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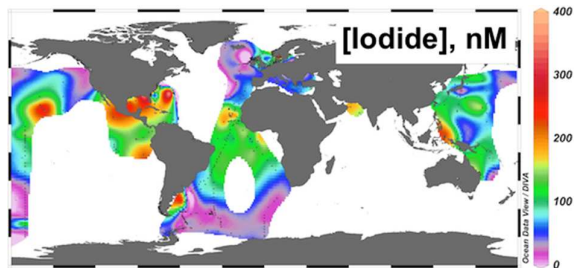
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An extensive compilation of sea surface iodide concentrations reveals a pronounced latitudinal gradient and associations with temperature, mixing and nitrate.



ARTICLE

The distribution of iodide at the sea surface

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Abstract

Recent studies have highlighted the impact of sea surface iodide concentrations on the deposition of ozone to the sea surface and the sea to air flux of reactive iodine. The use of models to predict this flux demands accurate, spatially distributed sea surface iodide concentrations, but to date, the observational data required to support this is sparse and mostly arises from independent studies conducted on small geographical and temporal scales. We have compiled the available measurements of sea surface iodide to produce a data set spanning latitudes from 69°S to 66°N, which reveals a coherent, large scale distribution pattern, with highest concentrations observed in tropical waters. Relationships between iodide concentration and more readily available parameters (chlorophyll, nitrate, sea surface temperature, salinity, mixed layer depth) are evaluated as tools to predict iodide concentration. Of the variables tested, sea surface temperature is the strongest predictor of iodide concentration. Nitrate was also strongly inversely associated with iodide concentration, but chlorophyll-a was not.

Environmental Impact

Atmospheric iodine chemistry impacts on climate, air quality and human health. The sea surface is the dominant source of atmospheric iodine. The reaction of iodide with ozone at the sea surface is thought to be an important sink for tropospheric ozone, and a major contributor to the sea-to-air flux of reactive iodine; seawater iodide concentrations are a source of uncertainty in quantifying these processes. In this review, we describe the distribution of iodide at the sea surface, based on a comprehensive compilation of the available measurements, and evaluate parameters that may be used as a proxy for iodide concentration, in order that iodide distributions may be incorporated into large-scale atmospheric and oceanic models.

1. Introduction

In the lower atmosphere, iodine is involved in catalytic ozone destruction cycles and particle formation reactions that impact upon both the oxidising capacity of the atmosphere and the Earth's radiative balance¹⁻⁷. Tropospheric ozone is a greenhouse gas and is harmful to both human health and vegetation, including food crops. As a key oxidant, ozone is also involved in reaction cycles that remove hydrocarbons from the troposphere. A detailed understanding of the controls on tropospheric ozone levels is thus a major goal in atmospheric

chemistry. Atmospheric iodine chemistry also has potential to perturb the balance of other important species such as peroxy radicals and nitrogen oxides^{6,8}, and may enhance rates of mercury oxidation and deposition at high latitudes⁸. A key species in these chemical cycles is the iodine oxide (IO) radical, which may also be involved in particle nucleation events where levels are sufficiently high^{7,9-12}. The particles formed in such events have potential to act as cloud condensation nuclei, and so can indirectly affect climate via impacts on the radiative properties of clouds. Iodine is also an essential nutrient for humans and many other animals, deficiency of which is the leading cause of preventable brain damage in children¹³. Sea-to-air transfer, followed by atmospheric transport and deposition onto land, is an important pathway by which iodine can enter the human food chain. It is also a route by which radionuclides of iodine discharged (intentionally or accidentally) to the

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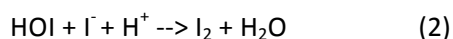
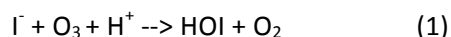
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oceans from nuclear facilities may be returned to the terrestrial environment.

The oceans are the largest reservoir of iodine after the Earth's crust, containing a total of around 7.93×10^{10} tonnes¹⁴. In seawater, the majority of iodine is found as one of two dissolved inorganic ions – iodide (I^-) and iodate (IO_3^-)¹⁵. The total amount of inorganic iodine (the sum of iodide and iodate) is close to constant across the oceans at ~ 450 to 500 nM¹⁵⁻¹⁷, but the ratio of iodide to iodate varies with both geographical location and depth (see section 3).

Sea-to-air exchange is the dominant source of iodine to the atmosphere^{1,8} with an estimated global flux of the order of 10^{12} g yr^{-1,8,18}. Until recently, fluxes of volatile organic iodine compounds (e.g. CH_3I , CH_2I_2) were thought to be the main source of iodine to the marine atmosphere (e.g.^{1,4,11}). However, it has become evident that known sources of organoiodines cannot sustain the observed concentrations of gas-phase iodine oxide^{6,19-22}, and consequently there has been a resurgence of interest in the reactions of inorganic iodine compounds at the sea surface.

At the air-sea interface, dissolved iodide (I^-) reacts with gas phase ozone to liberate molecular iodine via reactions (1) and (2) below^{18, 23, 24}:



Reaction (1) is one of a number of processes known to destroy ozone in the surface ocean²⁵, which together are thought to be responsible for the observed atmospheric ozone deposition velocity to the oceans being 40 times greater than that predicted from physical dissolution alone²⁶. Deposition to the sea surface is a significant ozone sink, accounting for around one third of total global ozone dry deposition flux ($600 - 1000$ Tg O_3 yr⁻¹; ²⁷). Estimates of the contribution of reaction (1) to the chemical enhancement of ozone deposition range from 20% ²⁸ to almost 100% ²⁵.

The reactive iodine (HOI and I_2) released to the atmosphere as a result of reactions (1) and (2) is photolysed to yield iodine atoms, which in turn react with ozone in the gas phase to form iodine oxide^{1, 8}. This gas phase chemistry represents a catalytic loss pathway for tropospheric ozone. Carpenter et al.²⁹ recently demonstrated that reactions (1) and (2) could explain around 75% of the iodine oxide levels measured over the tropical Atlantic. Inclusion of these reactions in atmospheric chemistry models has subsequently yielded good agreement between observed levels of molecular iodine and iodine oxide at Cape Verde²⁰, and reasonable agreement between modelled and observed iodine oxide levels over the eastern Pacific³⁰.

The strength of the reactive iodine source and the ozone deposition flux are related to sea surface iodide concentration^{24, 29, 31}, so to estimate the significance of these processes requires an accurate representation of sea surface iodide concentrations. Iodide concentrations are not constant at the sea surface; observations in different locations vary by approximately one

order of magnitude (see section 3). Measurements of iodide are sparse compared to parameters such as salinity or nutrient concentrations, and aqueous iodine species cannot yet be detected by either remote sensing or easily automated methods. The scarcity of oceanic iodide measurements and need for a synthesis of iodine biogeochemistry relevant to the atmospheric chemistry community has been highlighted in a number of recent publications^{21,32}. In the absence of comprehensive global and regional iodide data sets, sea surface iodide concentrations have instead been estimated as a function of more readily available oceanographic variables, specifically nitrate^{27,32} and chlorophyll-a^{32,33}, in the context of quantifying large-scale ozone deposition. Sea surface temperature has also been used as proxy for iodide concentration in order to estimate iodine emissions³⁰.

Here we present a geographically extensive compilation of the available sea surface iodide measurements, including data from the literature, archived resources and new, previously unpublished data collected during five research cruises. To the best of our knowledge, this is the largest and most detailed compilation of seawater iodide measurements presented to date. We describe the large-scale distribution of iodine compounds in the surface ocean, with a focus on iodide concentrations at the sea-surface, as it is this that impacts directly on atmospheric chemistry. Relationships between iodide concentration and more easily available oceanographic variables (chlorophyll, nitrate, sea surface temperature, salinity, mixed layer depth) are evaluated as tools to predict iodide concentration.

2. Compilation of the iodide data set

A large number of studies have examined the distribution of iodine compounds in the oceans over local, regional and basin wide scales. The results of these studies have been digitised where possible and supplemented by data kindly supplied directly by other investigators, data archives, and unpublished measurements made by the authors during five different field campaigns (see Table 1 for a list of data sets). Due to the small total number of measurements, the compiled data set has not been filtered according to season or time of day of sampling. The potential for temporal variation in dissolved iodine speciation is discussed in section 3.2. A total of 925

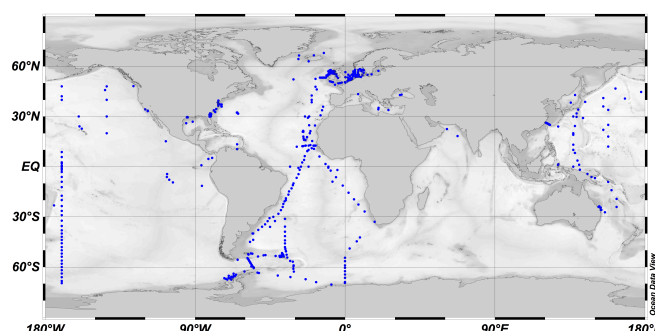


Fig 1. Locations of surface iodide measurements in the compilation; Fig. produced using Ocean Data View⁸⁰.

Table I. Contributions to iodide data set, including sampling platform and method used to measure iodide. * Indicates data sets provided directly by the originators, ** indicates data sets obtained from the British Oceanographic Data Centre (# 20, 37, 38) or online archives (# 12: <http://doi.pangaea.de/10.1594/PANGAEA.174586>; #22: <http://usjgofs.whoi.edu/jg/dir/jgofs/arabian/ttn-045/>); all other data sets were digitised from the publications listed. Abbreviations: CSSWV = cathodic stripping square wave voltammetry; NAA = neutron activation analysis; DPP = differential pulse polarography; HPLC = high performance liquid chromatography; ICP-MS = inductively coupled plasma-mass spectrometry; AMS= accelerator mass spectrometry.

#	Contributor	Location	Platform & Cruise	Method
1	*Chance, 2007 ³⁴	Southern Ocean (Atlantic sector)	RRS James Clark Ross (JR124)	CSSWV
2	*Chance, unpublished	Tropical east Atlantic	RRS Discovery (D325)	CSSWV
3	Elderfield&Truesdale, 1980 ¹⁶	Antarctic, Pacific, Atlantic	Various	Difference (spectrophotometric)
4	Truesdale et al., 2003 ³⁵	Skagerrak	RV G.M. Dannevig	CSSWV
5	Truesdale et al., 2000 ¹⁷	Atlantic meridional transect	RRS James Clark Ross (AMT3, AMT4)	Difference (spectrophotometric)
6	Truesdale et al., 2001 ³⁶	Baltic Sea	RV A.V. Humboldt	Difference (spectrophotometric)
7	Truesdale et al., 2003 ³⁷	Western Antarctic Peninsula	Juan Carlos I Antarctic base (mesocosm experiment)	Difference (spectrophotometric)
8	Waite et al., 2006 ³⁸	Seas around Iceland	RV Bjarni Saemundsson	CSSWV
9	Wong&Brewer, 1977 ^{39, 40}	Caribbean Sea, Black Sea	Various	Anion exchange + NAA
10	Campos et al., 1996 ⁴¹	Atlantic, Pacific	Bermuda Atlantic Time-series Study; Hawaii Ocean Time-series	CSSWV
11	Truesdale&Bailey, 2002 ⁴²	Eastern South Atlantic	RS Algoa (48)	Difference (spectrophotometric)
12	**Tian&Nicolas, 1995; Tian et al., 1996 ⁴³⁻⁴⁵	North west Mediterranean	DYFAMED time series	CSSWV
13	Truesdale, 1978 ⁴⁶	Indian Ocean, Atlantic, Irish Sea	Various	Difference (spectrophotometric)
14	*Jickells et al., 1988 ⁴⁷	Sargasso Sea, Bermuda inshore	RV Weatherbird	Difference (spectrophotometric)
15	Wong&Brewer, 1974 ⁴⁸	South Atlantic (Argentine basin, Angola basin)	RV Knorr (GEOSECS)	Difference (spectrophotometric)
16	McTaggart et al., 1994 ⁴⁹	Eastern Australian coast	RV Franklin	Ion chromatography
17	Truesdale&Upstill-Goddard, 2003 ⁵⁰	British east coast	RRS Challenger (C141)	Difference (spectrophotometric)
18	Wong&Zhang, 2003 ⁵¹	Southern East China Sea	RV Ocean Researcher I (314; KEEP)	CSSWV
19	Wong&Zhang, 1992 ⁵²	Southern Atlantic Bight	RV Iselin (FLEX)	Difference (DPP)
20	**Campos et al., 1999 ⁵³	South Atlantic, Weddell Sea	RRS James Clark Ross (JCR10; WOCE A23)	CSSWV
21	Nakayama et al., 1989; Nakayama et al., 1985 ^{54, 55}	North Pacific	RV Hakuohmaru (KH-84-3; KH-85-4)	Flow through electrode
22	**Farrenkopf&Luther, 2002 ⁵⁶	Arabian Sea	RV Thomas G. Thompson (TN045)	CSSWV
23	Wong et al., 1985 ⁵⁷	Orca Basin, Gulf of Mexico	USNS Lynch	Difference (DPP)
24	Ullman et al., 1990 ⁵⁸	Mediterranean	RV Tyro (87/3)	CSSWV
25	Woittiez et al., 1991 ⁵⁹	Kau Bay, Indonesian coast	RV Tyro (SNELLIUS II)	Precipitation + NAA
26	Schwehr&Santschi, 2003 ⁶⁰	Galveston Bay, Gulf of Mexico	RV Gyre	HPLC
27	Tsunogai, 1971 ⁶¹	North Pacific	RV Hakuoh Maru (KH70-1, KH70-2)	Precipitation + spectrophotometry
28	Wong&Cheng, 1998 ⁶²	Chesapeake Bay	Various	CSSWV
29	Huang et al., 2005 ⁶³	North Pacific	RV Mirai (MR03-K01)	Capillary electrophoresis
30	Bluhm et al., 2011 ⁶⁴	Southern Ocean (Atlantic sector)	RV Polarstern (ANTXXIV-3)	CSSWV

31	Wong&Cheng, 2008 ⁶⁵	Chesapeake Bay	RV Linwood Holton, RV Cape Hatteras	CSSWV Anion exchange + ICP-MS
32	Hou et al., 2007 ⁶⁶	North Sea	Not given	Precipitation + spectrophotometry
33	Tsunogai&Henmi, 1971 ⁶⁷	Pacific	RV Hakuho Maru (KH-88-4; KH-69-4; KH-70-1; KH-70-2; CSK-26)	
34	Liss, herring & Goldberg, 1973 ⁶⁸	Southern Californian coast	Not given	Difference (DPP)
35	Luther et al., 1988 ⁶⁹	North west Atlantic, Chesapeake Bay	Not given	CSSWV
36	*Baker, unpublished	Eastern North and South Atlantic	RV Polarstern (ANT18-1)	CSSWV
37	**Truesdale&Jones, 2000 ⁷⁰	Shelf seas off British Isles	RRS Challenger (CH125, C126)	Difference (spectrophotometric)
38	**Luther, unpublished	South west Atlantic	RRS Discovery (D199; WOCE A11)	CSSWV
39	*Chance, unpublished	Western Antarctic Peninsula	RV Laurence M. Gould (LMG1201)	CSSWV
40	*Chance, unpublished	Tropical Atlantic	RRS Discovery (D361)	CSSWV
41	Hou et al., 2013 ⁷¹	Offshore Fukushima	RV Kaimikai-O-Kanaloa	Anion exchange + AMS
42	Rue et al., 1997 ⁷²	Tropical North Pacific	VERTEX II and III sites	Difference (DPP)
43	*Chance et al., 2010 ⁷³	Western Antarctic Peninsula	Rothera Oceanographic and Biological Time Series	CSSWV
44	Wong, 1976, 1977 ^{40, 74}	Equatorial Atlantic	RV Atlantic II (AII-83)	NAA

surface data points collected from 44 sources have been collated into a single data set. The locations of data points included in the surface compilation are shown in Fig. 1.

Surface is here defined as the upper 20 m of the water column. This depth was selected as a compromise between maximising the number of data points included and attempting to represent concentrations at the actual surface accurately. At the air-sea interface itself, it has been suggested that iodide concentration may be enhanced or depleted compared to the bulk surface seawater immediately below; this is discussed in section 3.5. Iodide measurements made within a few millimetres of the ocean surface are extremely rare, so it was necessary to use bulk surface water measurements in this compilation. On ship-based campaigns, 'surface' water is usually collected from an underway pumped seawater inlet (typically at a depth of around 6 m on a 100 m length research ship), and/or sampling bottles mounted on a CTD rosette and closed within a few metres of the sea surface, but during some field campaigns (e.g. winter samples in the Antarctic⁷³), only data from 15 m depth was available. In most cases, the water column is thought to be sufficiently homogenous between 0 and 20 m that this choice of depth can be assumed to be representative of concentrations in the top few metres of the water column (see section 3.4 for a description of the changes in iodine speciation with depth).

A variety of different methods for the determination of iodine species in seawater have been reported in the literature. Details of the methods used in each study included in our compilation are summarised in Table 1. For all unpublished data included here, iodide was measured using cathodic stripping square wave voltammetry (CSSWV)^{69,75}, following protocols described in Chance et al., 2010⁷³. Direct

measurements of iodide are most commonly made by CSSWV, which is specific for the iodide ion. Other direct methods of iodide determination include ion chromatography⁴⁹, capillary electrophoresis⁶³ and flow through electrodes⁵⁵. Precision estimates for direct methods are 4 - 10% for CSSWV^{69,73,75}, 2% for ion chromatography⁴⁹, 3% for capillary electrophoresis⁶³ and 5% for the flow through electrode method⁵⁴. Other studies do not measure iodide directly, but infer it as the difference between total dissolved iodine and iodate concentrations, where these parameters have usually been determined by spectrophotometric^{47,70} or polarographic^{52,68} techniques. The precision of these methods is less than 5% for each species, and sometimes reported as better than 1%^{47,52,68,70}; propagation of errors leads to an uncertainty of between <6% to ~28% for an iodide concentration of 100 nM calculated by difference, and will increase as iodide concentration decreases. Depending on the analytical methods used, the difference approach may result in a small over-estimation of iodide, due to the presence of an unquantified organic iodine fraction with variable reactivity towards the total iodine method. In the open ocean, the dissolved organic iodine fraction is very small (less than 10%)^{15,58,76} and only a portion of this is may cause analytical interference, so this effect is negligible. However, in coastal waters where organic iodine may be high (40 to 80% e.g. ⁷⁶⁻⁷⁹) it could become significant. Generally, the analytical uncertainties for the iodine species are small compared to the observed environmental gradients. In some campaigns included in our compilation (e.g. Truesdale et al., 2000⁷⁰), iodide concentrations were not reported, and so we have calculated them by difference, using total iodine and iodate concentrations taken from the relevant publication.

3. The distribution of iodine compounds in seawater

3.1. Iodide and iodate concentrations at the sea surface

The 925 surface iodide concentrations in our compilation are shown in Figs. 2A and Fig. 3, and the corresponding iodate concentrations are shown in Fig. 2B. Fig. 2 was produced using the DIVA interpolation function in the Ocean Data View software⁸⁰. The estimated uncertainties for each iodide measurement are shown in Fig S1 (in the Supplementary Information). Observed iodide concentrations range from

undetectable (limits of detection were not always reported, but are typically around 1 nM) to 700 nM, with a median value of 77 nM and interquartile range of 28 to 140 nM (Fig. 4). Although coverage of iodide measurements is sparse compared to parameters such as nutrients and pigments, sufficient data exists to be able to describe the large scale distribution, which shows a clear and systematic spatial gradient. In general, highest iodide concentrations (greater than 100 nM) are observed at low latitudes and lower iodide concentrations (less than 50 nM) at latitudes greater than about 40 degrees north or

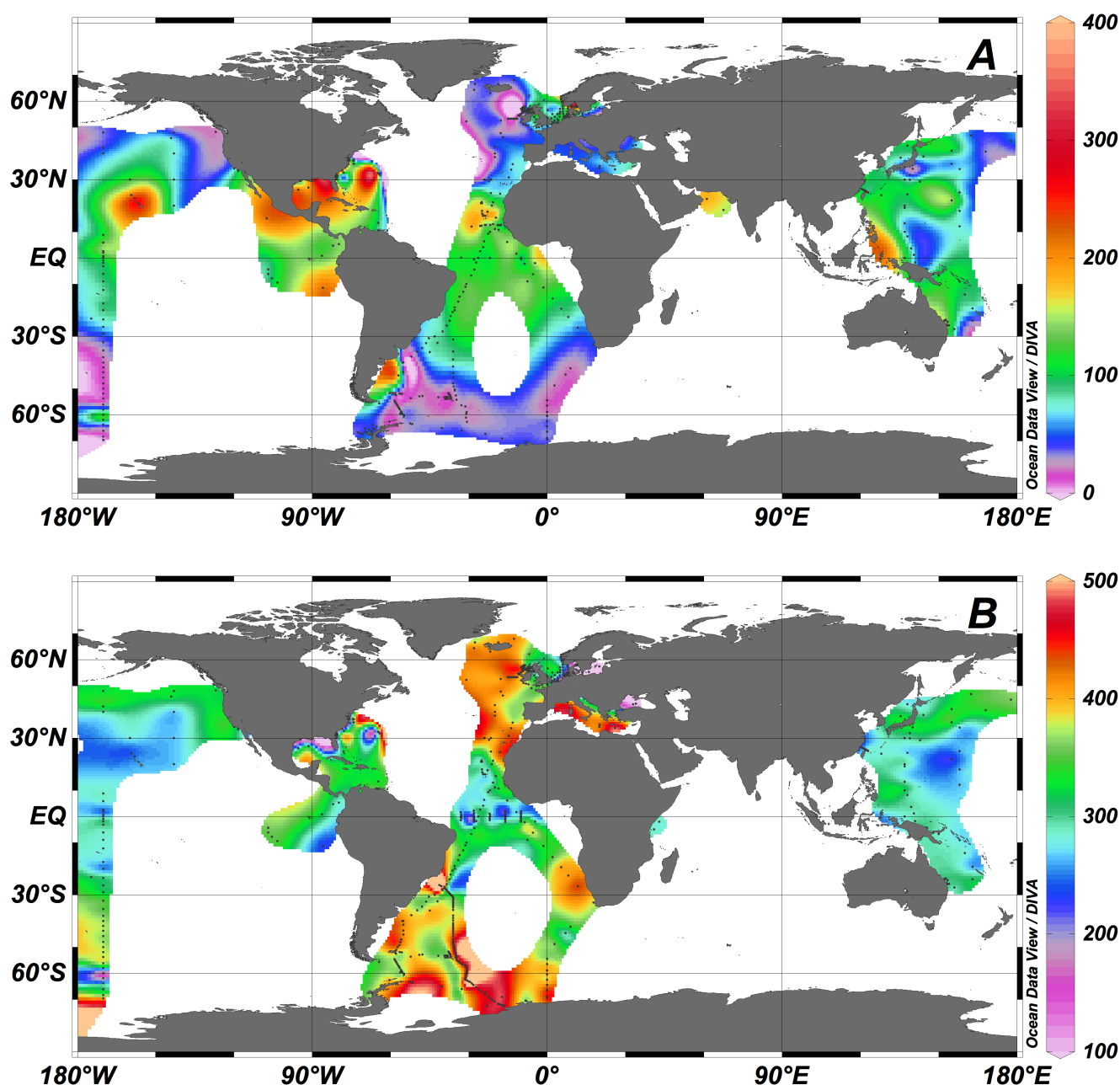


Fig 2. Sea surface iodide (A) and iodate (B) concentrations (nM), plotted and interpolated using Ocean Data View⁸⁰ with DIVA gridding at 10 °/° x and y scale length, bad estimates hidden at quality limit of 3.0. Note (B) displays some additional data points where iodate but not iodide measurements were available.

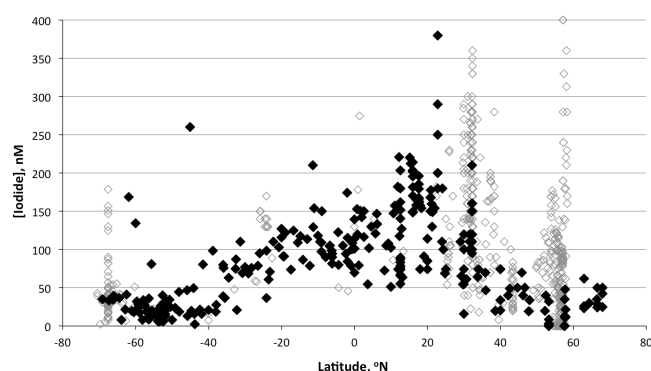


Fig 3. Variation of sea-surface iodide concentration with latitude for entire data set (open diamonds) and open ocean data only (filled diamonds). For clarity, one exceptionally high coastal iodide value (700 nM, 58.25°N) has been omitted.

or south (Figs. 2A, 3). Iodide concentrations were significantly correlated with absolute latitude (Tables 2 and 3). The increase in iodide concentrations with decreasing latitude is particularly pronounced between about 50° and 20°, while at tropical latitudes there is a slight indication of a levelling, or even a dip, in iodide concentrations moving toward the equator (Fig. 3). Iodate has an approximately opposite distribution to iodide (Fig. 2B), with highest levels typically observed at high latitudes. This large-scale latitudinal gradient in iodine speciation has been demonstrated during transects of the Atlantic^{17,53} and Pacific⁶⁷.

A number of studies have observed a decrease in the proportion of dissolved inorganic iodine present as iodate as the coast is approached^{46,47,52}, and it has been suggested that reduction of iodate to iodide may be particularly effective in coastal waters^{50,51,81}. We note that the highest iodide concentrations in our compilation often occur near coastlines (Fig. 2). In order to separate the effects of latitude and coastal proximity on iodide distribution, the data set was sub-divided into coastal and open ocean regions, where coastal data points were defined as those falling into coastal biogeochemical provinces⁸², plus Bermuda inshore waters which fall within an open ocean province (NAST-W) but are on the Bermuda platform⁴⁷. Exceptions to the latitudinal trend in iodide concentrations occur almost exclusively in coastal waters (Fig. 3). For a given latitude, iodide concentrations appear to have higher variability in coastal waters compared to the open ocean (Fig. 3). This may in part reflect a sampling bias, in that coastal waters may have been sampled at more different times of year (including time series studies) than open ocean locations, which may have only been visited during a single research cruise. Considering all latitudes, there is a modest difference in the spread of data between the open ocean and coastal sub-sets. Coastal waters have a larger range than open ocean waters, but this is due to the occurrence of a very high outlier with an iodide concentration of 700 nM (Fig. 4A). This sample was collected in the Skagerrak, and had a salinity of 27.7³⁵, so may be reasonably considered an unusual case. Excluding outliers, the range of coastal samples is 53 nM greater than the open

ocean samples and the interquartile range is 20 nM greater (Fig. 4A).

Further sub-division of the open ocean data-set into arbitrary latitudinal bands (0-23.4°; 23.5 - 35.5°, 36 - 60° and >60° north or south) also demonstrates the trend for decreasing iodide concentration with increasing latitude (Fig. 4B), although there is overlap between the range of the data, particularly at low latitudes. Interestingly, iodide concentrations at the highest latitudes (> 60°) appear to be a little higher than those in more temperate regions (35 - 60°) with median values of 33 and 18 nM respectively (Fig. 4B).

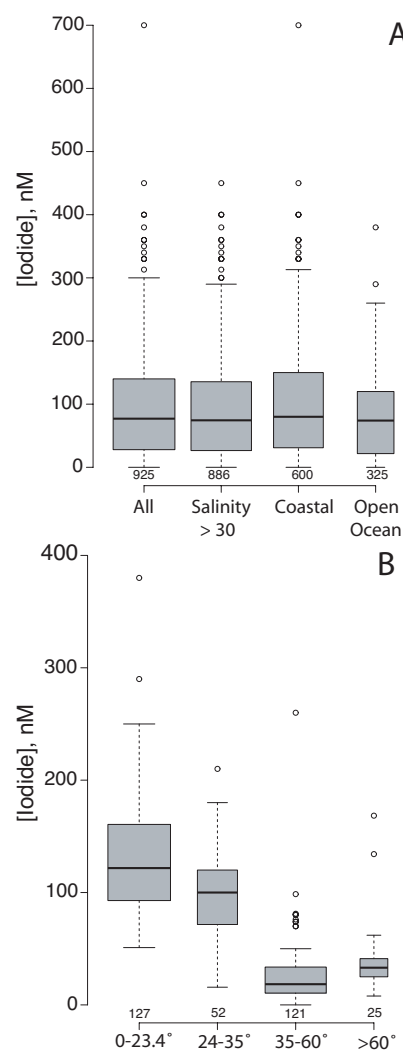


Fig. 4. Box and whisker plots showing: (A) the complete data set (n=925), all points with salinity greater than 30 (n=886), coastal data points (n=600) and open ocean data points (n=325); (B) shows open ocean data only, sub-divided according to absolute latitude into bands loosely corresponding to tropical (0-23°; n = 127), sub-tropical (24-35°; n=52), temperate (35-60°; n=121) and high latitude (>60°; n=25) regions. Centre lines show the medians, box limits show the 25th and 75th percentiles as determined by R software, whiskers extend to data points that are less than 1.5 x the interquartile range away from the 1st or 3rd quartile and dots show the outliers. Width of the boxes is proportional to the square root of the sample size. Figures produced using BoxPlotR (<http://boxplot.tyerslab.com/>)

3.2. Changes in iodine speciation with time

3.2.1. Rates of iodine redox transformations in seawater

The time scales for changes in dissolved iodine speciation in the surface ocean are quite poorly constrained. This is in part due to the scarcity of time series studies, and the need to account for external forcing such as advection and vertical mixing, as well as in-situ rates of change in a parcel of water. In general, the reduction of iodate to iodide is considered to occur more rapidly than the reverse reaction¹⁵. *Net* rates of iodide accumulation (and iodate depletion) of 0.27 to 0.55 nM day⁻¹ have been observed in the surface ocean over 78 days⁷³, but other studies have found no discernible net change over similar time periods³⁷. Under low oxygen conditions, much faster rates have been observed (~50 nM hr⁻¹; ⁸³), but these are not relevant to surface open ocean conditions. The oxidation of iodide to iodate in oxygenated seawater is slow^{15, 84}; this kinetic barrier allows iodide to persist alongside iodate in the surface ocean, despite it being thermodynamically less stable⁸⁵, and hence it is termed metastable. Estimates of the oceanic lifetime of iodide with respect to oxidation range from 40 years (~4 nM yr⁻¹; ⁶¹) to six months or less (with rates of 300 nM yr⁻¹; ⁸⁶, 270-560 nM yr⁻¹; ⁴¹ and 670 nM yr⁻¹; ⁸⁷ reported). These latter oxidation rates are too fast to be explained by suggested abiotic pathways^{15, 84, 88, 89}, so a biologically mediated route may need to be invoked, for example it has recently been suggested that iodide oxidation is associated with nitrification processes⁸⁷. Rates of change must be considered when searching for a suitable proxy for iodide concentration - a proxy which changes on an hourly or daily basis is likely to vary too rapidly to reflect significant changes in iodide concentration, while those that vary on a seasonal timescale may be more appropriate, since iodide production and loss processes appear to operate of over timescales of weeks to months.

3.2.2. Seasonal variation

The surface ocean is subject to seasonal cycles in mixing and biological production, which can in turn cause seasonal changes in concentrations of biogeochemically active chemical species⁹⁰. Very generally, vertical mixing of the water column tends to be deeper in winter, while in summer stratification causes isolation of a surface layer. In spring, increasing light levels and the onset of stratification drive an increase in phytoplankton growth (the 'spring bloom'), which consumes nutrients and may be associated with an increase in levels of biogenic compounds. Stratification prevents the resupply of nutrients by upward mixing, so eventually nutrients in the surface ocean may become exhausted, causing a decline in phytoplankton growth in the summer.

There is evidence both for and against a seasonal cycle in surface iodide (and iodate) concentrations. The spikes in iodide concentrations at 23°N, 32°N, 43°N and 67°S (Fig. 3) are the result of temporal variations observed during time series studies at stations in the tropical Pacific⁴¹, the Atlantic^{41,47}, the Mediterranean^{43,44} and the western Antarctic peninsula⁷³, respectively. Where these changes follow a discernible seasonal

cycle, surface iodide concentrations increase (and iodate concentrations decrease) over periods of stratification in summer, while minimum iodide (and maximum iodate) concentrations are observed during winter when vertical mixing is greatest^{43,47,73}. Changes in iodine speciation have not necessarily been in step with primary productivity⁴⁷, but have sometimes indicated a loss of iodate associated with the onset of phytoplankton growth in spring, and a concurrent or delayed increase in iodide concentration^{41,51,73}. Meanwhile, other studies have not found any evidence for seasonal changes in iodine speciation^{35, 38, 46, 70}.

Given the possibility of seasonal variation in iodine speciation, it would be desirable to create a climatology that is filtered by season; unfortunately, insufficient data is available to attempt this at present and the possibility of seasonal iodide variations should be considered as a source of uncertainty when modelling iodine chemistry at the sea surface. Note that the amplitudes of any unaccounted for seasonal variations in iodide concentration in the data compilation are not sufficient to mask the spatial patterns in iodide distribution described in section 3.1, and the same general trends remain even when the data is divided by season (see Figs S2a-d in the Supplementary Information). Furthermore, at the time series stations noted above, seasonal maxima and minima are lower at higher latitudes (Fig. 3).

3.2.3. Diel variation

As the measurements collated in our iodide data set were taken at many different times of day and night, and we have not attempted to filter the data set according to time of day of sampling, it is pertinent to consider whether iodine speciation in the surface ocean exhibits any diel variation. Though most incubation experiments and time-series measurements report rates of change too low to be detectable on a timescale of hours at typical marine chlorophyll-a levels^{37,41,73,91-93}, consistent with an absence of diel cycling, these rates are based on *net* changes in iodine speciation observed over timescales of a day or more. A slow net rate of change does not preclude the occurrence of

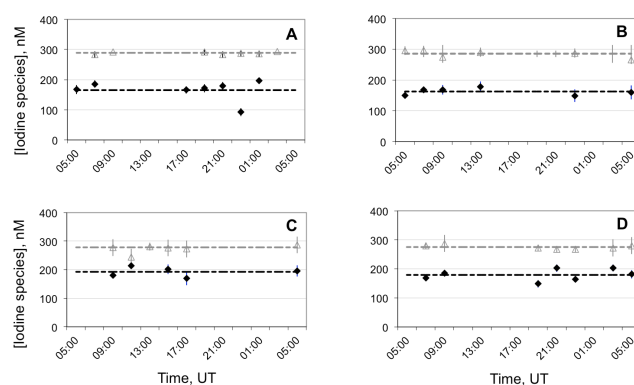


Fig 5. Concentrations of iodide (filled diamonds) and iodate (open triangles) sampled over 24 hour periods at three stations in the tropical east Atlantic: (A) 18°N, 23°W, ~2 m depth; (B) 21°N, 25°W, ~2 m depth; (C) 16°N, 24°W, ~2m depth; (D) 16°N, 24°W, ~9 m depth (chlorophyll maximum). Samples collected during cruise D325 of the RRS Discovery in 2007 (unpublished data).

diel cycling in these studies, because the net rates reflect the balance of iodide production and/or loss processes, either or both of which may exhibit a diel cycle. As any such cycles are unlikely to be synchronous, it is possible that daily fluctuations in iodide concentration may occur which are larger than the net change observed over a 24 period or multiple thereof.

In order to investigate the possibility of a diel cycle in iodine speciation, we conducted Lagrangian sampling of surface seawater over 24 hours at three sites in the tropical east Atlantic. The samples were collected during cruise D325 of the RRS Discovery⁹⁴. Iodide and iodate concentrations were found to be effectively constant over time (Fig. 5), suggesting iodine species do not undergo diel cycling in the oxygenated surface ocean. This supports our assumption that sampling time does not have a significant effect on iodine speciation. To the best of our knowledge, only three other studies have examined diel variation in iodine speciation specifically, though none under conditions directly relevant to the oxygenated surface ocean. Brandão et al.⁹⁵ reported diurnal changes in iodide and iodate concentrations in nutrient enriched unfiltered seawater incubated under natural light, but not in filtered seawater. The most striking change was an increase in iodide concentration associated with decreasing pH and oxygen levels, during night-time periods of net respiration. The high net primary productivity reported for these experiments (50 to 280 mg C m⁻³ hr⁻¹) suggest that phytoplankton density and/or growth rates in the experimental vessel (an 11 L glass vat) were very much greater than in the ocean. Beck and Bruland⁸³ observed diel variations in a shallow (~1.5 m maximum depth) tidal pool; as noted above, iodate was rapidly converted to iodide following the onset of sub-oxic conditions while the pool was isolated, while tidal flushing replenished the pool with higher iodate/lower iodide waters. Similar factors are likely to be the cause of changes in iodide and iodate concentration observed over periods of hours at a shallow, estuarine site⁹⁶. While further research is required to confirm whether or not iodine species undergo diel cycles in the surface ocean, the available evidence suggests it is unlikely to be important.

In addition to processes associated with photosynthesis, photochemistry is a potential driver of diel variation. The evidence for a photochemical influence on iodine speciation in seawater is mixed. Some incubations of cell-free seawater under natural sunlight have shown detectable increases in iodide concentration over periods of hours^{34,97} but others have not⁹⁵, and the amount and nature of organic matter present appears to be an important factor^{95,97,98}. Spokes and Liss⁹⁷ demonstrated that exposure of seawater to natural light caused an increase in iodide concentration, provided that organic matter was present. Photochemical reduction of iodate to dissolved organic iodine and iodide in the presence of humic acids and has also been demonstrated in salt-water solutions, using a light field replicating the UV-visible solar spectrum⁹⁹. Conversely, Brandao et al.⁹⁵ found iodate to be reduced by UV light at 254 nm, but not natural light, and further, that the UV photo-reduction was inhibited by the presence of organic matter. As iodate absorbs little light above 280 nm¹⁰⁰ and a

delay in the onset of iodide production has been observed in some experiments⁹⁷, an indirect mechanism of iodate photoreduction has been suggested, whereby dissolved organic iodine compounds are formed from iodate and organic matter, which are then photolysed to yield iodide^{97,99}. The iodine species reacting with the organic matter could be HOI or I₂, which may be formed by the reduction of iodate with solvated electrons generated from the irradiation of organic chromophores⁹⁹. The photolysis of organic iodine compounds to yield iodide has been demonstrated^{78,101,102}. In addition to photoreduction of iodate, there is also some evidence to suggest that iodide may also undergo photo-oxidation, particularly at low wavelengths^{89,98}. However, it is thought that the rate of iodide photo-oxidation in natural seawater is too slow to have a significant impact on dissolved iodine speciation⁸⁹. While it is evident that photochemical reactions can alter dissolved iodine speciation, and in particular may cause the reduction of iodate to iodide in the presence of organics, it is not clear whether or not these reactions are significant in the surface ocean. The absence of observable diel variation in the tropical Atlantic (Fig. 5), where the light-dark cycle is pronounced, suggests that photochemical reactions do not cause significant changes in iodine speciation on a daily timescale. Over longer periods, net rates of photochemical iodide production may be sufficient to make a significant contribution to net rates of iodide accumulation³⁴. The combined influence of light and organic matter on sea surface iodide concentrations requires further investigation.

3.4. Changes in iodine speciation with depth

This work is concerned with iodine speciation at the sea surface, as it is here that iodide is involved in sea-air exchange processes. However, it should be noted that iodine speciation also varies with depth. Typical depth profiles for oxygenated waters at high and low latitudes are shown in Fig. 6. In surface waters up to half of the iodine present may be found as iodide, while below the ocean mixed layer iodate dominates regardless of location, with only a few nM or less of iodide detectable. At the pH and pE of oxygenated seawater (8.1 and 12.5 respectively), iodate is predicted to be the thermodynamically stable form (based on an equilibrium constant for the interconversion of iodide and iodate of logK = 110.1)^{39,85,103}. While the preponderance of iodate in deep waters is in accordance with these simple thermodynamic predictions, the surface ocean appears to be in thermodynamic disequilibrium with respect to iodine speciation. This disequilibrium is assumed to be due to biological processes¹⁵, and is a key feature of the biogeochemical cycling of marine iodine. As exemplified in Fig 6A, the depth to which the iodide maximum/iodate minimum persists tends to loosely follow the depth of the thermocline^{43,47,49}. Under certain conditions, iodide profiles also display sub-surface maxima, which are related to anoxic³⁹ or sub-oxic conditions⁵⁶ or remineralisation processes occurring at depth^{34, 64}.

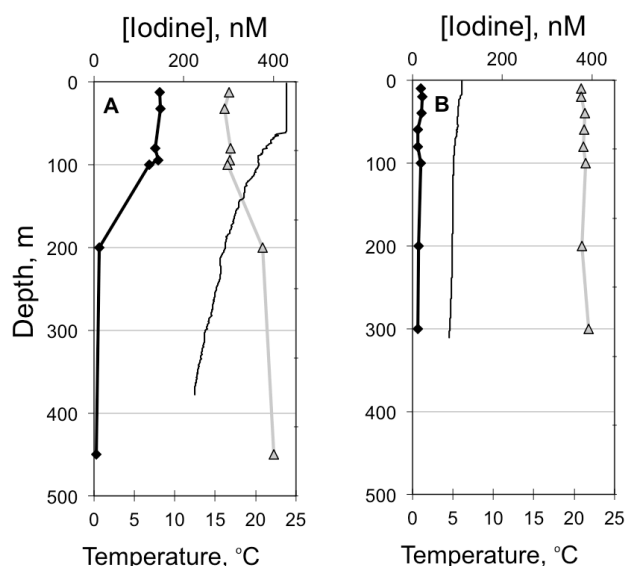


Fig 6. Vertical profiles of iodide (diamonds), iodate (triangles), temperature (solid black line) in (A) the tropical east Atlantic (20°N, 25°W) and (B) the Southern Ocean (55°S, 59°W). Samples were collected during cruise D325 of the RRS Discovery in 2007 and cruise JR124 of the RRS James Clark Ross in 2004, respectively (data unpublished).

3.5. Iodine speciation in the air-sea interface

When considering air-sea exchange processes, knowing the concentration of reactants at the interface is key, as these are not necessarily the same as in the bulk. This in turn requires consideration of the length scales over which the air-sea interface is defined. In the kinetic model of Carpenter et al.²⁹, an interfacial layer of a few μm is defined by the reacto-diffusive length over which the ozone-iodide reaction occurs. The thickness of this layer depends on the iodide concentration, for a typical bulk iodide concentration of 100 nM it is 2.6 μm . Within this layer, iodide ions may be enhanced in the immediate vicinity (~ 1 nm) of the sea surface^{104,105}. Such enhancement is a consequence of the polarisable nature of iodide ions, and has been observed in laboratory studies of salt solutions as well as being predicted in theoretical simulations^{104,105}. The partitioning of iodide to the surface can be described as a function of the bulk iodide concentration using the Langmuir isotherm¹⁰⁶.

For an interfacial layer of only a few μm , the 'bulk' seawater below may be more accurately represented by that in the sea surface micro layer (SML) than surface water at a few metres depth. The SML is a layer of water tens to hundreds of μm thick at the ocean surface, in which many physical, chemical and biological properties are distinctly different to those of the bulk seawater immediately below¹⁰⁷. Sampling the SML necessarily imposes an operational definition of microlayer thickness, which is dependent on the collection method chosen, and there is still debate as to the 'true' thickness of the microlayer¹⁰⁸. Only one study of inorganic iodine speciation in

the SML is described in the literature¹⁰⁹. Measurements of total dissolved iodine, iodate and iodide (by difference) suggested that none of these species is enriched or depleted in SML samples (~ 300 μm) relative to sub-surface water¹⁰⁹. Unpublished measurements made near Bermuda also found no significant enhancement or depletion of iodide in microlayer samples compared to water collected 1 m below the sea surface (L. Campos, pers. comm). Conversely, surface foams from marine lakes have been found to be enriched in organic iodine compounds, leading to the suggestion that organic forms of iodine might be enriched in the microlayer¹¹⁰. It has also been suggested that iodide might be depleted in the SML³². This idea was proposed to explain why modelled ozone deposition velocities were in better agreement with observations when iodide concentrations approximately one order of magnitude lower than typical oceanic levels were used³², but is not supported by observations¹⁰⁹. In summary, the available evidence suggests that iodide concentrations in the SML are similar to those in the bulk seawater below, but more measurements of iodine speciation in the SML are needed to confirm whether enrichment or depletion occurs in this important reaction zone.

4. Predicting iodide concentrations: Relationships with other oceanographic variables

Because existing iodide measurements are sparse, and current measurement techniques are time consuming and poorly suited to automation or remote sensing, a means by which to estimate iodide concentrations from some other parameter is desirable. As the controls on dissolved iodine speciation are not yet well understood, a theoretical basis by which to model iodide concentrations is lacking. Instead, we evaluate empirical relationships between iodide concentration and other oceanographic variables in order to find a suitable proxy for iodide levels.

Where available, measurements of salinity, water temperature, chlorophyll-a and nitrate made concurrently with iodide and iodate measurements have been included in our compilation of data. Additionally, climatological values for the same location (one-degree resolution) and the correct month (temperature, salinity, nitrate) or season (chlorophyll-a) have been extracted from the World Ocean Atlas 2009¹¹¹⁻¹¹³ for each iodide data point. Mixed layer depth, calculated according to three different criteria (see below for details) for the appropriate month and position (one degree resolution) were also obtained from the World Ocean Atlas¹¹⁴. Due to some iodide data points falling in grid squares designated as land in the World Ocean Atlas grid, not all iodide points could be associated with World Ocean Atlas parameters.

Statistical analysis was performed using Microsoft Excel and StatPlus:mac LE software. As the primary objective was to obtain an empirical relationship by which iodide concentration could be estimated from some other parameter, linear regression analysis was conducted. The coefficient of determination (R^2 ; Table 2) obtained by this analysis is the

Table 2. Coefficients of determination (R^2), slope (m), intercept (c) and significance ($p = 5\%$) for linear regression of [iodide] (regular font) and $\ln[\text{iodide}]$ (italic font) against variables taken from the World Ocean Atlas as described in the text. Where the dependent variable was iodide, $n = 673$, and for $\ln[\text{iodide}]$, $n = 608$.

Independent variable	R^2	m	c	$p < 5\%$?
SST ² (°C ²)	0.61 <i>0.54</i>	0.225 ± 0.007 <i>0.0030 ± 0.0001</i>	19 ± 3 <i>3.18 ± 0.05</i>	Yes <i>Yes</i>
SST (°C)	0.52 <i>0.48</i>	5.7 ± 0.2 <i>0.075 ± 0.003</i>	4 ± 4 <i>3.01 ± 0.06</i>	Yes <i>Yes</i>
SST ⁻¹ (K ⁻¹)	0.51 <i>0.49</i>	$-4.6 \times 10^5 \pm 1.7 \times 10^4$ <i>-6059 ± 263</i>	1690 ± 61 <i>25 ± 1</i>	Yes <i>Yes</i>
Latitude (°)	0.40 <i>0.37</i>	-2.7 ± 0.1 <i>-0.036 ± 0.002</i>	200 ± 6 <i>5.60 ± 0.09</i>	Yes <i>Yes</i>
Summed MLD _{pt}	0.37 <i>0.43</i>	-0.043 ± 0.002 <i>$-7.4 \times 10^{-4} \pm 3 \times 10^{-5}$</i>	144 ± 4 <i>5.00 ± 0.05</i>	Yes <i>Yes</i>
[NO ₃ ⁻], μM	0.36 <i>0.39</i>	-5.2 ± 0.3 <i>-0.074 ± 0.004</i>	125 ± 3 <i>4.67 ± 0.04</i>	Yes <i>Yes</i>
Maximum MLD _{pt}	0.34 <i>0.39</i>	-0.142 ± 0.008 <i>-0.0024 ± 0.0001</i>	131 ± 3 <i>4.78 ± 0.05</i>	Yes <i>Yes</i>
Salinity	0.18 <i>0.17</i>	23 ± 2 <i>0.31 ± 0.03</i>	-730 ± 67 <i>-6.6 ± 1</i>	Yes <i>Yes</i>
Monthly MLD _{pt}	0.17 <i>0.20</i>	-0.16 ± 0.01 <i>-0.0033 ± 0.0003</i>	106 ± 3 <i>4.4 ± 0.05</i>	Yes <i>Yes</i>
Summed MLD _{pd}	0.07 <i>0.10</i>	-0.034 ± 0.005 <i>$-5.8 \times 10^{-4} \pm 7 \times 10^{-5}$</i>	110 ± 4 <i>4.52 ± 0.06</i>	Yes <i>Yes</i>
Maximum MLD _{pd}	0.06 <i>0.07</i>	-0.12 ± 0.02 <i>-0.0020 ± 0.0003</i>	105 ± 4 <i>4.41 ± 0.06</i>	Yes <i>Yes</i>
Monthly MLD _{vd}	0.015 <i>0.009</i>	0.19 ± 0.06 <i>0.0021 ± 0.0009</i>	79 ± 4 <i>4.04 ± 0.05</i>	Yes <i>Yes</i>
Chlorophyll-a, μg l ⁻¹	0.004 <i>0.003</i>	-6 ± 4 <i>-0.07 ± 0.05</i>	89 ± 4 <i>4.16 ± 0.06</i>	No <i>No</i>
Summed MLD _{vd}	0.002 <i>0.0003</i>	0.009 ± 0.007 <i>$-0.5 \times 10^{-4} \pm 1 \times 10^{-4}$</i>	81 ± 5 <i>4.14 ± 0.07</i>	No <i>No</i>
Maximum MLD _{vd}	0.001 <i>9×10^{-5}</i>	0.03 ± 0.03 <i>$-1 \times 10^{-4} \pm 4 \times 10^{-4}$</i>	83 ± 4 <i>4.13 ± 0.06</i>	No <i>No</i>
Monthly MLD _{pd}	0.001 <i>0.005</i>	-0.04 ± 0.04 <i>-0.0011 ± 0.0006</i>	87 ± 3 <i>4.17 ± 0.05</i>	No <i>No</i>

same as the Pearson product-moment correlation coefficient (r^2). However, as neither iodide nor the dependent variables (e.g. SST) appeared to have a normal distribution, the non-parametric Spearman's rank correlation was also used to investigate associations between iodide and selected oceanographic parameters (Table 3). Analyses were conducted for a subset of the data ($n=674$) for which all independent variables were available, and salinity (observed and/or WOA) was greater than 30 (see section 4.1). This subset comprised 262 data points classified as 'Open Ocean' and 412 classified as 'coastal' (see section 3.1).

As the primary objective of this analysis was to identify robust relationships that could be used in global models without necessarily requiring in-situ oceanographic measurements, we present relationships between sea-surface iodide and ancillary parameters from the World Ocean Atlas in Tables 2 and 3. This approach also allows a larger data set to be used. The relationships between observed parameters and sea surface iodide, while not identical, are similar to those obtained using WOA parameters (Figs., 7, 8, 10 and 11, and Fig. S3 and Table 1 in the Supplementary Information). Regression analysis was conducted using both [iodide] and the natural logarithm of iodide concentration ($\ln[\text{iodide}]$) as the dependent variable. The

latter was found to be the more appropriate model as, although both yielded similar coefficients of determination (Table 2), the former gave residuals that changed as a function of the independent variable while the latter gave an approximately random distribution of residuals. Note that due to the existence of some zero values for iodide concentration, for which $\ln[\text{iodide}]$ cannot be calculated, sample size was smaller ($n=609$) for correlations of $\ln[\text{iodide}]$. The zero values occur for iodide concentrations calculated as the difference between total iodine and the iodate concentrations, where these parameters were effectively equal⁷⁰ and insufficient information was available to constrain the limit of detection (LoD). Note that for the Spearman's rank correlation analysis, [iodide] and $\ln[\text{iodide}]$ return identical results, so results are only reported for the former (with $n=674$).

4.1. Salinity

We find a comparatively strong relationship between salinity and iodide concentration at salinity values less than 30 ($R^2 = 0.65$; Fig. 7A). This reflects the mixing of coastal seawater (higher iodide, high salinity) and freshwater (lower iodide, negligible salinity) end members. In estuarine environments, iodide concentrations are sometimes strongly

Table 3: Spearman's rank correlation coefficients (ρ) and significance ($p = 5\%$) for non-parametric correlation of [iodide] against variables taken from the World Ocean Atlas as described in the text, $n = 674$.

Independent variable	ρ	$p < 5\%$?
$[\text{NO}_3^-]$, μM	-0.73	Yes
SST ($^{\circ}\text{C}$)	0.72	Yes
Latitude ($^{\circ}$)	-0.65	Yes
Summed MLD_{pt}	-0.65	Yes
Maximum MLD_{pt}	0.63	Yes
Salinity	0.46	Yes
Monthly MLD_{pt}	-0.44	Yes
Maximum MLD_{pd}	-0.30	Yes
Monthly MLD_{vd}	0.26	Yes
Summed MLD_{pd}	-0.25	Yes
Chlorophyll- a , $\mu\text{g l}^{-1}$	-0.24	Yes
Monthly MLD_{pd}	0.12	Yes
Summed MLD_{vd}	0.07	No
Maximum MLD_{vd}	0.05	No

correlated with salinity gradients (e.g. Chesapeake Bay, USA⁷⁷). However, in other estuaries iodide levels may be only very loosely related to salinity (e.g. Huon Estuary, Australia¹¹⁵), or more complex relationships involving both positive and negative correlations between iodide and salinity may occur (e.g. Guanabara Bay, Brazil⁹⁶ and the Nile River estuary, Egypt¹¹⁶).

In some estuaries, exceptionally high iodide (and as a consequence, total iodine) levels are occasionally encountered (e.g. the Skagerrak³⁵). These diverse findings likely arise from the large range of estuarine processes with potential to affect iodine speciation, most of which are not salinity dependent. For example, sediment interactions will be more important than in the open ocean, and low oxygen conditions may occur^{77, 116}. Such processes will cause deviations from conservative behaviour, and probably contribute to the scatter about the best-fit line for the low salinity samples (Fig. 7A). As low salinity samples represent a special case of iodine chemistry distinct from the open ocean, they have been excluded from further correlation analyses (section 4.2 - 4.6). Removal of these samples from the data set reduced the overall range of iodide concentrations to undetectable to 450 nM, but the distribution was otherwise little changed (median 74 nM, interquartile range 27 to 135 nM; see Fig. 4).

At salinities more typical of 'true' seawater (30–40; shaded area in Fig. 7A), we find iodide concentrations to be only very weakly associated with salinity ($R^2 = 0.15$, Table 2). This is consistent with the view that, while total dissolved iodine is approximately conservative, individual iodine species are biogeochemically reactive and so do not behave conservatively. The lack of a strong correlation between iodide and salinity on a large scale (Table 2, Fig. 7B) suggests that biogeochemical processes exert greater control on iodide speciation in the oceans than precipitation, evaporation and mixing. Although it is true that precipitation and evaporation will cause co-variation in total salinity and the concentrations of individual salt components such as iodide (via simple dilution and

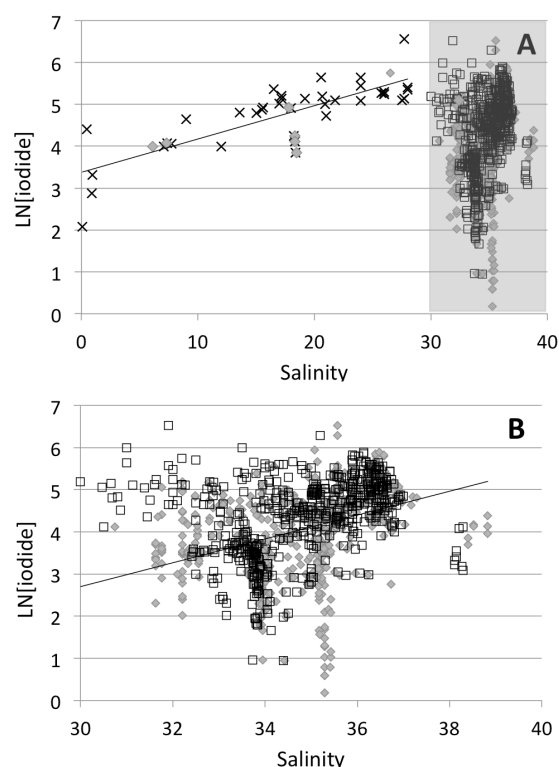


Fig. 7. LN[iodide] concentration plotted against observed salinity (X, \square) and climatological salinity (\blacklozenge) values obtained from the World Ocean Atlas as described in the text for: (A) all data; (B) samples with salinity greater than 30, shown in shaded area in (A). Note samples with salinity less than 30 have been excluded from further analysis and are not shown in Figs. 8 to 11.

concentration), in the open ocean, the magnitude of these effects is very small. For example, a change in salinity from 34 to 35 due to evaporation would only cause a 3% increase in iodide concentration. The mixing of water masses with different iodide and salinity signatures can also result in a relationship between the two on a regional or local scale, where mixing of water masses is the dominant control on their properties (e.g. the British Isles shelf seas⁷⁰). Positive correlations between atmospheric iodine (IO and IOx) and salinity have been observed and attributed to variation in iodide concentrations^{21,117}; despite the lack of a significant relationship in our large scale data set, regional scale correlations between iodide and salinity may have existed in these study areas. Alternatively, the relationship may arise because of the salinity dependence of iodine volatilisation^{29,30}, though the small change in salinity is estimated to cause only a 1% change in I_2 flux as a result of enhanced volatilisation rates³⁰. Concentrations of iodine species are sometimes reported as values normalised to salinity (rationalisation^{118,119}) to account for any dilution or concentration effects (see above). However, when attempting to quantify processes with a rate dependence on the iodide (or iodate) concentration, absolute concentrations are more appropriate and so have been used in the data compilation and regression analyses presented here. We have repeated the regression analyses using rationalised iodide

concentrations, and find the linear relationships (R^2 , slope and intercept) obtained are almost identical to those for absolute iodide concentration (data not shown).

4.2. Sea-surface temperature

Of the variables tested, the strongest parametric correlations (Table 2), and second strongest non-parametric correlations (Table 3) were between iodide concentration and sea-surface temperature (SST). This association between iodide and temperature is consistent with the observed latitudinal trends in iodide distribution (as, with the exception of upwelling waters, low latitude waters are warmer than high latitude waters). Where temperature is measured in degrees Celsius, rather than Kelvin, SST^2 is a stronger predictor of iodide than SST (Table 2). This is because there are some relatively high iodide values at negative sea surface temperatures (Fig. 8) that are effectively shifted to the right, and hence closer to the line of best fit, when the square function is applied. Conversely, for the case of SST^{-1} , the association with iodide is much stronger where temperature is measured in Kelvin rather than degrees Celsius (R^2 of 0.51 and 0.0006 respectively). MacDonald et al.³⁰ report an Arrhenius style dependency of $\ln[\text{iodide}]$ on SST^{-1} (K^{-1}) for a sub-set of the data presented here. Using our larger data set, a significant Arrhenius style relationship is also found ($R^2 = 0.49$; Table 2), but the slope and intercept fall outside the error bounds of the MacDonald et al. relationship and vice-versa.

There are a number of hypotheses that may explain the positive dependency of iodide concentration on SST. Firstly, SST may be positively correlated with iodide concentration because both are related to mixed layer depth (MLD). Vertical mixing is expected to affect iodide concentration, as it effectively determines the volume of seawater within which iodide is diluted. In warmer waters, stratification leads to a shallow mixed layer in which iodide could accumulate, while in cooler waters, deeper winter mixing would result in the dilution of iodide produced in surface waters with lower iodide, deep water (see section 3.4). Relationships between iodide and MLD are considered further in section 4.3. A second, related, explanation is that upwelling of cold, low iodide/high iodate deep waters could sometimes result in co-variation of iodide and temperature on a regional scale. Upwelling has sometimes been observed to have this effect on surface water iodine speciation^{17,81}. However, in many cases the low iodide signal of upwelled water may be altered, because upwelling regions are associated with high productivity, and the formation of iodide has been linked to productivity^{43,73,120}. Indeed, the impact of high productivity in upwelling zones could have the opposite effect on iodine speciation, leading to higher iodide concentrations in the colder, upwelling waters. Finally, a positive correlation between iodide and sea surface temperature could occur if either the rate of iodide production has a positive temperature dependency and/or the rate of iodide removal has a negative temperature dependency. As both these processes may be biologically mediated¹⁵, any such dependency could be

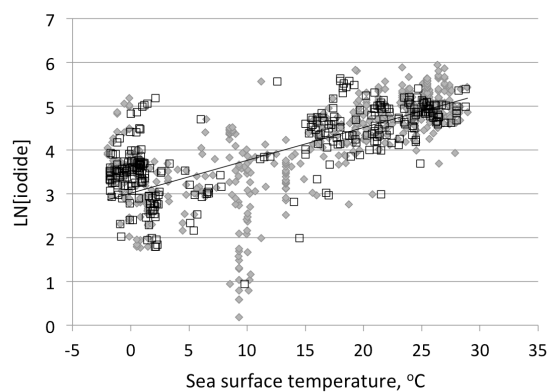


Fig. 8. $\ln[\text{iodide}]$ concentration plotted against observed sea surface temperature (\square) and climatological sea surface temperature (\blacklozenge) values obtained from the World Ocean Atlas as described in the text.

caused by an indirect link with temperature, rather than the direct effect of temperature on reaction kinetics. For example, plankton community composition varies with temperature, and these different communities may produce iodide at varying rates^{92,121}. Alternatively, as SST reflects the amount of solar irradiation reaching the ocean surface, photochemical reactions may influence the dissolved iodine distribution (see section 3.2.3).

The apparent relationship between iodide and SST may explain, at least in part, observed relationships between SST and both atmospheric iodine above the oceans, and ozone deposition to the oceans. Positive correlations between atmospheric iodine species (IO and IOx) and SST have been observed in the eastern Pacific^{21, 22, 117}. These could be partially a consequence of the correlation between iodide and SST in the surface ocean, given that iodide concentration affects the flux of reactive iodine from the sea surface³⁰. Our findings support the suggestion that observed correlations between atmospheric IOx and SST are due to higher concentrations of reactive iodine precursors in warmer waters^{21,22,117}. Helmig et al.³² found measured rates of oceanic ozone uptake to have a positive temperature dependency, while model predictions made assuming a fixed rate constant for chemical destruction of ozone displayed a negative or neutral temperature dependency, suggesting that reactivity may be weaker in regions with colder water. The lower levels of iodide present in colder waters may contribute to this reduced reactivity. Ozone deposition velocity increased up to threefold over an SST range of 0 to 33 °C³² while our results suggest at least a 12-fold increase in iodide concentration over the same temperature range (Table 2). Note a 12-fold increase in concentration equates to an approximately threefold increase in $\sqrt{[\text{concentration}]}$ and ozone deposition velocity is reported to be a function of $\sqrt{[\text{Iodide}]}$ ²⁹.

4.3. Mixed layer depth

As mixed layer depth (MLD) estimates vary according to the definition chosen^{114,122}, relationships between iodide concentration and all three of the mixed layer depth fields available in Monterey and Levitus¹¹⁴ were investigated. The

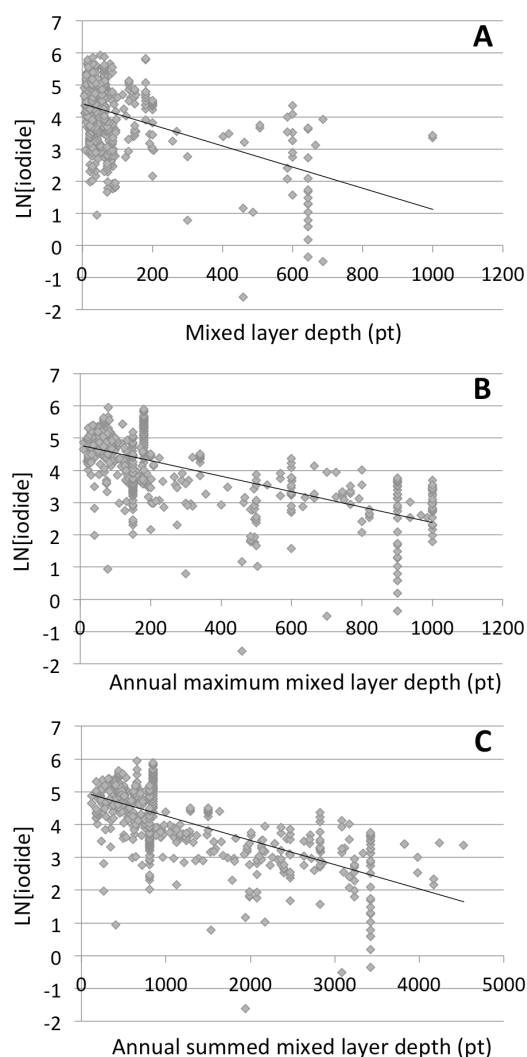


Fig. 9. $\ln[\text{iodide}]$ concentration plotted against: (A) mixed layer depth for the month of sampling; (B) annual maximum mixed layer depth; (C) sum of all mixed layer depths over one year. Mixed layer depths obtained from the World Ocean Atlas¹¹⁴, with MLD calculated using the potential temperature criteria.

three MLD criteria used in Monterey and Levitus¹¹⁴ are as follows: (i) a potential temperature change from the ocean surface of 0.5°C , here referred to as MLD_{pt} (ii) a potential density change from the ocean surface of 0.125 (sigma units), here referred to as MLD_{pd} (iii) a variable density change from the ocean surface equivalent to a temperature change of 0.5°C , taking account of the temperature dependence of the thermal expansion coefficient of seawater, here referred to as MLD_{vd} . For each MLD criteria, the relationship between iodide concentration and MLD was evaluated using climatological monthly mean MLD at the time of sampling ('monthly MLD'), the deepest climatological monthly mean MLD over the course of a year ('maximum MLD') and the sum of climatological monthly mean MLDs for a year ('summed MLD'). The latter parameter was selected as a simplistic indicator of the extent and duration of vertical mixing/stratification i.e. small values of summed MLD reflect prolonged periods of stratification, while

large values indicate deep mixing and/or deep mixing over many months.

Summed and maximum MLD_{pt} were relatively strongly inversely associated with iodide ($R^2 \geq 0.34$; $\rho \geq 0.34$), while monthly MLD_{pt} and all MLD_{pd} and MLD_{vd} parameters were only weakly associated with iodide and not all relationships were significant (Tables 2 and 3). For all MLD variables, the potential temperature criterion (i) yielded the strongest correlations (Tables 2 and 3). MLD definitions vary in their ability to capture different structures in the water column in both space and time^{114,122}. For example, compared to MLD definitions based on a smaller change in potential temperature, the MLD_{pt} definition is thought to sometimes detect deeper thermocline gradients, rather than weaker restratification events at shallower depths, and place the maximum MLD later in the season¹²². Of the three criteria used here, the potential temperature criterion appears to yield MLD values most relevant to iodide speciation. These findings are consistent with the *a priori* assumption that vertical mixing must have some effect on the concentration of relatively long-lived moieties such as iodide that are produced in surface waters. The results suggest that the deepest extent of the winter mixed layer, and the duration of stratification over the course of a year are more important than mixed layer depth at the time of sampling. Long periods of stratification are expected to allow iodide to accumulate at the ocean surface, while deep winter mixing will dilute the iodide signal, effectively resetting the iodide signal to a low winter value. The impact of changes in mixed layer depth on surface iodide (and iodate) concentrations was considered by Chance et al. (2010)⁷³, who found that observed changes in surface concentration over 100 days were similar to those calculated from the known deepening of the mixed layer in Antarctic coastal waters⁷³. Further investigation using more refined estimates of MLD may yield more insights into the relationship between iodine speciation and vertical mixing.

In section 4.2 it was hypothesised that the observed link between iodide and SST was the result of higher SST being associated with shallower mixed layer depths. An exploration of the links between mixed layer depth and sea surface temperature is beyond the scope of this work. However, we note that within our data set, maximum and summed MLD_{pt} were relatively strongly correlated with SST^2 (r^2 of 0.33 and 0.35 respectively), while maximum and summed MLD_{pd} and MLD_{vd} were not ($r^2 \leq 0.08$). Furthermore, none of the three monthly MLD parameters correlated strongly with SST^2 (r^2 of 0.13, 0.003 and 0.01 for MLD_{pt} , MLD_{pd} and MLD_{vd} respectively). Our results are broadly consistent with the view that iodide is related to SST because of the influence of SST on vertical mixing, where the potential density criterion identifies the most relevant mixing features. Of course a significant correlation cannot be taken as proof of cause and effect, so the possibility remains that iodide concentration is related to MLD_{pt} only because both are related to temperature. As the relationship between iodide concentration and SST is stronger than either that between iodide concentration and MLD_{pt} (see Table 2), or SST and MLD_{pt} (see above), it is also possible that

other factors in addition to mixing contribute to the link between iodide concentration and SST. Possible additional factors are suggested in section 4.2.

4.4. Chlorophyll-a

Regression analysis suggests that there is not a statistically significant relationship between iodide and chlorophyll-a concentrations on a large scale (Fig. 10; Table 2), while Spearman's rank correlation finds a weak but significant negative association between the two ($\rho = -0.24$; Table 3). The majority of regional and basin scale studies included in our compilation (see Table 1 for references) make no mention of a correlation, or lack thereof, between iodine speciation and chlorophyll-a. Only very rarely has a significant relationship between chlorophyll-a and iodide concentration been reported, and this has generally been in environments unrepresentative of the open ocean^{47,96}. Rebello et al.⁹⁶ report a positive correlation between iodide and chlorophyll-a (slope of 0.231 mM iodide per mg L⁻¹ chl-a, $r = 0.79$;) for a 5 m deep sampling site in Guanabara Bay, a polluted estuarine (average salinity 29) bay in southeastern Brazil. The observed relationship was derived from the average iodide and chlorophyll-a concentrations for each of four different depths, which were sampled at four time points over the course of one day only, and was not replicated on other sampling days. This relationship was extrapolated to estimate iodide concentration in the Gulf of Mexico in two modelling studies examining ozone deposition^{32,33}. Helmig et al.³² found that inferring iodide from chlorophyll-a (after Oh et al.³³) gave better agreement between modelled and observed values of ozone deposition velocity (Vd) than inferring iodide from nitrate concentrations (after Ganzeveld et al.²⁷), as the use of nitrate as an iodide proxy led to an over-estimate of Vd. However, as Helmig et al.³² note, the iodide concentrations obtained using chlorophyll-a were probably not realistic, as they were an order of magnitude lower than typical oceanic levels. Interestingly, anti-correlations between chlorophyll-a concentration and atmospheric iodine species (IO and IOx) have been observed^{21,22,117}. Given that we find sea surface iodide and chlorophyll-a are not related, an inverse relationship between atmospheric iodine and chlorophyll-a does not preclude the role of iodide as a precursor of IOx.

The results presented here suggest that chlorophyll-a concentration is a poor proxy for iodide concentration. However, the absence of a correlation between iodide and chlorophyll does not necessarily controvert a link between iodide production and biological activity. Although commonly used as an easily quantifiable indicator of biological activity, chlorophyll-a concentrations are a measure of the standing stock of phytoplankton biomass at a given point in time. Concentrations of metastable biogenic species (such as iodide is thought to be) are more likely to reflect integrated biological activity over a period of time than the net biomass. Links between iodine speciation and biological activity are discussed further in Section 4.5.

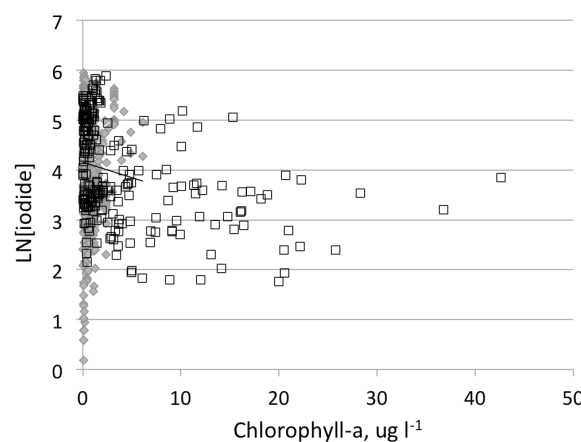


Fig. 10. Ln[iodide] concentration plotted against observed (\square) and climatological (\blacklozenge) chlorophyll-a concentration obtained from the World Ocean Atlas as described in the text.

4.5. Nitrate

Iodide is inversely related to nitrate, with a relatively large coefficient of determination ($R^2 = 0.36$; Fig. 10, Table 2) and the strongest non-parametric correlation coefficient ($\rho = -0.73$; Table 3). Negative correlations between iodide and nitrate have previously been identified in the southern Atlantic and Southern Ocean, with the exact relationship differing according to hydrographic region⁵³. Given that iodide exhibits an approximately inverse relationship to iodate (Figs. 2 and 6), these results are also in broad agreement with observations of tight coupling between iodate and nitrate in individual vertical profiles^{17,48,63}. However, correlations between iodine species and nutrients are not ubiquitously observed^{42,70}, and Bluhm et al.⁶⁴ did not find a relationship between iodide and nitrate in the Atlantic sector of the Southern Ocean. Though an inverse relationship between iodide and nutrient concentrations could arise as the result of hydrographic coupling¹⁷, it is also consistent with the view that iodide formation may be biologically mediated, as discussed in section 4.4. Both the biologically mediated production of iodide in association with nutrient uptake in the euphotic zone, and the upwelling of deep, low iodide/high nutrient waters, may contribute to an inverse relationship in surface waters.

Although it is generally accepted that there is a link between iodine speciation and biological activity¹⁵, this has not yet been unequivocally established and the mechanism remains unknown. The occurrence of iodide in the surface ocean (e.g. Fig. 6), where the majority of marine primary production also occurs, strongly suggests that iodide production might be biologically mediated. A number of laboratory studies have demonstrated iodate uptake and the conversion of iodate to iodide in phytoplankton cultures^{91-93,121,123,124}, but in other cases no link has been found^{93,98}. Similarly, a time series study in Antarctic waters found iodide accumulation to be correlated with primary productivity⁷³, while a mesocosm study at a similar location found no change in iodine speciation associated with phytoplankton growth³⁷. Elsewhere, associations between iodide concentrations and both new^{120,125} and regenerated

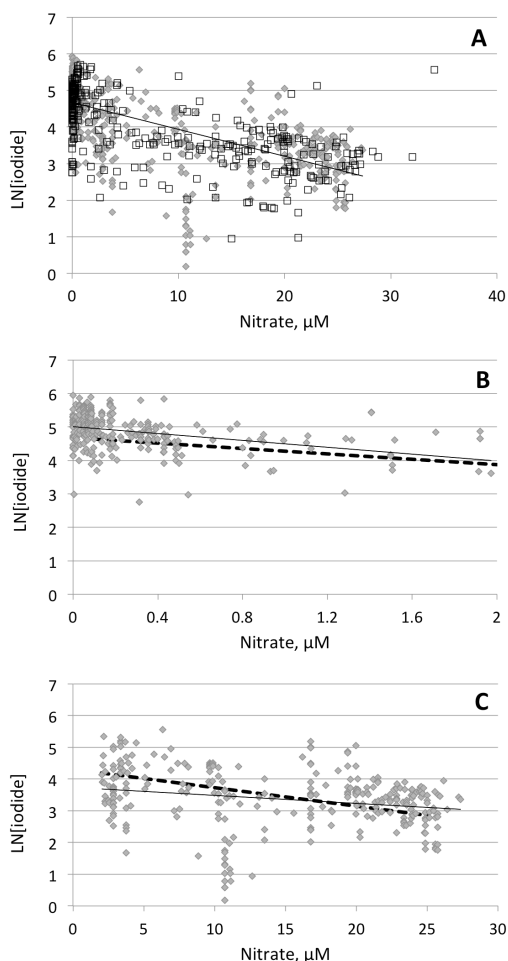


Fig. 11. $\text{LN}[\text{iodide}]$ concentration plotted against observed (\square) and climatological (\blacklozenge) nitrate concentration obtained from the World Ocean Atlas as described in the text for all data (A) and nitrate concentrations below 2 μM (B) and above 2 μM (C). Dashed lines in B and C show the relationships between iodide and nitrate adapted from Campos et al.⁴¹ by Ganzeveld et al.²⁷.

primary production⁴³ have been inferred from field measurements. It has been suggested that iodate could be reduced by nitrate reductase enzymes^{120,125,126}, which are widespread in marine micro-organisms¹²⁷, and an association between nitrate reductase activity and iodate reduction has been shown in cellular extracts^{126,128} and the East China Sea¹²⁰. However, deactivation of nitrate reductase activity in micro-algal cultures did not prevent the production of iodide⁹³, and conversely, bacterial cultures only reduced iodate under certain conditions, despite always displaying nitrate reductase activity¹²⁹, suggesting nitrate reductases are not involved in iodate reduction, or at least are not the sole control. More recently, it has been suggested that the reduction of iodate to iodide may be brought about sulphides or thiols^{87,91,130}, which may be released from leaking senescent cells⁹¹.

Considering the full water column, the existence of correlations between dissolved iodine species and nutrients has prompted an extension of the Redfield ratio approach to consider iodine^{16,48}. As dissolved iodine is present in multiple

Table 4. Comparison of slope (m) and intercept (c) for the linear relationships between iodide and nitrate used by Ganzeveld et al. (2009; derived from Campos et al., 1999) and those found in this work, for high and low nitrate concentrations.

$[\text{NO}_3^-]$, μM		Ganzeveld et al.	This work
< 2	m	-29 ± 15	-60 ± 9
	c	106 ± 22	163 ± 4
> 2	m	-2.12 ± 0.2	-1.68 ± 0.3
	c	70.4 ± 5	68 ± 4

oxidation states, which may themselves be interconverted by biological uptake and remineralisation, as well as additional extracellular processes, the Redfield approach is most appropriate for total dissolved iodine (i.e. iodide plus iodate)^{16,131}. Total iodine is coupled to phosphate, suggesting it is subject to the similar processes of assimilation and regeneration¹⁶, though the coupling breaks down at depth, indicating a greater proportion of iodine is recycled in shallower waters, compared to nitrogen and phosphorus¹³¹.

The relationships between iodide and nitrate in the south Atlantic reported by Campos et al.⁵³ were adapted by Ganzeveld et al.²⁷ to estimate iodide concentrations under 'in gyre' and 'out of gyre' conditions (defined as waters with surface concentrations less than and greater than 2 μM nitrate respectively), and hence model ozone deposition to the sea surface. Ganzeveld et al.²⁷ demonstrated that the equations of Campos et al.⁵³ yielded a latitudinal iodide distribution in reasonable agreement with observations made during meridional transects of the Atlantic¹⁷, but underpredicted iodide levels near Hawaii and Bermuda⁴¹. They attributed the latter discrepancy to the nitrate climatology used not resolving high biological activity in the coastal waters near these islands²⁷. Considering our data compilation, the relationship between iodide and nitrate at nitrate concentrations greater than 2 μM is very similar to that used by Ganzeveld et al.²⁷, with overlap between the error bounds of the gradient and slope (Fig. 11C; Table 3). Visual inspection also suggests reasonable agreement between the relationships for nitrate concentrations less than 2 μM (Fig. 11B), but in this case there is no overlap between the error bounds of the gradient and intercepts (Table 4).

4.6. Multiple linear regression

Multiple linear regression analysis of iodide against SST^2 , absolute latitude, MLD (summed MLD_{pt} , as this had strongest individual relationship, see Table 2), nitrate concentration, salinity and chlorophyll-a concentration was carried out using StatPlus software as an add on to Microsoft Excel. Analysis was carried out for different combinations and functions of the key variables, in order to find the combination that accounted for the greatest amount of variability in the dataset i.e. returned the largest value of R^2 .

As reported in Table 2, SST^2 , latitude, summed MLD_{pt} and nitrate concentration are the strongest individual predictors of iodide concentration, accounting for about ~40 to ~60% of the

observed variability. Combining these four variables increased R^2 for each variable added, to a maximum increase of $\sim 10\%$ for all four variables compared to SST^2 alone. The increases in R^2 caused by adding these variables were not cumulative because of the high interdependency of the variables e.g. latitude and SST. The inclusion of salinity caused an increase in R^2 of between ~ 1 to $\sim 5\%$. Chlorophyll-a was not found to be a significant contributor (5% significance level) in any of the multivariate combinations tested and its inclusion did not increase R^2 . For the dependent variables [iodide] and $\ln[\text{iodide}]$, maximum R^2 values of 0.676 and 0.642 respectively were achieved and relationships (1) and (2) identified:

$$[\text{iodide}] = 0.28 (\pm 0.02) * SST^2 + 1.7 (\pm 0.2) * |\text{Latitude}| + 0.9 (\pm 0.4) * [\text{NO}_3^-] - 0.020 * \text{sumMLD}_{\text{pt}} (\pm 0.002) + 7 (\pm 2) * \text{salinity} - 3 (\pm 8) \quad (1)$$

$$\ln[\text{iodide}] = 0.0026 (\pm 0.0003) * SST^2 + 0.016 (\pm 0.003) * |\text{Latitude}| - 0.009 (\pm 0.006) * [\text{NO}_3^-] - 0.00044 * \text{sumMLD}_{\text{pt}} (\pm 0.00004) + 0.05 (\pm 0.03) * \text{salinity} + 2 (\pm 1) \quad (2)$$

Where [iodide] is in nmol L^{-1} , SST is in $^{\circ}\text{C}$, $[\text{NO}_3^-]$ is in $\mu\text{mol L}^{-1}$ and $\text{sumMLD}_{\text{pt}}$ is the annual sum of monthly average mean mixed layer depths taken from Monterey and Levitus¹¹⁴ (potential temperature criterion). As for the individual correlations, the use of $\ln[\text{iodide}]$ rather than [iodide] as the dependent variable gave a more uniform distribution of residuals, suggesting equation (2) is the more appropriate model despite the lower R^2 value. In equation (1) all variables were significant (at $p=5\%$). In equation (2) neither nitrate concentration or salinity were significant, but each became significant when the other was excluded from the regression, and the inclusion of both increased the R^2 value slightly.

5. Concluding remarks

Knowledge of sea surface iodide concentrations is required in order to accurately predict both ozone deposition to the sea surface and the sea-to-air flux of reactive iodine arising from this reaction. Sea surface iodide concentrations from the literature and unpublished data sets have been compiled as a first step towards a global iodide climatology. Despite only patchy coverage of the world's oceans, the 925 data points reveal clear trends in the iodide distribution. Observed iodide concentrations in waters with salinities greater than 30 range from effectively zero to 450 nM, with 50% of measurements falling between 26 and 135 nM. There is a strong trend of increasing concentration with decreasing latitude, evident in both the Atlantic and the Pacific. Very large gaps in the data set remain, particularly in the eastern Pacific, Indian and Arctic Oceans, where further field measurements are required. For the purposes of studying air-sea exchange, it is important to consider concentrations in the sea surface microlayer; current evidence is limited but suggests iodide is neither enhanced nor depleted in the sea surface microlayer.

Relationships between iodide concentration and other, more widely measured oceanographic variables have been explored. Of the variables tested, SST^2 appears to be the strongest predictor of iodide surface concentration, and nitrate concentration the second best, and these variables are recommended for use where proxies of iodide concentration are required. Atmospheric iodine oxides (IO and IOx) are also positively correlated with $SST^{21,22,117}$; that both sea surface iodide and atmospheric IOx are related to SST suggests that the former may be an important predictor of the latter. Observed iodide concentrations in surface waters vary across approximately an order of magnitude, which would equate to an approximately three-fold variation in the reactive iodine flux, assuming that this is proportional to $\sqrt{[\text{iodide}]}$ ²⁹ and that all other factors are equal, with highest fluxes expected at lowest latitudes. No relationship between iodide and chlorophyll-a was found. Inclusion of additional variables in a multivariate linear regression gave only a slight increase in the amount of iodide variability accounted for, compared to SST alone. Given that the reasons for the link between iodide concentration and SST are not established, this relationship should be used with caution and any iodide fields generated should be checked against actual measurements to ensure they are realistic. For example, in highly productive upwelling regions, or situations where surface waters become hypoxic, higher iodide concentrations than predicted from SST may occur.

The controls on iodide concentration are still not fully understood, and further work is needed to provide a theoretical framework with which to explain and predict iodide concentrations. The observed link between iodide and nitrate concentration is in agreement with individual studies, and consistent with a biological role in determining iodine speciation. Meanwhile, the strong associations between SST and latitude and iodide remain somewhat enigmatic, particularly given that MLD was less strongly associated with iodide concentration. Annual patterns of vertical mixing can account for some of the variation in iodide concentration, but other factors related to temperature and/or latitude may also be important. The sea surface distribution of iodide is strikingly similar to that of dissolved organic carbon (DOC)¹³². Both show elevated levels in the tropics and lower levels at higher latitudes in the southern hemisphere. The same large scale physical and biogeochemical processes that determine the global DOC distribution may also control iodide concentrations, and indeed create the broader differences between oligotrophic warm water gyres and seasonally well mixed mid- and high latitude systems. The potential for shared drivers of both iodide and DOC distributions merits further investigation. It is hoped that the nascent compilation of iodine speciation measurements presented here may be a useful tool for probing iodine dynamics in seawater in future.

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