

## Reviewer 1:

Overall evaluation:

This manuscript presents a novel and well-designed calibration approach for quantifying hypiodous acid (HOI) based on its conversion to molecular iodine (I<sub>2</sub>) using a sodium iodide trap, coupled with bromide chemical ionization mass spectrometry (Br-CIMS). The authors systematically investigate the humidity dependence of the instrument's sensitivity to both HOI and I<sub>2</sub>, demonstrating that I<sub>2</sub> sensitivity becomes essentially independent of humidity above ~50% RH, while HOI exhibits a slight negative dependence. The study also highlights significant inlet-mediated losses and interconversion between HOI and I<sub>2</sub>, especially in bent or salted inlet configurations mimicking field setups. The manuscript is well written and easy to read. I would recommend it to be published in this journal after the following comments being addressed and revised.

### Comments

**1. The 1:1 conversion of HOI to I<sub>2</sub> via the NaI trap is assumed based on analogy with the HOBr-Br<sub>2</sub> system. However, small signals of HI and IBr were observed upon trap insertion. Could side reactions or impurities in the NaI trap lead to non-stoichiometric conversion? Is there additional experimental evidence (e.g., isotopic labeling, independent HOI quantification) to confirm the 1:1 conversion efficiency under varying humidity and concentration conditions?**

Thank you for these suggestions. However, we believe that HI is more likely to be produced through the aqueous reaction of NaI with HNO<sub>3</sub> than from a HOI reaction pathway, via:



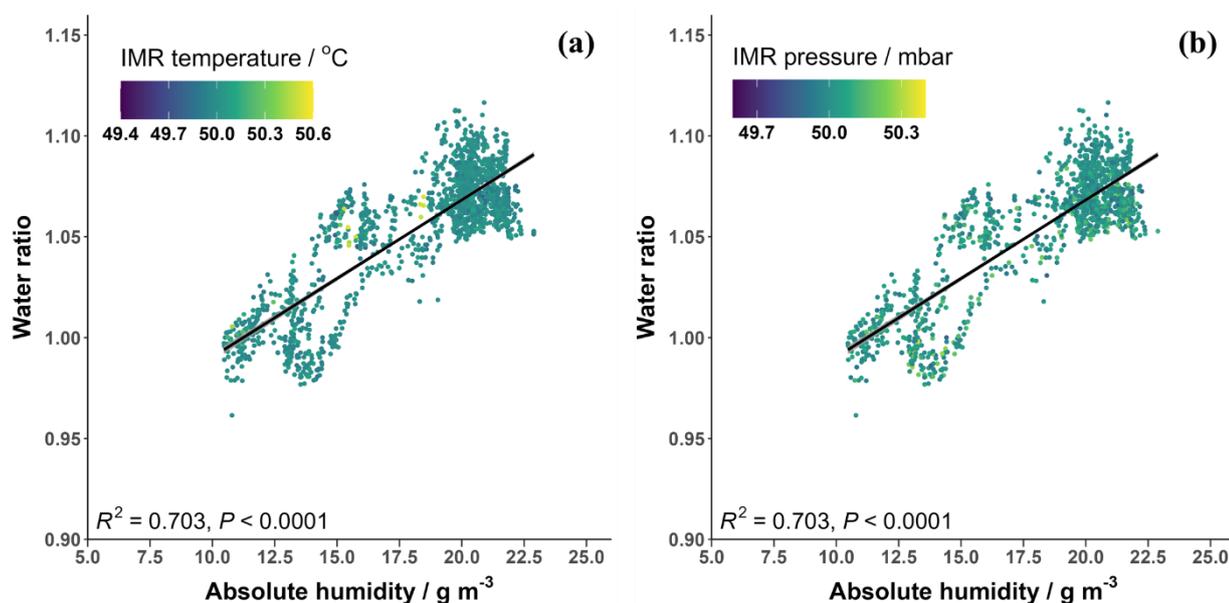
This is because HNO<sub>3</sub>, which is produced during the HOI generation step via (R12), decreases on addition of the NaI trap while HI increases, as shown in the table below. This additional experimental evidence has been added to the Appendix. The IBr signal also increases slightly. IBr can be formed either by HOI reacting with NaBr impurities or by contaminant bromine compounds reacting with NaI. However, the average change in the IBr signal is less than the average standard error of the I<sub>2</sub> signal change, therefore its potential contribution to I<sub>2</sub> is negligible compared to the I<sub>2</sub> uncertainty. We have updated the text in section 3.4 to reflect this.

**Table A1: The signal change (in normalised ion counts per second) of HNO<sub>3</sub>, HI, IBr and I<sub>2</sub> along with their calculated standard errors during the HOI calibration runs upon addition of the NaI trap.**

Run number	Signal change ( $\pm$ standard error) on addition of NaI trap / ncps			
	HNO <sub>3</sub>	HI	IBr	I <sub>2</sub>
1	-4902.1 ( $\pm$ 71.5)	36.49 ( $\pm$ 0.93)	6.84 ( $\pm$ 0.51)	430.04 ( $\pm$ 10.89)
2	-5274.0 ( $\pm$ 164.4)	20.25 ( $\pm$ 0.80)	5.07 ( $\pm$ 0.46)	451.62 ( $\pm$ 13.60)
3	-4543.7 ( $\pm$ 43.7)	11.96 ( $\pm$ 0.69)	4.73 ( $\pm$ 0.40)	519.53 ( $\pm$ 5.76)
4	-4129.3 ( $\pm$ 58.4)	10.72 ( $\pm$ 1.02)	5.82 ( $\pm$ 0.49)	573.95 ( $\pm$ 6.90)
5	-4051.3 ( $\pm$ 116.0)	13.98 ( $\pm$ 1.41)	7.24 ( $\pm$ 0.51)	517.84 ( $\pm$ 8.79)
6	-4865.5 ( $\pm$ 48.7)	6.77 ( $\pm$ 0.95)	6.98 ( $\pm$ 0.53)	662.69 ( $\pm$ 9.09)
7	-2812.2 ( $\pm$ 43.3)	6.57 ( $\pm$ 0.82)	10.66 ( $\pm$ 0.52)	424.65 ( $\pm$ 6.39)
8	-3742.2 ( $\pm$ 64.4)	24.76 ( $\pm$ 1.09)	6.89 ( $\pm$ 0.49)	391.72 ( $\pm$ 5.24)
9	-2413.3 ( $\pm$ 63.5)	6.67 ( $\pm$ 0.55)	11.63 ( $\pm$ 0.55)	553.02 ( $\pm$ 7.72)
10	-4725.2 ( $\pm$ 50.5)	4.26 ( $\pm$ 0.82)	7.35 ( $\pm$ 0.40)	516.05 ( $\pm$ 4.749)
11	-4555.5 ( $\pm$ 52.7)	2.27 ( $\pm$ 0.48)	8.04 ( $\pm$ 0.40)	884.80 ( $\pm$ 7.62)

**2(a).** The “water ratio” ( $\text{H}_2\text{OBr}^-/\text{Br}^-$ ) is used as a proxy for IMR humidity. While convenient, has this ratio been validated against direct humidity measurements (e.g., using a hygrometer) across the full range of conditions? Could temperature fluctuations in the IMR affect the relationship between the water ratio and actual  $\text{H}_2\text{O}$  mixing ratio?

The water ratio hasn't been directly validated against other humidity measurements. The water ratio has been compared to the absolute humidity measured during the BLEACH campaign and indicates that the water is a good proxy for IMR humidity, as shown below. This data is now included as figure A4 in the appendix. The figure is coloured by variations in temperature and pressure, showing the small deviations occurring during a field campaign.



**Figure A4:** The water ratio in the CIMS IMR plotted against the absolute humidity measured during the BLEACH campaign coloured by (a) the variation in IMR temperature and (b) the variation in IMR pressure.

Note that a previous study on the relationship between the IMR temperature and the proportions of the dry reagent ion and first water cluster only saw a noticeable change when using a wider range of temperatures than the  $\pm 0.6$   $^{\circ}\text{C}$  measured here (Robinson et al., 2022).

**2(b).** For I2, sensitivity becomes humidity-independent above a water ratio of  $\sim 0.7$ . The explanation involves a balance between the stabilizing effect of  $\text{H}_2\text{O}$  on the adduct and the lower formation enthalpy with  $\text{H}_2\text{OBr}^-$ . Is there quantitative kinetic or quantum-chemical modeling to support this interpretation? Could the second water cluster  $\text{Br}(\text{H}_2\text{O})_2^-$  play a non-negligible role at very high humidity?

There was no quantitative kinetic or quantum-chemical modelling performed here; the interpretation of the observed results is based on the findings of Lee et al. (2014) and Iyer et al. (2016) who performed similar analysis using the  $\text{I}^-$  reagent ion. Values for the formation enthalpy with the  $\text{Br}^-$  ion were taken from Wang et al. (2021) and He et al. (2023).

At very high humidity the second water cluster may have an indirect role in slowing down the increase in sensitivity. At these humidities, the proportion of  $\text{Br}(\text{H}_2\text{O})_2^-$  increases, whereas  $\text{BrH}_2\text{O}^-$  remains fairly constant and  $\text{Br}^-$  continues to decrease. This suggests that conversion from  $\text{Br}^-$  to  $\text{BrH}_2\text{O}^-$  is still occurring but there is also a similar rate of conversion of  $\text{BrH}_2\text{O}^-$  to  $\text{Br}(\text{H}_2\text{O})_2^-$ . Less  $\text{Br}^-$  will result in fewer adduct formation reactions occurring through the more exothermic pathway with no increase in the stabilisation pathway. We have updated the text in section 3.3 to better reflect the role the second water cluster can

play on the stabilisation. Additionally, a further figure has been added to demonstrate the change in proportion of the  $\text{Br}^-$ ,  $\text{BrH}_2\text{O}^-$  and  $\text{Br}(\text{H}_2\text{O})_2^-$  ions with increasing humidity, shown below:

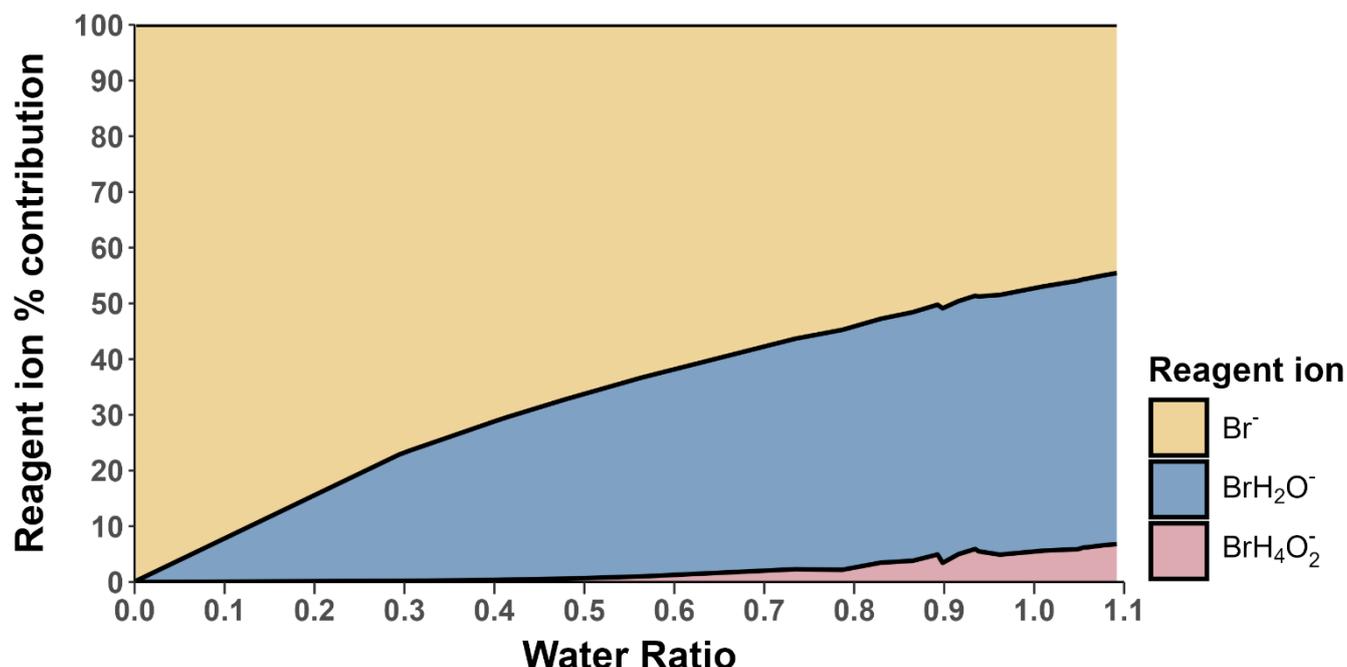


Figure 7: The percentage contribution of the  $\text{Br}^-$  ion (yellow),  $\text{BrH}_2\text{O}^-$  ion (blue) and  $\text{BrH}_4\text{O}_2^-$  ion (pink) at different water ratios. Values used are the average of these ions from the  $\text{I}_2$  calibration runs.

**2(c). For HOI, sensitivity decreases with humidity, explained by QRRK theory. Are there computational or experimental data on the binding energies, vibrational frequencies, or number of effective oscillators for  $\text{HOI}\cdot\text{Br}^-$  vs.  $\text{I}_2\cdot\text{Br}^-$  adducts to substantiate this argument?**

We have included some additional analysis from quantum chemical calculations using the Gaussian 16 program. This analysis provides values for the vibrational frequencies, binding energies, total thermal energies and effective oscillators for the  $\text{I}_2\cdot\text{Br}^-$  and  $\text{HOI}\cdot\text{Br}^-$  clusters, allowing for the calculation and comparison of the “decay rate” of these clusters. The introduction has been updated to include more information about the decay rate using QRRK theory. An additional section has been added to the Methods, discussing the calculation of these values using the Gaussian 16 program and includes a table shown below containing the values from the quantum chemical calculations. Section 3.4 has been updated to include references to this table.

Table 1: The calculated vibrational frequencies, binding energy, total thermal energy and vibrational modes of the  $\text{I}_2\cdot\text{Br}^-$  and  $\text{HOI}\cdot\text{Br}^-$  clusters. The decay rate is found using Eq. (1).

Cluster	Vibrational frequency / Hz	Binding energy / kcal mol <sup>-1</sup>	Total thermal energy / kcal mol <sup>-1</sup>	Vibrational modes (accessible)	Decay rate / s <sup>-1</sup>
$\text{I}_2\cdot\text{Br}^-$	$3.06 \times 10^{12}$	30.8	33.5	4 (2)	$2.66 \times 10^{11}$
$\text{HOI}\cdot\text{Br}^-$	$1.19 \times 10^{13}$	24.3	27.1	6 (3)	$2.38 \times 10^{11}$

**3(a). Inlet loss experiments using a T-piece and a salted PTFE guard show substantial HOI loss (65–75%) with concomitant  $\text{I}_2$  increase, attributed to reverse hydrolysis. How representative are these laboratory tests of real-world marine boundary layer conditions, where aerosol composition, surface acidity, and humidity vary continuously? Have you considered performing similar tests with authentic sea-salt aerosol or under varying RH/T conditions?**

The T-piece experiment showed that the majority effect on HOI loss is due to the physical shape of the inlet. A lack of time meant that further repeats were not able to be made on the inlet loss tests and so other conditions of the inlet were not tested. We regard the inlet used in this work as a prototype and future efforts are better focused on improving the inlet design to minimise inlet effects for these compounds.

**3(b). The HOI data are presented as an “upper limit” because background subtraction was not performed due to the lack of dry calibration. Could the use of isotope ratio filtering (as done for zeroing checks) or nighttime background estimation provide a way to constrain the background more rigorously? How might this affect the reported diurnal profile and peak mixing ratios?**

Thank you for this suggestion. We decided to repeat our calculations allowing for zero subtraction of the HOI data, using the dry  $I_2$  sensitivity as a conservative estimate for the HOI sensitivity. We regard this as a conservative estimate because, using the quantum chemical calculations, the predicted decay rate of the dry HOI.Br cluster is slightly slower than  $I_2.Br$ , indicating that the HOI sensitivity at the water ratios of the instrument zeros should be slightly higher. The text in section 3.7 has been updated to include this new analysis.

Figure 8 (now figure 11) has been updated to use the zero subtracted HOI data and the HOI and  $I_2$  diurnal cycles have been separated to improve clarity. More HOI data has also been included from earlier in the campaign. (Note that no additional  $I_2$  data has been added since an interferent in the zero data resulted in negative values from zero subtraction). The updated Figure is shown below:

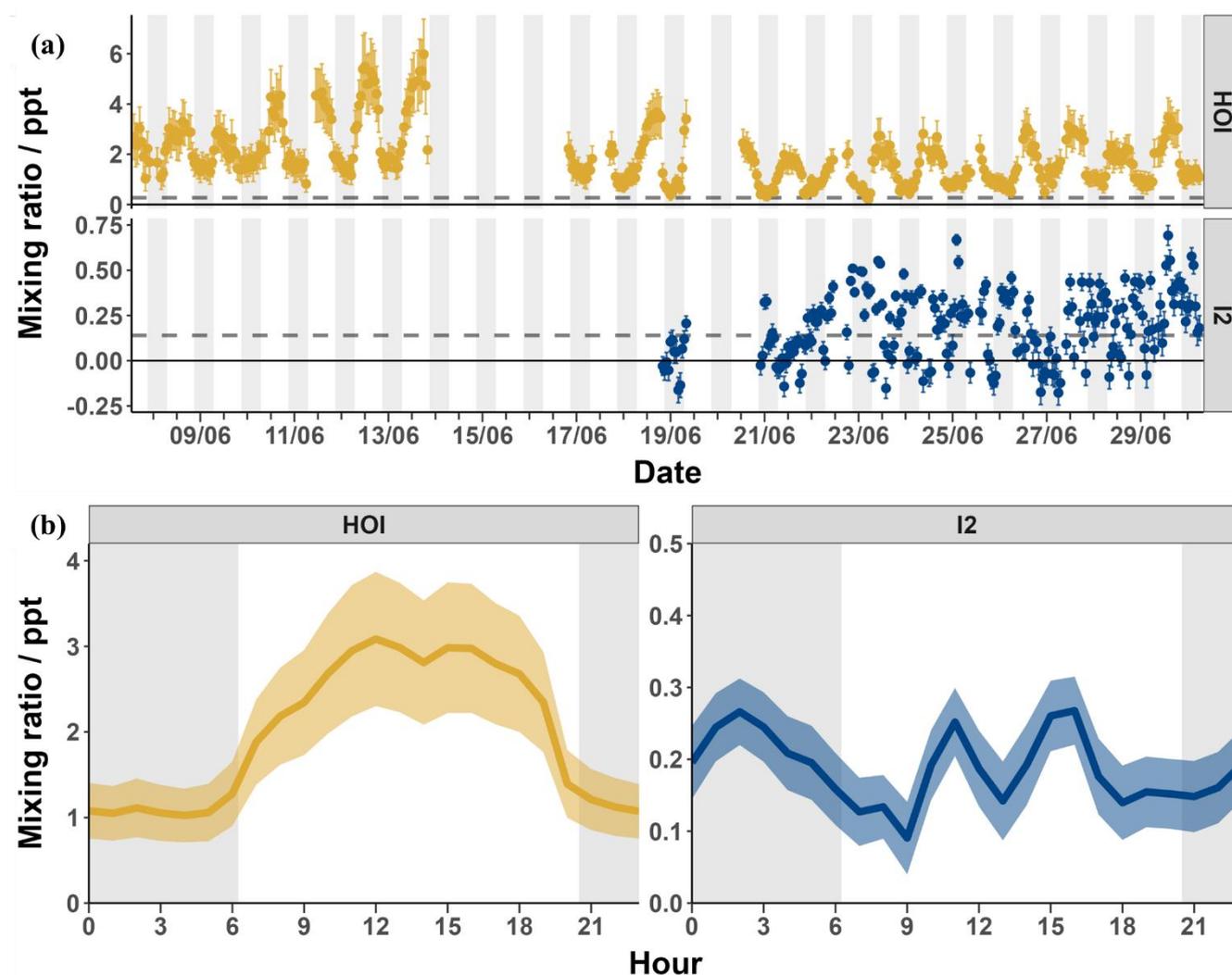


Figure 11: The timeseries (a) and diurnal cycle (b) of the mixing ratios of  $I_2$  (blue) and HOI (yellow) from the BLEACH campaign in June 2022 after zero subtraction and loss correction. The dashed line indicates the limit of detection for each compound. The average relative uncertainty of  $I_2$  was  $\pm 28.7\%$  and for HOI was  $\pm 27.7\%$ .

An additional timeseries showing the separated sample and zero mixing ratios of HOI and I<sub>2</sub> is shown below and has been included in the appendix:

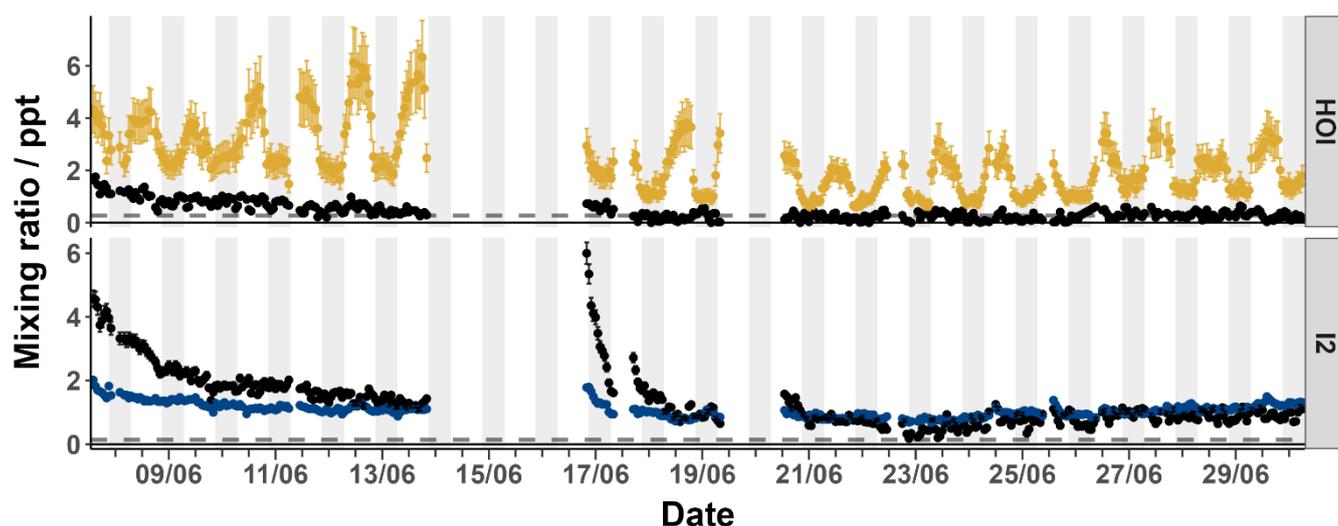


Figure A5: The timeseries of the sample mixing ratios of HOI (yellow) and I<sub>2</sub> (blue) along with their corresponding zero mixing ratios (black) from the BLEACH campaign in June 2022. The dashed line indicates the limit of detection for each compound.

**4(a). The overall uncertainties for I<sub>2</sub> and HOI are given as ~30%, but described as “lower limits” due to unquantified inlet effects. Could repeated loss experiments with different inlet configurations or flow rates help better constrain these uncertainties?**

A lack of time meant that further repeats were not able to be made on the inlet loss tests. In any case, and as highlighted in the “Summary and conclusions” section of the paper, we regard the inlet used in this work as a prototype and recommend that future efforts should focus on improved inlet designs inlets that can minimise inlet effects for these compounds.

**4(b). I<sub>2</sub> mixing ratios show no clear diurnal cycle, contrary to expectations from photolysis. The authors suggest inlet or background effects, but could there be a daytime source of I<sub>2</sub> (e.g., photochemical production or wind-driven emission) compensating for photolytic loss? Is there corroborative data (e.g., from DOAS, other CIMS, or model simulations during BLEACH) to contextualize this observation?**

There are a number of possible sources of I<sub>2</sub> which could be elevated during the daytime: (i) heterogeneous reactions of HOI with iodide on the surface of aerosols (Vogt et al., 1999) (Moon et al., 2025) or on the sea surface (Pound et al., 2024); (ii) photochemical oxidation of iodide (Raso et al., 2017), or (iii) photochemical reduction of iodate (Reza et al., 2024) However, these would have to be occurring close to the measurement site due to the fast photolytic lifetime of I<sub>2</sub>. It should be noted that I<sub>2</sub> release from aerosol may also occur from the buildup of aerosol on the inlet and we are unable to distinguish, with the inlet set up used in this work, the contribution of inlet artefacts. The work highlights the need for an improved inlet design and zeroing/calibration protocol. We have added further discussion in section 3.7 on potential daytime I<sub>2</sub> emission sources.

**5(a). The calibration and inlet loss corrections were developed for marine boundary layer conditions (high RH, sea-salt influence). How transferable is this method to other environments (e.g., polluted coasts, polar regions, forests) where humidity, aerosol composition, and oxidant levels differ significantly?**

For calibrations, it should be possible to lower the humidity of the N<sub>2</sub> gas that is used in the HOI generator, and this should allow for lower humidity calibrations. However, this risks lowering the yield of HOI produced in the generator as water is required for the I<sub>2</sub> hydrolysis to occur. This may make it more difficult to observe the change in I<sub>2</sub> signal, as the I<sub>2</sub> signal is already 5 times higher than HOI in the described setup. We have updated the text in section 2.3.2 to include this.

For inlet loss corrections, as stated in the paper, we recommend that future work focuses on inlet designs which can minimise artefacts. However, given that the condition of the inlet could change during a field campaign, we recommend that inlet loss corrections are performed before, during and just after field measurement collection to best characterise any inlet artefacts. We have updated section 4 to include this recommendation.

**4(b). For long-term field deployments, how stable is the Br<sup>-</sup> reagent ion source and the instrument sensitivity over weeks to months? What quality-control measures (e.g., regular permeation tube checks, humidity-adjustment protocols) are recommended for ongoing ambient monitoring of HOI and I<sub>2</sub>?**

The Br<sup>-</sup> reagent ion source is generally stable provided the temperature and gas flow for the permeation tube is consistent, though it is particularly sensitive to impurities in the N<sub>2</sub> gas. We have seen substantial drops in Br<sup>-</sup> reagent ion signal when using cylinder N<sub>2</sub> gas which we attributed to fluorinated compounds in the cylinder, such as TFA, scavenging the photoelectrons produced during the photoionisation stage (R7).

The ion source will experience minor fluctuations in signal over long term measurements, but these are accounted for using signal normalisation. Most drops in signal are when the instrument is restarted after a shutdown. The permeation tubes generally work consistently until they get close to end of life (generally 6-9 months). This is noticeable as the total ion current of the instrument will decrease and the proportion of the sum of the reagent ions (Br<sup>-</sup> + BrH<sub>2</sub>O<sup>-</sup>) compared to the total ion current also decreases. We recommend that the humidity of the zeroing gas is adjusted to be as close to the sample air as possible. This will reduce the work needed for humidity dependent sensitivity calibrations

We have updated the text in section 2.4 to include the method we used for providing clean N<sub>2</sub> gas to the reagent ion source.

## **Reviewer 2**

Overall evaluation:

This manuscript describes the development, characterization, and application of an optimized quantitative method for the calibration of I<sub>2</sub> and hypiodous acid (HOI) using bromide adduct chemical ionization mass spectrometry (CIMS). An indirect calibration method for HOI has been established where HOI is generated via the hydrolysis of I<sub>2</sub>, and a NaI trap is used to achieve the 1:1 conversion of HOI back to I<sub>2</sub>. This provides an alternative way for the calibration of HOI, which still remain very challenging to date. The manuscript is well written and the scope is suitable for Atmospheric Measurement Techniques. However, I have some concerns that need to be addressed prior to the consideration of publication.

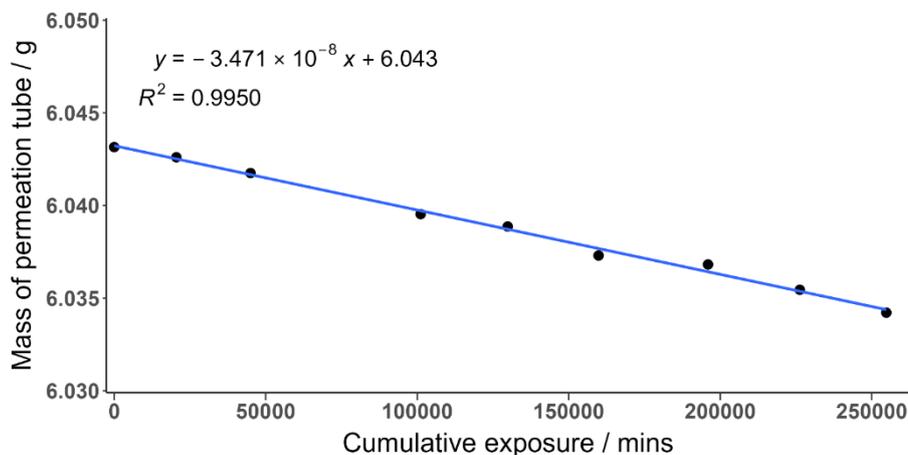
**1. Section 2.3.1: The emission rate of the permeation tube is reported as 34.7±0.21 ng/min, quantified via the gravimetric method. However, critical experimental details for validating the reliability and robustness of the permeation tube as a calibration standard are not adequately specified in the text.**

**1(a). What is the time interval adopted for weight loss determination? E.g., weekly, monthly, or predefined intervals, rather than mentioning over several months.**

Thank you for your comments. We performed 9 mass loss measurements of the permeation tube over a period of just under 6 months. The interval is on average just under every 3 weeks. Each mass loss data

point is the average of 6 sequential measurements. The text in section 2.3.1 has been updated to reflect this as follows;

“The emission rate was calculated gravimetrically by measuring the mass loss of the permeation tube over a period of 6 months. Measurements were taken on average every 3 weeks with each data point representing the average of 6 sequential mass measurements. The calibration curve from this is shown in Fig. A1.” A figure of the calibration curve for the emission rate has been included in the Appendix and is shown below:



**Figure A1: The mass loss of an I<sub>2</sub> permeation tube over time. The gradient represents the emission rate of the permeation tube. Each data point is the average of 6 measurements.**

**1(b). Please mention the precise characterization of the environment during the gravimetric measurement, particularly the temperature fluctuation.**

Measurements were performed in a temperature-controlled laboratory. We have updated section 2.3.1 with the following information:

“The permeation tube was kept in a temperature-controlled laboratory and held in a permeation holder at 40 °C. The temperature variation in the holder was minimal, at ± 0.1 °C, and is included in the uncertainty calculation. The permeation tube was continuously swept by 20 sccm high-purity oxygen-free N<sub>2</sub> gas.”

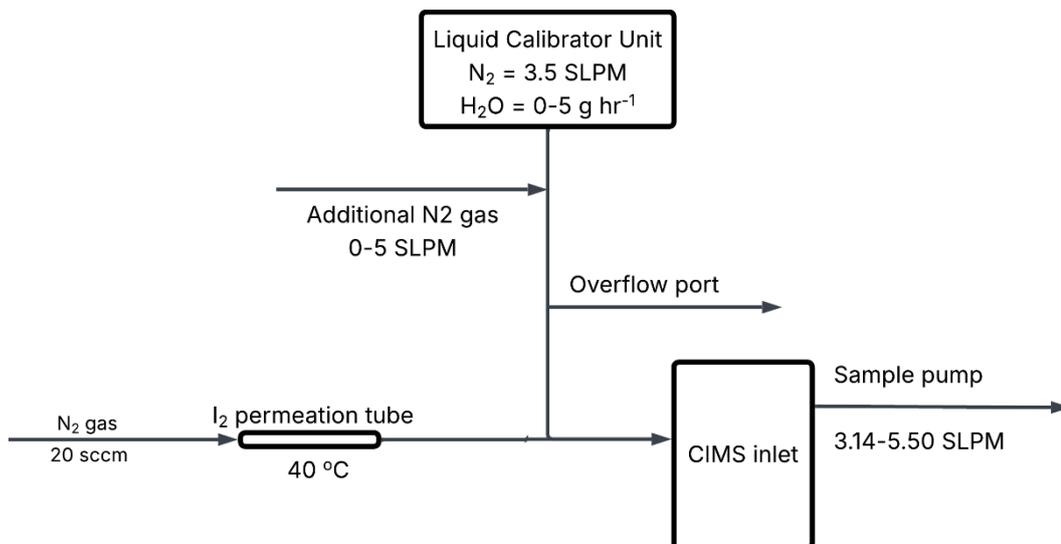
**1(c). How to validate the stability or drifting of the emission rate over time? Is there any validation from other method like the n-hexane absorption method? This will be a solid approach to validate the permeation rate, which is critical for determining the I<sub>2</sub> concentration.**

The lack of drift of the emission rate during the 6-month measuring time (as shown in Fig. A1) gives us high confidence that the emission rate was stable. We have updated the text in section 2.3.1 to state that little variation was seen during the emission period.

**1(d). What is the range of the dilution flowrate being used in this study? It is not clear how using different pump speeds altered the concentration of I<sub>2</sub>?**

We have updated the text in section 2.3.1 to provide clarity on this point, as follows:.

“Before mixing with the permeation gas, the dilution gas is first split, with some diluting the I<sub>2</sub> permeation gas and some passing through an overflow port. The amount of dilution gas mixing with the permeation gas depends on how much flow the CIMS sample pump pulls towards the instrument. Increasing the speed increases the amount of dilution gas pulled towards the instrument, with less dilution gas subsequently passing through the overflow port. By changing the amount of dilution gas, the concentration of I<sub>2</sub> is altered for the calibrations. The range of gas flow pulled by the sample pump was 3.14–5.50 SLPM. A schematic of this setup is shown in Fig. 1. This allowed for the construction of calibration curves at different humidity levels.” A figure of the dilution setup has been added and is shown below:



**Figure 1: Schematic of the I<sub>2</sub> calibration setup.**

**2(a). Section 2.3.2: Please state the range of humidity being used for the hydrolysis (Line 173).**

The humidity for the hydrolysis step was generated by passing 500 sccm nitrogen gas through a bubbler and then mixing with another 500 sccm from the I<sub>2</sub> permeation source. This was not measured and there may be some differences between calibration runs in how much humidity this generates based on how much water is remaining in the bubbler. The two calibrations that had no added water from the LCU had water ratios of 0.74 and 0.79. Knowledge of the actual humidity should not be necessary provided that the humidity for hydrolysis remains the same within a calibration run with and without the NaI trap.

**2(b). A 1:1 conversion of HOI to I<sub>2</sub> was assumed here. Did the authors conduct further testing to check on the validity of this assumption? It is also not clear if the HOI absorption efficiency on NaI agglomeration or deliquescence will change under different environment, such as the changes of humidity (i.e., high humidity) or temperature?**

Further analysis regarding the assumed 1:1 conversion is covered in more detail in comment 6. We think that changes in the HOI absorption efficiency should not matter. If the environment makes it more difficult for HOI to react with NaI, the change in HOI signal will reduce. However, this would also reduce the amount of I<sub>2</sub> released. This should not affect the HOI/I<sub>2</sub> ratio which is how the sensitivity of HOI is determined compared to I<sub>2</sub>.

**2(c). Figures 2: For the HOI peak fitting, how sure are the authors that the surrounding peaks will not interfere the HOI peak (i.e., in Fig 2b)? More details of the peak fittings are needed.**

The multi-peak fitting algorithm by the Tofware software is generally considered to be robust for separating overlapping peaks, as discussed in Stark et al., (2015). We have updated the images to include the isotope peaks of HOI and I<sub>2</sub> which can aid in verifying that the peak is correct and has the correct signal intensity. To aid in the clarity of this discussion, the figure has been split into two figures, one for I<sub>2</sub> and one for HOI, as shown below:

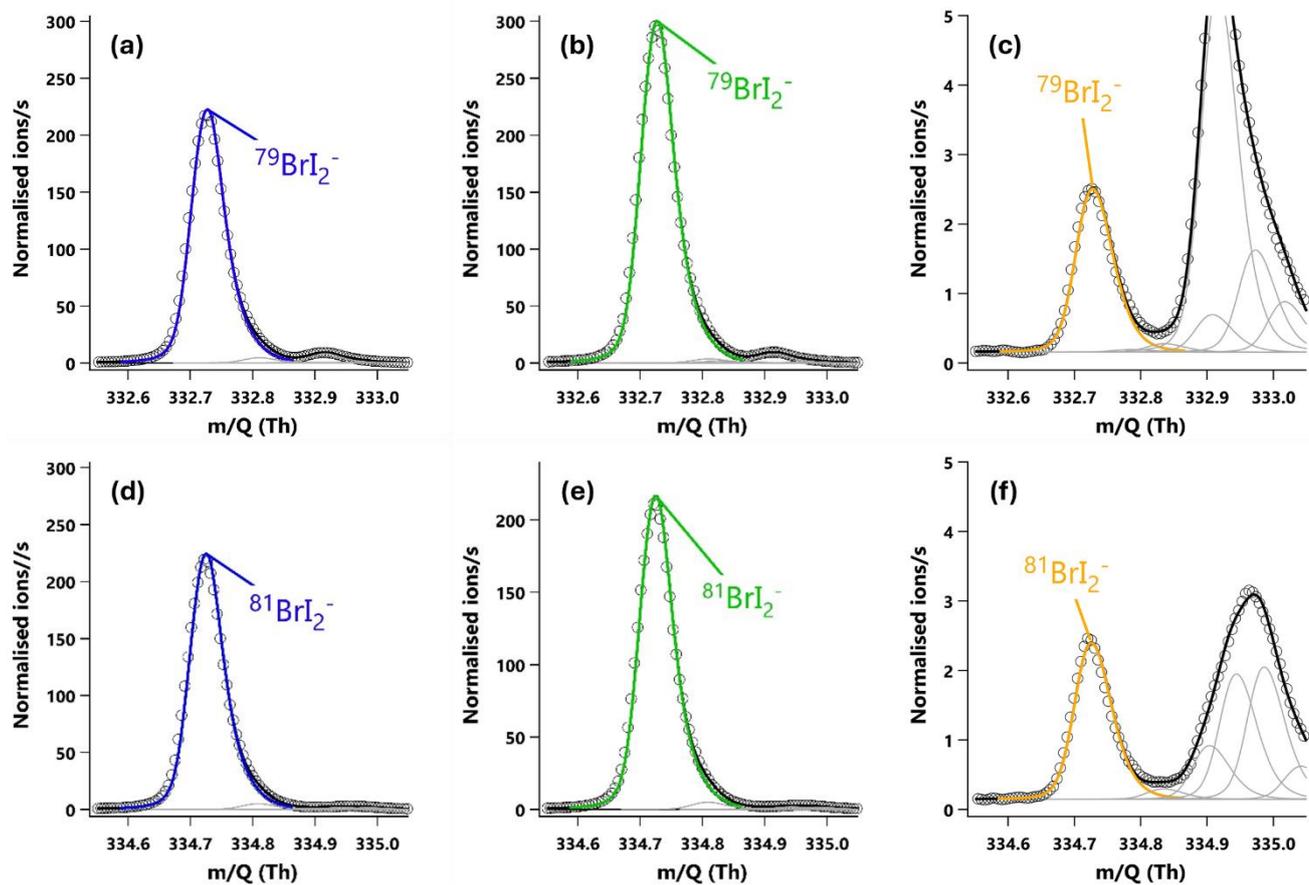


Figure 3: 20-minute averaged high resolution single peak mass spectra fits for the molecular ion peak (a,b,c) and primary isotope peak (d,e,f) for  $I_2$ . The signal intensities correspond to mixing ratios of (a) 190.2 ppt, (b) 254.0 ppt and (c) 1.37 ppt. (a, d) The signal  $I_2$  during an HOI calibration run without the NaI trap. (b, e) The signal of  $I_2$  during an HOI calibration run on addition of the NaI trap. (c, f) Ambient air measurements of  $I_2$  in a high humidity environment.

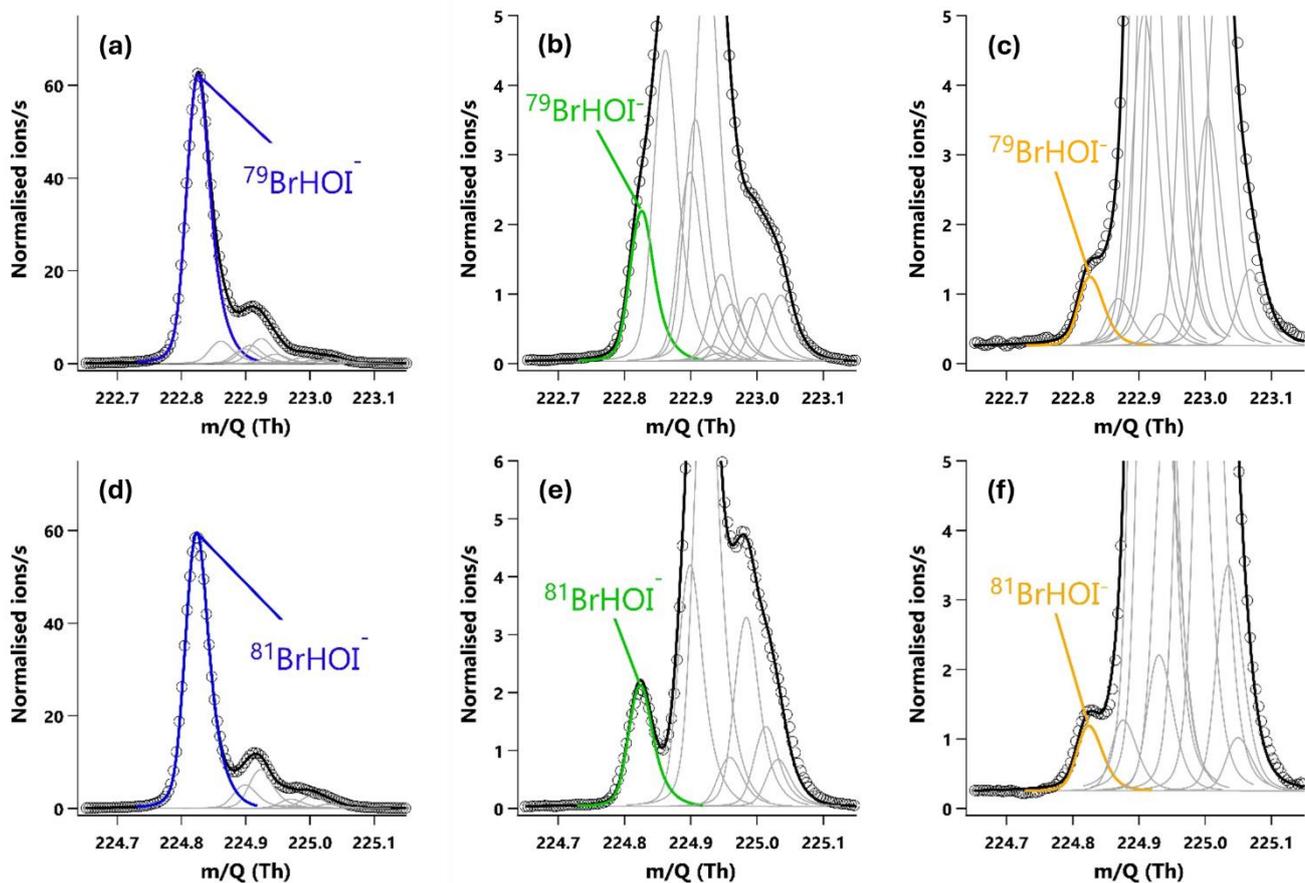


Figure 4: 20-minute averaged high resolution single peak mass spectra fits for the molecular ion peak (a,b,c) and primary isotope peak (d,e,f) for HOI. The signal intensities correspond to mixing ratios of (a) 60.8 ppt, (b) 2.2 ppt and (c) 0.87 ppt. (a, d) The signal of HOI during an HOI calibration run without the NaI trap. (b, e) The signal of HOI during an HOI calibration run on addition of the NaI trap. (c, f) Ambient air measurements of HOI in a high humidity environment.

4. Figure 3 and Figure 8: A major concern here is that the Bermuda observations reported  $I_2$  concentration of about less than 1 ppt, but the calibration for  $I_2$  used  $1-3 \times 10^{10}$  molecules  $cm^{-3}$ . Can the high concentration calibration represent the actual sensitivity to the ambient signal? How do the reagent ion ( $Br^-$ ) of CIMS reacts to the high  $I_2$  concentration? How much does it deplete and how much will the change of reagent ion affect the sensitivity of the CIMS? For CIMS, there is possible that the sensitivity to low concentration will response differently with the higher concentration.

The assumption that the concentrations of the calibrations, which were between 600 ppt and 1 ppb, fall within the linear range of the instrument is reasonable since it has been reported that other CIMS instruments operating at the same IMR pressure maintain linear ranges up to hundreds of ppb (Riva et al. 2024), providing the signal is normalised. Riva et al. (2024) also note that normalisation errors noticeably occur once you reach 50% reagent ion depletion. No reagent ion depletion was observed with changes to the  $I_2$  concentration during the calibrations in this work. Additional discussion of this has been added to the paper in sections 3.2 and 3.3.

5. Figure 4: Provide the  $R^2$  value for Fig 4a as well. At high humidity levels, does there exist a critical humidity threshold (Water ratio = 0.7)? Is there a direct correlation between this threshold and the change in the signal proportion of  $Br^-$  hydration clusters ( $Br^-$ ,  $H_2OBr^-$ ,  $Br(H_2O)_2^-$ )?

This figure has been updated to include the  $R^2$  value.

We find that there isn't necessarily a critical humidity threshold to reach humidity independence, but more of a range where the stabilisation of the formed adduct by the water molecule is in equal competition with the lower availability of the more exothermic adduct formation pathway with the dry  $\text{Br}^-$  reagent ion. Additionally, the increase in water ratio is accompanied by an increase in the 2<sup>nd</sup> water cluster,  $\text{Br}(\text{H}_2\text{O})_2^-$ , which can have an indirect effect on adduct formation by reducing the increase of the 1<sup>st</sup> water cluster but still reducing the dry reagent ion. It is possible that reaching an even higher water ratio may result in another humidity dependent region as these processes compete with each other.

We have added additional discussion of this in section 3.3 and added an additional figure shown in comment 2(b) for reviewer 1, which describes the change in the reagent ion distribution as the water ratio increases.

**6. Line 285: Increase in the signals of HI and IBr as observed by the NaI trap was noted. If the HI and IBr are produced from HOI, then the assumption of 1:1 is not absolutely true. The authors have noted that the impurities are negligible, but why not adjusting the ratio since they mentioned that the  $\text{I}_2$  which represented 96% of the change in signal? Or did the authors include this 'negligible' value in the uncertainty estimation?**

As discussed in the reply to Reviewer 1 comment 1, we conclude that the more likely source of HI is from the loss of nitric acid formed during the HOI generation step of the calibration (R12) rather than from an HOI loss pathway. The IBr produced is on average less than the average standard error of the  $\text{I}_2$  signal change so we consider the IBr production negligible compared to the uncertainty of the  $\text{I}_2$  signal.

We have updated the discussion in section 3.4 to include this as well as added the table from shown in comment 1 for reviewer 1 to the Appendix:

**7. Figure 5: Why not presenting the  $\text{I}_2$  in concentration rather than signal? It will give a better view on the concentration of  $\text{I}_2$  conversion.**

We have updated this figure to use mixing ratio rather than signal. We applied the general HOI/ $\text{I}_2$  ratio equation rather than the specific HOI/ $\text{I}_2$  ratio from this run. This results in a slight discrepancy in the mixing ratio deltas between HOI and  $\text{I}_2$ .

**8. Section 3.5.2: I am wondering whether the CIMS response linearly to the HOI concentrations? Suggest to add a figure for HOI calibration curve or to show how does the CIMS sensitivity response to various HOI concentrations. This is important information for the quantification of HOI in the ambient. Similar to my comments above, the calibration range should reflect the ambient levels.**

For HOI calibrations, we require a sufficiently large amount of HOI so that its conversion to  $\text{I}_2$  produces a substantial step change in the  $\text{I}_2$  signal and can be detected precisely. As with the  $\text{I}_2$  calibration, the HOI and  $\text{I}_2$  mixing ratios fall within the linear range described in Riva et al., (2024).

Figure 6 (now figure 9) has been updated to include a secondary axis showing HOI sensitivity in  $\text{ncps cm}^3 \text{ molecules}^{-1}$  to give a more direct view of how the sensitivity changes with water ratio. The equation of the regression line using the HOI/ $\text{I}_2$  ratio has been moved to the caption to prevent confusion with the two y-axis. This is shown below:

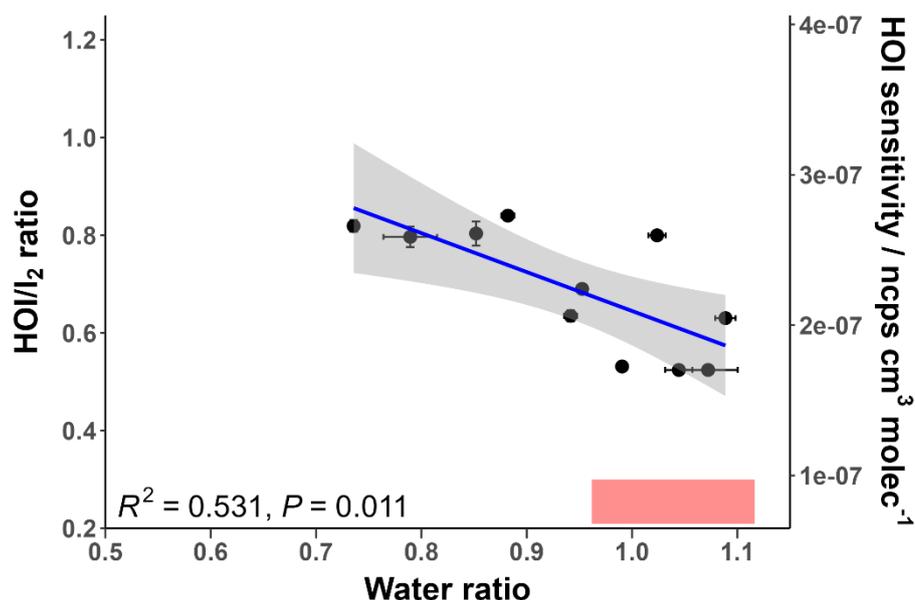


Figure 9: The relative sensitivity of HOI compared to I<sub>2</sub> (HOI/I<sub>2</sub> ratio) at different water ratio values. The regression line follows the equation  $y = 1.44 - 0.798x$ . The secondary y-axis shows the corresponding HOI sensitivity compared to the HOI/I<sub>2</sub> ratio. The shaded grey area represents the 95% confidence interval of the fitted regression line. The shaded red region represents the ambient water ratio observed in the marine boundary layer at Tudor Hill, Bermuda.

**9. Line 393-394: This statement is not clear. Please justify what is the basis that ICl and IBr could be from the I<sup>-</sup> present from the HOI production step.**

We have removed this sentence as we now do not think that this occurs.

**10. In the appendix, Figure A1 and A2: The authors should verify if the peaks for HI, INO<sub>2</sub>, ICl and HIO<sub>3</sub> are real and not interfered by the larger peaks. Will a longer averaged period for mass spectra will have better peaks for these iodine species, rather than using a 20-min averaged?**

We have updated the appendix figures to include the isotope peaks of the iodine compounds to help authenticate the peaks of the iodine compounds. The size of the interferent peaks and overlap of the interferent peaks means that it is unlikely that the HIO<sub>2</sub>, ICl, HIO<sub>3</sub>, INO<sub>2</sub> and IONO<sub>2</sub> peaks, detected at the resolution of the instrument, during the HOI calibration are real. We have updated the text in section 3.4 to include this.

We found that a longer averaging period did not improve the separation of the iodine compounds from the interferent peaks and so have kept the 20-min averaging.

**11. Double check the formatting of references.**

We have double checked the references.