

1 **Estimation of Reactive Inorganic Iodine Fluxes in the Indian and Southern Ocean Marine**  
2 **Boundary Layer**

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## 22 **Abstract**

23 Iodine chemistry has noteworthy impacts on the oxidising capacity of the marine boundary  
24 layer (MBL) through the depletion of ozone ( $O_3$ ) and changes to  $HO_x$  (OH/ $HO_2$ ) and  $NO_x$   
25 ( $NO/NO_2$ ) ratios. Hitherto, studies have shown that the reaction of atmospheric  $O_3$  with surface  
26 seawater iodide ( $I^-$ ) contributes to the flux of iodine species into the MBL mainly as hypoiodous  
27 acid (HOI) and molecular iodine ( $I_2$ ). Here, we present the first concomitant observations of  
28 iodine oxide (IO),  $O_3$  in the gas phase, and sea surface iodide concentrations. The results from  
29 three field campaigns in the Indian Ocean and the Southern Ocean during 2015-2017 are used  
30 to compute reactive iodine fluxes to the MBL. Observations of atmospheric IO by MAX-  
31 DOAS show active iodine chemistry in this environment, with IO values up to 1 pptv (parts  
32 per trillion by volume) below latitudes of  $40^\circ S$ . In order to compute the sea-to-air iodine flux  
33 supporting this chemistry, we compare previously established global sea surface iodide  
34 parameterisations with new, region-specific parameterisations based on the new iodide  
35 observations. This study shows that regional changes in salinity and sea surface temperature  
36 play a role in surface seawater iodide estimation. Sea-air fluxes of HOI and  $I_2$ , calculated from  
37 the atmospheric ozone and seawater iodide concentrations (observed and predicted), failed to  
38 adequately explain the detected IO in this region. This discrepancy highlights the need to  
39 measure direct fluxes of inorganic and organic iodine species in the marine environment.  
40 Amongst other potential drivers of reactive iodine chemistry investigated, chlorophyll-*a*  
41 showed a significant correlation with atmospheric IO ( $R = 0.7$  above the 99 % significance  
42 level) to the north of the polar front. This correlation might be indicative of a biogenic control  
43 on iodine sources in this region.

44

45 **Keywords:** iodine, Southern Ocean, Indian Ocean, marine boundary layer

## 46 **1. Introduction**

47 Iodine chemistry in the troposphere has gained interest over the last four decades after it was  
48 first discovered to cause depletion of tropospheric ozone ( $O_3$ ) (Chameides and Davis, 1980;  
49 Jenkin et al., 1985) and cause changes to the atmospheric oxidation capacity (Davis et al., 1996;  
50 Read et al., 2008). Iodine studies in the remote open ocean are important considering its role  
51 in tropospheric ozone destruction (Allan et al., 2000), the formation of potential cloud  
52 condensation nuclei and impact on cloud radiative properties (McFiggans, 2005; O'Dowd et  
53 al., 2002). However, iodine chemistry in the remote open ocean is still not completely  
54 understood, with uncertainties remaining around the sources and impacts of atmospheric iodine  
55 (Saiz-Lopez et al., 2012; Simpson et al., 2015).

56 Recent studies of atmospheric iodine chemistry have focused on the detection of iodine oxide  
57 (IO) in the marine boundary layer (MBL) as a fingerprint for active iodine chemistry. IO may  
58 itself also participate in particle nucleation if present at high concentrations (A. Saiz-Lopez et  
59 al., 2006). Iodine containing precursor compounds undergo photo dissociation to produce  
60 iodine atoms (I), which rapidly react with ambient ozone, forming IO (Chameides and Davis,  
61 1980). Until recently, fluxes of volatile organic iodine (e.g.  $CH_3I$ ,  $CH_2ICl$ ,  $CH_2I_2$ ) compounds  
62 including those originating from marine algae (Saiz-Lopez and Plane, 2004) were considered  
63 to be the primary source of iodine in the marine atmosphere (Carpenter, 2003; Vogt et al.,  
64 1999). However, the biogenic sources of atmospheric iodine could not account for the levels  
65 of IO detected in the tropical MBL (Mahajan et al., 2010a; Read et al., 2008). Currently,  
66 inorganic iodine emissions are considered to be the dominant sources contributing to the open  
67 ocean boundary layer iodine (Carpenter et al., 2013). A recent study by Koenig et al. (2020)  
68 concluded that inorganic iodine sources play major role in comparison to the organic iodine  
69 sources in contributing even to the upper troposphere iodine budget. Laboratory investigations  
70 revealed that at the ocean surface, iodide ( $I^-$ ) dissolved in the seawater reacts with the deposited

71 gas-phase ozone to release hypoiodous acid (HOI) and molecular iodine ( $I_2$ ) via the following  
72 reactions (Carpenter et al., 2013; Gálvez et al., 2016; MacDonald et al., 2014) :



77 The reaction of sea surface iodide (SSI) with ozone in (R1) is considered a major contributor  
78 (600-1000 Tg per year, (Ganzeveld et al., 2009)) to the loss of ozone at the surface ocean,  
79 contributing between 20 % (Garland et al., 1980) and 100 % (Chang et al., 2004) of the oceanic  
80 ozone dry deposition velocity. Reactions (R1) and (R2) result in the release of reactive iodine  
81 (HOI and  $I_2$ ) to the atmosphere, where they quickly photolyse to yield I atoms, which react  
82 with ozone in the gas phase to form IO (Carpenter, 2003; Saiz-Lopez et al., 2012). Carpenter  
83 et al. (2013) showed that the reactions (R1) and (R2) could account for about 75 % of the IO  
84 levels detected over the tropical Atlantic Ocean. Further studies have shown that including  
85 these reactions and the resulting fluxes of HOI and  $I_2$  in atmospheric chemistry models has  
86 results in good agreement between observed and modelled iodine levels over the Atlantic and  
87 the Pacific Ocean, but not for the Indian and Southern Ocean. For example, the sea-air flux of  
88 HOI and  $I_2$  could explain the observed levels of molecular iodine and IO at Cape Verde (Lawler  
89 et al., 2014a), and observed IO levels over the eastern Pacific were in reasonable agreement  
90 with those modelled from estimated  $I_2$  and HOI fluxes (MacDonald et al., 2014). In contrast,  
91 the inorganic iodine fluxes estimated for the Indian Ocean and Indian sector of the Southern  
92 Ocean marine boundary layer could not fully explain the observed IO concentrations (Mahajan  
93 et al., 2019a, 2019b). Similarly, in the Pacific observations of IO and halocarbons have shown

94 that the contribution of combined iodocarbon fluxes to IO is between 30 to 80% assuming an  
95 inorganic iodine lifetime of between 1 and 3 days (Hepach et al., 2016).

96 Predicted global emissions of iodine compounds show a large sensitivity (~ 50 %) to the SSI  
97 field used (Saiz-Lopez et al., 2014; Sherwen et al., 2016c, 2016b); an improved and accurate  
98 system for simulating SSI concentration is imperative. Existing global parameterisations  
99 discussed in this study follow three different methods for SSI estimation. The first is a linear  
100 regression approach against biogeochemical and oceanographic variables (Chance et al.,  
101 2014), the second uses an exponential relationship with sea surface temperature as a proxy for  
102 SSI (MacDonald et al., 2014), and the third is a recent machine-learning-based model (Sherwen  
103 et al., 2019a) that predicts monthly global SSI fields for the present-day. Where such  
104 approaches are based on large scale relationships, they may not properly capture smaller scale,  
105 regional differences in SSI (as observed for Chance et al., 2014; MacDonald et al., 2014) or  
106 underestimate surface iodide concentration (in case of Sherwen et al., 2019). Furthermore, there  
107 are large differences in predicted iodide concentrations between these parametrisations in some  
108 regions (refer Sect. 3.2). Thus, estimation of seawater iodide based on the existing  
109 parameterisations may not always be sufficiently accurate.

110 At present, there is a paucity of measurements of SSI, and remote sensing techniques cannot  
111 detect iodine species in seawater (Chance et al., 2014; Sherwen et al., 2019a). In particular,  
112 regions of the Indian Ocean and the Southern Ocean have been under-sampled in terms of  
113 iodine observations in the atmosphere and ocean (Chance et al., 2014; Mahajan et al., 2019a,  
114 2019b). It is important to remember that the most widely used parameterisation (MacDonald  
115 et al., 2014) is built on a limited observational dataset from the Atlantic and Pacific Ocean  
116 completely excluding the Indian Ocean and the Southern Ocean. As they have not been tested  
117 in the Indian Ocean, they may not be suitable for accurate estimation of SSI in the distinct and  
118 highly variable salinity and temperature regimes of the Indian Ocean region. The

119 parameterisations presented in Chance et al. (2014), are based on a larger data set including  
120 Southern Ocean observations, but still only make use of two data points in the Indian Ocean.  
121 Furthermore, the Sherwen et al. (2019) parameterisation uses the updated data set including  
122 the new Indian Ocean SSI observations used in this study. Compounding the lack of Indian  
123 Ocean SSI observations is the fact that parts and in particular the Arabian Sea and the Bay of  
124 Bengal, do not follow the same seasonal trends in salinity (D’Addezio et al., 2015) and sea  
125 surface temperature (Dinesh Kumar et al., 2016) as each other on the same latitudinal band and  
126 hence the currently used global iodide parameterisations in models i.e. MacDonald et al. (2014)  
127 may not be appropriate for these areas. Here we use new SSI observations made as part of this  
128 study (described in full in (Chance et al., 2020) and included in Chance et al. (2019)) to test  
129 whether the existing parameterisations can be directly applied to the Indian Ocean and if  
130 regional specific parameterisations are more accurate compared to the former.

131 Although several measurements of IO have been reported around the globe, including in the  
132 open ocean (Alicke et al., 1999; Allan et al., 2000; Frieß et al., 2001; Großmann et al., 2013;  
133 Mahajan et al., 2010b, 2010a, 2009; Prados-Roman et al., 2015), the remote open ocean still  
134 remains under-sampled. The two documented observations of IO in the Indian Ocean and the  
135 Indian sector (Jan-Feb 2015 and December 2015) of the Southern Ocean were interpreted using  
136 parameterisations to estimate the SSI concentrations in combination with observed ozone  
137 concentrations, to subsequently calculate the resulting inorganic iodine fluxes. This approach  
138 suggested that the observed atmospheric IO may not be well correlated with the inorganic  
139 fluxes and that biogenic fluxes could play an important role (Mahajan et al., 2019a, 2019b).  
140 Here, we present measurements of IO in the MBL of the Indian Ocean and the Southern Ocean  
141 during the 9<sup>th</sup> Indian Southern Ocean Expedition (ISOE-9) conducted in January-February  
142 2017, alongside the first simultaneous SSI observations along the cruise track (Chance et al.,  
143 2019). The iodide observations were used to compute the inorganic iodine fluxes to compare

144 with IO observations along the cruise tracks. Further, observed SSI concentrations are used to  
145 compute region-specific parameterisations for SSI concentrations, following the approaches  
146 taken by Chance et al. (2014) and MacDonald et al. (2014). The iodide concentrations obtained  
147 with these region-specific modified parameterisations are compared to the iodide estimates  
148 using their original counterparts and the global machine-learning-based prediction of SSI  
149 concentration (Sherwen et al., 2019a). The resulting estimated reactive iodine fluxes (HOI and  
150 I<sub>2</sub>) are then used to see if the inorganic fluxes can explain the IO loading in the atmospheric  
151 MBL.

## 152 **2. Measurement techniques and methodology**

153 The 9<sup>th</sup> Indian Southern Ocean Expedition (ISOE-9) was conducted from January to February  
154 2017 in the Southern Ocean and the Indian Ocean sector of the Southern Ocean. The expedition  
155 started from Port Louis, Mauritius, and spanned the remote open ocean area till the coast of  
156 Antarctica. Observations of IO, SSI and O<sub>3</sub> were made along the cruise track during ISOE-9.  
157 For further analysis we also include IO observations from the 2<sup>nd</sup> International Indian Ocean  
158 Expedition (IIOE-2) and the 8<sup>th</sup> Indian Southern Ocean Expedition (ISOE-8) conducted in the  
159 Indian and Southern Ocean region during austral summer of 2015 (Mahajan et al., 2019a,  
160 2019b). We also include SSI observations in the northern Indian Ocean from two expeditions  
161 namely, the Sagar Kanya-333 cruise (SK-333) and the Bay of Bengal Boundary Layer  
162 Experiment (BoBBLE) conducted during June-July and September 2016 respectively (Chance  
163 et al., 2020). Table 1 includes details of the expeditions, including the locations, dates of the  
164 expeditions and the meridional transect for each expedition. Figure 1a shows a map with the  
165 cruise tracks for the five expeditions. Figure 1b shows the seawater iodide sampling locations  
166 during ISOE-9, SK-333 and BoBBLE expeditions. The track of the ship during ISOE-9 along  
167 with the air mass back trajectories arriving at noon each day is given in the supplementary text  
168 Fig. S1. The HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model

169 (Rolph et al., 2017; Stein et al., 2015) was used to calculate the back trajectories. Similar back  
170 trajectory plots and full cruise tracks for ISOE-8 and IIOE-2 are given in Mahajan et al. (2019a,  
171 2019b). During the three expeditions, meteorological parameters of ocean and atmosphere were  
172 measured using an on-board automatic weather station and manual observation techniques.

## 173 **2.1. Sea surface iodide (SSI)**

174 In this section, we focus on developing region-specific parameterisation for SSI estimation by  
175 adapting previously established methods. The SSI concentrations obtained from the original  
176 and newly developed region-specific parameterisation and SSI model predictions are used for  
177 a comparison study, and further to calculate the inorganic iodine emissions.

### 178 **2.1.1 Observed SSI in the Indian Ocean and the Southern Ocean**

179 Historically, few observations of SSI are available for the Indian Ocean basin with reports of  
180 only 3 data points in the open ocean from the Arabian Sea sector of the Indian Ocean  
181 (Farrenkopf and Luther, 2002). Two of these values are coastal, and they lack supporting sea  
182 surface temperature and salinity data; thus, they have been excluded from this study. However,  
183 recent work has led to a large increase in the number of SSI observations available for the  
184 Indian Ocean and Southern Ocean (Indian ocean sector) (Chance et al., 2020). Specifically,  
185 111 new observations were made during the 2016 ISOE-9 and 18 during the SK-333 and  
186 BoBBLE. During the ISOE-9, SSI measurements in seawater were made concomitant with  
187 observations of O<sub>3</sub> and IO in the gas phase for the first time. Observations of SSI made during  
188 this expedition used the cathodic stripping voltammetry method with a hanging mercury drop  
189 electrode as a working electrode (Campos, 1997; Luther et al., 1988). The errors reported on  
190 the concentrations reflect the standard deviation of the repeat scans and the standard error on  
191 the intercept and slope of the calibration. The seawater samples were collected during the  
192 ISOE-9 at a 3-6-hour interval between 23° S and 70° S. Seawater samples from the SK-333



193 cruise and BoBBLE were analysed following the same technique for surface iodide  
194 concentrations. Iodide data from SK-333 and BoBBLE contributed to 18 additional data points  
195 between 10° N and 4° S making a total of 129 new locations (excluding coastal and extremely  
196 high values above 400 nM; see (Chance et al., 2020) for details) for observed SSI in the Indian  
197 Ocean and Southern Ocean region. This is a major sample size compared to the global 2014  
198 database (n=925) across all the global oceans (Chance et al., 2014), and these data points  
199 contribute substantially to the recently updated iodide dataset (Chance et al., 2019) (n=1342).  
200 From here onwards, the iodide concentrations obtained from sampling observations will be  
201 referred to as measured SSI as opposed to modelled SSI to differentiate between the observed  
202 iodide concentrations and those calculated using the parametrisations. All available  
203 observations made in the Indian Ocean basin as presented in Chance et al. (2019) have been  
204 included for the development of the region-specific parameterisation presented in this work.  
205 Further details about the measurement technique and the observations used can be found in  
206 (Chance et al., 2020).

### 207 **2.1.2 Iodide parametrisations**

208 Due to the sparsity of SSI measurements, different empirical parametrisations have been  
209 proposed to estimate SSI concentrations. Parameters like SST and salinity (only for SK-333  
210 and BoBBLE;  $R^2 = 0.3$ ,  $P = 0.018$ ) show a positive correlation with the SSI concentrations.  
211 However, a global parameterisation scheme may not capture the specificities of these required  
212 for regional studies. The northern Indian Ocean has markedly different sea surface salinity  
213 (D'Addezio et al., 2015) and SST (Dinesh Kumar et al., 2016) in its two basins, the Arabian  
214 Sea and the Bay of Bengal, that share the same latitude bands separated by the Indian sub-  
215 continental landmass. These basins experience the biannually reversing monsoonal winds,  
216 which greatly influence their SST and salinity structure. Strong winds in the Arabian Sea  
217 associated with the summer monsoon dissipate heat via overturning and turbulent mixing.

218 Whereas weaker winds in the Bay of Bengal imply high SST due to the formation of stable and  
219 shallow surface mixed layer (Shenoi, 2002). The Arabian Sea exhibits much higher salinity  
220 compared to the Bay of Bengal due to greater evaporation and lower river runoff (Rao and  
221 Sivakumar, 2003). As mentioned earlier, the current global SSI parameterisations are based  
222 almost entirely on observations from the Atlantic, Pacific and Southern Oceans, and have not  
223 been tested in the Indian Ocean region.

224 Here, we aim to create region-specific parameterisations for the Indian and Southern Ocean  
225 and conduct a comparison between these and the existing global parameterisations, further  
226 discussed in Sect. 4.2. The existing (Eq. (1), Eq. (4), and Eq. (6)) global and the new region-  
227 specific parameterisations are listed in Table 2. Below we describe briefly the modified  
228 parameterisations. Details about the original parameterisations can be found in their respective  
229 publications (Chance et al., 2014; MacDonald et al., 2014; Sherwen et al., 2019a).

230 (a) Linear regression analysis was performed, on each parameter, namely, SST, mixed layer  
231 depth (MLD), latitude, sea surface nitrate concentration (as it has been suggested that iodate  
232 could be reduced by nitrate based enzymes (Chance et al., 2014)), and salinity against the  
233 measured SSI concentrations from ISOE-9, SK-333, and BoBBLE campaigns, similar to the  
234 Chance et al. (2014) technique, but using in situ SST and salinity observations instead of  
235 climatological values. More details on the approach taken can be found in the supplementary  
236 text. The combination with the largest  $R^2$  and uniform distribution of residuals from the  
237 statistically significant dependent variables, as detailed in Table S1 resulted in Eq. (2) of Table  
238 2. Eq. (2) thus represents a region-specific (the Indian Ocean and the Southern Ocean region  
239 abbreviated as Ind. O. + Sou. O. in the figures) variant of the Chance et al. (2014)  
240 parameterisation for the estimation of SSI concentrations. Similarly, keeping in mind the  
241 difference in the SST and salinity for the Indian Ocean and the Southern Ocean, another  
242 parameterisation was derived only for the Southern Ocean region using the ISOE-9 iodide

243 observations and for the Indian Ocean using the SK-333 and BoBBLE iodide observations,  
244 respectively. The parameterisation for the Southern Ocean region using ISOE-9 iodide  
245 observations is given in Table 2 as Eq. (3). A similar Indian Ocean parameterisation is  
246 formulated and listed in the last row of Table 2 as Eq. (3a). However, this parameterisation is  
247 not valid, and it is omitted from analysis in this text due to statistical insignificance inferred  
248 from ANOVA test using StatPlus statistical analysis software. In this method, the F ratio from  
249 ANOVA analysis is compared with the critical F value from the standard f-distribution table  
250 (at 0.05 significance level) to confirm the statistical robustness. Results of ANOVA test on the  
251 datasets for Eq. (2), (3) and (3a) is discussed in the supplementary text.

252 (b) A second method for the estimation of SSI concentration was proposed by MacDonald et  
253 al. (2014) that uses the correlation between sea surface iodide and SST. At present, this is the  
254 most commonly used parameterisation in global models (Sherwen et al., 2016b, 2016a, 2016c;  
255 Stone et al., 2018). Similar to MacDonald et al. (MacDonald et al., 2014) (Table 2, Eq. 4), we  
256 derived an Arrhenius-type, region-specific expression using iodide and SST data from ISOE-  
257 9, SK-333 and BoBBLE. Figure 2 shows the typical linear dependence of  $\ln[I^-]$ , for observed  
258 SSI in the Indian Ocean and the Southern Ocean, with  $SST^{-1}$ , which resulted in the Arrhenius  
259 form expression given as Eq. (5) in Table 2.

260 Figure 3 shows the iodide concentrations for the three campaigns, ISOE-8, IIOE-2 and ISOE-  
261 9, calculated using equations (1) to (5), the measured iodide concentrations from ISOE-9, SK-  
262 333 and BoBBLE, and the global iodide model predictions obtained from Sherwen et al. (2019)  
263 (Table 2.). From here on, region-specific parameterisations developed for SSI concentrations  
264 are referred to as the modified versions of the original parameterisations; Eq. (2) and (3) are  
265 called the modified Chance et al. (2014) parameterisation for the Indian Ocean and Southern  
266 Ocean region and only the Southern Ocean region, respectively. Eq. (5) is called the modified

267 Macdonald et al. (2014) parameterisation. The machine-learning-based model proposed in  
268 Sherwen et al. (2019) is referred to as ‘SSI model’ results.

## 269 **2.2. Ozone**

270 Surface ozone was monitored using a US-EPA approved nondispersive photometric UV  
271 analyser (Ecotech EC9810B) installed on the ship during the expeditions to detect surface  
272 ozone values at a one-minute temporal resolution. A Teflon tube ~ 4 m long fixed towards the  
273 front of the ship acted as an inlet for the analyser. The analyser is equipped with a selective  
274 ozone scrubber, which was alternatively switched in and out of the measuring stream. The  
275 analyser has a lower detection limit of 0.5 ppbv and a precision of 1 ppbv. A 5-micron PTFE  
276 filter membrane installed in the sample inlet tube was changed regularly. Zero and span  
277 calibration were done every alternate day to ensure accurate O<sub>3</sub> measurements. The ozone data  
278 collected was cleaned to remove the data points under the influence of the ship’s smokestack  
279 by referring to the measured apparent wind direction on the ship. Apparent wind approaching  
280 the ship from 0 ° to 90° or 270 ° to 360° (front hemisphere of the ship) was considered free from  
281 smokestack emission influence, where 0° or 360° represents the bow of the ship. Ozone data  
282 recorded when the ship was stationary showed major smokestack emission influence and was  
283 excluded from the data.

## 284 **2.3. Estimation of inorganic iodine fluxes**

285 In order to estimate the contribution of inorganic iodine chemistry to active iodine chemistry  
286 in the atmosphere, the atmospheric fluxes for the main product species, I<sub>2</sub> and HOI, need to be  
287 calculated, since direct flux measurements of I<sub>2</sub> and HOI have not been done anywhere in the  
288 world to date. While there are reported observations of marine I<sub>2</sub> emission, they are few in  
289 number and mostly from coastal regions (Atkinson et al., 2012; Huang et al., 2010; a Saiz-  
290 Lopez et al., 2006) and one observation in the open ocean (Lawler et al., 2014b), although these

291 are all observations of atmospheric concentrations and not of fluxes. As observed SSI is not  
 292 available for all cruises, we used the following scenarios for SSI to estimate the inorganic  
 293 iodine fluxes:

294 (a) Using measured SSI: Observations of sea surface iodide from ISOE-9, SK-333, and  
 295 BoBBLE.

296 (b) Using calculated SSI from:

297 1. Chance et al. (2014) parameterisation Eq. (1)

298 2. Modified Chance et al. (2014) parameterisation for the Indian Ocean and  
 299 Southern Ocean (Ind. O. + Sou. O.) region Eq. (2)

300 3. Modified Chance et al. (2014) parameterisation for the Southern Ocean (Sou.  
 301 O.) region Eq. (3)

302 4. MacDonald et al. (2014) parameterisation using SST Eq. (4)

303 5. Modified MacDonald et al. (2014) parameterisation Eq. (5)

304 6. Machine-learning-based model prediction (Sherwen et al., 2019a) Eq. (6)

305 Ozone was measured on all three cruises (ISOE-9, IIOE-2 and ISOE-8). The fluxes for HOI  
 306 and  $I_2$  were then calculated for all the above scenarios except for the observations from SK-  
 307 333 and BoBBLE as IO observations were not taken during these cruises. The following  
 308 algorithm was used for estimating iodine fluxes (Carpenter et al., 2013),

$$309 \text{ flux}_{I_2} = [O_{3(g)}] * [I_{(aq)}^-]^{1.3} * (1.74 \times 10^9 - 6.54 \times 10^8 * \ln(ws)) \quad \text{Eq. (7)}$$

$$310 \text{ flux}_{HOI} = [O_{3(g)}] * \left( 4.15 \times 10^5 * \frac{\sqrt{[I_{(aq)}^-]}}{ws} - \frac{20.6}{ws} - 2.36 \times 10^4 * \sqrt{[I_{(aq)}^-]} \right) \text{Eq. (8)}$$

311 where, the fluxes are in  $\text{nmol m}^{-2} \text{d}^{-1}$ ,  $[O_3]$  in  $\text{nmol mol}^{-1}$  (ppbv),  $[I^-]$  in  $\text{mol dm}^{-3}$  and the wind  
 312 speed (WS) in  $\text{m s}^{-1}$ . Carpenter et al. (2013) did not consider the effect of temperature in the  
 313 interfacial layer of the sea-surface model on activation energies for the reaction R1 (i.e.,

314 assumed the temperature dependence for  $k(\Gamma + O_3)$  to be zero). Although  $I_2$  and HOI fluxes  
315 are expected to increase with the temperature of the interfacial layer,  $I_2$  production has a  
316 negative activation energy, as noted by MacDonald et al. (2014). In Carpenter et al. (2013)  
317 (specific to the tropical Atlantic), a seawater temperature of 15°C and air temperature of 20° C  
318 were used to calculate Henry's law constants, diffusion constants, and mass transfer velocities.  
319 Again assuming the temperature dependence of  $k(\Gamma + O_3)$  to be zero, but including the  
320 temperature-dependence of Henry's law constants, diffusion constants, and mass transfer  
321 velocities, the same interfacial layer model predicted effective activation energies for  $I_2$  and  
322 HOI emissions of  $-2 \text{ kJ mol}^{-1}$  and  $25 \text{ kJ mol}^{-1}$  (Macdonald et al. (2014). Using these  
323 activation energies, Macdonald et al. (2014) calculated differences in  $I_2$  and HOI fluxes of 3 %  
324 and 31-41 %, respectively, at SSTs of 10° C and 30° C compared to the room-temperature  
325 parameterisations presented in Carpenter et al. (2013). Experimentally derived activation  
326 energies for  $I_2$  and HOI emissions were  $-7 \pm 18 \text{ kJ mol}^{-1}$  and  $17 \pm 50 \text{ kJ mol}^{-1}$  (MacDonald  
327 et al., 2014). As HOI represents the larger iodine flux, the higher relative uncertainty in the  
328 activation energy should be kept in mind when calculating temperature-dependent emissions.  
329 It should be noted that a recent study suggested that the activation energies from MacDonald  
330 et al. (2014) are better summarized as approximately zero (e.g. (Moreno and Baeza-Romero,  
331 2019) as the overall temperature dependence remains unresolved.

332 HOI and  $I_2$  fluxes are also influenced by the wind speed as seen from equations (7) and (8),  
333 and the modelled iodine fluxes (HOI and  $I_2$ ) are highest for high  $[O_3]$ , high  $[I^-]$  and low wind  
334 speed. This is explained by the assumption that wind shear drives mixing of the interfacial layer  
335 to bulk seawater, reducing the efflux of HOI and  $I_2$  into the atmosphere (Carpenter et al., 2013).  
336 Negative fluxes are obtained from equations (7) and (8) for both HOI and  $I_2$  when the wind  
337 speed is higher than  $14 \text{ m s}^{-1}$ , which is not physically possible and therefore the model output  
338 is limited to wind speeds below  $14 \text{ ms}^{-1}$  (Mahajan et al., 2019a). Iodine fluxes calculated from

339 equations (7) and (8) using SSI concentrations from the scenarios (a) and (b 1-6) are shown in  
340 Fig. 4 (c and d).

## 341 **2.4. Iodine Oxide**

### 342 **2.4.1 Observations**

343 Ship-based measurements of IO were made using the Multi-Axis Differential Optical  
344 Absorption Spectroscopy (MAX-DOAS) technique (Hönninger et al., 2004; Platt and Stutz,  
345 2008). The MAX-DOAS was installed at the bow of the ship with a direct line of sight towards  
346 the front of the ship to avoid the ship's plume in the detection path of the telescope. The MAX-  
347 DOAS was programmed to capture scattered sunlight spectra at every 1 second at set elevation  
348 angles of 0, 1, 2, 3, 5, 7, 20, 40, and 90-degrees during daylight hours. Mercury line calibration  
349 offset, and dark current spectra were recorded after sunset on each day. Elevation angles  
350 outside a range of  $\pm 0.2$  degree from the set value were eliminated from the 30 minutes averaged  
351 spectra for increased accuracy. Figure S2 shows the resultant IO and O<sub>4</sub> differential slant  
352 column densities (DSCDs) for ISOE-9 campaign, similar plots are available for ISOE-8  
353 (Mahajan et al., 2019a) and IIOE-2 (Mahajan et al., 2019b). The QDOAS software (Danckaert  
354 et al., 2017) was used for DOAS retrieval of IO from the spectra using the optical density fitting  
355 analysis method. The spectra were fitted with a 3<sup>rd</sup> order polynomial using fitting interval of  
356 415 to 440 nm with cross-sections of NO<sub>2</sub> (Vandaele et al., 1998), O<sub>3</sub> (Bogumil et al., 2003),  
357 O<sub>4</sub> (Thalman and Volkamer, 2013), H<sub>2</sub>O (Rothman et al., 2013), two ring spectra, first as  
358 recommended by Chance and Spurr, (1997) and second following Wagner et al., (2009) and a  
359 liquid water spectrum for seawater (Pope and Fry, 1997). To remove the influence of  
360 stratospheric absorption a spectrum corresponding to 90° (zenith) from each scan was used as  
361 a reference for the analysis. The raw spectra were analysed to obtain differential slant column  
362 densities (DSCDs), and values with a root mean square error (RMS) of greater than  $10^{-3}$  were

363 eliminated. Similarly, DOAS retrieval of O<sub>4</sub> in 350 to 386 nm spectral window was performed,  
364 and DSCDs were obtained. The optical density fits for IO and O<sub>4</sub> from ISOE-9 are shown in  
365 Fig. S3. The IO DSCDs were then converted to volume mixing ratios using the O<sub>4</sub> slant  
366 columns following the previously used "O<sub>4</sub> method" (Mahajan et al., 2012; Prados-Roman et  
367 al., 2015; Sinreich et al., 2010; Wagner et al., 2004). Further details of the instrument, retrieval  
368 procedure and conversion into mixing ratios can be found in previous works (Mahajan et al.,  
369 2019a, 2019b).

#### 370 **2.4.2 Modelled atmospheric IO**

371 We use outputs from two global models for a comparison with the observations conducted  
372 during the three cruises. The first model is the GEOS-Chem chemical transport model (version  
373 10-01, 4x5 degrees horizontal resolution, <http://www.geos-chem.org>), which includes detailed  
374 HO<sub>x</sub>-NO<sub>x</sub>-VOC-ozone-halogen-aerosol tropospheric chemistry (Sherwen et al., 2017, 2016b)  
375 and is driven by offline meteorology from NASA's Global Modelling and Assimilation Office  
376 (<http://gmao.gsfc.nasa.gov>) forward processing product (GEOS-FP).

377 The second model is the 3D chemistry-climate model CAM-Chem version 4 (Community  
378 Atmospheric Model with Chemistry) <https://www2.acom.ucar.edu/gcm/cam-chem>, which is  
379 included in the CESM framework (Community Earth System Model, CAM-Chem, version  
380 4.0). The model includes a state-of-the-art halogen chemistry scheme (chlorine, bromine and  
381 iodine) (Saiz-Lopez and Fernandez, 2016). The current configuration includes an explicit  
382 scheme of organic and inorganic iodine emissions and photochemistry. These halogen sources  
383 comprise the photochemical breakdown of five very short-lived bromocarbons (CHBr<sub>3</sub>,  
384 CH<sub>2</sub>Br<sub>2</sub>, CH<sub>2</sub>BrCl, CHBrCl<sub>2</sub> and CHBr<sub>2</sub>Cl) naturally emitted by phytoplankton from the  
385 oceans (Ordóñez et al., 2012). The model was run in specified dynamic mode (Ordóñez et al.,



386 2012), with a spatial resolution of 1.9° latitude by 2.5° longitude and 26 vertical levels from the  
387 surface to up to 40 km.

388 Both models include biotic emissions of four iodocarbons (CH<sub>3</sub>I, CH<sub>2</sub>ICl, CH<sub>2</sub>IBr and CH<sub>2</sub>I<sub>2</sub>)  
389 as described by (Ordóñez et al., 2012) and abiotic oceanic sources of HOI and I<sub>2</sub> based on the  
390 Carpenter et al. (2013) and MacDonald et al. (2014) laboratory studies of the oxidation of  
391 aqueous iodide by atmospheric ozone at the ocean surface. Both models here use the  
392 MacDonald parameterisation expression (Eq. (4), MacDonald et al., 2014) discussed in Section  
393 2.1.2 to predict surface iodide used for calculating iodine emissions and the organo-halogen  
394 emissions from Ordóñez et al. (2012). IO surface concentrations for the three campaigns (IIOE-  
395 2, ISOE-8 and ISOE-9) were extracted from the model runs and used for comparison.  
396 Currently, these two global models include reactive iodine chemistry (along with TOMCAT,  
397 which includes the tropospheric iodine chemistry (Hossaini et al., 2016)).

### 398 **3. Results**

#### 399 **3.1 Ozone, Meteorological and Oceanic parameters**

400 The latitudinal distribution of hourly average values of U10 wind speed (WS), O<sub>3</sub>, SST, and  
401 salinity from all the campaigns are shown in Fig. 5. Winds arriving at the ship, shown in the  
402 first panel (Fig. 5a), remained low for most of the duration of all three expeditions with wind  
403 speed ranging from 1 m s<sup>-1</sup> to stronger winds of 24 m s<sup>-1</sup> on a few days. Even stronger winds  
404 (above 30 m s<sup>-1</sup>) were observed during the ISOE-9 in the region between 64 ° and 65° S with  
405 the highest wind speed of 32 m s<sup>-1</sup> at 66° S on the night of 8<sup>th</sup> February 2017. Ozone mixing  
406 ratios, (Fig. 5b) during all three expeditions showed a similar trend exhibiting a large reduction  
407 in values in the open ocean environment compared to coastal environments. The back  
408 trajectories (supplementary text) show that for most of the expeditions, air masses arriving at  
409 the cruise were from the open ocean environment and did not have any anthropogenic influence

410 for the last five days. This is reflected in the O<sub>3</sub> values, which range between 8 and 20 ppbv in  
411 the open ocean but were between 30 and 50 ppbv near the coastal regions, where the air mass  
412 back trajectories confirm anthropogenic origins. Close to the Indian sub-continent ozone levels  
413 peaked at about 50 ppbv during the ISOE-8. It also showed a distinct diurnal variation with  
414 higher ozone values during the daytime due to photochemical production. However, in the open  
415 ocean environment, ozone mixing ratios did not show this diurnal variation, and indeed values  
416 of ozone dropped during daytime indicating photochemical destruction during both ISOE-8  
417 and ISOE-9 (Fig. 5b).

418 As already noted, SST is widely used to predict SSI (Eq. 4 and 5). Combined SST data (Fig.  
419 5c) reveal a steady decrease in sea surface temperature from 15° S to 68° S for all the  
420 campaigns. During January 2015 (ISOE-8) seawater north of 6° N displays slightly lower SST  
421 (~ 3° C) compared to that in December 2015 (IIOE-2). Salinity is also an important parameter  
422 for the prediction of SSI (higher coefficient in Eq. 1, 2 and 3). The Southern Ocean region  
423 explored during ISOE-8 and ISOE-9 reveals similar salinity values (Fig. 5d) for the austral  
424 summer months of 2015 and 2016 (January-February). The salinity data shows relatively lower  
425 values for ISOE-8 compared to those for IIOE-2 for the region 15° N to 20° S. Despite the inter-  
426 annual differences in the northern Indian Ocean region, salinity values of ~ 35 PSU overlap for  
427 the IIOE-2 and ISOE-8 in a small window of 7° N to the equator. Below the equator, the salinity  
428 values for IIOE-2 increase while for ISOE-8 salinity remains lower than 35 PSU until 20° S.  
429 Seawater between 20° S and 44° S has a near-constant salinity of 35 PSU which decreases to  
430 ~33.5 PSU after 44° S and remains the same until 65° S after which the salinity begins to drop  
431 to 31.5 PSU near 67° S close to Antarctica.

### 432 **3.2 Sea surface iodide concentration**

433 Latitudinal averages of SSI concentrations estimated from seven scenarios (listed in Sect. 2.3)  
434 are shown in Fig. 3. SSI estimates from the IIOE-2 campaign are marked separately to  
435 differentiate from the ISOE estimates for the Indian Ocean region. There is a clear difference  
436 in the estimated SSI in different scenarios. All the estimates and the model follow a similar  
437 pattern showing elevated levels in the tropics as compared to the higher latitudes. SSI estimates  
438 from parameterisations (Eq. 1, 3, 4, and 5) show nearly constant values for SSI from 15° N to  
439 25° S, after which a steady decline is noted until 70° S. Thus, the parameterisations based on Eq.  
440 1, 3, 4 and 5 do not capture the decreasing trend observed for iodide around the equator. Eq. 2,  
441 which was derived specifically for the Indian Ocean and Southern Ocean region better captures  
442 this trend, and also shows a better match with the measured SSI from SK-333 and BoBBLE in  
443 the Indian Ocean. Eqn. 6 also predicts lower concentrations around the equator than in the  
444 northern Indian Ocean. SSI concentrations estimated using the Chance et al. (2014)  
445 parameterisation (Eq. 1) show a small increase in iodide concentrations south of 47° S (polar  
446 front), which is not observed in the other parameterisations, but there is some suggestion of an  
447 increase in the observations. Eq. 1 also resulted in a large difference (~ 50 nM) of SSI estimates  
448 north of 10° N between the IIOE-2 and ISOE-8 cruises; while this difference was lower for the  
449 other parameterisations. This difference between the SSI estimates for the IIOE-2 and ISOE-8  
450 cruises is due to the large difference in salinity values for this region (Sect. 4.1). SSI estimates  
451 using Eq. 2 shows good agreement with the model prediction of Sherwen et al. (2019), both  
452 indicating a decrease in SSI concentrations near the equator during the IIOE-2 and ISOE-8  
453 expeditions. Some high SSI concentrations (up to ~250 nM) were observed around 10° N, these  
454 were best replicated by Eqn.3. The highest SSI concentrations estimated using Eq. 3 were 244  
455 nM at 7° N during IIOE-2 and 242 nM at 12° S during ISOE-8. At the equator, Eq. 2 performs  
456 better in predicting the SSI concentrations with a difference of ~75 nM compared to the  
457 observations. SSI estimates from Eq. 4, i.e. MacDonald et al. (2014) parameterisation, were

458 lower than the measured iodide concentrations and all other parameterisation, including the  
459 model (Eq. 7) predictions. Overall, all modified parameterisations (Eq. 2, 3 and 5) estimate  
460 higher SSI compared to the original parameterisation (Eq. 1 and 4), with the exception of the  
461 region south of 20° S, where Eq. 3 predicts lower SSI than Eq. 1. The modified MacDonald  
462 parameterisation (Eq. 5) estimated iodide concentrations to be greater by 50 nM for the entire  
463 dataset in comparison to the existing MacDonald parameterisation given by Eq. 4. For Eq. 5,  
464 the uncertainty in the iodide concentration from the 95 % prediction band is ~15 % of the  
465 predicted value.

### 466 **3.3 Iodine fluxes**

467 Figure 4 shows the latitudinal variation in IO mixing ratios, inorganic iodine emissions (HOI  
468 and I<sub>2</sub>), chl-*a* and ozone mixing ratios for the entire dataset comprising of the three campaigns.  
469 All the panels in Fig. 4 are plots of daily averaged values during each expedition, except for  
470 the HOI and I<sub>2</sub> fluxes; these are latitudinal averages from each campaign. Emissions calculated  
471 using the measured SSI concentrations (represented by filled spheres in Fig. 4 c & d) from  
472 ISOE-9 correspond to the data points of the measured SSI concentration. Oceanic inorganic  
473 iodine emission fluxes of HOI and I<sub>2</sub> were estimated using the Carpenter et al. (2013)  
474 parameterisation given in Eq. (7) and (8) limited to wind speeds below 14 m s<sup>-1</sup>. Thus, the  
475 fluxes estimated from the measured SSI concentrations were reduced to 56 points (out of 111  
476 measured SSI data points). The seven different datasets of iodide concentrations (listed in Sect.  
477 2.3) have been used for estimation of HOI and I<sub>2</sub> fluxes. For the entire dataset, the highest  
478 fluxes were obtained when using the SSI concentrations from the modified Chance et al. (2014)  
479 parameterisation (Eq. 3), derived from measured SSI from the Southern Ocean region, i.e.  
480 during ISOE-9. The second highest fluxes were estimated using SSI from Eq. 2, obtained from  
481 measured SSI from the Indian Ocean and Southern Ocean. Comparatively lower iodine  
482 emissions were estimated using SSI concentration from MacDonald et al. (2014)

483 parameterisation (Eq. 4). The estimated inorganic iodine fluxes in the Southern Ocean region  
484 ( $30^{\circ}$  S and below) are much lower compared to the Indian Ocean (Fig. 5), driven by the higher  
485 estimated SSI in the latter. Maximum inorganic emissions are predicted in the tropical region,  
486 specifically, north of the equator. HOI is the dominant reactive iodine precursor species for the  
487 entire dataset, with calculated flux values 20 times higher than those for  $I_2$ . Emissions estimated  
488 using SSI from Eq. (3), resulted in a peak HOI flux of  $1.5 \times 10^9$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  at  $9^{\circ}$  N during  
489 ISOE-8. The lowest HOI flux of  $1.7 \times 10^6$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  was obtained at  $61^{\circ}$  S during ISOE-  
490 9. For the same latitudes ( $9^{\circ}$  N and  $61^{\circ}$  S), a maximum  $I_2$  flux of  $7.0 \times 10^7$  molecules  $\text{cm}^{-2} \text{s}^{-1}$   
491 and a minimum of  $1.3 \times 10^5$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  were estimated, respectively. Flux estimates from  
492 Eq. 2 are slightly lower, with a maximum HOI flux of  $1.3 \times 10^9$  and a minimum of  $5.8 \times 10^5$   
493 molecules  $\text{cm}^{-2} \text{s}^{-1}$  and maximum  $I_2$  flux of  $5.2 \times 10^7$  with minimum of  $8.3 \times 10^4$  molecules  $\text{cm}^{-2}$   
494  $\text{s}^{-1}$  at the same latitudes. The estimated HOI and  $I_2$  emissions are notably lower (by  $\sim 50\%$ )  
495 during IIOE-2 to the north of  $5^{\circ}$  S compared to emissions from ISOE-8. Between  $5^{\circ}$  S and  $20^{\circ}$   
496 S, the emissions from IIOE-2 and ISOE-8 are similar. Fluxes estimated using measured SSI  
497 concentrations for the ISOE-9 campaign ( $20^{\circ}$  S to  $70^{\circ}$  S) show no strong latitudinal trend for  
498 both HOI and  $I_2$  emissions. The maximum calculated HOI flux was  $5.8 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$   
499 at  $68^{\circ}$  S and the minimum was  $1.1 \times 10^7$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  at  $33^{\circ}$  S. Similarly,  $I_2$  fluxes  
500 estimated from measured SSI concentrations peaked at  $1.5 \times 10^7$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  at  $32^{\circ}$  S with  
501 a minimum of  $3.5 \times 10^5$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  at  $67^{\circ}$  S. Inorganic iodine emissions estimated using  
502 model predictions for SSI concentrations from Sherwen et al. (2019) match well with the fluxes  
503 estimated using the iodide parameterisation tools. Despite the differences in SSI concentrations  
504 from existing and region-specific parameterisations, all result in similar values for iodine  
505 fluxes. The fluxes were calculated using the hourly wind speeds for the results to be comparable  
506 with model outputs as described below. This would result in a loss of high temporal resolution

507 emission variability, but considering the frequency of the iodide and IO observations,  
508 computing the fluxes at a higher resolution would not give any extra information.

### 509 **3.4 Iodine oxide**

#### 510 **3.4.1 Observations**

511 IO was detected above the instrument detection limit ( $2.1 - 3.5 \times 10^{13}$  molec.  $\text{cm}^{-2}$  i.e. 0.4 – 0.7  
512 pptv) in all three campaigns. The expeditions covered a track from the Indian Ocean to the  
513 Antarctic coast in the Southern Ocean and showed lower IO DSCDs in the tropics compared  
514 to the Southern Ocean, with a peak of about  $3 \times 10^{13}$  molec.  $\text{cm}^{-2}$  at  $40^\circ$  S. Figure 4a shows  
515 daily averaged IO mixing ratios for all the three cruises combined. IO mixing ratios of up to 1  
516 pptv were observed in the region  $50^\circ - 55^\circ$  S and slightly higher values of IO mixing ratios were  
517 observed in the region below  $65^\circ$  S close to the Antarctic coast. North of the polar front region,  
518 the maximum IO average mixing ratio of  $\sim 1$  pptv was observed at  $40^\circ$  S. The highest values of  
519 IO were observed close to the Antarctic coast, with up to 1.5 pptv measured during ISOE-9  
520 and similar values are reported for the ISOE-8 expedition south of the polar front (Mahajan et  
521 al., 2019a). The IO mixing ratios in the Southern Ocean region for ISOE-9 ranged between 0.1  
522 and a maximum of  $1.57 (\pm 0.37)$  pptv observed on 18 Feb 2017 at  $50^\circ$  S on a clear sky day.  
523 This maximum value was observed only on one day, and preceded by foggy and misty days,  
524 later followed by overcast for several days evidencing the role of photochemistry in IO  
525 production from its precursor gases.

#### 526 **3.4.2 Modelled IO**

527 Based on the current understanding of iodine chemistry, regional and global models consider  
528 inorganic fluxes of iodine (HOI and  $\text{I}_2$ ) as major contributors of iodine in the marine boundary  
529 layer. It is important to verify if the models using the existing parameterisation for these source  
530 gases can replicate observations of IO in the region of study. Thus, we have included model IO

531 output from GEOS-Chem and CAM-Chem, both of which use the SST based MacDonald et  
532 al. (2014) parameterisation for SSI (Fig. 4b). The surface IO output from GEOS-Chem predicts  
533 the highest levels of IO up to 1.7 pptv to the north of the equator at 11° N for the time period  
534 of the IIOE-2 campaign. For the same latitudes, the model suggests lower IO levels, of less  
535 than 0.5 pptv, during the ISOE-8 campaign. Conversely, south of the equator to 10° S, the  
536 model predicts higher IO levels during the ISOE-8 and lower IO values during the IIOE-2, in  
537 agreement with the observations. Below 10° S, IO predictions for both campaigns match well  
538 until 20° S, which was the latitudinal limit for the IIOE-2 campaign. To the south of 20° S,  
539 modelled IO levels remained below 1 pptv and exhibited a decreasing trend to the south of the  
540 polar front, in disagreement with IO observations. At locations between 40° S and 43° S,  
541 GEOS-Chem underestimates the observed IO levels by 50 %. These locations are close to the  
542 Kerguelen Islands, and high IO values were observed here only during the ISOE-8. These  
543 locations have been omitted in the correlation study between modelled and observed IO as they  
544 could be impacted by coastal or upwelling emissions, which are not well prescribed in the  
545 models.

546 The CAM-Chem IO surface output suggests consistently higher levels of IO during IIOE-2  
547 compared to the ISOE-8 for the same latitudinal band (Fig. 4b). Contrary to the observations,  
548 the CAM-Chem model suggests that IO levels during the IIOE-2 are up to 1 pptv higher than  
549 the ISOE-8 campaign near 7° S latitude. The model also shows elevated IO levels of 2.7 pptv  
550 at 7.9° N during the IIOE-2 campaign, which does not match the observations during the IIOE-  
551 2 or the ISOE-8 for that region. IO levels below 1.5 pptv (11° N to 20° S) are indicated for the  
552 ISOE-8 campaign. In addition, the region between 0° and 1.5° S has similar IO levels for the  
553 IIOE-2 and ISOE-8 campaigns. The model predicts lower IO levels for the south Indian Ocean  
554 and the Southern Ocean (less than 1 pptv) with decreasing IO to the south of the polar front.  
555 However, at 43° S, the model suggests higher IO (2.4 pptv) during the ISOE-9, which matches

556 the increase in observed IO for that region during the ISOE-8 expedition, with this region being  
557 close to the Kerguelen Islands Both models show consistently higher absolute concentrations  
558 overall compared to the observations north of the polar front.

## 559 **4. Discussion**

### 560 **4.1 Seawater iodide**

561 To improve the estimation of SSI in the study region, previously established parameterisations  
562 (Eq. 1 and 4) were modified to obtain a region-specific parameterisation for SSI concentrations.  
563 SSI estimated using these modified parameterisations were less sensitive to seasonal salinity  
564 and SST changes for the north Indian Ocean basin compared to the existing parameterisation  
565 (Fig 3). Figure 6 shows the correlations of all the calculated SSI concentrations with the  
566 observations. The SSI estimates from Eq. 1 to 6 correlate positively (significantly) to the  
567 measured SSI concentrations (observations) from ISOE-9 (Fig. 6). Out of the six  
568 parameterisation tools compared in this study, as expected, SSI from Eq. (2) i.e. the modified  
569 Chance equations for the Indian Ocean and the Southern Ocean showed the best correlation  
570 with the measured SSI because they were created using datasets from these campaigns (Fig. 6  
571 and Table 2). Although the region-specific parameterisations were expected to match with the  
572 observations they are based on, there was a notable difference between predictions and  
573 observations when this approach was applied only to Indian Ocean SSI measurements from  
574 SK-333 and BoBBLE ( $R^2 = 0.5$  for Indian Ocean parameterisation, analysis not shown). This  
575 could be attributed to the lack of SSI measurements in this region ( $n=18$ ), and it highlights the  
576 fact that there may be not only seasonally but regionally varying complexities in SSI which  
577 should be considered when estimating SSI. All parameterisation methods used for SSI  
578 estimations show that SSI concentrations are directly proportional to seawater salinity (listed  
579 in Sect. 2.3). It is evident from Fig. 5d and Fig. 3a that to the north of the equator, the



580 parameterisations (Eq. 1 to 5) show lower SSI concentrations in regions with lower salinity (up  
581 to 5° N during ISOE-8 – filled symbols Fig. 3) and higher SSI concentrations in regions with  
582 comparatively higher salinity (during IIOE-2 – unfilled symbols Fig. 3). Only the modelled  
583 SSI concentrations using Eq. 6 (Fig. 3a, data in purple) reveal an inversely proportional  
584 relationship for salinity and SSI concentration in this region. The Sherwen et al. (2019)  
585 parametrisation (Eq. 6) produces lower SSI concentrations in high salinity Arabian Sea waters  
586 during IIOE-2 (Fig. 3a) north of 5° N, compared to the low salinity Bay of Bengal waters during  
587 ISOE-8 which contradicts all the other parameterisation (Eq. 1 to 5). Further, the SSI  
588 concentrations obtained from Sherwen et al. (2019) reverse their trend to the south of 6° N,  
589 with higher concentrations during IIOE-2 and lower during ISOE-8. It should be noted that  
590 only a few observations of SSI exist in this region to confirm this trend. Further discussion on  
591 the relationship between salinity and other biogeochemical variables with SSI concentrations  
592 at a global and regional scale can be found elsewhere (Chance et al., 2014, 2019).

593 SSI estimates considering only SST as a proxy for iodide concentration (Eq. 4), reveal positive  
594 correlations with measured SSI concentration ( $R = 0.86$ ,  $P < 0.001$ ,  $n = 129$ ; Fig. 6d). The  
595 modified MacDonald parameterisation (Eq. 5) also correlates positively to the measured SSI  
596 concentration but has a slightly lower coefficient of correlation ( $R = 0.83$ ,  $P < 0.001$ ,  $n = 129$ ;  
597 Fig. 6e). When using the SST as a proxy for SSI, a large intercept was obtained for the SSI  
598 values, evidencing the discrepancy in absolute value between this parametrisation and the  
599 observations. Eq. (5) resulted in a lower intercept, approximately half of that for Eq. (4), and a  
600 lower absolute slope value of  $|-3763 \pm 218|$  compared to the  $|-9134 \pm 613|$  of Eq. (4) given in  
601 MacDonald et al. (2014). The lower absolute slope value for Eq. (5) implies that the SSI  
602 concentrations for this region were less sensitive to the changes in SST compared to that in Eq.  
603 (4).

604 Despite the lower R-value, the SSI estimates from Eq. 5 in Fig. 3 are closer to the measured  
605 SSI concentration than the estimates from Eq. 2 and 3 for the region from 25° S to 70° S.  
606 However, north of 25° S, the SSI estimates from Eq. 3 and Eq. 5 differ by ~40 %. Both SST  
607 based parameterisation (Eq. 4 and 5) did not show the observed latitudinal variation in the SSI  
608 concentrations near the equator. Linear regression of SSI with SST for only the Indian Ocean  
609 region revealed that there was no correlation between the two ( $R^2 = 0.07$ ,  $P = 0.3$ ,  $n = 18$ ). The  
610 SSI in this region only showed dependence on the salinity and latitude, correlations with the  
611 other parameters were not significant. This highlights that SST may not be a very good proxy  
612 for SSI in the Indian Ocean, especially near the equator. This is explored further in Chance et  
613 al. (2020). The original Chance et al. (2014) parameterisation displays higher sensitivity to  
614 seasonal salinity changes compared to the existing and modified parameterisation in the Indian  
615 Ocean region (Sect. 3.3). However, this method predicted increasing iodide concentration to  
616 the south of the polar front (47° S), which is not supported by observations in this region (Fig.  
617 3). In conclusion, considering the correlation with measured SSI concentration and dependence  
618 on seawater salinity, the region-specific modified Chance parameterisation (Eq. 2) is a suitable  
619 method to estimate SSI concentration for the Indian Ocean and Southern Ocean region. The  
620 modelled SSI estimates by Sherwen et al. (2019) capture SSI trend close to equator better than  
621 other existing schemes but it fails to replicate higher SSI observations at locations 8° N, 40° S  
622 and to the south of 65° S close to the Antarctic coast (Fig. 3).

## 623 **4.2 Atmospheric iodine**

624 Combined IO observations from IIOE-2, ISOE-8, and ISOE-9 (Fig. 4a) show that the Indian  
625 Ocean region has comparatively less IO in its MBL than the Southern Ocean region. IO  
626 remained below 1 pptv up to 40° S and reached a maximum IO of 1.6 pptv south of the polar  
627 front. Modelled surface IO output from GEOS-Chem and from CAM-Chem using the  
628 Macdonald et al. (2014) parameterisation (Fig. 4b) do not match the observations of IO,

629 although they generally show good agreement with each other. The models show similar spatial  
630 patterns across the entire dataset, except for two periods of very high IO levels predicted by  
631 CAM-Chem (Fig. 4b). As well as structural differences between CAM-Chem and GEOS-  
632 Chem, there are many halogen specific differences in rate constants, heterogeneous  
633 parameters, cross-sections and photolysis of species (e.g. higher iodine oxides) which could  
634 explain differences in predicted gas-phase IO. Considering the generally lower wind speeds  
635 and higher ozone concentrations seen in IIOE-2 versus SOE-8 and SOE-9, the calculated fluxes  
636 are higher and therefore more sensitive to assumptions, such as minimum wind speeds provided  
637 to the Carpenter et al. (2013) parameterisation. GEOS-Chem uses a minimum wind speed of 5  
638  $\text{m s}^{-1}$ ; however, CAM-Chem uses a minimum wind speed of  $3 \text{ m s}^{-1}$  and hence fluxes calculated  
639 using the surface winds in these models are expected to be slightly different.

640 Both models suggest higher than observed IO levels in the Indian Ocean region but under-  
641 predict IO for the Southern Ocean region. The highest detected IO levels, both in the Southern  
642 Ocean and in a narrow band around  $43^\circ \text{ S}$ , were not reflected in the model predictions. We note  
643 these occurred in regions of elevated chl-*a* values (Fig. 4e) close to the Kerguelen Islands.  
644 Mahajan et al. (2019a) also reported positive correlations for IO with chl-*a* for the Indian Ocean  
645 region, above the polar front for a subset of the dataset (ISOE-8). Calculated fluxes of HOI and  
646  $\text{I}_2$  (Fig. 4c and d) fail to directly explain trends in the detected IO levels for the entire dataset,  
647 regardless of the method used to estimate SSI. Maximum levels of HOI and  $\text{I}_2$  predicted to the  
648 north of  $5^\circ \text{ N}$  correspond to rather low levels of IO ( $< 0.5 \text{ pptv}$ ) in this region. However, this  
649 has been attributed to  $\text{NO}_x$  titration of IO (Mahajan et al., 2019b). The models, however, do  
650 not capture this iodine titration by  $\text{NO}_x$  as seen in the observations; even though the reactions  
651 of IO with  $\text{NO}_x$  are included (Ordóñez et al., 2012). Similarly, for the region south of the polar  
652 front, the calculated iodine fluxes remain low in the region of the maximum detected IO  
653 concentrations during the ISOE-8 and ISOE-9 campaigns. Iodine fluxes estimated for the

654 Indian Ocean region (15° N to 5° N) during IIOE-2 and ISOE-8 show large differences with  
655 much higher values during ISOE-8. However, the modelled IO is in fact higher for IIOE-2 than  
656 during ISOE-8 (5°-15°N). Considering that the models do not reflect the fluxes, this indicates  
657 that either photochemistry or dynamical dilution of the fluxes led to this difference in the  
658 model. Additionally, the elevated levels of IO predicted in the models suggest that CAM-Chem  
659 and GEOS-Chem overestimate the impact of iodine chemistry in the northern Indian Ocean.

660 In Fig. 7, correlations of iodine fluxes estimated using the measured SSI concentrations (Eq.  
661 2) show that fluxes of HOI correlate positively with tropospheric ozone ( $R = 0.56$ ,  $P < 0.001$ )  
662 and negatively to wind speed ( $R = -0.62$ ,  $P < 0.001$ ) and  $I_2$  fluxes correlate positively with SSI  
663 concentration ( $R = 0.56$ ,  $P = P < 0.001$ ) and ozone ( $R = 0.59$ ,  $P < 0.001$ ) and negatively to wind  
664 speed ( $R = -0.4$ ,  $P < 0.001$ ). This indicates that although there is positive correlation of  $I_2$  with  
665 SSI, the dominant inorganic iodine flux i.e. HOI does not show significant correlation with SSI  
666 concentration, although the flux equation includes an iodide term (Eq. 8). We analysed the  
667 correlation of daily averaged observed IO during the three campaigns with daily averaged  
668 values of oceanic parameters (SST, chl-*a*, salinity, SSI concentration), meteorological  
669 parameters (wind speed, ozone) and calculated inorganic iodine fluxes. We divided the  
670 combined dataset from three campaigns into two regional subsets for the north (Fig. 8a) and  
671 south (Fig. 8b) of the polar front (47° S). The correlation for SSI concentrations is included for  
672 all the seven methods for SSI estimation listed in Sect. 2.3. The fluxes of HOI and  $I_2$  obtained  
673 using the seven different datasets for SSI are included and listed in Fig. 8 in the same order as  
674 the SSI concentration (labelled 1 to 7). IO model output from GEOS-Chem (labelled 8) and  
675 CAM-Chem (labelled 9) is included for the correlation analysis, along with chl-*a* data from  
676 observations during ISOE-8 and ISOE-9 and satellite dataset obtained from MODIS Aqua  
677 (Oceancolor, NASA-GSFC, 2017).

678 For the entire dataset (Fig. 8c), only wind speed shows a statistically significant, positive  
679 correlation with observed IO above the 99 % confidence limit ( $R = 0.4$ ,  $P < 0.001$ ,  $n = 115$ ). A  
680 similar positive correlation with wind speed was found in the subset of data south of the polar  
681 front (Fig. 8b) ( $R = 0.49$ ,  $P = 0.01$ ,  $n = 48$ ), with observations north of the polar front showing  
682 a weaker positive correlation ( $R = 0.27$ ,  $P = 0.08$ ,  $n = 67$ ). Mahajan et al. (2012) showed that  
683 no correlation existed between IO and wind speed over the eastern Pacific Ocean, contrary to  
684 the results in this study. Current estimation methods for iodine emissions have a negative  
685 dependence on wind speed (Eq. 7 and 8). A positive correlation of IO with wind speed could  
686 suggest that increased vertical mixing enables emission of HOI and  $I_2$ , and/or other iodine  
687 gases, thus enhancing IO production in the MBL. However, the interfacial model still over  
688 predicts IO concentrations at low wind speeds due to over prediction of HOI and  $I_2$  emission  
689 (MacDonald et al., 2014). The apparently contradictory results from different studies call for  
690 more observations of IO in the MBL over a range of wind speeds.

691 Salinity and SST show a weak negative correlation with atmospheric IO for the entire dataset  
692 and for the north of the polar front region. This indicates that even if the physical parameters  
693 are significant for the initial parametrisation for SSI and inorganic flux estimation, there is no  
694 direct and significant correlation of these parameters with the atmospheric IO. However, south  
695 of the polar front, SST correlates positively above the 99 % limit ( $R = 0.52$ ,  $P = 0.01$ ,  $n = 48$ )  
696 and salinity correlates positively above the 95 % limit ( $R = 0.44$ ,  $P = 0.03$ ,  $n = 48$ ). Ozone  
697 correlates negatively with IO above 95 % limit ( $R = -0.4$ ,  $P = 0.046$ ,  $n = 47$ ), which could  
698 indicate catalytic destruction of tropospheric ozone through atmospheric iodine cycling in the  
699 south of the polar front. This highlights that although these physical parameters may be  
700 required for iodine fluxes, IO levels may only be weakly related to them.

701 The calculated SSI concentrations and the HOI and  $I_2$  fluxes calculated using these SSIs all  
702 show a significant negative correlation with the observed IO concentrations above the 95 %

703 confidence limit for the entire dataset (except for the HOI flux estimated from the MacDonald  
704 et al. (2014) parameterisation, which shows no significant correlation). The positive correlation  
705 of the observed IO with wind speed is a potential driver for the negative correlation of observed  
706 IO with the calculated HOI and I<sub>2</sub> fluxes, which decrease with wind speed.

707 Measured iodide levels (labelled 4) and the I<sub>2</sub> and HOI fluxes calculated from them (also  
708 labelled 4) show no correlation with the observed IO levels across the entire dataset, although  
709 iodide shows a significant positive correlation ( $R = 0.55$ ,  $P = 0.04$ ,  $n = 32$ ) for IO measured  
710 south of the polar front. Mahajan et al. (2019a) pointed out that SST negatively correlated with  
711 IO for the ISOE-8 campaign, contradicting the previous results for observations in the Pacific  
712 Ocean (Großmann et al., 2013; Mahajan et al., 2012). Here, SST shows a significant positive  
713 correlation with observed IO ( $R = 0.52$ ,  $P = 0.006$ ,  $n = 48$ ) south of the polar front above the  
714 99 % confidence limit, but there is no correlation north of the polar front and only a weak  
715 negative correlation using the combined dataset from the three campaigns ( $R = -0.18$ ,  $P = 0.13$ ,  
716  $n = 119$ ).

717 Despite the above-mentioned point regarding the increase in observed IO levels in regions of  
718 elevated chl-*a*, there is only a weak and negative correlation of IO with chl-*a* (both from  
719 observations and satellite data) south of the polar front. However, there is a strong positive  
720 relationship north of the polar front ( $R = 0.696$ ,  $P = 2.3 \times 10^{-4}$ ,  $n = 29$ ). In fact, for the region  
721 north of the polar front, chl-*a* shows a significant positive correlation with observed IO above  
722 the 99 % confidence limit ( $P < 0.001$ ). The GEOS-Chem and CAM-Chem output also shows a  
723 significant positive correlation (Fig. 8) which may result from the dependency of organic iodine  
724 species on oceanic chl-*a* in both GEOS-Chem and CAM-Chem. Figure 8 shows a large  
725 difference in correlation values for chl-*a* data obtained from observations and satellite (MODIS  
726 Aqua, NASA, GSFC; <https://oceancolor.gsfc.nasa.gov>; extracted for the same locations as the  
727 [in situ data](#)). In situ, observed chl-*a* showed an improved correlation with IO compared to those

728 with satellite chl-*a*. Figure 9 shows linear fits for chl-*a* from in situ observations and satellite  
729 against IO for the entire dataset and north of polar front subset. For the entire dataset,  
730 correlation of chl-*a* with IO from both observations and satellite data is not significant. Chl-*a*  
731 from in situ observations positively correlates with IO ( $R = 0.15$ ,  $P = 0.32$ ) while chl-*a* from  
732 satellite data correlates negatively ( $R = -0.13$ ,  $P = 0.26$ ). Correlations of chl-*a* with IO improves  
733 for the north of polar front for chl-*a* from observations ( $R = 0.696$ ,  $P = 0.0002$ ), but chl-*a* from  
734 satellite data shows a statistically insignificant correlation with IO ( $R = 0.08$ ,  $P = 0.57$ ). The  
735 discrepancies in chl-*a* from observations and satellite data will make it difficult to identify links  
736 between the organic parameter and atmospheric IO and expand this to a global scale. It should  
737 be noted that one study in the Pacific has shown that the contribution of combined biogenic  
738 iodocarbon fluxes to IO does not explain the observed IO (Hepach et al., 2016).

739

740 Despite the observed negative relationship of IO with wind speed noted above, note that the  
741 GEOS-Chem IO model output (which is dependent on the calculated HOI and I<sub>2</sub> fluxes) shows  
742 a significant positive correlation with observed IO above the 99 % confidence limit for data  
743 south ( $R = 0.78$ ,  $P = P < 0.001$ ,  $n = 48$ ) and north ( $R = 0.69$ ,  $P = P < 0.001$ ,  $n = 68$ ) of the polar  
744 front, although there is no correlation across the entire dataset. Note that the model  
745 underestimates IO values by 1 pptv south of the polar front and generally overestimates IO, by  
746 ~1.5 pptv, north of the polar front (Fig. 4). A linear fit for observed IO against modelled IO for  
747 north and south of the polar front (Fig. 10) shows significant positive correlation of GEOS-  
748 Chem output with observed IO, but with very different slopes north of the polar front (where  
749 the models overestimate IO) and south of the polar front (where the models underestimate IO).  
750 Hence, even though the correlations are good in the individual regions, the model does not  
751 accurately reproduce the observed absolute concentrations.

## 752 **5. Conclusions**

753 In this study, region-specific parameterisation tools were devised for sea surface iodide (SSI)  
754 estimation following previous SSI estimation methods from Chance et al. (2014) and  
755 MacDonald et al. (2014). New observations of SSI from ISOE-9, SK-333 and BoBBLE (Indian  
756 and the Southern Ocean) were used to create region-specific SSI parameterisations. An average  
757 difference of up to 40 % in SSI concentration was observed among the existing  
758 parameterisations (Eq. 1, 4, and 6) and the difference was 21 % for the region-specific ones  
759 (Eq. 2, 3, and 5). Comparison of estimated SSI concentrations from various parameterisations  
760 with observed SSI and sensitivity to seasonal salinity changes showed that the modified Chance  
761 parameterisation (Eq. 2) was most suitable relative to the SST based parameterisation (Eq. 5)  
762 for SSI estimation in the Indian Ocean and Southern Ocean region. Since the existing global  
763 parameterisation schemes (Eq. 1 and 3) fail to match measured SSI in this region, it highlights  
764 the need to conduct more observations of SSI in the Indian Ocean and Southern Ocean region  
765 to fully understand and estimate the impact of seasonally varying, region-specific parameters  
766 (like salinity, reversing winds patterns) influencing the seawater iodide concentration in this  
767 region. Alternatively, a region-specific parameterisation scheme may be included in the global  
768 models for better representation of seawater iodine chemistry in the Indian and Southern Ocean  
769 region. Modelled estimates from Sherwen et al. (2019) also captured SSI well, although some  
770 high concentrations in the northern Indian Ocean region were not captured. SSI estimation from  
771 SST alone under-predicts SSI for the Indian Ocean, and so is not considered to be suitable for  
772 SSI estimation in the Indian Ocean region. Although, improving SSI concentration in models  
773 for the Indian Ocean and Southern Ocean region may improve the estimation of seawater iodine  
774 chemistry, it does not translate to estimating the atmospheric iodine chemistry in this region.  
775 An accurate estimation of inorganic iodine fluxes (HOI and I<sub>2</sub>) is hence necessary to explain  
776 observed levels of IO in the remote open ocean marine boundary layer. However, these first



777 concomitant observations of SSI and IO show that these inorganic fluxes, estimated in this  
778 study, fail to explain detected IO levels for the entire dataset. No significant correlation was  
779 seen between the SSI from different parameterisation techniques or estimated inorganic iodine  
780 fluxes with observed IO levels. Fluxes estimated using iodide from different parameterisation  
781 and measured iodide did not show large variation in values and followed a similar latitudinal  
782 trend. This is indicative that the inorganic iodine flux parameterisation is not highly sensitive  
783 to the SSI parameterisation. Predicted inorganic iodine fluxes did not explain iodine chemistry,  
784 as indicated by IO levels, in the atmosphere above the Indian and Southern Ocean (Indian  
785 Ocean sector). Chl-*a* shows a positive correlation with IO for the north of the polar front region,  
786 suggesting that biologically emitted species could also play a role in addition to ozone and  
787 iodide derived inorganic emissions of HOI and I<sub>2</sub>. Finally, model predictions of IO  
788 underestimate IO levels for the Southern Ocean region but overestimate IO in the Indian Ocean.  
789 Models greatly underestimate IO in regions with higher chl-*a* concentration which could be  
790 indicative of organic species playing a role (close to the Kerguelen Islands, refer Sect. 3.4.2).  
791 This study suggests that the fluxes of iodine in the MBL are more complex than considered at  
792 present and further studies are necessary in order to parameterise accurate inorganic and  
793 organic fluxes that can be used in models. Using seawater iodide measurements and  
794 calculations from different parameterisations did not alter the inorganic iodide flux estimate  
795 greatly. Direct observations of HOI and I<sub>2</sub>, alongside volatile organic iodine measurements in  
796 the MBL are necessary in order to reduce the uncertainty in the impacts of iodine chemistry.

## 797 **6. Author contributions:**

798 ASM conceptualised the research plan and methodology. SI did the data curation, analysis, and  
799 writing of the original draft. LT and RC did the iodide measurements provided unpublished  
800 iodide data from ISOE-9, SK-333 and BoBBLE. PS and RCo provided salinity data for ISOE-  
801 9. SCT and AUK provided chl-*a* data for ISOE-9. AKS and PVB provided chl-*a* data for SK-

802 333. AS and RR provided chl-a data from BoBBLE. CC and ASL did the CAM-Chem model  
803 run for ISOE-9 and IIOE-2. TS did the GEOS-Chem model run for ISOE-9, IIOE-2 and ISOE-  
804 8.

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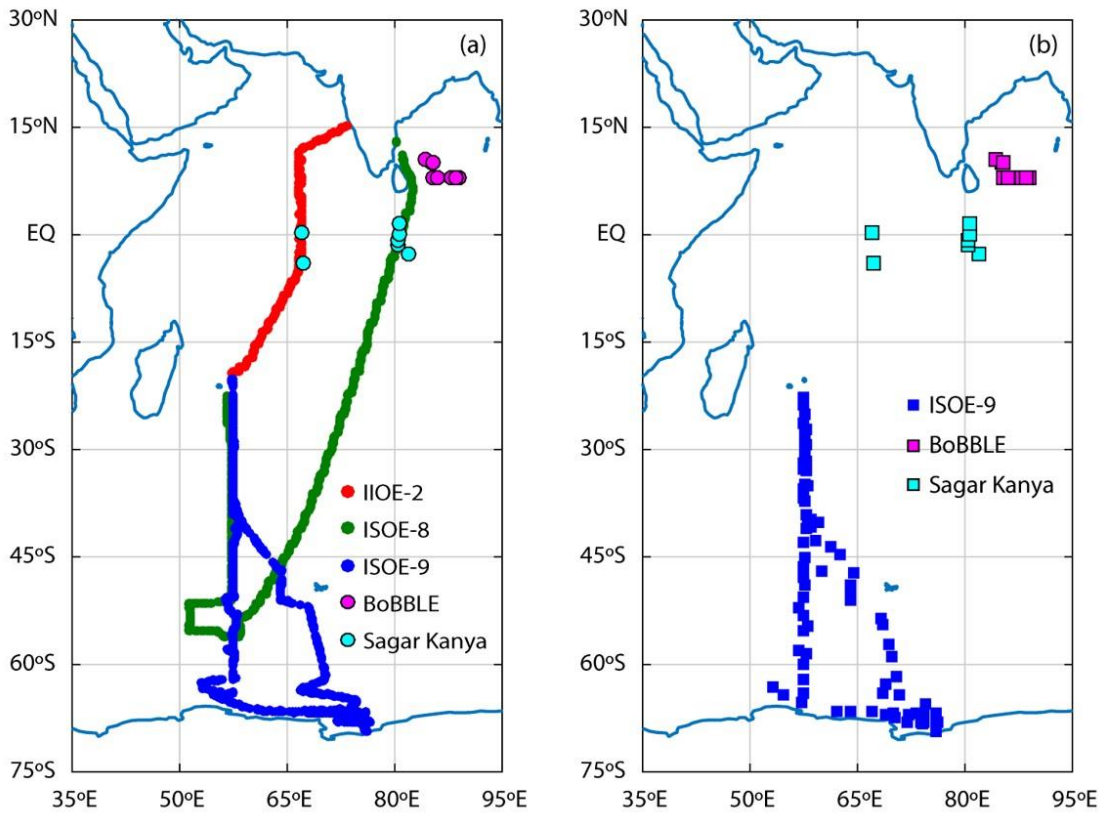
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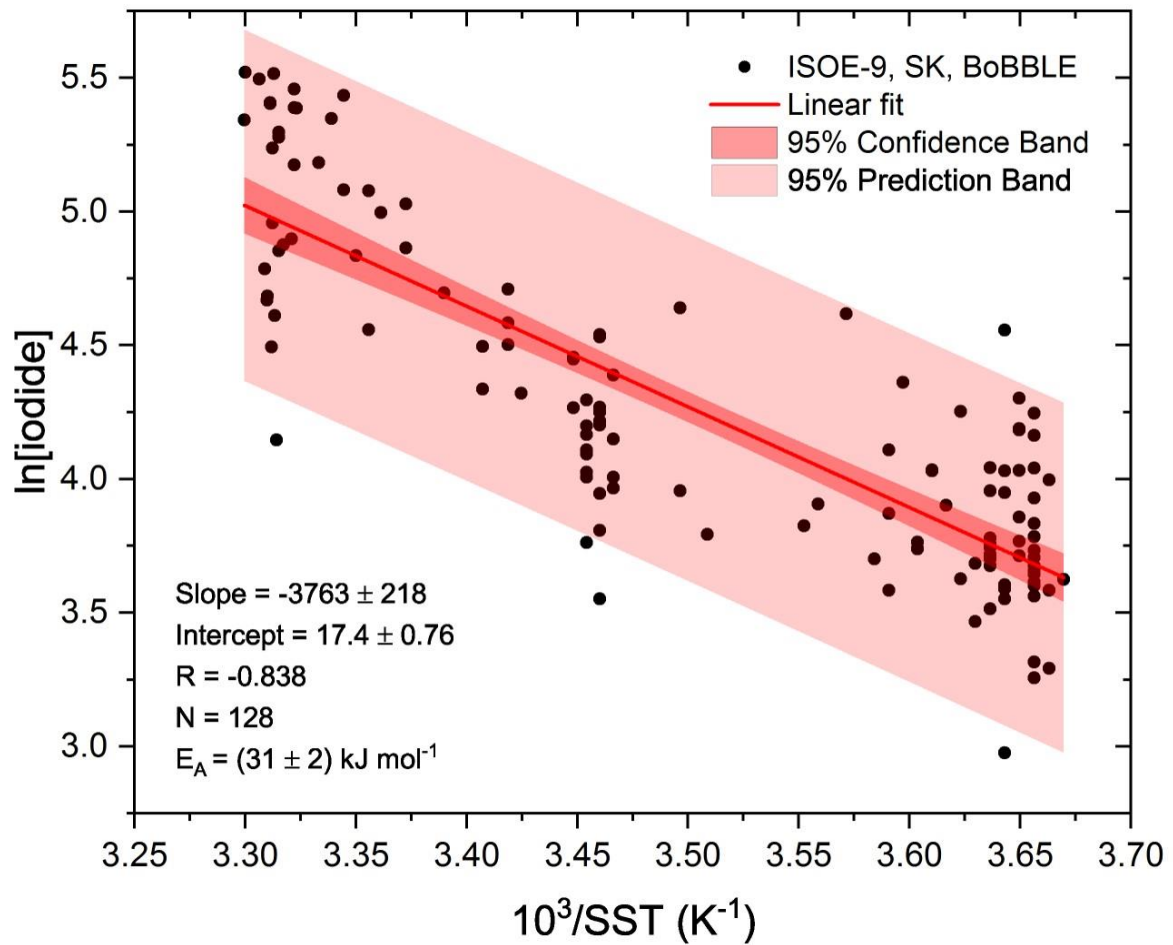
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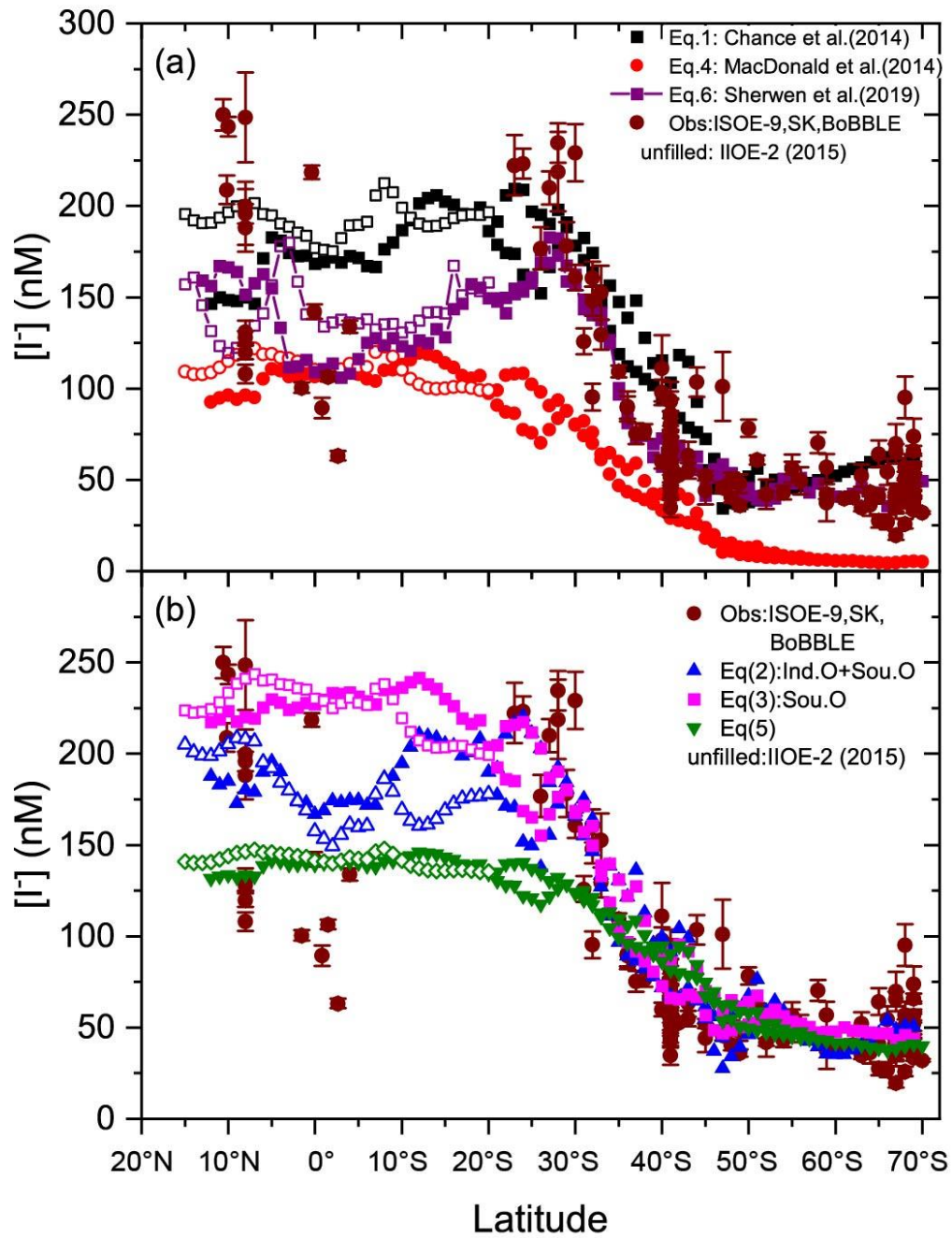
1070 **Figure 1: Map of the Indian Ocean and the Southern Ocean (a) with cruise tracks for**  
 1071 **campaigns conducted during the austral summer of 2014-2016. Green circles indicate the**  
 1072 **cruise track for ISOE-8, red circles show the cruise track for IIOE-2, and blue circles**  
 1073 **indicate the cruise track for ISOE-9. Magenta and cyan circles indicate sample locations**  
 1074 **for the BoBBLE and SK-333 expeditions respectively. (b) boxes represent 129 seawater**  
 1075 **iodide sampling locations from 3 expeditions following the colour code in (a).**



1076

1077 **Figure 2: Arrhenius form plot of sea surface iodide concentrations against SST from all**  
 1078 **available seawater iodide field observations in the Indian Ocean and Southern Ocean.**  
 1079 **The red line represents a linear fit., the shaded region in dark red (inner) indicates the**  
 1080 **95% confidence bands and shaded area in light red (outer) indicates the 95% prediction**  
 1081 **bands.**

1082

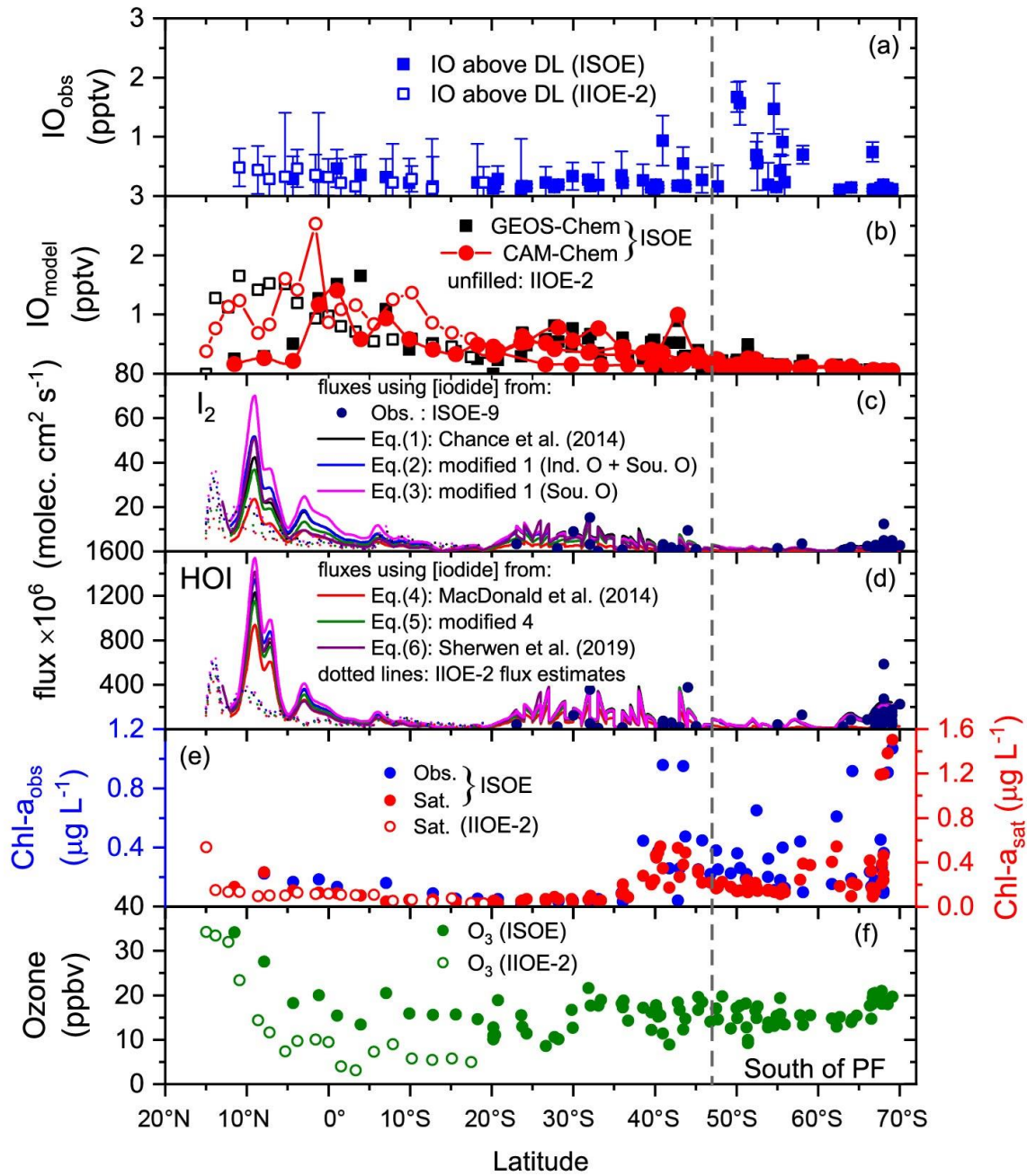


1083

1084 **Figure 3: Latitudinal averages of calculated sea surface iodide (SSI) concentrations for**  
 1085 **each campaign using (a) existing, (b) new parameterisation tools and observations from**  
 1086 **ISOE-9, SK-333, and BoBBLE. Filled markers represent combined SSI from ISOE-8 and**  
 1087 **ISOE-9, unfilled markers represent SSI from IIOE-2 campaign.**

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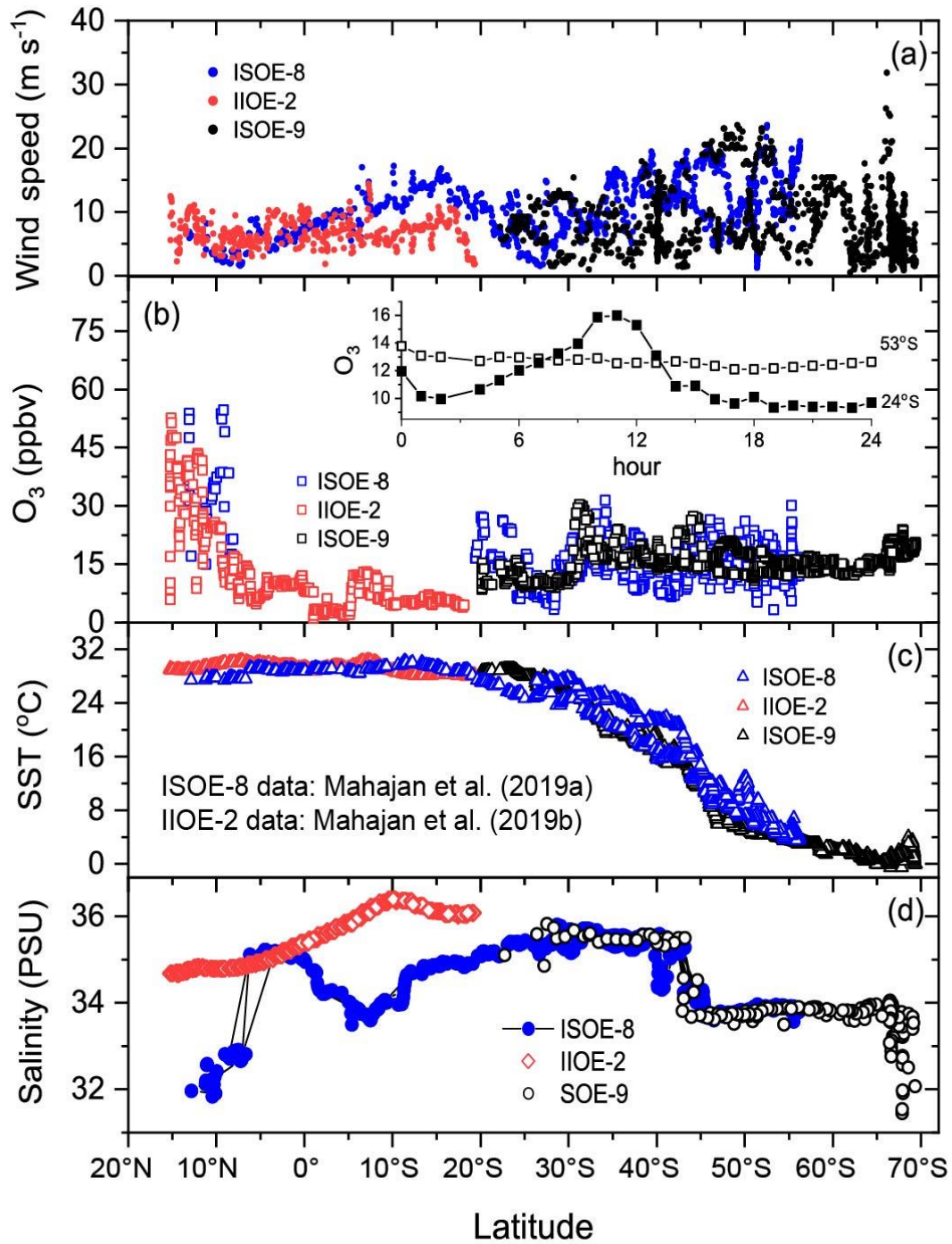


1089

1090 **Figure 4: Daily averaged atmospheric and oceanic parameters combined from ISOE-8,**  
 1091 **IIOE-2, and ISOE-9 field campaigns. Data marked ISOE represents combined data from**  
 1092 **ISOE-8 and ISOE-9. Unfilled markers and dotted lines show values for IIOE-2. (a)**  
 1093 **IO above detection limit from ISOE-8, ISOE-9 and IIOE-2. (b) Surface IO values from**  
 1094 **GEOS-Chem and CAM-Chem models. (c) and (d) comprise of HOI and I<sub>2</sub> fluxes**  
 1095 **estimated from Eq. (7) and (6) respectively. Fluxes are colour coded for different sea**  
 1096 **surface iodide (SSI) datasets used for their estimation. Colours black, blue, red and green**  
 1097 **correspond to fluxes calculated using SSI estimation from Eq. (1) to (5), purple colour**  
 1098 **represents the use of model SSI predictions (Sherwen et al., 2019b), filled circles in dark**  
 1099 **blue correspond to measured SSI from ISOE-9 for each observation, (e) chlorophyll-*a***  
 1100 **observations from ISOE-8 and ISOE-9 (blue circles) and satellite data for all campaigns**

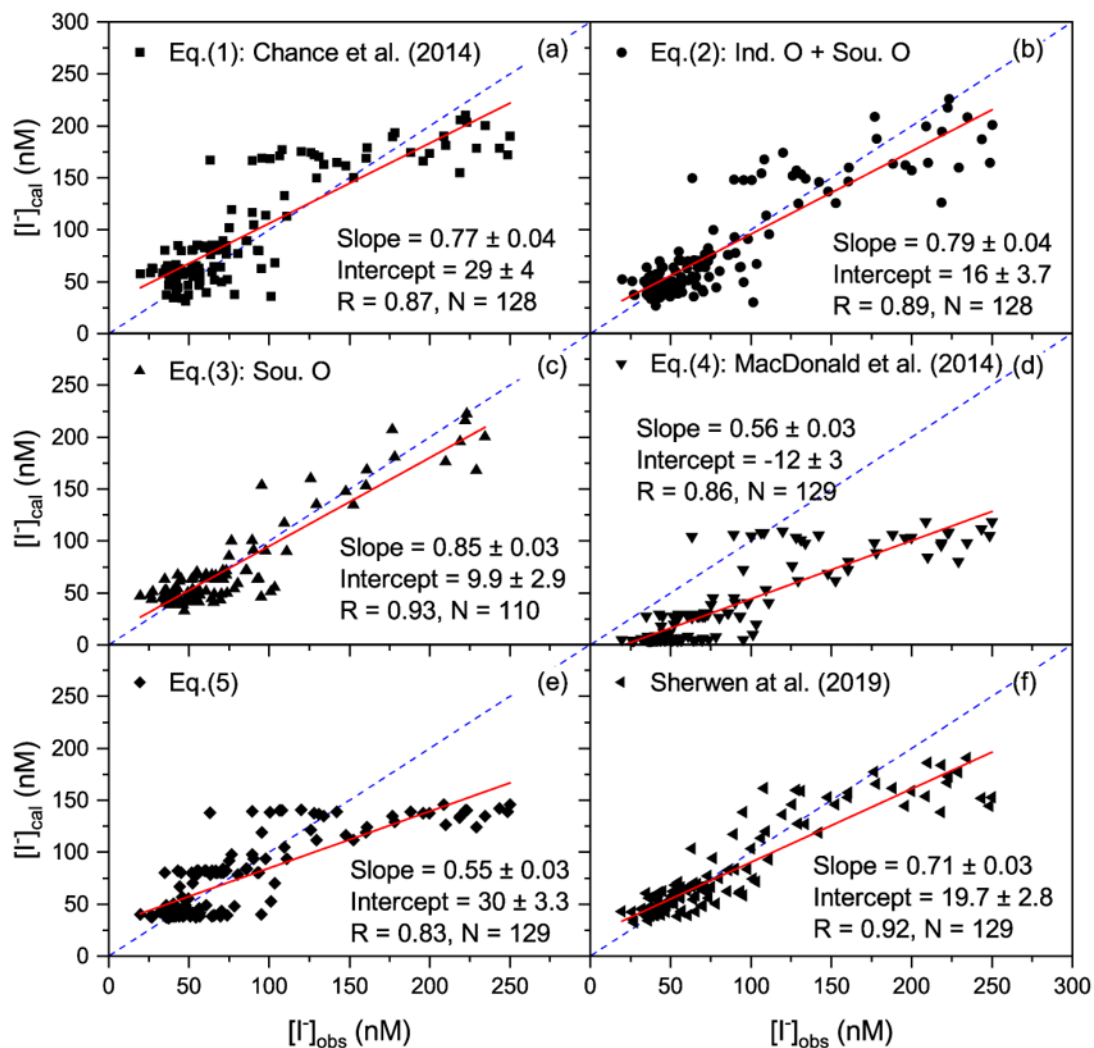
1101 (red circles). (f) ozone mixing ratios from campaigns ISOE and IIOE-2. The dashed line  
 1102 marks the polar front at 47° S. Observational plots for ISOE-8 and IIOE-2 were adapted  
 1103 from Mahajan et al. 2019 a & b. The vertical dashed line through the figure indicates the  
 1104 PF (Polar Front).

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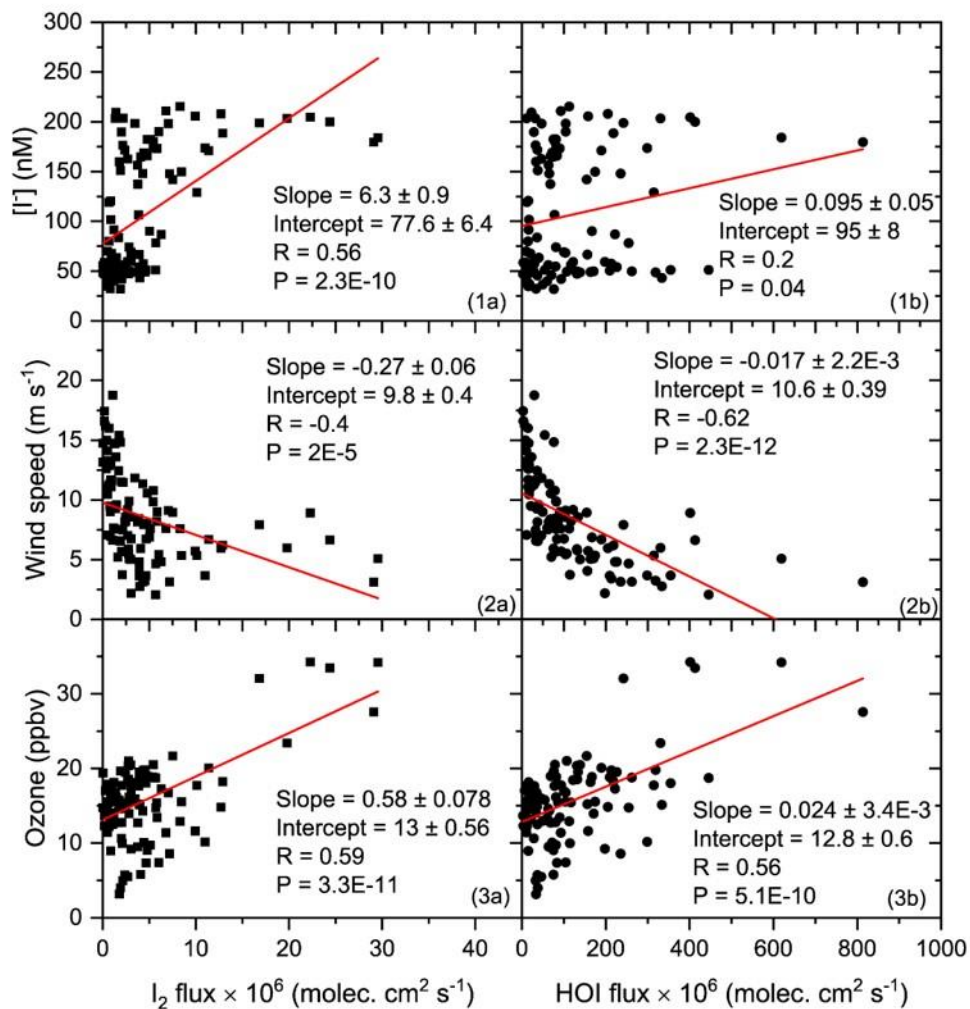
1107 **Figure 5: Latitudinal plot of hourly-averaged field measurements of wind speed, ozone**  
 1108 **mixing ratios, SST and salinity<sup>†</sup> from ISOE-8, IIOE-2, and ISOE-9 campaigns. Data**  
 1109 **markers in red belong to the IIOE-2 campaign; those in blue belong to the ISOE-8 and**  
 1110 **markers in black are from ISOE-9 for all the panels. Observational plots for ISOE-8 and**  
 1111 **IIOE-2 were adapted from Mahajan et al. 2019 a &b.**



1112  
 1113 **Figure 6: Linear fit analysis of estimated sea surface iodide (SSI) concentrations (y axis)**  
 1114 **from parameterisation methods in Eq. (1) to (5) and model prediction (Sherwen et al.,**  
 1115 **2019) against measured SSI concentration (x axis) from ISOE-9, SK-333 and BoBBLE.**

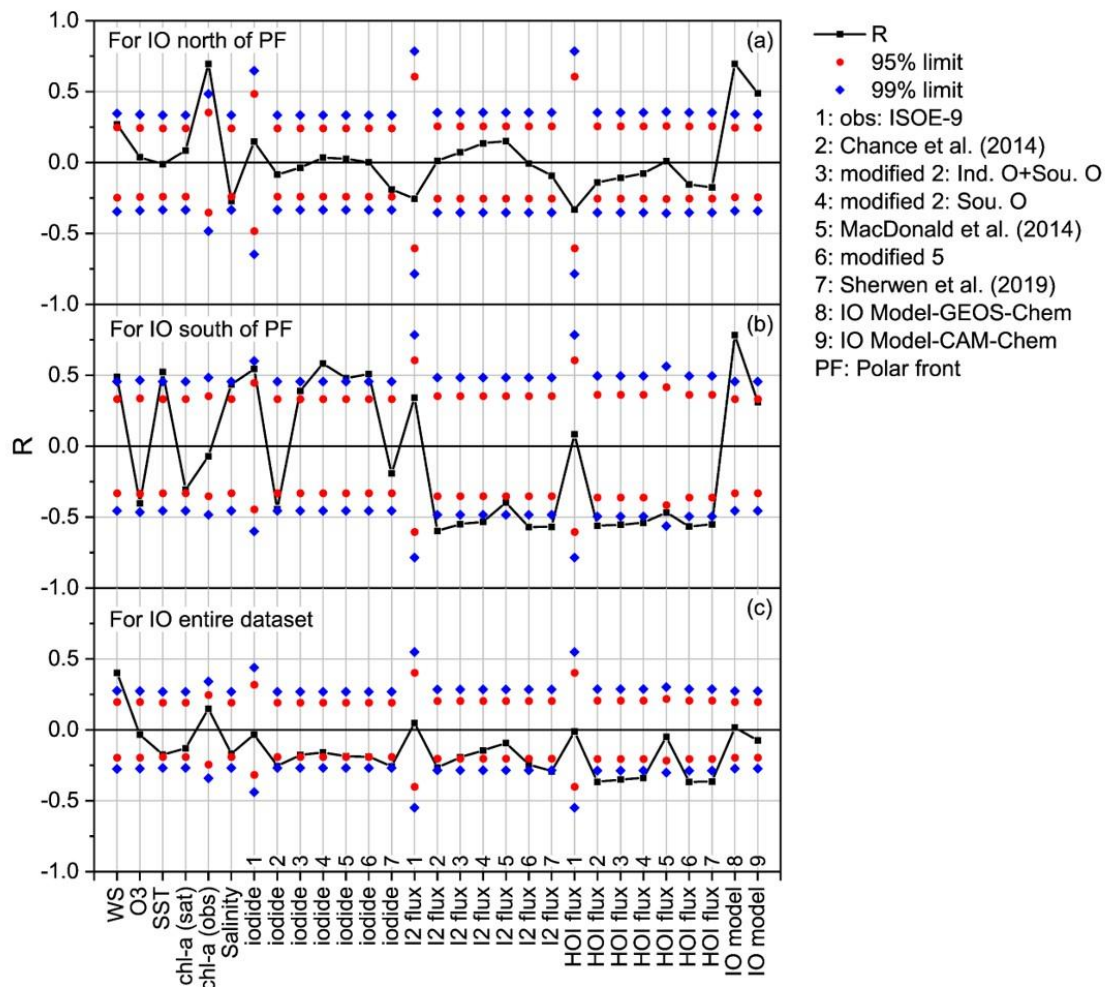
<sup>†</sup> Salinity data for IIOE-2 are monthly climatological means from World Ocean Atlas as described in the supplementary text.

1116 In panel (c) SSI are compared only with ISOE-9 observations for Southern Ocean specific  
 1117 parameterisation. R represents Pearson's correlation coefficient and N is the size of the  
 1118 dataset. Dashed blue line represents identity (1:1) line.  
 1119  
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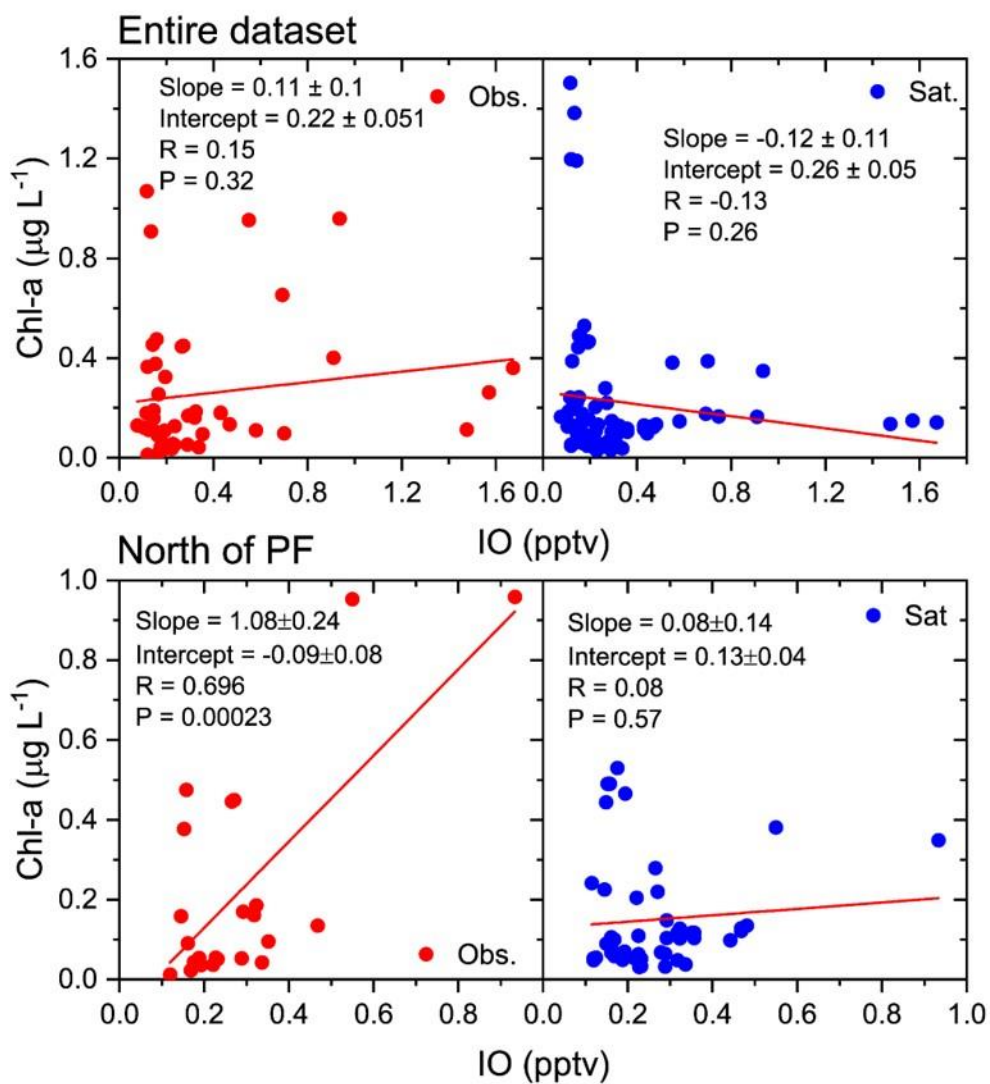


1121  
 1122 **Figure 7: Linear fit of daily average sea surface iodide (SSI) concentration, wind speed**  
 1123 **and ozone mixing ratio (y axis) against calculated I<sub>2</sub> and HOI flux (x axis) against for all**  
 1124 **the campaign. HOI and I<sub>2</sub> are calculated using SSI estimated using the modified Chance**  
 1125 **parameterisation for Indian Ocean and Southern Ocean in Eq. (2).**  
 1126





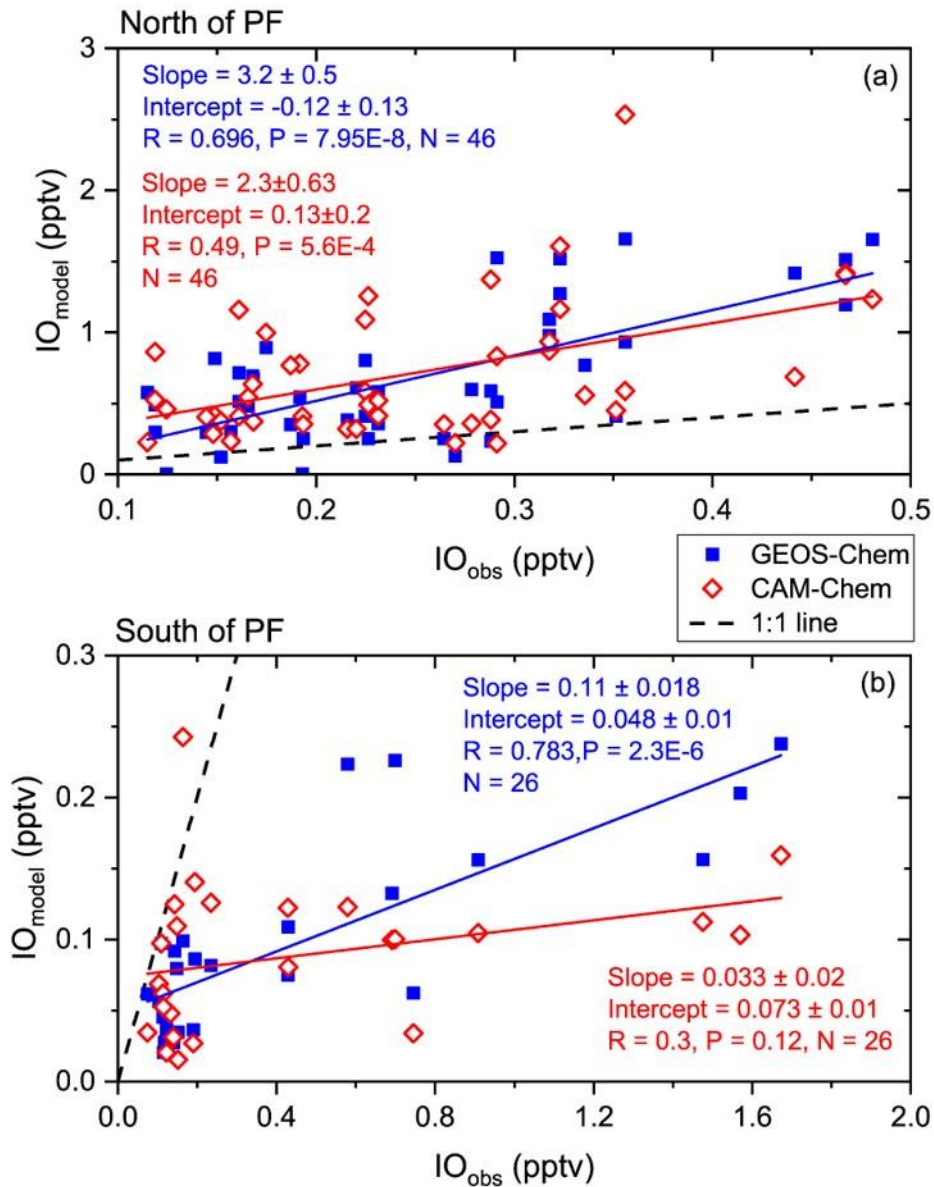
1127  
 1128 **Figure 8: Pearson's correlation coefficient of observed iodine monoxide (IO) with oceanic**  
 1129 **and atmospheric parameters combined for ISOE-8, IIOE-2, and ISOE-9 campaigns.**  
 1130 **Correlations are performed for daily averages of IO and corresponding parameters listed**  
 1131 **on the X axis. The black squares represent Pearson's correlation coefficients (R), the**  
 1132 **diamonds (blue) mark the 99% confidence limit, and the circles (red) correspond to the**  
 1133 **95% confidence limits in all the panels, (a) includes data from all campaigns to the north**  
 1134 **of the polar front (PF) (n = 72), (b) represents combined data for the south of the polar**  
 1135 **front (n = 48), the last panel (c) includes the entire dataset from three campaigns (n =**  
 1136 **120).**  
 1137



1138

1139 **Figure 9: Linear fit of daily averaged field observations of chlorophyll-*a* (red circles) and**  
 1140 **chlorophyll-*a* satellite data (blue circles) (y axis) against observed iodine monoxide (IO)**  
 1141 **(x axis) from ISOE-8, IIOE-2, and ISOE-9 campaigns. The top panel includes**  
 1142 **chlorophyll-*a* for the entire dataset; the bottom panel includes data to the north of the**  
 1143 **polar front.**

1144



1145

1146 **Figure 10: Linear fit of daily averages of modelled surface iodine monoxide (IO) output**

1147 **(y axis) from GEOS-Chem (filled blue squares) and CAM-Chem (unfilled red diamonds)**

1148 **against observed IO (x axis) for ISOE-8, IIOE-2 and ISOE-9 campaigns. (a) includes**

1149 **linear fits of both GEOS-Chem and CAM-Chem for IO detected to the north of the polar**

1150 **front, (b) shows the same for the region south of the polar front. Two data points in panel**

1151 **(a) at 41° S and 43° S are removed due to large differences between observation and**

1152 **modelled values.**

1153

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1156

1157 **10. Tables**

Expedition	Research Vessel	Duration	Location	Meridional Transect	Observations
8 <sup>th</sup> Indian Southern Ocean Expedition (ISOE-8)	Sagar Nidhi, India	7 Jan 2015 to 22 Feb 2015	Indian Ocean from Chennai, India to Port Louis, Mauritius	13° N to 56° S	IO, O <sub>3</sub>
2 <sup>nd</sup> International Indian Ocean Expedition (IIOE-2)	Sagar Nidhi, India	4 to 22 Dec 2015	Indian Ocean from Goa, India to Port Louis, Mauritius	15° N to 20° S	IO, O <sub>3</sub>
Bay of Bengal Boundary Layer Experiment (BoBBLE)	R.V. Sindhu Sadhana	23 June 2016 to 24 July 2016	Southern Bay of Bengal	8° N to 10° N	Seawater samples for I <sup>-</sup>
Sagar Kanya-333 (SK-333)	Sagar Kanya, India	5 Sept 2016 to 20 Sept 2016	Southern Arabian Sea and Southern Bay of Bengal	1.6° N to 4° S	Seawater samples for I <sup>-</sup>
9 <sup>th</sup> Indian Southern Ocean Expedition (ISOE-9)	S A Agulhas, South Africa	6 Jan 2017 to 26 Feb 2017	Indian and Southern Ocean from Port Louis, Mauritius to Antarctica	20° S to 70° S	IO, O <sub>3</sub> , I <sup>-</sup>

1158

1159 **Table 1: Details of the three expeditions contributing to the IO and seawater iodide**  
 1160 **dataset in this study. Expeditions are listed in chronological order from 2015 to 2017.**

1161



Eq. No	Database location	Reference	Parametric equation ([iodide] in nM)	Data points	R <sup>2*</sup>	R <sup>2</sup>
Eq. (1)	Majorly Atlantic and Pacific Ocean	<i>Chance et al. (2014)</i>	$[\text{iodide}] = 0.28(\pm 0.002) \times \text{SST}^2 + 1.7(\pm 0.2) \times  \text{latitude}  + 0.9(\pm 0.4) \times [\text{NO}_3^-] - 0.02(\pm 0.002) \times \text{MLD}_{\text{pt}} + 7(\pm 2) \times \text{salinity} - 309(\pm 75)$	n = 673	0.676	0.758
Eq. (2)	Indian and Southern Ocean	This study	$[\text{iodide}] = 0.36(\pm 0.04) \times \text{SST}^2 - 2.7(\pm 0.5) \times  \text{latitude}  + 0.28(\pm 0.57) \times [\text{NO}_3^-] + 0.64(\pm 0.17) \times \text{MLD}_{\text{pt}} - 5.4(\pm 3.82) \times \text{salinity} + 22(\pm 137)$	n = 128	0.794	0.794 <sup>^</sup>
Eq. (3)	Southern Ocean	This study	$[\text{iodide}] = 0.25(\pm 0.017) \times \text{SST}^2 - 0.6(\pm 0.4) \times  \text{latitude}  + 2.2(\pm 0.4) \times [\text{NO}_3^-] - 5.5(\pm 3.3) \times \text{salinity} + 212(\pm 123)$	n = 110	0.859	0.859 <sup>^</sup>
Eq. (3a)	Indian Ocean	This study	$[\text{iodide}] = 4.56(\pm 6.45) \times  \text{latitude}  - 23.7(\pm 31) \times \text{salinity} + 944(\pm 1096)$	n = 18	0.325	NA
Eq. (4)	Atlantic, Central and West Pacific Ocean	<i>MacDonald et al. (2014)</i>	$[\text{iodide}] = 1.46 \times 10^{15} \times \exp\left(\frac{-9134}{\text{SST}}\right)$	n = ~88	0.71	0.739
Eq. (5)	Indian and Southern Ocean	This study	$[\text{iodide}] = 3.6 \times 10^7 \times \exp\left(\frac{-3763}{\text{SST}}\right)$	n = 129	0.702	0.697 <sup>^</sup>
Eq. (6)	Atlantic, Pacific, Indian and Southern Oceans	<i>Sherwen et al. (2019)</i>	Machine learning based regression approach	n = 1293	NA	0.842

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1163 **Table 2: List of existing global (italicised reference column) and new region-specific**  
1164 **(regular font in reference column) parameterisations for sea surface iodide concentration**  
1165 **indicating data location and number of data points used to formulate each equation. Here**  
1166 **[iodide] represents sea surface iodide concentration in nM, sea surface temperature as**  
1167 **SST (in °C for Eq. (1) to (3), and in K for Eq. (4) to (5)). Nitrate concentration ([NO<sub>3</sub><sup>-</sup>]) is**  
1168 **given in μM, mixed layer depth as MLD<sub>pt</sub> in m, subscript ‘pt’ indicates potential**  
1169 **temperature implying a temperature change of 0.5 °C from the ocean surface (Monterey**  
1170 **and Levitus, 1997), and salinity in PSU. Further details on individual parameters and the**  
1171 **choice of Eq. (1) over others proposed in Chance et al. (2014) are discussed in the**  
1172 **supplementary text. R<sup>2\*</sup> represents the initial coefficient of determination (COD) while**  
1173 **deriving each parameterisation, and R<sup>2</sup> represents COD from correlation analysis of the**  
1174 **calculated iodide with observations in this study (ISOE-9, SK-333, BoBBLE).**

1175 <sup>^</sup>**Higher R<sup>2</sup> values for the modified parameterisations reflect the fact that they have been**  
1176 **derived using the same observational data as they are tested on.**