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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 hypiodous
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 2014-2017 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 (Saiz-Lopez et al.,
59 2006b). Iodine containing precursor compounds undergo photo dissociation to produce iodine
60 atoms (I), which rapidly react with ambient ozone, forming IO (Chameides and Davis, 1980).
61 Until recently, fluxes of volatile organic iodine (e.g. CH_3I , 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., 2010b; 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., 2014b), 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).



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

108 At present, there is a paucity of measurements of SSI, and remote sensing techniques cannot
109 detect iodine species in seawater (Chance et al., 2014; Sherwen et al., 2019a). In particular,
110 regions of the Indian Ocean and the Southern Ocean have been under-sampled in terms of
111 iodine observations in the atmosphere and ocean (Chance et al., 2014; Mahajan et al., 2019a,
112 2019b). It is important to remember that the most widely used parameterisation (MacDonald
113 et al., 2014) is built on a limited observational dataset from the Atlantic and Pacific Ocean
114 completely excluding the Indian Ocean and the Southern Ocean. The parameterisations
115 presented in Chance et al. (2014), are based on a larger data set including Southern Ocean
116 observations, but still only make use of two data points in the Indian Ocean. Furthermore, the
117 Sherwen et al. (2019) parameterisation uses the updated data set including the new Indian
118 Ocean SSI observations used in this study. Compounding the lack of Indian Ocean SSI



119 observations is the fact that parts and in particular the Arabian Sea and the Bay of Bengal, do
120 not follow the same seasonal trends in salinity (D'Addezio et al., 2015) and sea surface
121 temperature (Dinesh Kumar et al., 2016) as each other on the same latitudinal band and hence
122 the currently used global iodide parameterisations in models i.e. MacDonald et al. (2014) may
123 not be appropriate for these areas. Here we use new SSI observations made as part of this study
124 (described in full in Chance et al. (2019b) and included in Chance et al. (2019a)) to test whether
125 the existing parameterisations can be directly applied to the Indian Ocean and if regional
126 specific parameterisations are more accurate compared to the former.

127 Although several measurements of IO have been reported around the globe (Alicke et al., 1999;
128 Allan et al., 2000; Frieß et al., 2001; Großmann et al., 2013; Mahajan et al., 2009, 2010a,
129 2010b; Prados-Roman et al., 2015), the remote open ocean still remains under-sampled. The
130 two documented observations of IO in the Indian Ocean and the Indian sector (Jan-Feb 2015
131 and December 2015) of the Southern Ocean were interpreted using parameterisations to
132 estimate the SSI concentrations in combination with observed ozone concentrations, to
133 subsequently calculate the resulting inorganic iodine fluxes. This approach suggested that the
134 observed atmospheric IO may not be well correlated with the inorganic fluxes and that biogenic
135 fluxes could play an important role (Mahajan et al., 2019a, 2019b). Here, we present
136 measurements of IO in the MBL of the Indian Ocean and the Southern Ocean during the 9th
137 Indian Southern Ocean Expedition (ISOE-9) conducted in January-February 2017, alongside
138 the first simultaneous SSI observations along the cruise track (Chance et al., 2019a). The iodide
139 observations were used to compute the inorganic iodine fluxes to compare with IO observations
140 along the cruise tracks. Further, observed SSI concentrations are used to compute region-
141 specific parameterisations for SSI concentrations, following the approaches taken by Chance
142 et al. (2014) and MacDonald et al. (2014). The iodide concentrations obtained with these
143 region-specific modified parameterisations are compared to the iodide estimates using their



original counterparts and the global machine-learning-based prediction of SSI concentration (Sherwen et al., 2019a). The resulting estimated reactive iodine fluxes (HOI and I₂) are then used to see if the inorganic fluxes can explain the IO loading in the atmospheric MBL.

2. Measurement techniques and methodology

The 9th Indian Southern Ocean Expedition (ISOE-9) was conducted from January to February 2017 in the Southern Ocean and the Indian Ocean sector of the Southern Ocean. The expedition started from Port Louis, Mauritius, and spanned the remote open ocean area till the coast of Antarctica. Observations of IO, SSI and O₃ were made along the cruise track during ISOE-9. For further analysis we also include IO observations from the 2nd International Indian Ocean Expedition (IIOE-2) and the 8th Indian Southern Ocean Expedition (ISOE-8) conducted in the Indian and Southern Ocean region during austral summer of 2014-2015 (Mahajan et al., 2019a, 2019b). We also include SSI observations in the northern Indian Ocean from two expeditions namely, the Sagar Kanya-333 cruise (SK-333) and the Bay of Bengal Boundary Layer Experiment (BoBBLE) conducted during June-July and September 2016 respectively (Chance et al., 2019b). Table 1 includes details of the expeditions, including the locations, dates of the expeditions and the meridional transect for each expedition. Figure 1a shows a map with the cruise tracks for the five expeditions. Figure 1b shows the seawater iodide sampling locations during ISOE-9, SK-333 and BoBBLE expeditions. The track of the ship during ISOE-9 along with the air mass back trajectories arriving at noon each day is given in the supplementary text Fig. S1. The HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Rolph et al., 2017; Stein et al., 2015) was used to calculate the back trajectories. Similar back trajectory plots and full cruise tracks for ISOE-8 and IIOE-2 are given in Mahajan et al. (2019a, 2019b). During the three expeditions, meteorological parameters of ocean and atmosphere were measured using an on-board automatic weather station and manual observation techniques.



168 **2.1. Sea surface iodide (SSI)**

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

173 **2.1.1 Observed SSI in the Indian Ocean and the Southern Ocean**

174 Historically, few observations of SSI are available for the Indian Ocean basin with reports of
175 only 3 data points in the open ocean from the Arabian Sea sector of the Indian Ocean
176 (Farrenkopf and Luther, 2002). Two of these values are coastal, and they lack supporting sea
177 surface temperature and salinity data; thus, they have been excluded from this study. However,
178 recent work has led to a large increase in the number of SSI observations available for the
179 Indian Ocean and Southern Ocean (Indian ocean sector) (Chance et al., 2019b). Specifically,
180 111 new observations were made during the 2016 ISOE-9 and 18 during the SK-333 and
181 BoBBLE. During the ISOE-9, SSI measurements in seawater were made concomitant with
182 observations of O₃ and IO in the gas phase for the first time. Observations of SSI made during
183 this expedition used the cathodic stripping voltammetry method with a hanging mercury drop
184 electrode as a working electrode (Campos, 1997; Luther et al., 1988). The seawater samples
185 were collected during the ISOE-9 at a 3-6-hour interval between 23° S and 70° S. Seawater
186 samples from the SK-333 cruise and BoBBLE were analysed following the same technique for
187 surface iodide concentrations. Iodide data from SK-333 and BoBBLE contributed to 18
188 additional data points between 10° N and 4° S making a total of 129 new locations (excluding
189 coastal and extremely high values above 400 nM; see Chance et al. (2019b) for details) for
190 observed SSI in the Indian Ocean and Southern Ocean region. This is a major sample size
191 compared to the global 2014 database (n=925) across all the global oceans (Chance et al.,



2014), and these data points contribute substantially to the recently updated iodide dataset (Chance et al., 2019a) ($n=1342$). From here onwards, the iodide concentrations obtained from sampling observations will be referred to as measured SSI as opposed to modelled SSI to differentiate between the observed iodide concentrations and those calculated using the parametrisations. All available observations made in the Indian Ocean basin as presented in Chance et al. (2019a) have been included for the development of the region-specific parameterisation presented in this work. Further details about the measurement technique and the observations used can be found in Chance et al. (2019b).

2.1.2 Iodide parametrisations

Due to the sparsity of SSI measurements, different empirical parametrisations have been proposed to estimate SSI concentrations. Parameters like SST and salinity (only for SK-333 and BoBBLE; $R^2 = 0.3$, $P = 0.018$) show a positive correlation with the SSI concentrations. However, a global parameterisation scheme may not capture the specificities of these required for regional studies. The northern Indian Ocean has markedly different sea surface salinity (D'Addezio et al., 2015) and SST (Dinesh Kumar et al., 2016) in its two basins, the Arabian Sea and the Bay of Bengal, that share the same latitude bands separated by the Indian sub-continental landmass. These basins experience the biannually reversing monsoonal winds, which greatly influence their SST and salinity structure. Strong winds in the Arabian Sea associated with the summer monsoon dissipate heat via overturning and turbulent mixing. Whereas weaker winds in the Bay of Bengal imply high SST due to the formation of stable and shallow surface mixed layer (Shenoi, 2002). The Arabian Sea exhibits much higher salinity compared to the Bay of Bengal due to greater evaporation and lower river runoff (Rao and Sivakumar, 2003). Current global SSI parameterisations (MacDonald et al., 2014; Chance et al., 2014) are based almost entirely on observations from the Atlantic, Pacific and Southern (excluding the Indian ocean sector) Oceans, they may not be suitable for accurate estimation



217 of SSI in the distinct and highly variable salinity and temperature regimes of the Indian Ocean
218 region.

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

225 (a) Linear regression analysis was performed, on each parameter, namely, SST, mixed layer
226 depth (MLD), latitude, sea surface nitrate concentration, and salinity against the measured SSI
227 concentrations from ISOE-9, SK-333, and BoBBLE campaigns, similar to the Chance et al.
228 (2014) technique, but using in situ SST and salinity observations instead of climatological
229 values. More details on the approach taken can be found in the supplementary text. The
230 combination with the largest R^2 and uniform distribution of residuals from the statistically
231 significant dependent variables, as detailed in Table S1 resulted in Eq. 2 of Table 2. Eq. 2 thus
232 represents a region-specific (the Indian Ocean and the Southern Ocean region abbreviated as
233 Ind. O. + Sou. O. in the figures) variant of the Chance et al. (2014) parameterisation for the
234 estimation of SSI concentrations. Similarly, keeping in mind the difference in the SST and
235 salinity for the Indian Ocean and the Southern Ocean, another parameterisation was derived
236 only for the Southern Ocean region using the ISOE-9 iodide observations and for the Indian
237 Ocean using the SK-333 and BoBBLE iodide observations, respectively. The parameterisation
238 for the Southern Ocean region using ISOE-9 iodide observations is given in Table 2 as Eq. (3).
239 A similar Indian Ocean parameterisation is not included in this text as the linear regression
240 analysis fails to obtain a parametric equation for this region. This may be due to fewer data
241 points ($n=18$) combined for the Arabian Sea and Bay of Bengal basins.



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

Figure 3 shows the iodide concentrations for the three campaigns, ISOE-8, IIOE-2 and ISOE-9, calculated using equations (1) to (5), the measured iodide concentrations from ISOE-9, SK-333 and BoBBLE, and the global iodide model predictions obtained from Sherwen et al. (2019) (Table 2.). From here on, region-specific parameterisations developed for SSI concentrations are referred to as the modified versions of the original parameterisations; Eq. (2) and (3) are called the modified Chance et al. (2014) parameterisation for the Indian Ocean and Southern Ocean region and only the Southern Ocean region, respectively. Eq. (5) is called the modified Macdonald et al. (2014) parameterisation. The machine-learning-based model proposed in Sherwen et al. (2019) is referred to as ‘SSI model’ results.

2.2. Ozone

Surface ozone was monitored using a US-EPA approved nondispersive photometric UV analyser (Ecotech EC9810B) installed on the ship during the expeditions to detect surface ozone values at a one-minute temporal resolution. A Teflon tube ~ 4 m long fixed towards the front of the ship acted as an inlet for the analyser. The analyser is equipped with a selective ozone scrubber, which was alternatively switched in and out of the measuring stream. The analyser has a lower detection limit of 0.5 ppbv and a precision of 0.001 ppmv. A 5-micron



PTFE filter membrane installed in the sample inlet tube was changed regularly. Zero and span calibration were done every alternate day to ensure accurate O_3 measurements. The ozone data collected was cleaned to remove the data points under the influence of the ship's smokestack by referring to the measured apparent wind direction on the ship. Apparent wind approaching the ship from 0 to 90° or 270 to 360° was considered free from smokestack emission influence, where 0 or 360° represents the bow of the ship. Ozone data recorded when the ship was stationary showed major smokestack emission influence and was excluded from the data.

2.3. Estimation of inorganic iodine fluxes

In order to estimate the contribution of inorganic iodine chemistry to active iodine chemistry in the atmosphere, the atmospheric fluxes for the main product species, I_2 and HOI, need to be calculated, since direct flux measurements of I_2 and HOI have not been done anywhere in the world to date. While there are reported observations of marine I_2 emission, they are few in number and mostly from coastal regions (Atkinson et al., 2012; Huang et al., 2010; Saiz-Lopez et al., 2006a) and one observation in the open ocean (Lawler et al., 2014a), although these are all observations of atmospheric concentrations and not of fluxes. As observed SSI is not available for all cruises, we used the following scenarios for SSI to estimate the inorganic iodine fluxes:

- (a) Using measured SSI: Observations of sea surface iodide from ISOE-9, SK-333, and BoBBLE.
- (b) Using calculated SSI from:
 1. Chance et al. (2014) parameterisation Eq. (1)
 2. Modified Chance et al. (2014) parameterisation for the Indian Ocean and Southern Ocean (Ind. O. + Sou. O.) region Eq. (2)



- 289 3. Modified Chance et al. (2014) parameterisation for the Southern Ocean (Sou.
 290 O.) region Eq. (3)
- 291 4. MacDonald et al. (2014) parameterisation using SST Eq. (4)
- 292 5. Modified MacDonald et al. (2014) parameterisation Eq. (5)
- 293 6. Using machine learning SSI model predictions (Sherwen et al., 2019a) Eq. (6)

294 Ozone was measured on all three cruises (ISOE-9, IIOE-2 and ISOE-8). The fluxes for HOI
 295 and I₂ were then calculated for all the above scenarios except for the observations from SK-
 296 333 and BoBBLE as IO observations were not taken during these cruises. The following
 297 algorithm was used for estimating iodine fluxes (Carpenter et al., 2013),

$$298 \text{ flux}_{I_2} = [O_3(g)] * [I_{(aq)}^-]^{1.3} * (1.74 \times 10^9 - 6.54 \times 10^8 * \ln(ws)) \quad \text{Eq. (7)}$$

$$299 \text{ flux}_{HOI} = [O_3(g)] * \left(4.15 \times 10^5 * \frac{\sqrt{[I_{(aq)}^-]}}{ws} - \frac{20.6}{ws} - 2.36 \times 10^4 * \sqrt{[I_{(aq)}^-]} \right) \quad \text{Eq. (8)}$$

300 where, the fluxes are in nmol m⁻² d⁻¹, [O₃] in nmol mol⁻¹ (ppbv), [I⁻] in mol dm⁻³ and the wind
 301 speed (WS) in m s⁻¹. Carpenter et al. (2013) did not consider the effect of temperature in the
 302 interfacial layer of the sea-surface model on activation energies for the reaction R1 (i.e.,
 303 assumed the temperature dependence for k (I⁻ + O₃) to be zero). Although I₂ and HOI fluxes
 304 are expected to increase with the temperature of the interfacial layer, I₂ production has a
 305 negative activation energy, as noted by MacDonald et al. (2014). In Carpenter et al. (2013)
 306 (specific to the tropical Atlantic), a seawater temperature of 15°C and air temperature of 20°C
 307 were used to calculate Henry's law constants, diffusion constants, and mass transfer velocities.
 308 Again assuming the temperature dependence of k(I⁻ + O₃) to be zero, but including the
 309 temperature-dependence of Henry's law constants, diffusion constants, and mass transfer
 310 velocities, the same interfacial layer model predicted effective activation energies for I₂ and
 311 HOI emissions of -2 kJ mol⁻¹ and 25 kJ mol⁻¹ (Macdonald et al. (2014). Using these



activation energies, Macdonald et al. (2014) calculated differences in I_2 and HOI fluxes of 3 % and 31-41 %, respectively, at SSTs of 10° C and 30° C compared to the room-temperature parameterisations presented in Carpenter et al. (2013). Experimentally derived activation energies for I_2 and HOI emissions were $-7 \pm 18 \text{ kJ mol}^{-1}$ and $17 \pm 50 \text{ kJ mol}^{-1}$ (MacDonald et al., 2014). As HOI represents the larger iodine flux, the higher relative uncertainty in the activation energy should be kept in mind when calculating temperature-dependent emissions.

HOI and I_2 fluxes are also influenced by the wind speed as seen from equations (7) and (8), and the modelled iodine fluxes (HOI and I_2) are highest for high $[O_3]$, high $[I^-]$ and low wind speed. This is explained by the assumption that wind shear drives mixing of the interfacial layer to bulk seawater, reducing the efflux of HOI and I_2 into the atmosphere (Carpenter et al., 2013). Negative fluxes are obtained from equations (7) and (8) for both HOI and I_2 when the wind speed is higher than 14 m s^{-1} , which is not physically possible and therefore the model output is limited to wind speeds below 14 m s^{-1} (Mahajan et al., 2019a). Iodine fluxes calculated from equations (7) and (8) using SSI concentrations from the scenarios (a) and (b 1-6) are shown in Fig. 4 (c and d).

2.4. Iodine Oxide

2.4.1 Observations

Ship-based measurements of IO were made using the Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) technique (Hönninger et al., 2004; Platt and Stutz, 2008). The MAX-DOAS was installed at the bow of the ship with a direct line of sight towards the front of the ship to avoid the ship's plume in the detection path of the telescope. The MAX-DOAS was programmed to capture scattered sunlight spectra at every 1 second at set elevation angles of 0, 1, 2, 3, 5, 7, 20, 40, and 90-degrees during daylight hours. Mercury line calibration offset, and dark current spectra were recorded after sunset on each day. Elevation angles



336 outside a range of ± 0.2 degree from the set value were eliminated from the 30 minutes averaged
337 spectra for increased accuracy. Figure S2 shows the resultant IO and O₄ differential slant
338 column densities (DSCDs) for ISOE-9 campaign, similar plots are available for ISOE-8
339 (Mahajan et al., 2019a) and IIOE-2 (Mahajan et al., 2019b). The QDOAS software (Danckaert
340 et al., 2017) was used for DOAS retrieval of IO from the spectra using the optical density fitting
341 analysis method. The spectra were fitted with a 3rd order polynomial using fitting interval of
342 415 to 440 nm with cross-sections of NO₂ (Vandaele et al., 1998), O₃ (Bogumil et al., 2003),
343 O₄ (Thalman and Volkamer, 2013), H₂O (Rothman et al., 2013), two ring spectra, first as
344 recommended by Chance and Spurr, (1997) and second following Wagner et al., (2009) and a
345 liquid water spectrum for seawater (Pope and Fry, 1997). To remove the influence of
346 stratospheric absorption a spectrum corresponding to 90° (zenith) from each scan was used as
347 a reference for the analysis. The raw spectra were analysed to obtain differential slant column
348 densities (DSCDs), and values with a root mean square error (RMS) of greater than 10⁻³ were
349 eliminated. Similarly, DOAS retrieval of O₄ in 350 to 386 nm spectral window was performed,
350 and DSCDs were obtained. The optical density fits for IO and O₄ from ISOE-9 are shown in
351 Fig. S3. The IO DSCDs were then converted to volume mixing ratios using the O₄ slant
352 columns following the previously used "O₄ method" (Mahajan et al., 2012; Prados-Roman et
353 al., 2015; Sinreich et al., 2010; Wagner et al., 2004). Further details of the instrument, retrieval
354 procedure and conversion into mixing ratios can be found in previous works (Mahajan et al.,
355 2019a, 2019b).

356 2.4.2 Modelled atmospheric IO

357 We use outputs from two global models for a comparison with the observations conducted
358 during the three cruises. The first model is the GEOS-Chem chemical transport model (version
359 10-01, 4x5 degrees horizontal resolution, <http://www.geos-chem.org>), which includes detailed
360 HOx-NOx-VOC-ozone-halogen-aerosol tropospheric chemistry (Sherwen et al., 2016c, 2017)



361 and is driven by offline meteorology from NASA's Global Modelling and Assimilation Office
362 (<http://gmao.gsfc.nasa.gov>) forward processing product (GEOS-FP).

363 The second model is the 3D chemistry-climate model CAM-Chem version 4 (Community
364 Atmospheric Model with Chemistry) (<https://www2.aom.ucar.edu/gcm/cam-chem>), which is
365 included in the CESM framework (Community Earth System Model, CAM-Chem, version
366 4.0). The model includes a state-of-the-art halogen chemistry scheme (chlorine, bromine and
367 iodine) (Saiz-Lopez and Fernandez, 2016). The current configuration includes an explicit
368 scheme of organic and inorganic iodine emissions and photochemistry. These halogen sources
369 comprise the photochemical breakdown of five very short-lived bromocarbons (CHBr_3 ,
370 CH_2Br_2 , CH_2BrCl , CHBrCl_2 and CHBr_2Cl) naturally emitted by phytoplankton from the
371 oceans (Ordóñez et al., 2012). The model was run in specified dynamic mode (Ordóñez et al.,
372 2012), with a spatial resolution of 1.9° latitude by 2.5° longitude and 26 vertical levels from the
373 surface to up to 40 km.

374 Both models include biotic emissions of four iodocarbons (CH_3I , CH_2ICl , CH_2IBr and CH_2I_2)
375 as described by (Ordóñez et al., 2012) and abiotic oceanic sources of HOI and I_2 based on the
376 Carpenter et al. (2013) and MacDonald et al. (2014) laboratory studies of the oxidation of
377 aqueous iodide by atmospheric ozone at the ocean surface. Both models here use the
378 MacDonald parameterisation expression (Eq. (4), MacDonald et al., 2014) discussed in Section
379 2.1.2 to predict surface iodide used for calculating iodine emissions and the organo-halogen
380 emissions from Ordóñez et al. (2012). IO surface concentrations for the three campaigns (IIOE-
381 2, ISOE-8 and ISOE-9) were extracted from the model runs and used for comparison.
382 Currently, these two global models include reactive iodine chemistry (along with TOMCAT,
383 which includes the tropospheric iodine chemistry (Hossaini et al., 2016)).

384 3. Results



3.1 Ozone, Meteorological and Oceanic parameters

The latitudinal distribution of hourly average values of wind speed (WS), O₃, SST, and salinity from all the campaigns are shown in Fig. 5. Winds arriving at the ship, shown in the first panel (Fig. 5a), remained low for most of the duration of all three expeditions with wind speed ranging from 1 m s⁻¹ to stronger winds of 24 m s⁻¹ on a few days. Even stronger winds (above 30 m s⁻¹) were observed during the ISOE-9 in the region between 64° and 65° S with the highest wind speed of 32 m s⁻¹ at 66° S on the night of 8th February 2017. Ozone mixing ratios, (Fig. 5b) during all three expeditions showed a similar trend exhibiting a large reduction in values in the open ocean environment compared to coastal environments. The back trajectories (supplementary text) show that for most of the expeditions, air masses arriving at the cruise were from the open ocean environment and did not have any anthropogenic influence for the last five days. This is reflected in the O₃ values, which range between 8 and 20 ppbv in the open ocean but were between 30 and 50 ppbv near the coastal regions, where the air mass back trajectories confirm anthropogenic origins. Close to the Indian sub-continent ozone levels peaked at about 50 ppbv during the ISOE-8. It also showed a distinct diurnal variation with higher ozone values during the daytime due to photochemical production. However, in the open ocean environment, ozone mixing ratios did not show this diurnal variation, and indeed values of ozone dropped during daytime indicating photochemical destruction during both ISOE-8 and ISOE-9 (Fig. 5b).

As already noted, SST is widely used to predict SSI (Eq. 4 and 5). Combined SST data (Fig. 5c) reveal a steady decrease in sea surface temperature from 15° S to 68° S for all the campaigns. During January 2015 (ISOE-8) seawater north of 6° N displays slightly lower SST (~ 3° C) compared to that in December 2015 (HIOE-2). Salinity is also an important parameter for the prediction of SSI (higher coefficient in Eq. 1, 2 and 3). The Southern Ocean region explored during ISOE-8 and ISOE-9 reveals similar salinity values (Fig. 5d) for the austral



summer months of 2014 and 2016 (January-February). The salinity data shows relatively lower values for ISOE-8 compared to those for IIOE-2 for the region 15° N to 20° S. Despite the inter-annual differences in the northern Indian Ocean region, salinity values of ~ 35 PSU overlap for the IIOE-2 and ISOE-8 in a small window of 7° N to the equator. Below the equator, the salinity values for IIOE-2 increase while for ISOE-8 salinity remains lower than 35 PSU until 20° S. Seawater between 20° S and 44° S has a near-constant salinity of 35 PSU which decreases to ~33.5 PSU after 44° S and remains the same until 65° S after which the salinity begins to drop to 31.5 PSU near 67° S close to Antarctica.

3.2 Sea surface iodide concentration

Latitudinal averages of SSI concentrations estimated from seven scenarios (listed in Sect. 2.3) are shown in Fig. 3. SSI estimates from the IIOE-2 campaign are marked separately to differentiate from the ISOE estimates for the Indian Ocean region. There is a clear difference in the estimated SSI in different scenarios. All the estimates and the model follow a similar pattern showing elevated levels in the tropics as compared to the higher latitudes. SSI estimates from parameterisations (Eq. 1, 3, 4, and 5) show nearly constant values for SSI from 15° N to 25° S, after which a steady decline is noted until 70° S. Thus, the parameterisations based on Eq. 1, 3, 4 and 5 do not capture the decreasing trend observed for iodide around the equator. Eq. 2, which was derived specifically for the Indian Ocean and Southern Ocean region better captures this trend, and also shows a better match with the measured SSI from SK-333 and BoBBLE in the Indian Ocean. Eqn. 6 also predicts lower concentrations around the equator than in the northern Indian Ocean. SSI concentrations estimated using the Chance et al. (2014) parameterisation (Eq. 1) show a small increase in iodide concentrations south of 47° S (polar front), which is not observed in the other parameterisations, but there is some suggestion of in the observations. Eq. 1 also resulted in a large difference (~ 50 nM) of SSI estimates north of 10° N between the IIOE-2 and ISOE-8 cruises; while this difference was lower for the other



parameterisations. This difference between the SSI estimates for the IIOE-2 and ISOE-8 cruises is due to the large difference in salinity values for this region (Sect. 4.1). SSI estimates using Eq. 2 shows good agreement with the model prediction of Sherwen et al. (2019), both indicating a decrease in SSI concentrations near the equator during the IIOE-2 and ISOE-8 expeditions. Some high SSI concentrations (up to ~250 nM) were observed around 10° N, these were best replicated by Eqn.3. The highest SSI concentrations estimated using Eq. 3 were 244 nM at 7° N during IIOE-2 and 242 nM at 12° S during ISOE-8. At the equator, Eq. 2 performs better in predicting the SSI concentrations with a difference of ~75 nM compared to the observations. SSI estimates from Eq. 4, i.e. MacDonald et al. (2014) parameterisation, were lower than the measured iodide concentrations and all other parameterisation, including the model (Eq. 7) predictions. Overall, all modified parameterisations (Eq. 2, 3 and 5) estimate higher SSI compared to the original parameterisation (Eq. 1 and 4), with the exception of the region south of 20° S, where Eq. 3 predicts lower SSI than Eq. 1. The modified MacDonald parameterisation (Eq. 5) estimated iodide concentrations to be greater by 50 nM for the entire dataset in comparison to the existing MacDonald parameterisation given by Eq. 4. For Eq. 5, the uncertainty in the iodide concentration from the 95 % prediction band is ~15 % of the predicted value.

3.3 Iodine fluxes

Figure 4 shows the latitudinal variation in IO mixing ratios, inorganic iodine emissions (HOI and I₂), chl-*a* and ozone mixing ratios for the entire dataset comprising of the three campaigns. All the panels in Fig. 4 are plots of daily averaged values during each expedition, except for the HOI and I₂ fluxes; these are latitudinal averages from each campaign. Emissions calculated using the measured SSI concentrations (represented by filled spheres in Fig. 4 c & d) from ISOE-9 correspond to the data points of the measured SSI concentration. Oceanic inorganic iodine emission fluxes of HOI and I₂ were estimated using the Carpenter et al. (2013)



parameterisation given in Eq. (7) and (8) limited to wind speeds below 14 m s^{-1} . Thus, the fluxes estimated from the measured SSI concentrations were reduced to 56 points (out of 111 measured SSI data points). The seven different datasets of iodide concentrations (listed in Sect. 2.3) have been used for estimation of HOI and I_2 fluxes. For the entire dataset, the highest fluxes were obtained when using the SSI concentrations from the modified Chance et al. (2014) parameterisation (Eq. 3), derived from measured SSI from the Southern Ocean region, i.e. during ISOE-9. The second highest fluxes were estimated using SSI from Eq. 2, obtained from measured SSI from the Indian Ocean and Southern Ocean. Comparatively lower iodine emissions were estimated using SSI concentration from MacDonald et al. (2014) parameterisation (Eq. 4). The estimated inorganic iodine fluxes in the Southern Ocean region (30° S and below) are much lower compared to the Indian Ocean (Fig. 5), driven by the higher estimated SSI in the latter. Maximum inorganic emissions are predicted in the tropical region, specifically, north of the equator. HOI is the dominant reactive iodine precursor species for the entire dataset, with calculated flux values 20 times higher than those for I_2 . Emissions estimated using SSI from Eq. (3), resulted in a peak HOI flux of $1.5 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$ at 9° N during ISOE-8. The lowest HOI flux of $1.7 \times 10^6 \text{ molecules cm}^{-2} \text{ s}^{-1}$ was obtained at 61° S during ISOE-9. For the same latitudes (9° N and 61° S), a maximum I_2 flux of $7.0 \times 10^7 \text{ molecules cm}^{-2} \text{ s}^{-1}$ and a minimum of $1.3 \times 10^5 \text{ molecules cm}^{-2} \text{ s}^{-1}$ were estimated, respectively. Flux estimates from Eq. 2 are slightly lower, with a maximum HOI flux of 1.3×10^9 and a minimum of $5.8 \times 10^5 \text{ molecules cm}^{-2} \text{ s}^{-1}$ and maximum I_2 flux of 5.2×10^7 with minimum of $8.3 \times 10^4 \text{ molecules cm}^{-2} \text{ s}^{-1}$ at the same latitudes. The estimated HOI and I_2 emissions are notably lower (by $\sim 50 \%$) during IIOE-2 to the north of 5° S compared to emissions from ISOE-8. Between 5° S and 20° S , the emissions from IIOE-2 and ISOE-8 are similar. Fluxes estimated using measured SSI concentrations for the ISOE-9 campaign (20° S to 70° S) show no strong latitudinal trend for both HOI and I_2 emissions. The maximum calculated HOI flux was $5.8 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$.



¹ at 68° S and the minimum was 1.1×10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$ at 33° S. Similarly, I_2 fluxes estimated from measured SSI concentrations peaked at 1.5×10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$ at 32° S with a minimum of 3.5×10^5 molecules $\text{cm}^{-2} \text{s}^{-1}$ at 67° S. Inorganic iodine emissions estimated using model predictions for SSI concentrations from Sherwen et al. (2019) match well with the fluxes estimated using the iodide parametrisation tools. Despite the differences in SSI concentrations from existing and region-specific parameterisations, all result in similar values for iodine fluxes and so SSI cannot explain discrepancies in the observed and modelled IO levels in this region.

3.4 Iodine oxide

3.4.1 Observations

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



509 3.4.2 Modelled IO

510 Based on the current understanding of iodine chemistry, regional and global models consider
511 inorganic fluxes of iodine (HOI and I₂) as major contributors of iodine in the marine boundary
512 layer. It is important to verify if the models using the existing parameterisation for these source
513 gases can replicate observations of IO in the region of study. Thus, we have included model IO
514 output from GEOS-Chem and CAM-Chem, both of which use the SST based MacDonald et
515 al. (2014) parameterisation for SSI (Fig. 4b). The surface IO output from GEOS-Chem predicts
516 the highest levels of IO up to 1.7 pptv to the north of the equator at 11° N for the time period
517 of the IIOE-2 campaign. For the same latitudes, the model suggests lower IO levels, of less
518 than 0.5 pptv, during the ISOE-8 campaign. Conversely, south of the equator to 10° S, the
519 model predicts higher IO levels during the ISOE-8 and lower IO values during the IIOE-2, in
520 agreement with the observations. Below 10° S, IO predictions for both campaigns match well
521 until 20° S, which was the latitudinal limit for the IIOE-2 campaign. To the south of 20° S,
522 modelled IO levels remained below 1 pptv and exhibited a decreasing trend to the south of the
523 polar front, in disagreement with IO observations. At locations between 40° S and 43° S,
524 GEOS-Chem underestimates the observed IO levels by 50 %. These locations are close to the
525 Kerguelen Islands, and high IO values were observed here only during the ISOE-8. These
526 locations have been omitted in the correlation study between modelled and observed IO as they
527 could be impacted by coastal or upwelling emissions, which are not well prescribed in the
528 models.

529 The CAM-Chem IO surface output suggests consistently higher levels of IO during IIOE-2
530 compared to the ISOE-8 for the same latitudinal band (Fig. 4b). Contrary to the observations,
531 the CAM-Chem model suggests that IO levels during the IIOE-2 are up to 1 pptv higher than
532 the ISOE-8 campaign near 7° S latitude. The model also shows elevated IO levels of 2.7 pptv
533 at 7.9° N during the IIOE-2 campaign, which does not match the observations during the IIOE-



2 or the ISOE-8 for that region. IO levels below 1.5 pptv (11° N to 20° S) are indicated for the ISOE-8 campaign. In addition, the region between 0° and 1.5° S has similar IO levels for the HIOE-2 and ISOE-8 campaigns. The model predicts lower IO levels for the south Indian Ocean and the Southern Ocean (less than 1 pptv) with decreasing IO to the south of the polar front. However, at 43° S, the model suggests higher IO (2.4 pptv) during the ISOE-9, which matches the increase in observed IO for that region during the ISOE-8 expedition, with this region being close to the Kerguelen Islands Both models show consistently higher absolute concentrations overall compared to the observations north of the polar front.

4. Discussion

4.1 Seawater iodide

To improve the estimation of SSI in the study region, previously established parameterisations (Eq. 1 and 4) were modified to obtain a region-specific parameterisation for SSI concentrations. SSI estimated using these modified parameterisations were less sensitive to seasonal salinity and SST changes for the north Indian Ocean basin compared to the existing parameterisation (Fig 3). Figure 6 shows the correlations of all the calculated SSI concentrations with the observations. The SSI estimates from Eq. 1 to 6 correlate positively (significantly) to the measured SSI concentrations (observations) from ISOE-9 (Fig. 6). Out of the six parameterisation tools compared in this study, as expected, SSI from Eq. (2) i.e. the modified Chance equations for the Indian Ocean and the Southern Ocean showed the best correlation with the measured SSI because they were created using datasets from these campaigns (Fig. 6 and Table 2). Although the region-specific parameterisations were expected to match with the observations they are based on, there was a notable difference between predictions and observations when this approach was applied only to Indian Ocean SSI measurements from SK-333 and BoBBLE ($R^2 = 0.5$ for Indian Ocean parameterisation, analysis not shown). This



could be attributed to the lack of SSI measurements in this region ($n=18$), and it highlights the fact that there may be not only seasonally but regionally varying complexities in SSI which should be considered when estimating SSI. All parameterisation methods used for SSI estimations show that SSI concentrations are directly proportional to seawater salinity (listed in Sect. 2.3). It is evident from Fig. 5d and Fig. 3a that to the north of the equator, the parameterisations (Eq. 1 to 5) show lower SSI concentrations in regions with lower salinity (up to 5° N during ISOE-8 – filled symbols Fig. 3) and higher SSI concentrations in regions with comparatively higher salinity (during IIOE-2 – unfilled symbols Fig. 3). Only the modelled SSI concentrations using Eq. 6 (Fig. 3a, data in purple) reveal an inversely proportional relationship for salinity and SSI concentration in this region. The Sherwen et al. (2019) parametrisation (Eq. 6) produces lower SSI concentrations in high salinity Arabian Sea waters during IIOE-2 (Fig. 3a) north of 5° N, compared to the low salinity Bay of Bengal waters during ISOE-8 which contradicts all the other parameterisation (Eq. 1 to 5). Further, the SSI concentrations obtained from Sherwen et al. (2019) reverse their trend to the south of 6° N, with higher concentrations during IIOE-2 and lower during ISOE-8. It should be noted that only a few observations of SSI exist in this region to confirm this trend. Further discussion on the relationship between salinity and other biogeochemical variables with SSI concentrations at a global and regional scale can be found elsewhere (Chance et al., 2014, 2019a).

SSI estimates considering only SST as a proxy for iodide concentration (Eq. 4), reveal positive correlations with measured SSI concentration ($R = 0.86$, $P < 0.001$, $n = 129$; Fig. 6d). The modified MacDonald parameterisation (Eq. 5) also correlates positively to the measured SSI concentration but has a slightly lower coefficient of correlation ($R = 0.83$, $P < 0.001$, $n = 129$; Fig. 6e). When using the SST as a proxy for SSI, a large intercept was obtained for the SSI values, evidencing the discrepancy in absolute value between this parametrisation and the observations. Eq. (5) resulted in a lower intercept, approximately half of that for Eq. (4), and a



583 lower absolute slope value of $|-3763 \pm 218|$ compared to the $|-9134 \pm 613|$ of Eq. (4) given in
584 MacDonald et al. (2014). The lower absolute slope value for Eq. (5) implies that the SSI
585 concentrations for this region were less sensitive to the changes in SST compared to that in Eq.
586 (4).

587 Despite the lower R-value, the SSI estimates from Eq. 5 in Fig. 3 are closer to the measured
588 SSI concentration than the estimates from Eq. 2 and 3 for the region from 25° S to 70° S.
589 However, north of 25° S, the SSI estimates from Eq. 3 and Eq. 5 differ by $\sim 40\%$. Both SST
590 based parameterisation (Eq. 4 and 5) did not show the observed latitudinal variation in the SSI
591 concentrations near the equator. Linear regression of SSI with SST for only the Indian Ocean
592 region revealed that there was no correlation between the two ($R^2 = 0.07$, $P = 0.3$, $n = 18$). The
593 SSI in this region only showed dependence on the salinity and latitude, correlations with the
594 other parameters were not significant. This highlights that SST may not be a very good proxy
595 for SSI in the Indian Ocean, especially near the equator. This is explored further in Chance et
596 al. (2019b). The original Chance et al. (2014) parameterisation displays higher sensitivity to
597 seasonal salinity changes compared to the existing and modified parameterisation in the Indian
598 Ocean region (Sect. 3.3). However, this method predicted increasing iodide concentration to
599 the south of the polar front (47° S), which is not supported by observations in this region (Fig.
600 3). In conclusion, considering the correlation with measured SSI concentration and dependence
601 on seawater salinity, the region-specific modified Chance parameterisation (Eq. 2) is a suitable
602 method to estimate SSI concentration for the Indian Ocean and Southern Ocean region. The
603 modelled SSI estimates by Sherwen et al. (2019) capture SSI trend close to equator better than
604 other existing schemes but it fails to replicate higher SSI observations at locations 8° N, 40° S
605 and to the south of 65° S close to the Antarctic coast (Fig. 3).

606 4.2 Atmospheric iodine



607 Combined IO observations from IIOE-2, ISOE-8, and ISOE-9 (Fig. 4a) show that the Indian
608 Ocean region has comparatively less IO in its MBL than the Southern Ocean region. IO
609 remained below 1 pptv up to 40° S and reached a maximum IO of 1.6 pptv south of the polar
610 front. Modelled surface IO output from GEOS-Chem and from CAM-Chem using the
611 Macdonald et al. (2014) parameterisation (Fig. 4b) do not match the observations of IO,
612 although they generally show good agreement with each other. The models show similar spatial
613 patterns across the entire dataset, except for two periods of very high IO levels predicted by
614 CAM-Chem (Fig. 4b). As well as structural differences between CAM-Chem and GEOS-
615 Chem, there are many halogen specific differences in rate constants, heterogeneous
616 parameters, cross-sections and photolysis of species (e.g. higher iodine oxides) which could
617 explain differences in predicted gas-phase IO. Considering the generally lower wind speeds
618 and higher ozone concentrations seen in IIOE-2 versus SOE-8 and SOE-9, the calculated fluxes
619 are higher and therefore more sensitive to assumptions, such as minimum wind speeds provided
620 to the Carpenter et al. (2013) parameterisation. GEOS-Chem uses a minimum wind speed of
621 5 m s⁻¹; however, CAM-Chem uses a minimum wind speed of 3 m s⁻¹.

622 Both models suggest higher than observed IO levels in the Indian Ocean region but under-
623 predict IO for the Southern Ocean region. The highest detected IO levels, both in the Southern
624 Ocean and in a narrow band around 43° S, were not reflected in the model predictions. We note
625 these occurred in regions of elevated chl-*a* values (Fig. 5), and that Mahajan et al. (2019a) also
626 reported positive correlations for IO with chl-*a* for the Indian Ocean region, above the polar
627 front for a subset of the dataset (ISOE-8). Calculated fluxes of HOI and I₂ (Fig. 4c and d) fail
628 to directly explain trends in the detected IO levels for the entire dataset, regardless of the
629 method used to estimate SSI. Maximum levels of HOI and I₂ predicted to the north of 5° N
630 correspond to rather low levels of IO (< 0.5 pptv) in this region. However, this has been
631 attributed to NO_x titration of IO (Mahajan et al., 2019b). The models, however, do not capture



632 this iodine titration by NO_x as seen in the observations; even though the reactions of IO with
633 NO_x are included (Ordóñez et al., 2012). Similarly, for the region south of the polar front, the
634 calculated iodine fluxes remain low in the region of the maximum detected IO concentrations
635 during the ISOE-8 and ISOE-9 campaigns. Iodine fluxes estimated for the Indian Ocean region
636 (15°N to 5°N) during IIOE-2 and ISOE-8 show large differences with much higher values
637 during ISOE-8. However, the modelled IO is in fact higher for IIOE-2 than during ISOE-8 (5° -
638 15°N). Considering that the models do not reflect the fluxes, this indicates that photochemistry
639 led to this difference in the model. Additionally, the elevated levels of IO predicted in the
640 models suggest that CAM-Chem and GEOS-Chem overestimate the impact of iodine chemistry
641 in the northern Indian Ocean.

642 In Fig. 7, correlations of iodine fluxes estimated using the measured SSI concentrations (Eq.
643 2) show that fluxes of HOI correlate positively with tropospheric ozone ($R = 0.56$, $P < 0.001$)
644 and negatively to wind speed ($R = -0.62$, $P < 0.001$) and I_2 fluxes correlate positively with SSI
645 concentration ($R = 0.56$, $P = P < 0.001$) and ozone ($R = 0.59$, $P < 0.001$) and negatively to wind
646 speed ($R = -0.4$, $P < 0.001$). This indicates that although there is positive correlation of I_2 with
647 SSI, the dominant inorganic iodine flux i.e. HOI does not show significant correlation with SSI
648 concentration, although the flux equation includes an iodide term (Eq. 8). We analysed the
649 correlation of daily averaged observed IO during the three campaigns with daily averaged
650 values of oceanic parameters (SST, chl-*a*, salinity, SSI concentration), meteorological
651 parameters (wind speed, ozone) and calculated inorganic iodine fluxes. We divided the
652 combined dataset from three campaigns into two regional subsets for the north (Fig. 8a) and
653 south (Fig. 8b) of the polar front (47°S). The correlation for SSI concentrations is included for
654 all the seven methods for SSI estimation listed in Sect. 2.3. The fluxes of HOI and I_2 obtained
655 using the seven different datasets for SSI are included and listed in Fig. 8 in the same order as
656 the SSI concentration (labelled 1 to 7). IO model output from GEOS-Chem (labelled 8) and



657 CAM-Chem (labelled 9) is included for the correlation analysis, along with chl-*a* data from
658 observations during ISOE-8 and ISOE-9 and satellite dataset obtained from MODIS Aqua
659 (Oceancolor, NASA-GSFC, 2017).

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

673 Salinity and SST show a weak negative correlation with atmospheric IO for the entire dataset
674 and for the north of the polar front region. This indicates that even if the physical parameters
675 are significant for the initial parametrisation for SSI and inorganic flux estimation, there is no
676 direct and significant correlation of these parameters with the atmospheric IO. However, south
677 of the polar front, SST correlates positively above the 99 % limit ($R = 0.52$, $P = 0.01$, $n = 48$)
678 and salinity correlates positively above the 95 % limit ($R = 0.44$, $P = 0.03$, $n = 48$). Ozone
679 correlates negatively with IO above 95 % limit ($R = -0.4$, $P = 0.046$, $n = 47$), which could
680 indicate catalytic destruction of tropospheric ozone through atmospheric iodine cycling in the



681 south of the polar front. This highlights that although these physical parameters may be
682 required for iodine fluxes, IO levels may only be weakly related to them.

683 The calculated SSI concentrations and the HOI and I₂ fluxes calculated using these SSIs all
684 show a significant negative correlation with the observed IO concentrations above the 95 %
685 confidence limit for the entire dataset (except for the HOI flux estimated from the MacDonald
686 et al. (2014) parameterisation, which shows no significant correlation). The positive correlation
687 of the observed IO with wind speed is a potential driver for the negative correlation of observed
688 IO with the calculated HOI and I₂ fluxes, which decrease with wind speed.

689 Measured iodide levels (labelled 4) and the I₂ and HOI fluxes calculated from them (also
690 labelled 4) show no correlation with the observed IO levels across the entire dataset, although
691 iodide shows a significant positive correlation ($R = 0.55$, $P = 0.04$, $n = 32$) for IO measured
692 south of the polar front. Mahajan et al. (2019a) pointed out that SST negatively correlated with
693 IO for the ISOE-8 campaign, contradicting the previous results for observations in the Pacific
694 Ocean (Großmann et al., 2013; Mahajan et al., 2012). Here, SST shows a significant positive
695 correlation with observed IO ($R = 0.52$, $P = 0.006$, $n = 48$) south of the polar front above the
696 99 % confidence limit, but there is no correlation north of the polar front and only a weak
697 negative correlation using the combined dataset from the three campaigns ($R = -0.18$, $P = 0.13$,
698 $n = 119$).

699 Despite the above-mentioned point regarding the increase in observed IO levels in regions of
700 elevated chl-*a*, there is only a weak and negative correlation of IO with chl-*a* (both from
701 observations and satellite data) south of the polar front. However, there is a strong positive
702 relationship north of the polar front ($R = 0.696$, $P = 2.3 \times 10^{-4}$, $n = 29$). In fact, for the region
703 north of the polar front, chl-*a* shows a significant positive correlation with observed IO above
704 the 99 % confidence limit ($P < 0.001$). The GEOS-Chem and CAM-Chem output also shows a



705 significant positive correlation (Fig. 8) which may result from the dependency of organic iodine
 706 species on oceanic chl-*a* in both GEOS-Chem and CAM-Chem. Figure 8 shows a large
 707 difference in correlation values for chl-*a* data obtained from observations and satellite (MODIS
 708 Aqua, NASA, GSFC; <https://oceancolor.gsfc.nasa.gov>). In situ, observed chl-*a* showed an
 709 improved correlation with IO compared to those with satellite chl-*a*. Figure 9 shows linear fits
 710 for chl-*a* from in situ observations and satellite against IO for the entire dataset and north of
 711 polar front subset. For the entire dataset, correlation of chl-*a* with IO from both observations
 712 and satellite data is not significant. Chl-*a* from in situ observations positively correlates with
 713 IO ($R = 0.15$, $P = 0.32$) while chl-*a* from satellite data correlates negatively ($R = -0.13$, $P =$
 714 0.26). Correlations of chl-*a* with IO improves for the north of polar front for chl-*a* from
 715 observations ($R = 0.696$, $P = 0.0002$), but chl-*a* from satellite data shows a statistically
 716 insignificant correlation with IO ($R = 0.08$, $P = 0.57$). The discrepancies in chl-*a* from
 717 observations and satellite data will make it difficult to identify links between the organic
 718 parameter and atmospheric IO and expand this to a global scale.

719 Despite the observed negative relationship of IO with wind speed noted above, note that the
 720 GEOS-Chem IO model output (which is dependent on the calculated HOI and I_2 fluxes) shows
 721 a significant positive correlation with observed IO above the 99 % confidence limit for data
 722 south ($R = 0.78$, $P = P < 0.001$, $n = 48$) and north ($R = 0.69$, $P = P < 0.001$, $n = 68$) of the polar
 723 front, although there is no correlation across the entire dataset. Note that the model
 724 underestimates IO values by 1 pptv south of the polar front and generally overestimates IO, by
 725 ~ 1.5 pptv, north of the polar front (Fig. 4). A linear fit for observed IO against modelled IO for
 726 north and south of the polar front (Fig. 10) shows significant positive correlation of GEOS-
 727 Chem output with observed IO, but with very different slopes north of the polar front (where
 728 the models overestimate IO) and south of the polar front (where the models underestimate IO).



Hence, even though the correlations are good in the individual regions, the model does not accurately reproduce the observed absolute concentrations.

5. Conclusions

In this study, region-specific parameterisation tools were devised for sea surface iodide (SSI) estimation following previous SSI estimation methods from Chance et al. (2014) and MacDonald et al. (2014). New observations of SSI from ISOE-9, SK-333 and BoBBLE (Indian and the Southern Ocean) were used to create region-specific SSI parameterisations. An average difference of up to 40 % in SSI concentration was observed among the existing parameterisations (Eq. 1, 4, and 6) and the difference was 21 % for the region-specific ones (Eq. 2, 3, and 5). Comparison of estimated SSI concentrations from various parameterisations with observed SSI and sensitivity to seasonal salinity changes showed that the modified Chance parameterisation (Eq. 2) was most suitable relative to the SST based parameterisation (Eq. 5) for SSI estimation in the Indian Ocean and Southern Ocean region. Since the existing global parameterisation schemes (Eq. 1 and 3) fail to match measured SSI in this region, it highlights the need to conduct more observations of SSI in the Indian Ocean and Southern Ocean region to fully understand and estimate the impact of seasonally varying, region-specific parameters (like salinity, reversing winds patterns) influencing the seawater iodide concentration in this region. Alternatively, a region-specific parameterisation scheme may be included in the global models for better representation of seawater iodine chemistry in the Indian and Southern Ocean region. Modelled estimates from Sherwen et al. (2019) also captured SSI well, although some high concentrations in the northern Indian Ocean region were not captured. SSI estimation from SST alone under-predicts SSI for the Indian Ocean, and so is not considered to be suitable for SSI estimation in the Indian Ocean region. Although, improving SSI concentration in models for the Indian Ocean and Southern Ocean region may improve the estimation of seawater iodine chemistry, it does not translate to estimating the atmospheric iodine chemistry in this region.



754 An accurate estimation of inorganic iodine fluxes (HOI and I₂) is hence necessary to explain
755 observed levels of IO in the remote open ocean marine boundary layer. However, these first
756 concomitant observations of SSI and IO show that these inorganic fluxes, estimated in this
757 study, fail to explain detected IO levels for the entire dataset. No significant correlation was
758 seen between the SSI from different parameterisation techniques or estimated inorganic iodine
759 fluxes with observed IO levels. Fluxes estimated using iodide from different parameterisation
760 and measured iodide did not show large variation in values and followed a similar latitudinal
761 trend. This is indicative that the inorganic iodine flux parameterisation is not highly sensitive
762 to the SSI parameterisation. Predicted inorganic iodine fluxes did not explain iodine chemistry,
763 as indicated by IO levels, in the atmosphere above the Indian and Southern Ocean (Indian
764 Ocean sector). Chl-*a* shows a positive correlation with IO for the north of the polar front region,
765 suggesting that biologically emitted species could also play a role in addition to ozone and
766 iodide derived inorganic emissions of HOI and I₂. Finally, model predictions of IO
767 underestimate IO levels for the Southern Ocean region but overestimate IO in the Indian Ocean.
768 Models greatly underestimate IO in regions with higher chl-*a* concentration which could be
769 indicative of organic species playing a role (close to the Kerguelen Islands, refer Sect. 3.4.2).
770 This study suggests that the fluxes of iodine in the MBL are more complex than considered at
771 present and further studies are necessary in order to parameterise accurate inorganic and
772 organic fluxes that can be used in models. Using seawater iodide measurements and
773 calculations from different parameterisations did not alter the inorganic iodide flux estimate
774 greatly. Direct observations of HOI and I₂, alongside volatile organic iodine measurements in
775 the MBL are necessary in order to reduce the uncertainty in the impacts of iodine chemistry.

776 **6. Author contributions:**

777 ASM conceptualised the research plan and methodology. SI did the data curation, analysis, and
778 writing of the original draft. LT and RC did the iodide measurements provided unpublished



779 iodide data from ISOE-9, SK-333 and BoBBLE. PS and RCo provided salinity data for ISOE-
780 9. SCT and AUK provided chl-a data for ISOE-9. AKS and PVB provided chl-a data for SK-
781 333. AS and RR provided chl-a data from BoBBLE. CC and ASL did the CAM-Chem model
782 run for ISOE-9 and IIOE-2. TS did the GEOS-Chem model run for ISOE-9, IIOE-2 and ISOE-
783 8.

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791 **8. References**

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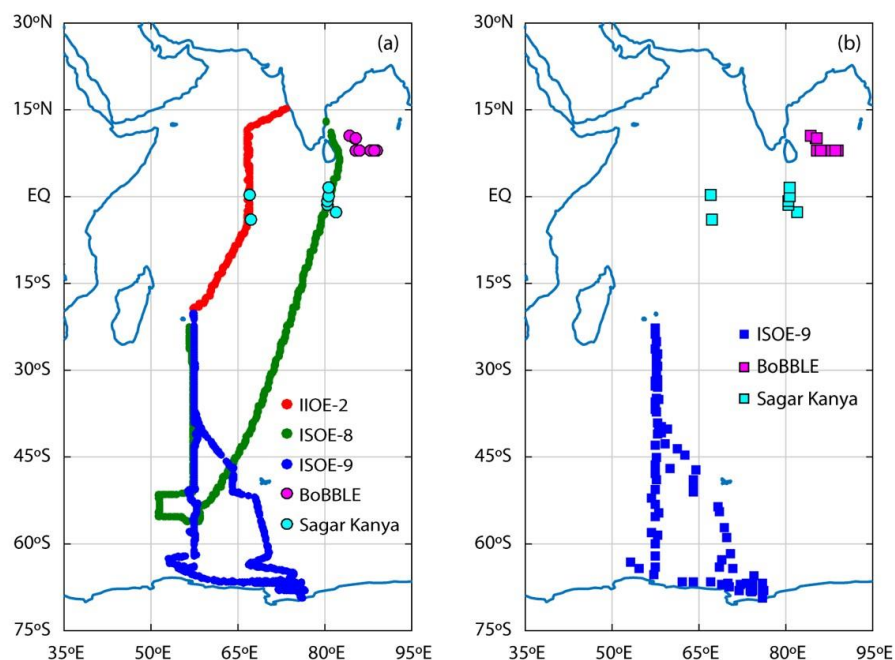


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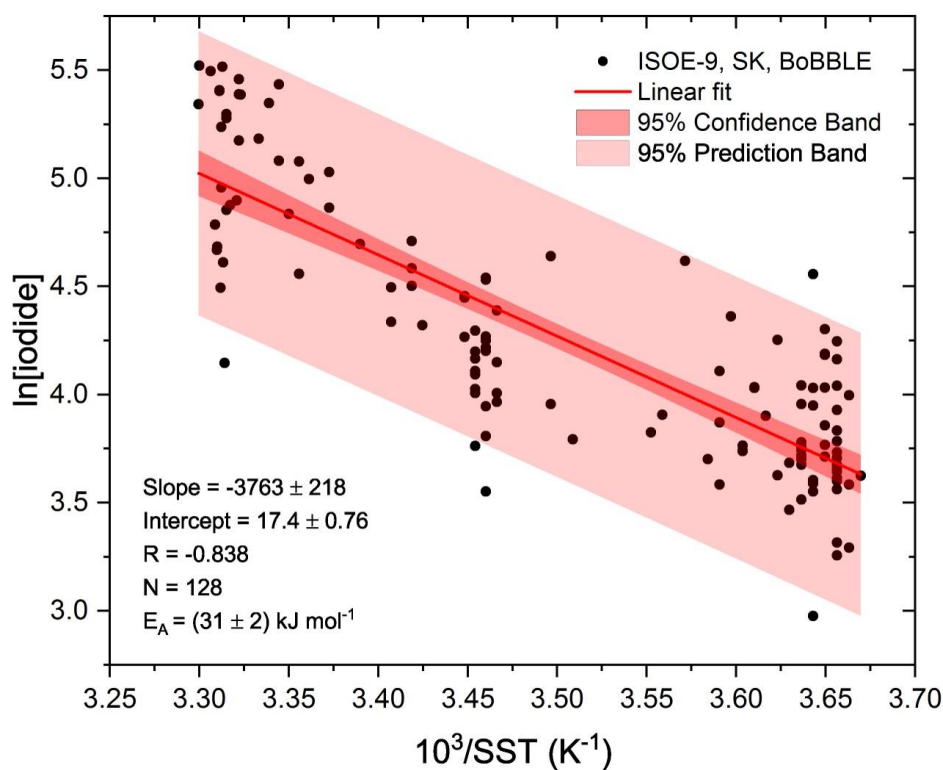


1038 9. Figures



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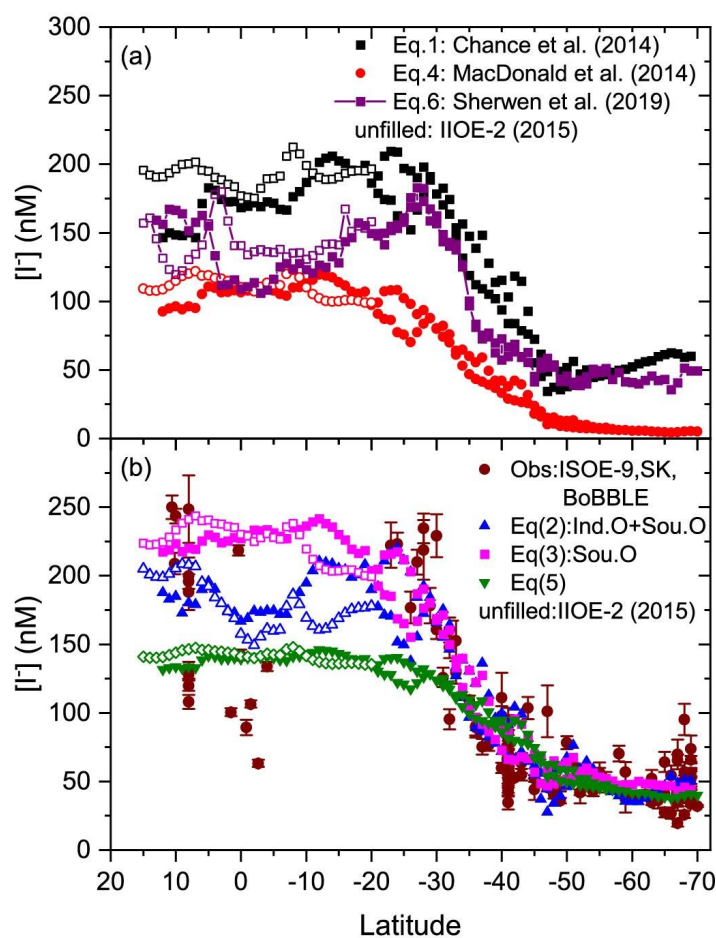
1040 **Figure 1: Map of the Indian Ocean and the Southern Ocean (a) with cruise tracks for**
 1041 **campaigns conducted during the austral summer of 2014-2016. Green circles indicate the**
 1042 **cruise track for ISOE-8, red circles show the cruise track for IIOE-2, and blue circles**
 1043 **indicate the cruise track for ISOE-9. Magenta and cyan circles indicate sample locations**
 1044 **for the BoBBLE and SK-333 expeditions respectively. (b) boxes represent 129 seawater**
 1045 **iodide sampling locations from 3 expeditions following the colour code in (a).**



1046

1047 **Figure 2: Arrhenius form plot of sea surface iodide concentrations against SST from all**
 1048 **available seawater iodide field observations in the Indian Ocean and Southern Ocean.**
 1049 **The red line represents a linear fit., the shaded region in dark red (inner) indicates the**
 1050 **95% confidence bands and shaded area in light red (outer) indicates the 95% prediction**
 1051 **bands.**

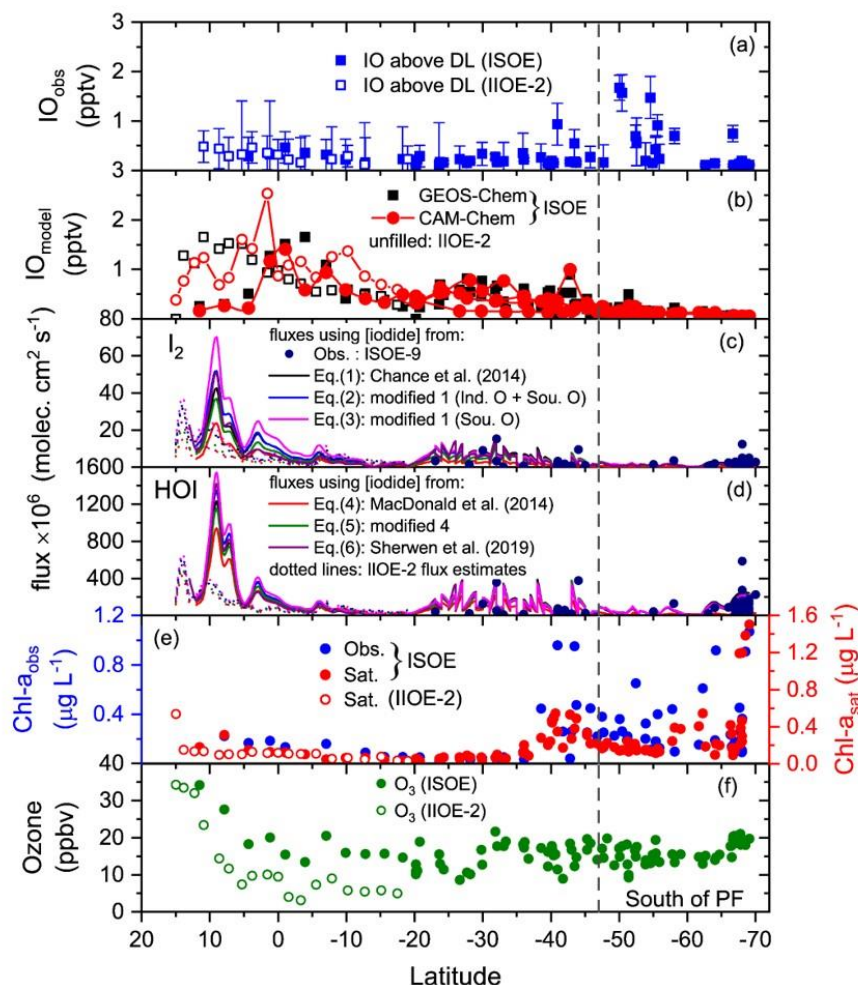
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1054 **Figure 3: Latitudinal averages of calculated sea surface iodide (SSI) concentrations for**
 1055 **each campaign using (a) existing, (b) new parameterisation tools and observations from**
 1056 **ISOE-9, SK-333, and BoBBLE. Filled markers represent combined SSI from ISOE-8 and**
 1057 **ISOE-9, unfilled markers represent SSI from IIOE-2 campaign.**

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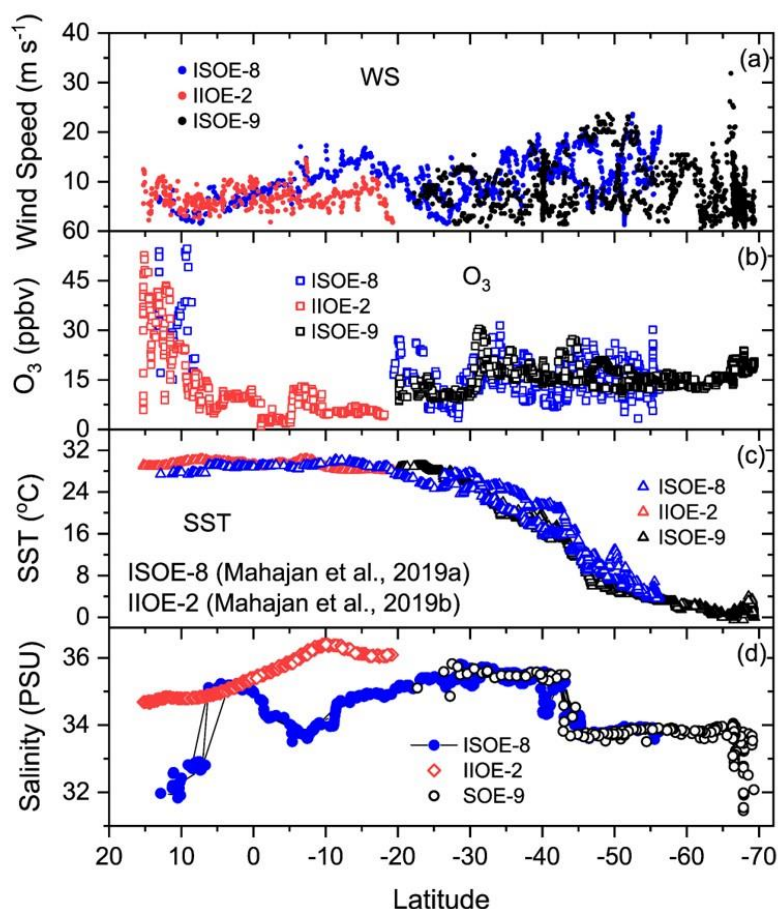
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1060 **Figure 4: Daily averaged atmospheric and oceanic parameters combined from ISOE-8,**
 1061 **IIOE-2, and ISOE-9 field campaigns. Data marked ISOE represents combined data from**
 1062 **ISOE-8 and ISOE-9. Unfilled markers and dotted lines show values for IIOE-2. (a) IO**
 1063 **above detection limit from ISOE-8, ISOE-9 and IIOE-2. (b) Surface IO values from**
 1064 **GEOS-Chem and CAM-Chem models. (c) and (d) comprise of HOI and I₂ fluxes**
 1065 **estimated from Eq. (7) and (6) respectively. Fluxes are colour coded for different sea**
 1066 **surface iodide (SSI) datasets used for their estimation. Colours black, blue, red and green**
 1067 **correspond to fluxes calculated using SSI estimation from Eq. (1) to (5), purple colour**
 1068 **represents the use of model SSI predictions (Sherwen et al., 2019b), filled circles in dark**
 1069 **blue correspond to measured SSI from ISOE-9 for each observation, (e) chlorophyll-*a***
 1070 **observations from ISOE-8 and ISOE-9 (blue circles) and satellite data for all campaigns**
 1071 **(red circles). (f) ozone mixing ratios from campaigns ISOE and IIOE-2. The dashed line**



marks the polar front at 47° S. Observational plots for ISOE-8 and IIOE-2 were adapted
 from Mahajan et al. 2019 a & b.

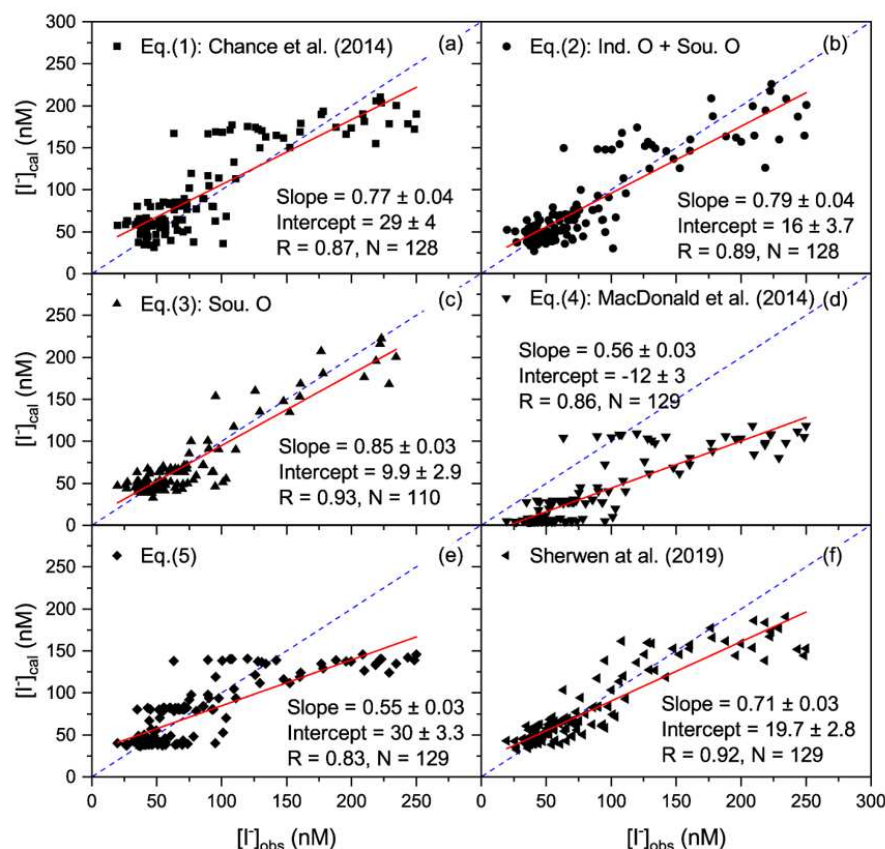
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1076 **Figure 5: Latitudinal plot of hourly-averaged field measurements of wind speed, ozone**
 1077 **mixing ratios, SST and salinity[†] from ISOE-8, IIOE-2, and ISOE-9 campaigns. Data**
 1078 **markers in red belong to the IIOE-2 campaign; those in blue belong to the ISOE-8 and**
 1079 **markers in black are from ISOE-9 for all the panels. Observational plots for ISOE-8 and**
 1080 **IIOE-2 were adapted from Mahajan et al. 2019 a & b.**

[†] Salinity data for IIOE-2 are monthly climatological means from World Ocean Atlas as described in the supplementary text.

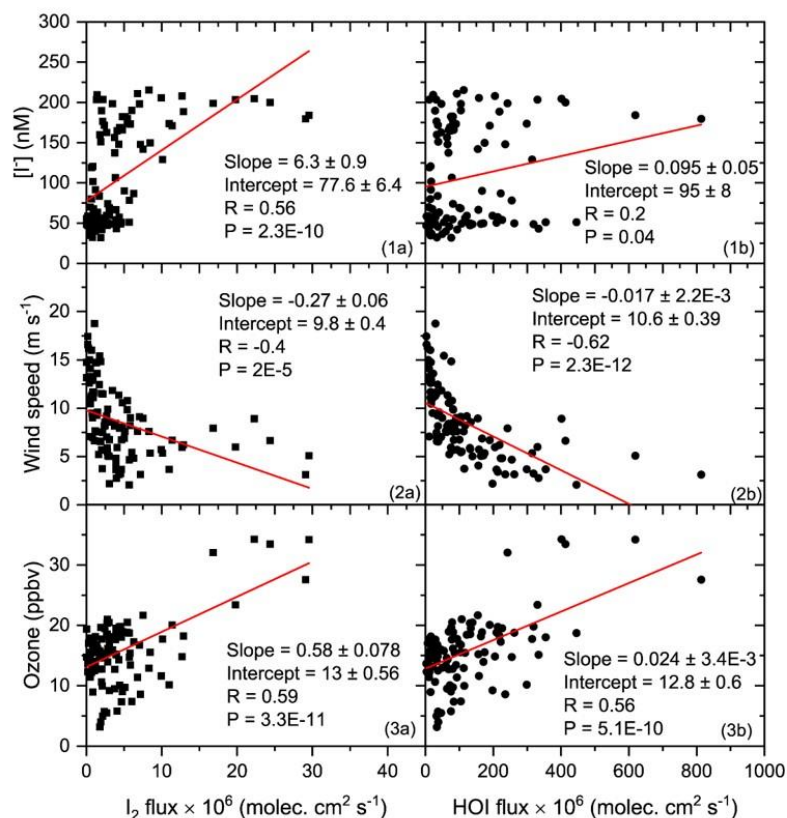


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1082 **Figure 6: Linear fit analysis of estimated sea surface iodide (SSI) concentrations (y axis)**
 1083 **from parameterisation methods in Eq. (1) to (5) and model prediction (Sherwen et al.,**
 1084 **2019) against measured SSI concentration (x axis) from ISOE-9, SK-333 and BoBBLE.**
 1085 **In panel (c) SSI are compared only with ISOE-9 observations for Southern Ocean specific**
 1086 **parameterisation. R represents Pearson's correlation coefficient and N is the size of the**
 1087 **dataset. Dashed blue line represents identity (1:1) line.**

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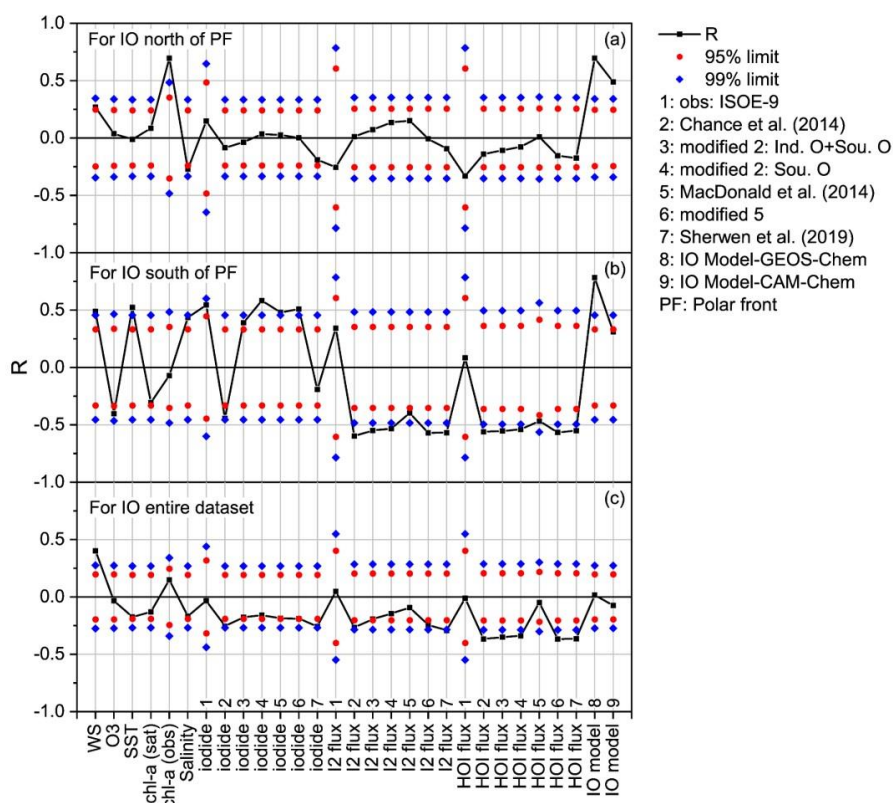
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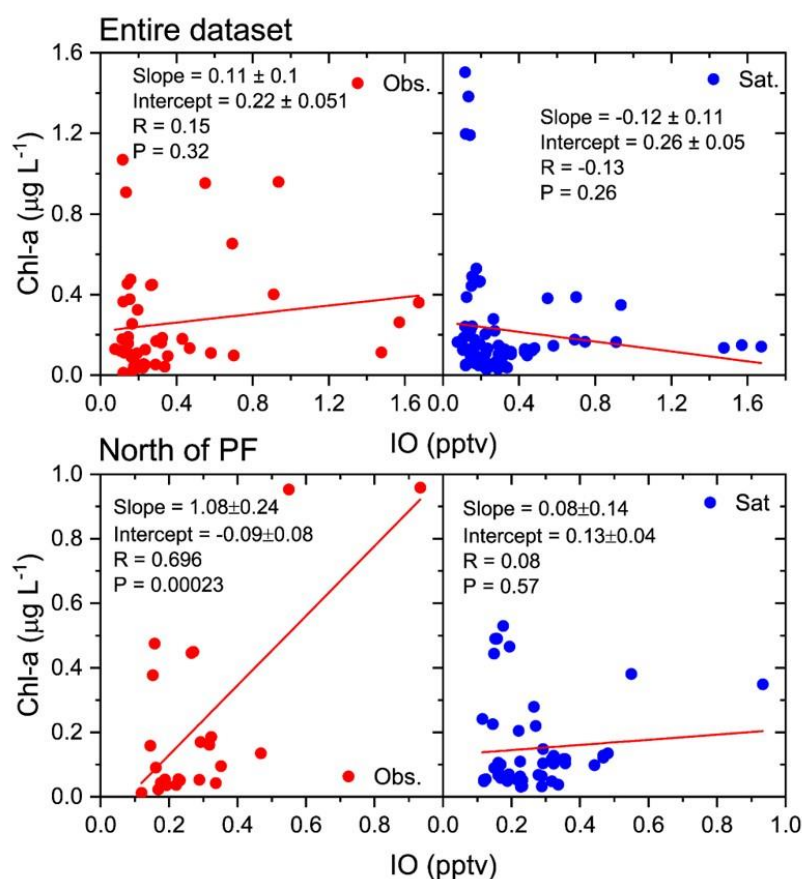
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1091 **Figure 7: Linear fit of daily average sea surface iodide (SSI) concentration, wind speed**
 1092 **and ozone mixing ratio (y axis) against calculated I_2 and HOI flux (x axis) against for all**
 1093 **the campaign. HOI and I_2 are calculated using SSI estimated using the modified Chance**
 1094 **parameterisation for Indian Ocean and Southern Ocean in Eq. (2).**

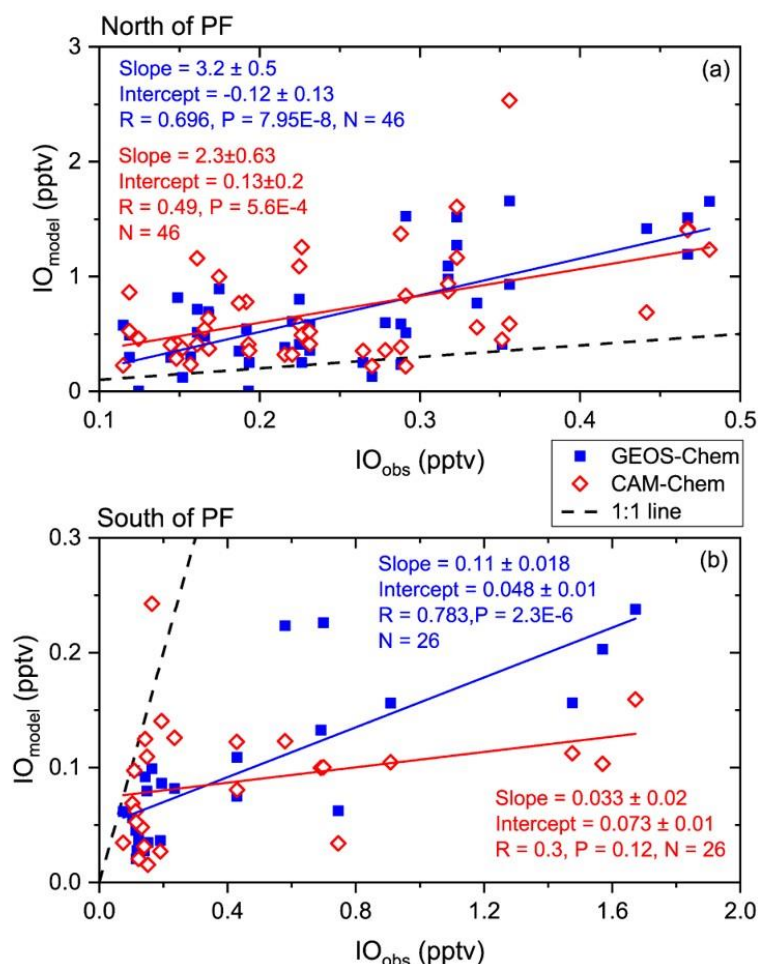
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 1097 **Figure 8: Pearson's correlation coefficient of observed iodine monoxide (IO) with oceanic**
 1098 **and atmospheric parameters combined for ISOE-8, IOE-2, and ISOE-9 campaigns.**
 1099 **Correlations are performed for daily averages of IO and corresponding parameters listed**
 1100 **on the X axis. The black squares represent Pearson's correlation coefficients (R), the**
 1101 **diamonds (blue) mark the 99% confidence limit, and the circles (red) correspond to the**
 1102 **95% confidence limits in all the panels, (a) includes data from all campaigns to the north**
 1103 **of the polar front (n = 72), (b) represents combined data for the south of the polar front**
 1104 **(n = 48), the last panel (c) includes the entire dataset from three campaigns (n = 120).**
 1105



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 1107 **Figure 9: Linear fit of daily averaged field observations of chlorophyll-a (red circles) and**
 1108 **chlorophyll-a satellite data (blue circles) (y axis) against observed iodine monoxide (IO)**
 1109 **(x axis) from ISOE-8, HIOE-2, and ISOE-9 campaigns. The top panel includes**
 1110 **chlorophyll-a for the entire dataset; the bottom panel includes data to the north of the**
 1111 **polar front.**
 1112



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1114 **Figure 10: Linear fit of daily averages of modelled surface iodine monoxide (IO) output**
 1115 **(y axis) from GEOS-Chem (filled blue squares) and CAM-Chem (unfilled red diamonds)**
 1116 **against observed IO (x axis) for ISOE-8, IIOE-2 and ISOE-9 campaigns. (a) includes**
 1117 **linear fits of both GEOS-Chem and CAM-Chem for IO detected to the north of the polar**
 1118 **front, (b) shows the same for the region south of the polar front. Two data points in panel**
 1119 **(a) at 41° S and 43° S are removed due to large differences between observation and**
 1120 **modelled values.**

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1125 **10. Tables**

Expedition	Research Vessel	Duration	Location	Meridional Transect	Observations
8 th 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 ₃
2 nd 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 ₃
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 ⁻
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 ⁻
9 th 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 ₃ , I ⁻

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1127 **Table 1: Details of the three expeditions contributing to the IO and seawater iodide**
 1128 **dataset in this study. Expeditions are listed in chronological order from 2014 to 2016.**

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Eq. No	Reference	Parametric equation ([iodide] in nM)	Database location	Data points	R ^{2*}	R ²
Eq. 1	Chance <i>et al.</i> (2014)	$[iodide] = 0.28(\pm 0.002) \times sst^2 + 1.7(\pm 0.2) \times latitude + 0.9(\pm 0.4) \times [NO_3^-] - 0.02(\pm 0.002) \times MLD_{pt} + 7(\pm 2) \times salinity - 309(\pm 75)$	Majorly Atlantic and Pacific Ocean	$n = 673$	0.676	0.758
Eq. 2	This study	$[iodide] = 0.36(\pm 0.04) \times sst^2 - 2.7(\pm 0.5) \times latitude + 0.28(\pm 0.57) \times [NO_3^-] + 0.64(\pm 0.17) \times MLD_{pt} - 5.4(\pm 3.82) \times salinity + 22(\pm 137)$	Indian and Southern Ocean	$n = 128$	0.794	0.794 [^]
Eq. 3	This study	$[iodide] = 0.25(\pm 0.017) \times sst^2 - 0.6(\pm 0.4) \times latitude + 2.2(\pm 0.4) \times [NO_3^-] - 5.5(\pm 3.3) \times salinity + 212(\pm 123)$	Southern Ocean	$n = 110$	0.859	0.859 [^]
Eq. 4	MacDonald <i>et al.</i> (2014)	$[iodide] = 1.46 \times 10^{15} \times \exp\left(\frac{-9134}{SST}\right)$	Atlantic, Central and West Pacific Ocean	$n = \sim 88$	0.71	0.739
Eq. 5	This study	$[iodide] = 3.6 \times 10^7 \times \exp\left(\frac{-3763}{SST}\right)$	Indian and Southern Ocean	$n = 129$	0.702	0.697 [^]
Eq. 6	Sherwen <i>et al.</i> (2019)	Machine learning based regression approach	Atlantic, Pacific, Indian and Southern Oceans	$n = 1293$	-	0.842

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1134 **Table 2: List of existing global (italics) and new region-specific (regular)**
 1135 **parameterisations for sea surface iodide concentration indicating data location and**
 1136 **number of data points used to formulate each equation. Here [iodide] represents sea**
 1137 **surface iodide concentration in nM, sea surface temperature as ‘sst’ in °C, and SST in K.**
 1138 **Nitrate concentration ([NO₃⁻]) is given in μmol L⁻¹, mixed layer depth as *MLD_{pt}* in m,**
 1139 **subscript ‘pt’ indicates potential temperature implying a temperature change of 0.5 °C**
 1140 **from the ocean surface (Monterey and Levitus, 1997), and salinity in PSU. Further details**
 1141 **on individual parameters and the choice of Eq. (1) over others proposed in Chance et al.**
 1142 **(2014) are discussed further in the supplementary text. R^{2*} represents the initial**
 1143 **coefficient of determination (COD) while deriving each parameterisation, and R²**
 1144 **represents COD from correlation analysis of the calculated iodide with observations in**
 1145 **this study (ISOE-9, SK-333, BoBBLE).**



1146 **^Higher R^2 values for the modified parameterisations reflect the fact that they have been**
1147 **derived using the same observational data as they are tested on.**