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

community comments

Wan et al. have performed an interesting laboratory study showing that the organic compounds co-emitted with iodine bearing molecules by exposed tidal macroalgae dominate particle growth in iodine-triggered NPF events. The chemical evolution of the emitted organic precursors is investigated by means of iodide-CIMS, showing that alkene ozonolysis and criegee intermediate gas-phase reactions and particle-phase accretion reactions increase the number of carbon and oxygen atoms of the organic compounds observed. Some information about inorganic iodine molecular cluster precursors is also obtained.

I have listed a few comments below that the authors may want to consider to improve their manuscript.

Page 2, line 35. Here and elsewhere: Mart *n* et al., 2020 -> G ómez Mart *n* et al., 2020

Re: corrected.

Page 2, line 38. A previous study also examined the growth of iodine oxide clusters in the presence of condensable vapours such as H2SO4 or oxalic acid (Saunders et al., 2010)

Page 2, line 47. An opening sentence indicating that organic compounds have been observed in particles formed in I-NPF events (Vaattovaara et al., 2006; Yu et al., 2019) would be useful.

Re: we add the citations in line 46-50:

"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 uptake of meso-erythritol, glyoxal, dimethylamine and oxalic acid on the growth of iodine oxide nanoparticles. However, no prior work has investigated the exact chemical identity of organic compounds (other than iodomethane) and their role in I-NPF."

Page 2, line 48. More common names for this compound are iodomethane and methyl iodide

Re: iodomethane is used now.

Page 3, line 81. Indicate in this paragraph an estimate of water vapour concentration or RH in the experiment.

Re: we add in line 86-87:

"*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 air flow."

Page 3, line 84. Note that even though up to 10% of O1D may end up as OH under atmospheric conditions, the rest will be quenched to O3P, and that O3P reacts both with I2 and iodomethane to make IO. Moreover, it is well known that OH reacts quickly with I2 to make HOI. Therefore, in these experiments additional photolytic sources of IO are present, plus a source of HOI. This may obscure the interpretation of the "OH-enhanced" experiments.

Re: we add the following description (line 89-93, 245-247) to explain the oxidants in the OH enhanced experiment.

"OH radicals were produced via the reaction $O_3 + hv \rightarrow O_2 + O({}^1D)$ and $O({}^1D) + H_2O \rightarrow 2OH...$ Other oxidants may include $O({}^3P)$ resulted from the quenching of $O({}^1D)$ (Li et al., 2015)."

"These differences indicate that more iodine nuclei were produced with enhanced oxidation capacity, probably via $OIO+OH \rightarrow HOIO_2$ (Plane et al., 2006) and $O(^{3}P)+CH_{3}I \rightarrow IO+CH_{3}$ (Teruel et al., 2004)."

In the "OH-enhanced" experiments, we showed bulk TOC and TI results only, interpreting that more iodine nuclei and particulate products were generated with enhanced oxidation capacity, while organic compounds still overwhelmingly dominated over iodine in the mass contribution to new particle growth. These interpretations were not obscured by more complicated oxidant species.

Page 4, line 117. Indicate ultrasonication time and power.

Re: We add in line 127:

"Ultrasonication time and power were 20 minutes and 150 Watt."

Page 5, line 145. It is likely that this effect is rather due to the presence of ground state oxygen atoms in the flow. O3P will free additional iodine atoms by reaction with I2 and CH3I.

Re: We add in line 245-247:

"These differences indicate that more iodine nuclei were produced with enhanced oxidation capacity, probably via $OIO+OH \rightarrow HOIO_2$ (Plane et al., 2006) and $O({}^3P)+CH_3I \rightarrow IO+CH_3$ (Teruel et al., 2004)."

Page 6, line 171. Is HNO3 then emitted by algae? I think explaining a bit more about the source of HNO3 is necessary, since it indirectly allows detection of most of the inorganic compounds reported. In fact the iodide CIMS in practice operates in these experiments as a nitrate CIMS for inorganic iodine compounds.

Re: NO_3^- sometimes exists as contaminant in the CIMS system, probably from air leak or contaminated air supply tubes of the CIMS. The system has to be cleaned before each experiment to eliminate background contaminant. Therefore, elevated NO_3^- signal did not surprise us very much when the sample air was from the bottle containing "dirty" algae and natural seawater.

In line 161-164, we add

"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."

Page 6, line 174. While iodide CIMS maybe a good technique for detecting organics, it is probably not be the best technique for detecting inorganic iodine compounds, for the obvious reason that the source

of charge is the iodide anion, which may obscure the interpretation of the observed ion clusters. No discussion of this potential interference has been included in this paper.

Re:

We add the following discuss in line 209-217:

"We noticed that CH_3I vapor was added as ion source reagent to the ion molecule reactor (IMR) of iodide-CIMS. It is likely that this extra CH_3I in the IMR might obscure the interpretation of the observed iodine containing clusters. We believed that ion source reagent CH_3I should have relatively small interference with inorganic iodine compounds from the bag reactor, on the basis of 2 facts: (1) ion source reagent CH_3I was added directly from permeation tube into the IMR. Without photolysis, ion source reagent CH_3I in the IMR should not become a source of I and I_xO_y . (2) the concentration of ion source reagent CH_3I and its potential products should be quite constant as long as O_3 was present in the IMR, which was not supported by the variable signals of I, CII, IO₂, IO, CIIO, HIO₃, INO₂ and INO₃ in Figure 2."

Page 6, line 177. Alongside Figure 4, it would be very useful showing a table with the correspondences between observed anions and proposed parent neutral molecules. Such correspondence is not always straightforward, as we have argued recently (Gómez Mart ń et al., 2022).

Re:

Thank you for pointing this out. Ion clusters were labeled alongside the signal dots of Figure 4. For each ion cluster, parent neutral molecule is on the left hand side of middle dot, while the clustering ion I° or NO₃⁻ is on the right hand side. Those without a clustering ion are shown as bare anions.

These descriptions are now added to Figure 4 caption.

Page 6, line 182. What about I2 and HOI photolysis? Why are you ruling out I2 and HOI as iodine sources?

Re: we did not include I_2 and HOI because they were not observed in the gas flow by either GC-MS or I-CIMS.

In line 175-178, we add

"we suggested the photolysis of CH_2Cl_2 , CHBrCl, CH_3I and C_3H_7I was the source of halogen atoms (e.g., $CH_3I+hv \rightarrow CH_3+I$), although we could not exclude the photolysis of other precursors like I_2 and HOI that are invisible to GC-MS and I-CIMS."

Page 6, line 184. Unlikely. Much faster reactions are:

Cl+I2->ICl+I

Cl+ICl->Cl2+I

The time traces in Figure 2b are qualitatively consistent with this sequence of reactions

Re: thank you for pointing it out.

In line 178-180 we update to:

"There was a time lag of 20-25 minutes between the appearances of Cl and I and those of ClI and Cl₂, which were probably resulted from anion exchange reactions of Cl I and II with Cl atoms."

Page 6, line 188. These experiments employ UHP air. What is then the source of NO2 in this system? There is no easy route from HNO3 to NO2.

Page 7, line 193. Again, what is the source of NO2 in this system? This must be discussed, since you are concluding that IONO2 is contributing to particle growth. In our recent work on the nitrate CIMS system in the context of I-NPF (Gomez Martin et al., 2022), we have found that IO3-, HIO3.NO3- (or rather HNO3.IO3-) and IONO2.NO3- are products of the reaction between NO3- and I2O3. I am skeptical about the presence of IONO and IONO2 in this system because of the unlikely presence of NO and NO2, and I suspect that IONO.NO3- and IONO2.NO3- could be products of IxOy+NO3- also in these experiments.

Re: thank you for the comments on IONO and IONO₂. Now we cite Gomez Martin et al., 2020 and 2022 and add the following paragraph in line 185-193.

3. INO_2 , $CINO_2$ and INO_3 : INO_2 and $CINO_2$ were detected in gas phase with similar time evolution with halogen atoms and halogen oxides. INO_3 was found in both gas and particle phases. INO_2 and INO_3 were usually thought to form upon the reactions $I+NO_2+M \rightarrow IONO+M$ and $IO+NO_2+M \rightarrow IONO_2+M$ in the atmosphere (Saiz-Lopez et al., 2012), which seems to be unlikely in our bag reactor because NO_2 was not added. Considering NO_3^- was ubiquitous in the bag reactor of our experiment, it is likely that INO_2 and INO_3 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 supported by theoretical calculation and flow tube mass spectrometry experiments (G ómez Mart ń et al., 2022; G ómez Mart ń et al., 2020). $CINO_2$ was likely to form upon similar reaction between Cl_2O_2 and NO_3^- in the bag reactor.

Page 7, line 193. Following my previous comment, at least part of the signal attributed to HIO3 results from I2Oy+NO3- (Gómez Mart ń et al., 2022)

Page 7, line 194. Note that Gomez Martin et al., 2020 never argued in that HOIO2 would form from I + H2O + O3 -they rather argued the opposite. The source of HOIO2 remains to be confirmed, although the reaction between I2O5 and the water dimer is currently our best candidate, where I2O5 would be a photolysis product of a higher iodine oxide (Gómez Mart n et al., 2022).

Page 7, line 196. This is in disagreement with the observations by He et al. 2022 using a Br-CIMS FIGAERO. They did observe HIO3 in the particles. This disagreement should be discussed.

Heating of HIO3 between 100 °C *and 200* °C *results in dehydration and formation of I2O5 (Selte and Kjekshus 1968), so the desorption temperature in is critical.*

The IO- and IO2- signals may be secondary products of the reaction between I2O5 and I-.

Re: thank you for the comments on HIO, HIO₂ and HIO₃. The following paragraph is updated in line 194-203:

3. HIO, HIO_2 and HIO_3 : HIO_3 seems to be the end product of above intermediates, because its gas-phase ion intensity kept on increasing during new particle growth. Based on this fact, we

assume that HIO₃ 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 hand, HIO₃ was not detected in particle phase by iodide-CIMS, which is contrary to the offline analysis of quartz filter by HPLC-ICP-MS showing that total iodine was mostly dominated by IO_3^- peak. We speculate that HIO₃ might have been dehydrated to I_2O_5 under thermal desorption temperature up to 180 °C in FIGAERO. The signals of IO^- , IO_2^- and HIONO₃⁻ (corresponding to HIO and HIO₂) were found in particle phase, but not in gas phase. He et al. (2021) proposed HIO₂ formation via $\Gamma + H_2O + O_3 \rightarrow HIO_2$ or $I_2O_2 + H_2O \rightarrow HIO + HIO_2$. With limit experimental evidence of our work, the exact formation pathways of HIO_x remains to be explored in future.