra CH<sub>3</sub>I in the IMR might obscure the interpretation of the 214 observed iodine containing clusters. We believed that ion source reagent CH<sub>3</sub>I should have relatively 215 small interference with inorganic iodine compounds from the bag reactor, on the basis of 2 facts: (1) 216 ion source reagent CH<sub>3</sub>I was added directly from permeation tube into the IMR. Without photolysis, 217 ion source reagent CH<sub>3</sub>I in the IMR should not become a source of I and I<sub>x</sub>O<sub>y</sub>. (2) the concentration 218 of ion source reagent  $CH_3I$  and its potential products should be quite constant as long as  $O_3$  was 219 present in the IMR, which was not supported by the variable signals of I, CII, IO<sub>2</sub>, IO, CIIO, HIO<sub>3</sub>,

220 INO<sub>2</sub> and INO<sub>3</sub> in Figure 2.

### 221 **3.2.2 Gaseous organic products**

222 After ozone addition, a gradual transformation from  $C_1$ - $C_3$  precursors to  $C_5$ - $C_8$  gaseous products 223 was observed during the NPF process (Figure 2h). In the meanwhile, the oxygen atom number of the 224 compounds increased from 2-3 to 4-7 (Figure 2g). The formation of compounds with more carbon 225 atoms than the parent VOCs is unlikely in the gas phase, except bimolecular reactions of stabilized 226 Criegee intermediates (SCIs) that typically form upon alkene ozonolysis. Similar to isoprene ozonolysis (Riva et al., 2017; Inomata et al., 2014), we propose the SCI addition mechanism can 227 also explain the transformation observed in our case: (1) C<sub>4</sub> SCIs formed upon the ozonolysis of 228 229 CHO precursors with C=C double bonds (e.g., those observed by GC-MS in Table 1). (2) the 230 insertion of C<sub>4</sub> SCIs into carboxylic acid precursors (e.g., those observed by CIMS in Table 1) 231 produced oligomeric hydroperoxides. An example was shown in Scheme I for the reactions of most 232 abundant ethyl vinyl carbinol ( $C_5H_{10}O$ ), ozone and formic acid ( $CH_2O_2$ ), but the same mechanism is also applicable for ethyl vinyl ketone (C5H8O) and other abundant C2-C5 carboxylic acids and 233 234 hydroxyl carboxylic acids. As a result, a series of gaseous oligomeric hydroperoxides  $C_5H_{10}O_5$ ,  $C_6H_{10}O_5$ ,  $C_6H_{12}O_5$ ,  $C_7H_{12}O_6$ ,  $C_7H_{14}O_6$ ,  $C_8H_{14}O_5$ ,  $C_8H_{16}O_6$ ,  $C_8H_{16}O_5$  and  $C_9H_{16}O_6$  were observed with 235 236 high intensity by iodide-CIMS.



Scheme I

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### 238 **3.3 Particulate products**

# 239 **3.3.1 Relative mass contribution of organic carbon and iodine to new particles**

In the dynamic mode experiments,  $O_3$  in the bag reactor was kept at its maximum concentration 200 ppbv. With a prolonged residential time of 67 min, the particles grew to  $102\pm23$  nm, which was measured by the SMPS at the outlet of the bag reactor. The TOC and TI measurements show that organic compounds contributed more particle mass than iodine with TOC/(I+TOC) ratio of 96.1±2.9% (Table 2).

In the OH-enhanced experiment (dynamic mode), more particulate products were generated with enhanced oxidation capacity: TI in the particles increased by a factor of 10.8; TOC increased by a factor of 2.7; particle number concentration increased by a factor of 7.4. On the other hand, particle size decreased to 73 nm and TOC/(TI+TOC) ratio decreased to 92.9% (Table 2). These differences indicate that more iodine nuclei were produced with enhanced oxidation capacity, probably via OIO+OH $\rightarrow$  HOIO<sub>2</sub> (Plane et al., 2006) and O(<sup>3</sup>P)+CH<sub>3</sub>I $\rightarrow$ IO+CH<sub>3</sub> (Teruel et al., 2004). Competitive uptake of condensing organic vapors onto these iodine nuclei limited the growth of individual new particles. Nevertheless, organic compounds overwhelmingly dominated over iodine in the mass contribution to new particle growth.

The significant organic contribution observed in the laboratory condition is generally consistent with TOC/(I+TOC) ratio of 98.2% in 10-56 nm new particles collected during a coastal I-NPF event in China (Yu et al., 2019), although TOC and TI during the field event are two orders of magnitude lower than those in the bag reactor (Table 2). Mean diameter of new particles was observed to be only 16 nm during the field event. But those small new particles are expected to grow into CCN active sizes, given longer residence time and uptake of more condensing vapors in the atmosphere (He et al., 2021).

# 261 **3.3.2 Particulate organic products**

262 In the end of a typical ozonolysis experiment (dynamic mode), 100 and 364 new formulas were observed in the gas and particle phases, respectively, including 73 semi-VOCs appeared in both gas 263 264 and particle phases. Those semi-VOCs accounted for 81 and 20% of total ion intensities of gaseous and particulate products, respectively. Being different from unimodal atom number distributions of 265 gaseous products ( $C_{max}$ = 7 and  $O_{max}$ =5, Figure 3b), particulate products were characterized by 266 distinct bimodal or trimodal distribution of carbon number (C<sub>max</sub>=8, 14 and 16, Figure 3c) and 267 268 oxygen number (O<sub>max</sub>=4 and 8), implying possible dimer formation via accretion reactions in the 269 particle phase.

270 ESI-Orbitrap MS differs from FIGAERO-iodide-CIMS in extraction method (ultrasonic solvent 271 extraction from quartz fiber filter vs. thermal desorption from PTFE membrane filter), ionization 272 source (electrospray ionization vs. iodide-adduct chemical ionization) and MS resolving power 273 (70000 vs. 4500). The result showed that ESI-orbitrap MS and FIGAERO-iodide-CIMS detected 336 274 and 364 organic formulas, respectively, in the particle phase. 167 organic formulas were commonly 275 observed by both methods, which accounted for 87% and 54% of total ion intensity of organic 276 formulas by the two methods, respectively (Figure S1). As shown in Figure 3c and 3d, 277 FIGAERO-iodide-CIMS had better sensitivity toward the organic compounds with more oxygen 278 atoms (e.g.,  $0 \ge 8$ ) and carbon atoms (e.g.,  $C \ge 10$ ). As a result, bimodal carbon and oxygen atom 279 number distributions were observed by FIGAERO-iodide-CIMS, but not ESI-orbitrap MS.

The measurement by ESI-orbitrap MS provided more insights about the formation mechanism of particulate products. We compared the 336 formulas detected by ESI-orbitrap MS in our study with the 414 formulas of isoprene ozonolysis SOA products (Nguyen et al., 2010) and 922 formulas of alpha-pinene ozonolysis SOA products (Putman et al., 2012) measured by the ESI-orbitrap MS. It was found that 72% of the formulas in this study can also be found in isoprene SOA, but only 39% can be found in alpha-pinene SOA. This seems to imply that some similar alkene ozonolysis reactions occurred in our system and isoprene ozonolysis.

287 For such a highly complex system full of various algae-emitted precursors, it is impossible to 288 simply propose a reaction mechanism to explain the formation of all particulate products, nor to list 289 all reactions occurring in the bag reactor. On the basis of particle-phase oligomer chemistry (Seinfeld 290 and Pandis, 2016), especially the well-understood isoprene ozonolysis SOA chemistry (Nguyen et al., 291 2010; Inomata et al., 2014; Riva et al., 2017), we suggest a variety of accretion reactions without 292 uniform oligomerization pattern (e.g., esterification, aldol condensation, hemiacetal reactions, peroxyhemiacetal formation and SCI reactions, etc.) transformed Omax=4 and Cmax=8 multifunctional 293 294 monomers (like alcohols, carbonyls, hydroperoxides, carboxylic acids) to O<sub>max</sub>=8 and C<sub>max</sub>=14 or 16 295 dimers. As an example, we used two simplified reaction equations to illustrate addition-type 296 cross-oligomerization between C<sub>6</sub> and C<sub>8</sub> monomers and self-oligomerization of C<sub>8</sub> monomers, 297 respectively:

$$C_6H_{6-12}O_{3-6}+C_8H_{10-16}O_{3-6} \rightarrow C_{14}H_{16-26}O_{6-12}$$

299 
$$C_8H_{10-16}O_{3-6}+C_8H_{10-16}O_{3-6}\rightarrow C_{16}H_{20-32}O_{6-12},$$

in which the  $C_6$ ,  $C_8$ ,  $C_{14}$  and  $C_{16}$  formulas in the equations are among the most abundant ones observed in the particle phase by the iodide-CIMS.

### **302 4.** Conclusions

Using a suite of mass spectrometers, we reported, for the first time, the chemical compositions of volatile precursors emitted by real-world coastal macroalgae and their gaseous and particulate oxidation products. In the presence of room light and ozone, the photolysis of halogenated  $C_{1,3,5}$ alkanes ends up as HIO<sub>3</sub> and INO<sub>3</sub>. It was most likely HIO<sub>3</sub> initiated NPF and provided nuclei for the further condensation of other products like MSA and CHO compounds. Gas-phase SCI reactions and particle-phase accretion reactions transformed  $C_1$ - $C_6$  and  $O_2$ - $O_3$  precursors gradually to particulate products with  $C_{max}$ =8, 14 and 16 and  $O_{max}$ =4 and 8. As a result, organic carbon were found to

overwhelmingly dominated over iodine in the mass contribution to the new particle growth. 310 Although our instruments did not allow the detection of nucleating clusters of iodine oxides or 311 312 oxyacids, our study provided important complementary information to the ongoing laboratory and 313 field researches of coastal I-NPF.

#### 314 **Data Availability**

315 All data related to figures and tables in this study are archived and made available through 316 Zenodo data repository https://doi.org/10.5281/zenodo.6965859.

#### 317 **Financial support.**

318 This work was supported by the National Science Foundation of China (grant no. 41975831 and

42175131) and Start-up research funding from China University of Geosciences. 319

#### 320 **Competing Interests.**

321 The authors declare that they have no conflict of interest.

#### 322 **Author contributions**

323 HY designed the experiment. YW, XH and CX conducted the experiments. YW and HY analyzed

324 the data and wrote the manuscript. QW and XG reviewed and revised the manuscript.

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	Formula	Structure	Peak area/MS peak intensity						
GC/MS, non-CHO compounds									
1	$C_{5}H_{12}$	$\downarrow$	$1.90 \times 10^{6}$						
2	$C_{5}H_{10}$		$1.59 \times 10^{6}$						
3	CH <sub>3</sub> I	<u>_</u> I	$1.37 \times 10^{6}$						
4	$C_3H_7I$		$7.60 \times 10^5$						
5	CHBr <sub>3</sub>	Br Br	$4.71 \times 10^{5}$						
6	$C_5H_{11}I$		$3.75 \times 10^{5}$						
7	CHBr <sub>2</sub> Cl	Br Br	$2.71 \times 10^{5}$						
8	$CH_2Cl_2$		$2.55 \times 10^{5}$						
9	$C_{10}H_{16}$	TX-	2.26×10 <sup>5</sup>						
GC/MS, CHO compounds									
1	$C_2H_6O$	ОН	$1.70 \times 10^{7}$						
2	$C_3H_6O$	~O	$1.38 \times 10^{7}$						
3	$C_4H_6O_2$		$1.30 \times 10^{7}$						
4	$C_6H_{12}O$	$\sim \sim \sim_0$	$1.03 \times 10^{7}$						
5	$C_5H_{10}O$	OH	$1.00 \times 10^{7}$						
6	$C_4H_{10}O$	ОН	$5.16 \times 10^{7}$						
8	$C_2H_4O$	~~ <sub>0</sub>	3.46×10 <sup>7</sup>						
9	$C_6H_{10}O$	$\sim \sim \sim_0$	$2.88 \times 10^{7}$						
7	C <sub>5</sub> H <sub>8</sub> O	O V	$1.45 \times 10^{7}$						
10	$C_4H_8O$		$1.37 \times 10^{7}$						
Iodide-CIMS									
1	$CH_2O_2$	о Н ОН	1.58×10 <sup>6</sup>						
2	$C_2H_4O_2$	ОН	9.52×10 <sup>5</sup>						
3	$C_3H_6O_3$	он Он Он	9.21×10 <sup>5</sup>						
4	$C_{6}H_{10}O_{3}$	HO	4.44×10 <sup>5</sup>						

Table 1. Major volatile organic compounds emitted by macroalgae as potential NPF precursors, sorted by TIC peak area measured by GC/MS or MS peak intensity measured by iodide-CIMS

5	$C_2H_6O_2$	НО	2.88×10 <sup>5</sup>
6	$C_4H_8O_2$	HOHO	1.17×10 <sup>5</sup>
7	$C_{6}H_{12}O_{3}$	ОН	1.12×10 <sup>5</sup>

Table 2. Particle number concentration (*N*), mean diameter ( $D_p$ ), total organic carbon (TOC) and total iodine (TI) of new particles with a residential time of 67 min in the bag reactor in the ozonolysis experiments and OH-enhanced experiment (dynamic mode). Those of 10-56 nm new particles collected by a nano Micro-Orifice Uniform Deposit Impactor (nano-MOUDI, MSP, Inc.) during an I-NPF event at a coastal site of Ningbo, China (Yu *et al.*, 2019) were also listed.

	TOC ( $\mu g m^{-3}$ )	TI (μg m <sup>-3</sup> )	TOC/(TI+TOC)	$N (\mathrm{cm}^{-3})$	$D_p$ (nm)
ozonolysis experiments	45.6±9.7	0.88±0.34	96.1±2.9%	$(5.58\pm2.04)\times10^4$	102±23
OH-enhanced experiment	125.3	9.5	92.9%	4.16×10 <sup>5</sup>	73
I-NPF event at a coastal site of China	0.7	0.0135	98.2%	6.00×10 <sup>5</sup>	16



Figure 1. Schematic of experimental setup. Solid line: air flows. Dashed lines: sent for offline chemical analysis.



Figure 2. Time evolution of particle number size distribution (a) and relative intensities of gaseous molecules and radicals (b-f); the fractions of organic compounds grouped by O and C atom numbers in the selected time points (g-h) in a typical ozonolysis experiment (static mode). Time zero was set as the time when gaseous products first appeared.



Figure 3. Oxygen and carbon atom number distributions of potential VOC precursors (a), gaseous products (b) and particulate products measured by iodide-CIMS (c), as well as the particulate products measured by ESI-orbitrap MS (d) in a typical ozonolysis experiment (dynamic mode). Hatched bars indicate the fractions of organic formulas observed in both gas and particle phases by iodide-CIMS.



Figure 4. Integrated ion intensities of inorganic molecules and radicals in the gas phase (static mode) and particle phase (dynamic mode) measured by iodide-CIMS in a typical ozonolysis experiment. The ions were coded in color according to their elemental composition. For each ion cluster, parent neutral molecule is on the left hand side of middle dot, while the clustering ion  $\Gamma$  or NO<sub>3</sub><sup>-</sup> is on the right hand side. Those without a clustering ion are shown as bare anions.