A point-to-point response and relevant changes made in the revised manuscript

Anonymous Referee #2

The manuscript provides useful insights into chemical composition of newly formed particles and indicates iodine role in coastal nucleation events. Moreover, it shows a presence of organic iodine species in the nucleation mode particles and gives their semi-quantitative estimate. The manuscript gives valuable input into understanding of marine new particle formation and growth and, given the potential importance of new particle formation for clouds and climate, I would support the publication after the comments listed below are addressed.

We thank the referee for his important comments and careful examination of the manuscript. Point-to-point responses are given below. All relevant changes made in the revised manuscript are highlighted in yellow color.

General remarks

It is nice to see the evidence for organic iodine being present in the nucleation mode particles, however, it is still not clear whether these contribute to the formation of the new particles or the growth by iodine reactions with organics. The latter would actually be consistent with previous studies (Sipilä et al., 2016) that point to iodine oxoacids and iodine oxide vapours being the main drivers of particle formation and initial growth. Similarly, in your figure 9, I-organic adducts are present in the larger particle sizes than inorganic I (IOx and I+I3). Moreover, as shown in Figure 8, the difference between I-NPF and non-NPF events is mainly in relative contribution from inorganic I compounds (IO and I+I3), which would support them being the drivers of NPF's. I would, therefore, recommend stating this point clearly in the abstract and conclusions or provide more extensive discussion.

Re:
We completely agree with the referee on his remarks here. Actually, we also pointed out that inorganic iodine, especially HIO_3, is likely the drivers of NPF, which is consistent with Sipilä et al., 2016. For example, in line 364 of the section 3.3, we stated "The most remarkable iodine species during the I-NPF days is IO_3^- with a mole fraction of 42.5%. This is consistent with the recent observation that HIO_3 is the key nucleating precursor in I-NPF event (Sipilä et al., 2016)."

Now we add the following two statements:
Lines 25-26 Abstract: "Iodide and organic iodine compounds were found in the nucleation mode particles, however, it is still not clear whether they contributed to nucleation or just new particle growth."

Line 455-456 Conclusion: “It is still not clear whether organic iodine compounds contributed to nucleation or just the growth of new particles via iodine reactions with organics.”

Likewise, it doesn’t seem that any iodine compounds were important for continental-NPF’s, but this point is not clearly covered in the paper. Add more discussion on the drivers of continental-NPF’s. Be clear what other than I- compounds are driving the continental-NPF as I- is not important here (Figures 8 and 9, also line 343). Also, lines 374-375: the hypothesis state that ‘that iodine species in the accumulation mode during the continental NPF days were from the aging process of small iodine-containing particles’ – where do these iodine particles come from in the continental air masses, are there iodine sources over the continent, elaborate? Lines 437-438 point to importance of aromatic iodine, but how relevant it is to NPF if existing in accumulation mode?

Re: we clarify the two misunderstandings pointed out by the referee:

1. Now we clearly state in line 388 that iodine is not important for continental NPF.
“The absence of nucleation mode for most of iodine compounds implies that iodine was unlikely to be an important NPF precursor in the continental NPF.”

Lines 437-438 simply spell out our observation that the percent of aromatic iodine concentration in total iodine was higher during the continental NPF days as compared to I-NPF and non-NPF days. We don’t mean aromatic iodine was important for continental NPF. Now the sentence in lines 456-459 was adjusted slightly to:

“During the continental NPF days, the outstanding iodine species is aromatic iodine compounds in the accumulation mode that accounted for 30% of total iodine. Those aromatic iodine compounds were probably formed from aqueous phase reactions between I^-, H_2O_2/O_3, HOI and aromatic organic compounds during in-cloud processing.”

Unfortunately we didn’t have any data on what other than iodine were the drivers of continental NPF, because our study measured only iodine species.

2. Considering the much lower iodine concentration at the inland site, we also agree with the referee that the iodine during the continental NPF days were unlikely from the sources over the continent. Instead, they are more likely from the uptake of gaseous HI, HOI or $IONO_2$ onto the anthropogenic aromatic particles that were transported to the coastal atmosphere. Now the hypothesis of aromatic iodine compound formation is elaborated in line 391-396:

“The outstanding species in the continental NPF days were aromatic iodine compounds that accounted for 30% of total iodine. This is not surprising because air masses from inland areas of China on these days might contain a large amount of anthropogenic aromatic substances. Upon arrival in the coastal region, the uptake of gaseous HI, HOI or $IONO_2$ onto these anthropogenic particles and the subsequent aerosol phase reactions between I^-, H_2O_2/O_3, HOI and aromatic compounds are hypothesized to be the formation mechanism of aromatic iodine compounds."

Abstract and conclusions state that farmed microalgae, as well as wild algae, could be an important source of new particle formation in the coastal areas of China, but statistics on the nucleation events is not provided, the statement that 'unless it was cloudy or rainy, strong NPF events were observed almost every day in April and May' is vague, provide frequency distributions or other quantitative information to evaluate that account. Move the text in lines 103-109 from experimental to result section and add more quantitative information on the occurrence of the NPF events.

Re:
Now we move the lines 103-109 from experimental to result section 3.1. Quantitative information on the occurrence of two types of NPF events is added:

Lines 160-168 "Based on the particle size distribution data, we identified two types of NPF events. The first type of NPF events was observed on 7 out of 54 non-raining observation days during the cold season from January to March…… These features, together with the air mass backward trajectories originating from northwest inland of China (Figure S2), confirm that this was a regional-scale continental NPF event."

Lines 173-176 "Strong NPF events were observed on 24 out of 33 non-raining observation days in April and May, which is the growth and farming season of seaweed. That is, the second type of NPF events occurred almost every day from April to May unless it was cloudy or rainy. As would be discussed in Section 3.3, high nucleation-mode iodine concentration suggests these NPF events were induced by iodine."

Add figures for back trajectories to supplementary and references to them (e.g. line 167, 360 and elsewhere); I would suggest moving section 3.2 to methods rather than results as it describes the measurement method development.

Re:
Now we add back trajectory as Figure S2 in Supporting Materials.

One focus of Section 3.2 is how we identified iodide-organic adducts and unknown organic iodine compounds. This method development is not established prior to the conduction of our experiments. Therefore, we think it is also reasonable to keep section 3.2 in *Section 3 Result and discussion*. In the meanwhile, general description of filter sampling, instrumental parameters and conditions was shown in *Section 2.2 Chemical analysis*.

I commend authors for being open with advantages and limitations of the technique, but more information is still needed. Material on lines 211-226 is very important, but difficult to follow for non-specialists, please provide more details on RT and its relevance to conclusions, elaborate, why longer RT points to bonds with organic. For example, the link between in-source fragmentation and weakly bond iodine-organic adducts is not so obvious, give more details and explanations. Similarly, provide explanation why 'all m/z 126.9039 peaks after RT=1 min in a sample by low energy MS scan can be deemed iodide-organic adducts and their total peak area should be proportional to the total concentration of the adducts.' (lines 224-226). It might be obvious for ion chromatography person, but not everyone. E.g. why RT of 1 min is important? (line 312 as well);

Re:

Now we add the following sentences in lines 218-227 to explain (1) why I^- peaks in low energy MS scan mode (in-source fragmentation only) can be attributed to iodine-organic adducts and (2) why RT of 1 min is important.

"For reversed phase HPLC, ionic compounds elute earliest followed by non-ionic organics with longer retention time. In our case, ionic I^-, IO_x^- and other strong Lewis acids elute with RT<1 min, as can be seen from the extracted m/z 126.9039 chromatogram of pure potassium iodide solution (1 mmol L^{-1}) in Figure 3b. The I^- peaks that eluted at RT>1 min in low energy MS scan mode (Figure 3a), on the other hand, can only be resulted from the dissociation of weakly bound iodine-containing organic precursors via in-source fragmentation. I^- is an electronegative weak base, which can bind with hydroxyl, acid or keto- groups to form adducts depending upon the polarity and H-bonding capability of organic compounds (Lee et al., 2014). These iodine-containing organics that dissociated to release I^- in the ESI source are thus attributed to iodide-organic adducts in our study and the total peak area of extracted ion chromatogram of m/z 126.9039 after RT 1 min is assumed to be proportional to their total concentration."

Provide more information on deductions from Figure 5, e.g. elaborate on the statement 'Therefore, each red circle without a black dot in -0.3_0 mass defect regime in Figure 5 should stand for an organic iodine compound.' (Lines 245-246);

Re: the following elaboration is added in lines 252-257:

"All ions above background intensity of 10^4 are shown in Figure 5 as dots and circles to stand for the samples before and after H_2O_2 addition, respectively. Benefiting from the large negative mass defect of iodine (-0.0961), the mass defects of newly-formed organic iodine compound should be in the range of -0.3~0, which makes them to be distinguished easily from non-iodine containing ions. Therefore, each red circle without a black dot in -0.3~0 mass defect range in Figure 5 should stand for an organic iodine compound that was newly formed after the addition of H_2O_2 into aerosol extract+KI mixture."

The statement in the conclusions 'Our study provided important information of iodine speciation, concentration and its role in NPF' does not have any specific info, spell out that 'important information' here;

Re: the important information means all the contents about iodine speciation, concentration and size distribution described in the previous paragraph (lines 445-460).

Now we change the entire statement in lines 461-463 to:
"Our study provided important information of iodine speciation, concentration and size distribution in the context of heavy air pollution China's coastal areas. However, source, gas-particle partitioning and the role of these iodine species in NPF are largely speculative."

Specific comments

Lines 99-100: be consistent in dimensions; use either cm or m when describing inlet lengths;

Re: cm is now used consistently.

Line 193: clarify what you mean by 'the contribution of ions were negligible';
Re: what we mean is the percentage of ions in total particles was negligible. The sentence is updated to "the ion/neutral particle ratios were on the order of 10^{-5} (2-7 nm) and 10^{-4} (7-20 nm) during the I-NPF events and 10^{-3} (2-7 nm) and 10^{-2} (7-20 nm) during the continental NPF events, indicating the contribution of ions to total particles was negligible at least in > 2 nm size range in both types of NPF events."

Line: 233: what aerosol extract – high I or low?

Re:
"low iodine" is now added before "aerosol extract+KI mixture"

Lines 244-246: add '-' for mass defect of 0.0961 to be consistent with the ones below.

Re:
Thanks for reminding this. It is now change to -0.0961

Line 248: Elaborate what are the 'typical' aerosol samples;

Re:
The aerosol samples here were used to provide a typical aerosol organic matrix for organics-KI-H_2O_2 reactions. Two $PM_{2.5}$ samples collected at the urban site and two $PM_{2.5}$ samples at the coastal site were selected. In lines 262-264, we change to:

“Following the same procedure, two $PM_{2.5}$ samples collected at the inland site and two $PM_{2.5}$ samples collected at the coastal site were treated using KI and H_2O_2 (or O_3 solution) and analyzed using MD vs. m/z diagrams in both ESI+ and ESI- modes”

Lines 262-263: What MOUDI stages were analysed to produce the results in Table1, all? Provide info here;

Re: yes, the samples from all MOUDI stages were analyzed to produce Table 1. Now more specific information is shown in lines 373-375:

“At last, 35 organic iodine formulas were detected, at least once, in our aerosol samples including the $PM_{2.5}$ samples and the size-segregated aerosol samples from all nano-MOUDI stages (Table 1).”

Lines 321-322: provide info on the significance of the blank concentrations, where they comparable to the sample or significantly lower?

Re: the following lines 333-338 are added

“Field blank filters were processed in the same way as sample filters. No signals above MS background were detected in the field blank filters for the iodine species other than I^- and IO_3^-. The MS signals of I^- and IO_3^- in the field blanks were comparable to those in the sample filters without iodine loading (e.g., the nano-MOUDI filters in the size bins larger than nucleation mode during the I-NPF days), but less than 1.3% of those in the sample filters with iodine loading. The MS signals of I^- and IO_3^- in the field blank were then subtracted from the aerosol samples.”

Lines 328-329: Provide info on what samples were used for regression analysis;

Re: after QTOF measurement, 13 samples with relatively high iodine concentrations were selected for ICP-MS analysis. Now in lines 344-346 we add:

“After UPLC/Q-TOF-MS measurement, we selected 13 samples with relatively high iodine concentrations for ICP-MS analysis, including 3 $PM_{2.5}$ samples and 10 size-segregated samples from 10 nm to 1.8 µm collected during the NPF days.”

Figure 8: typo in ‘continental’;

Re: Corrected.

Figure 9: Is it possible to provide overall mass size distribution calculated from SMPS here for reference by say using a constant density. It would give a feeling on how much mass was reconstructed. Otherwise, provide this information in the caption or description of the figure. Reference to Fig.2 is not very useful as it is very much time consuming to compare different figures (one is distribution over time, the other is averaged distribution);

Re: we agree with the referee that it will be interesting to see how much the iodine species contributed to total aerosol mass. However, we realised such rough estimation is subject to many uncertainties: (1) particle density and shape (2) water content in wet particles measured by SMPS, which depends on chemical composition (3) the conversion of electrical mobility diameter (SMPS) and aerodynamic diameter (MOUDI) to volume equivalent diameter, which again depends on density and shape factor (4) SMPS counts both iodine-containing particles and non-iodine containing particles and (5) the limitations of our semi-quantification method of iodine using UPLC-QTOF-MS.

Considering these unknown factors, it becomes unrealistic to obtain the percentage of iodine in aerosol dry mass. In our future study, we plan to reconstruct aerosol dry mass by analyzing (1) total organic carbon, (2) major inorganic ions using IC or IC-MS and (3) total iodine using ICP-MS. It is better not to be included in the current manuscript, the focus of which is developing a MS technique for iodine speciation and size distribution.

Table 2: Explain what the percentage in the table is referring to (22.8 % of what?) as adding all lines gives higher percentage than 100%.

Re: now one sentence is added in Table 2 caption:
"%: the percentages of iodine species in total iodine."
According to its definition (SOI=total iodine-I^--IO_x^-), SOI (soluble organic iodine) in the table actually includes all the species listed in the lines below SOI: I-organic adducts, CH_2I^-, I-AA, etc. This is why adding all lines gives higher percentage than 100%. We showed SOI in Table 2 just in order to compare with old studies like Gilfedder et al. 2008, which showed measured only I-, IO_3^- and SOI.