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# Seasonal and interannual variation of dissolved iodine speciation at a coastal Antarctic site

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ABSTRACT

Dissolved iodine speciation in surface seawater at a coastal Antarctic site has been studied over a period spanning three austral summers. The sampling site is biologically productive, with a summertime algal bloom accompanying strong seasonal variations in physical and chemical parameters. The results suggest a seasonal cycle in which iodide concentrations increase and iodate concentrations decrease during the summer, though the magnitude of these changes appears to be subject to considerable interannual variability. Iodide concentrations were typically very low, with minimum values of 10 to 20 nM at the beginning and end of the ice-free summer periods and summertime maxima of about 35 nM in 2005/06, 150 nM in 2006/07 and 82 nM in 2007/08. More detailed observations of iodide and iodate concentrations made during summer 2005/06 demonstrated that the accumulation of iodide was strongly correlated with integrated biological primary productivity, with an implied I/C assimilation ratio of $1.6 \times 10^{-4}$.

## 1. Introduction

Iodine is a bio-philic, redox sensitive element that is ubiquitous in seawater. Total dissolved iodine concentrations are in the range of 400 to 500 nM, with a surface depletion that is assumed to be caused by biological uptake (Elderfield and Truesdale, 1980; Wong, 1991). Throughout most of the oceans, iodate predominates, as predicted by thermodynamic considerations (Sillen, 1961). However, in surface waters up to 50% of the dissolved iodine may be present as iodide (e.g. Wong, 1991; Campos et al., 1996). Once formed, iodide is kinetically stable because the oxidation reaction is slow (Luther et al., 1995). The oceanic lifetime of iodide with respect to oxidation is between 70 and 180 days (Campos et al., 1996; Edwards and Truesdale, 1997). Understanding the controls on dissolved inorganic iodine speciation in seawater is important because of the potential impact on volatilisation of iodine to the lower atmosphere. In the atmosphere, iodine is involved in ozone destruction and particle formation reactions and may thus affect climate (von Glasow, 2005). The biogeochemical cycling of iodine is also of interest because iodine is an essential human micronutrient, and the long-lived radionuclide iodine-129 is released to the environment by the nuclear industry.

Within the euphotic zone, the proportion of iodine present as iodide appears to be greatest in temperate coastal, tropical and subtropical waters and lowest at high latitudes (Campos et al., 1996; Campos et al., 1999; Truesdale et al., 2000; Waite et al., 2006). The reasons for the latitudinal gradient in iodide concentrations are not fully understood. It has been speculated that it may be the result of differences in vertical mixing (Truesdale et al., 2000) or differences in biological assemblages (Campos et al., 1999). In shallow waters, interactions with sediments have also been proposed as a means of reducing iodate to iodide (Nakayama et al., 1989; Truesdale et al., 2003b), though this cannot explain the pronounced and ubiquitous surface iodide maximum observed in the open ocean.

The presence of iodide in surface seawater is consistent with a link between iodide formation and biological activity (presumably phytoplankton growth) occurring in the euphotic zone, and some laboratory studies support this view (Sugawara and Terada, 1967; Moisan et al., 1994; Wong et al., 2002; Chance et al., 2007). However, other studies have not found that phytoplankton growth leads to changes in dissolved iodine speciation (Butler et al., 1981; Waite and Truesdale, 2003; Truesdale et al., 2003a). The evidence from oceanographic observations for a link between iodine speciation and biological activity is similarly contradictory. Many studies have found

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water column concentrations of nutrients and either total iodine or iodate–iodine to be closely coupled (e.g. Elderfield and Truesdale, 1980; Campos et al., 1999; Truesdale et al., 2000; Huang et al., 2005), though in some cases this may have been caused by common hydrographic controls rather than direct chemical coupling (Truesdale et al., 2000). Conversely, during an upwelling episode in the Southern Benguela system, nutrient uptake and iodate depletion were not related (Truesdale and Bailey, 2002). Seasonal cycles in iodine speciation that appear to be at least partly caused by some component of the surface water micro-organism community have been observed in the tropics (Jickells et al., 1988; Campos et al., 1996), but data from polar and temperate coastal waters have thus far suggested an absence of seasonal variation (Truesdale, 1978; Truesdale and Jones, 2000; Truesdale and Upstill-Goddard, 2003; Waite et al., 2006). A number of studies have attempted to link dissolved iodine speciation and biological productivity directly (Campos et al., 1996; Tian et al., 1996; Wong, 2001; Farrenkopf and Luther, 2002) and, for certain oceanographic situations, the use of iodide concentrations as an integrated indicator of nitrogen assimilation has been proposed (Wong and Hung, 2001). Tian et al. (1996) proposed that iodine cycling was related to regenerated production (the fraction of primary production that is driven by recycled rather than exogenous nutrients), although their data set was subsequently found to also be consistent with a model in which iodate depletion and iodide enrichment were proportional to nitrate uptake, implying a link with new production (Wong, 2001).

Alternatively, the photochemical formation of iodide might be the cause of the iodide maximum in surface seawater in both coastal and open ocean waters. Experiments have demonstrated iodide formation in seawater exposed to natural and high UV light (Brandao et al., 1994; Spokes and Liss, 1996; Wong and Cheng, 2001), though there is also evidence for the photo-oxidation of iodide (Spokes and Liss, 1996; Truesdale, 2007).

In this paper we present a detailed study of the changes in iodine speciation over three years at a productive coastal Antarctic site. Because of the low background iodide concentrations encountered at high latitudes, it was possible to observe small changes in iodide concentration occurring over a period of months. To the best of our knowledge, this is the first evidence of a seasonal cycle in dissolved iodine speciation in high latitude surface waters.

## 2. Field setting

The Rothera Oceanographic and Biological Time Series (RaTS) site lies approximately 4 km off shore in Ryder Bay, at the northern end of Marguerite Bay on the western Antarctic Peninsula (Fig. 1). The location is close to the British Antarctic Survey research station at Rothera. The depth at the RaTS sampling site is 520 m. At this site, biogeochemical and physical parameters such as chlorophyll, nutrients, salinity and temperature have been continuously monitored for the past twelve years, with whole-water column profiling conducted with a Conductivity–Temperature–Depth (CTD) instrument, and discrete water sampling conducted using Niskin bottles lowered to 15 m depth. The physical and biogeochemical environments of the western Peninsula as they relate to RaTS have been detailed extensively elsewhere (Meredith et al., 2004; Clarke et al., 2008) and so are only described briefly here.

The west Antarctic Peninsula lies very close to the waters of the Antarctic Circumpolar Current (ACC), the strong eastward-flowing current system that dominates the horizontal circulation in the Southern Ocean. This enables warm, saline Circumpolar Deep Water (CDW) from the ACC to intrude in relatively unmodified form onto the continental shelf and enter Marguerite Bay via a deep glacial canyon known as the Marguerite Trough (Fig. 1; Klinck et al., 2004; Martinson et al., 2008). Although the CDW is modified by mixing once it is on the shelf, the relatively easy access of this water mass, and the heat and nutrients it contains, lead to the western Peninsula shelf having a relatively warm marine climate for Antarctica and being biologically very productive (Ducklow et al., 2006).

Above the CDW lies Antarctic Surface Water (AASW), the properties of which vary seasonally. During the austral winter, Ryder Bay is typically covered in sea ice, and the upper water column is homogenised to 100 m or more (Meredith et al., 2004; Clarke et al., 2008). At this time, mixed layer temperatures are close to the freezing point for seawater, and salinities are around 33.5–34.0. Unlike some other shelf regions of Antarctica (e.g. the Weddell and Ross Seas), sea ice production in autumn and winter at the western Peninsula is not sufficiently strong to create saline waters that are sufficiently dense for the winter mixed layer to reach to the seabed, and there is no pooling of high-salinity shelf water that could ultimately be involved in Antarctic Bottom Water formation.

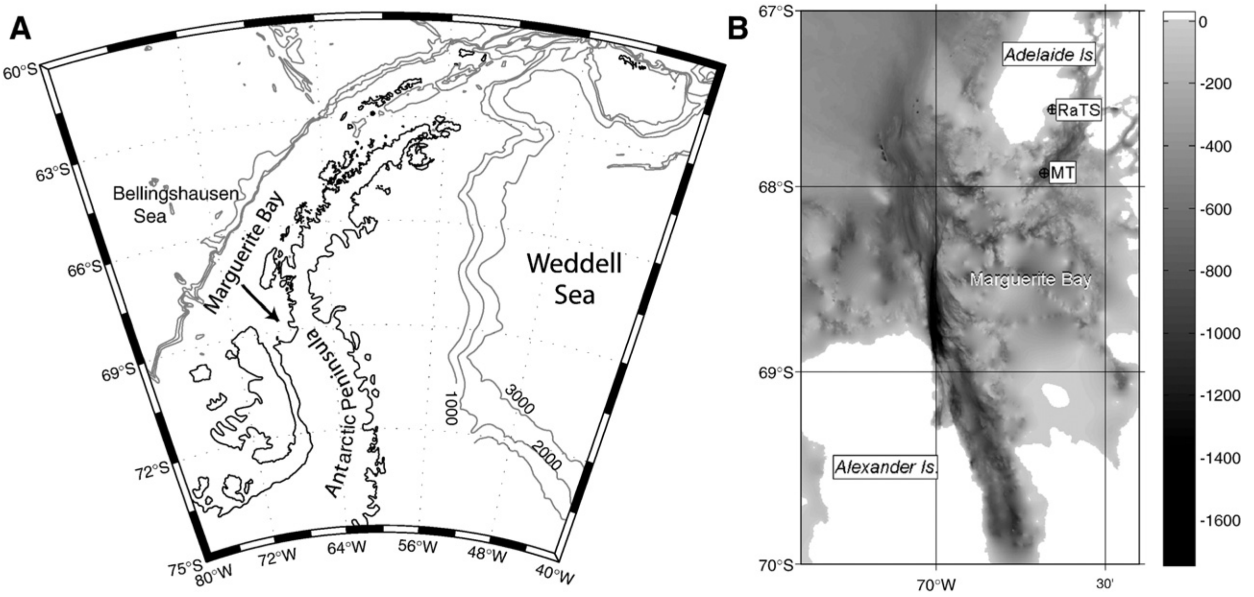

**Fig. 1.** A. Location of Marguerite Bay on the western Antarctic Peninsula B. Map of Marguerite Bay, showing the location of the RaTS sampling site (67.57°S, 68.22°W) and the MT deep mooring sampling site (67.93°S, 68.40°W).

During spring/summer, a combination of freshwater input from ice melt and solar warming of surface waters causes the upper water column to become more stratified, with a warm fresher surface layer a few metres thick created. This thin summer surface layer overlies the remnant of the winter mixed layer, which is marked by a distinct temperature minimum at around 50–100 m depth and is now called Winter Water (WW; Mosby, 1934). As summer progresses into autumn, the mixed layer deepens in response to sea ice production, entraining CDW and providing a vertical supply of heat, salt and nutrients (Meredith et al., 2004). Other potential mechanisms for vertical mixing include internal tides and coastal upwelling (Wallace et al., 2008).

The freshwater budget of coastal waters to the west of the Antarctic Peninsula is particularly important, both through its impact on the stratification of the water column, and via its potential influence on the marine ecosystem (Dierssen et al., 2002). Meteoric water, largely from glacial ice melt, is a significant source of freshwater to surface waters in Ryder Bay, contributing up to 5–6% of the near-surface ocean during late summer (Meredith et al., 2008). Sea ice is usually blown out of the Bay in spring rather than melting in situ (Clarke et al., 2008) and contributes less freshwater than glacial run off (up to 1–2%; Meredith et al., 2008).

In terms of horizontal circulation, an Antarctic Peninsula Coastal Current (APCC) has been reported flowing southward along the western side of Adelaide Island, and also along the western side of Alexander Island (Moffat et al., 2008; Fig. 1). The circulation of the APCC within Marguerite Bay is not well known, but the hydrography at the RaTS site is characteristic of waters inshore of the western-most edge of the APCC, so some level of horizontal advection from outside Marguerite Bay to the RaTS site is expected. This is consistent with earlier depictions of the circulation containing a generally cyclonic flow within Marguerite Bay, connecting boundary currents adjacent to Adelaide and Alexander Islands (Beardsley et al., 2004; Klinck et al., 2004). Alongside other evidence, this potential connectivity has been used to argue that the RaTS site is characteristic of the broader western Peninsula shelf (Meredith et al., 2004).

The RaTS site is biologically productive during summer, with chlorophyll concentrations of between 10 and 20 μg chl-a $l^{-1}$ being maintained for sustained periods (Clarke et al., 2008). During winter, chlorophyll concentrations fall below 1 μg chl-a $l^{-1}$, often by one or two orders of magnitude. Large diatoms and colonial phytoplankton dominate the summer bloom, while in winter nanophytoplankton become relatively more important (Clarke et al., 2008). Seasonal and interannual variations in biological activity at the RaTS station are typical of the western Antarctic Peninsula continental shelf in general (Smith et al., 1998; Ducklow et al., 2006). Dissolved oxygen is not measured routinely at the RaTS site, but data from other cruises in the region (available on the US Globec data base system, http://globec.whoi.edu/jg/dir/globec/soglobec/) indicate oxygen saturation (~350 μmol $O_2$ $l^{-1}$) in the upper 100 m of the water column and undersaturation (~160 μmol $O_2$ $l^{-1}$) at greater depths.

## 3. Sampling and methodology

### 3.1. Sampling

Seawater samples for determination of iodine speciation were collected from 15 m depth at the RaTS site between 14/3/05 and 03/03/08 (days 77 to 1162; note day count begins as day 1 on 28/12/04 when the 2004/05 summer field season began, sampling began at the end of the growing season and extended through three successive summers). 15 m is typically close to the chlorophyll-a maximum and within the euphotic zone (Clarke et al., 2008) and is the standard depth from which a water sample is recovered each time the RaTS site is occupied; samples for chlorophyll-a determination are collected from here routinely. The frequency of sampling was determined by weather and ice conditions as in the RaTS protocol (Clarke et al., 2008); during summer, samples were taken from a small boat at approximately weekly intervals, while winter sampling through holes cut in the sea ice took place less often. Water sampling events were accompanied by CTD casts to 500 m depth, from which salinity, temperature and chlorophyll fluorescence data were collected using a SeaBird SBE19+ instrument fitted with a WetLabs fluorometer. Further details of sampling protocols at the RaTS site are given in Clarke et al., 2008 (see also www.antarctica.ac.uk/rats).

From 04/01/06 until 13/02/06 (days 373 to 412), additional samples from depths up to 100 m were collected. During the more intensive sampling period of summer 2005/06, biological productivity measurements were also made on water collected during the same sampling events as those from which iodine samples were taken. The RaTS site and a second, deeper water site in Marguerite Bay (MT, see Fig. 1) were also sampled from the research ship RRS James Clark Ross on 15/02/06 (cruise JR136/7). A full depth CTD cast was conducted at each site (to 500 and 810 m respectively) using a SeaBird SBE911+ instrument, and water samples from discrete depths were collected using Niskin bottles.

Following collection, seawater samples were gently filtered under vacuum through GF/F (Whatman) papers and were usually frozen for later determination of iodide and iodate at either the Bonner Laboratory at Rothera research station (Antarctica), or our laboratories in the UK. Samples collected between 28/12/05 and 13/02/06 were filtered and stored at +4 °C prior to iodide analysis, which usually took place within 24 h of sample collection, while iodate samples collected during this period were filtered and frozen, and analysis conducted within 6 weeks of collection. These protocols have previously been established as suitable for the preservation of iodine speciation (Campos, 1997). Chlorophyll-a and biological productivity measurements were made at the Bonner Laboratory within a few hours of sample collection.

### 3.2. Analytical techniques

Iodide was determined by cathodic stripping square wave voltammetry (Luther et al., 1988; Campos, 1997). The overall precision of iodide measurements was determined by repeat analysis of selected samples and found to be between 4 and 10% relative standard deviation (RSD). The sum of inorganic iodine in oxidation states between 0 and +5 was determined spectrophotometrically (Jickells et al., 1988); in seawater this iodine fraction is dominated by iodate (Wong, 1991) so here it is defined operationally as iodate and is referred to as iodate hereafter. The overall iodate precision was found to be 5% RSD (around 15 to 20 nM) or better, based on repeat analyses of selected samples. Total dissolved inorganic iodine (TDII) was defined as the sum of iodide and iodate.

Chlorophyll-a from 15 m depth samples was measured by methanol extraction followed by fluorometric detection (Wood, 1985). To obtain a broader picture these results were then used to convert the CTD fluorescence data to chlorophyll-a concentrations for the entire depth profile (Clarke et al., 2008). Photosynthesis rates were measured by incubating 24×5 ml seawater samples spiked with a $^{14}$C tracer for 1 h under a range of light intensities (1–2000 μmol $m^{-2}$ $s^{-1}$) using a photosynthetron (Lewis and Smith, 1983). Photosynthesis versus irradiance curves were fitted by nonlinear regression, as per Platt et al. (1980). Calculation of daily water column primary production was calculated as in Walsby (1997) without the correction for wind speed. Briefly, this involved photosynthetic parameters being normalised to chlorophyll concentration. Calibrated fluorescence was used to scale these parameters at 1 m depth intervals. I was then calculated according to Walsby (1997), with correction for water reflectance by incorporating solar elevation and zenith angle. Daily water column integrated production P was calculated to the depth of net photocompensation irradiance (NPI). NPI is the value of photosynthetically active radiation (PAR) which results in a net phytoplankton growth rate of zero, in the presence of most naturally occurring losses. NPI was used due to the extreme seasonality of photoperiod and irradiance flux at high latitudes, together with the confounding effect of surface ice and surficial snow. An NPI of 15 μEm$^{-2}$ s$^{-1}$ was used based on measurements made in the Bellingshausen Sea (Boyd et al., 1995) and ranged from 6 to 11 m (average 9.1 m) during the sampling period. Full details of the collection and analysis of oxygen isotope samples is given in Meredith et al. (2008).

## 4. Results

### 4.1. Physical and biological oceanography

Vertical sections of potential temperature, salinity and density covering the upper 200 m of the water column for the time period of this study are shown in Fig. 2. This depth range shows clearly the seasonal and interannual variability associated with upper ocean processes. Surface temperatures typically peak around January at around 0–1 °C, while during winter there are long periods when surface waters are close to the freezing point (Fig. 2). Surface waters are freshest during the summer period as a consequence of ice melt, dropping to 33.0 or less. During the winter salinities reach as high as 33.5–34.0. Density strongly mimics salinity, due to the controlling role of salinity in the equation of state for seawater at low temperatures. In terms of physical oceanography, 2005 and 2006 were broadly similar, albeit with slightly fresher surface waters in summer 2005/06. Conversely, the winter of 2007 was very different, with a much thicker slab of water close to the freezing point (Fig. 2; around 150 m in 2007 compared with around 50 m in both 2005 and 2006). This difference is also apparent in salinity and density, which show near-homogeneous waters in winter 2007 compared with much more stratified conditions in 2005 and 2006. The greater homogenisation in 2007 is reflected in the mixed layer depth (Fig. 3A).

The much deeper mixed layer in Ryder Bay in 2007 is linked to pronounced interannual differences in sea ice behaviour (Fig. 3A). During 2005 and 2006, near-complete fast ice cover persisted for several months during winter, whereas during 2007 ice cover was incomplete and highly variable. Complete fast ice was only present for a few days during 2007 and the greater open-water percentage enabled more persistent heat loss to the atmosphere and stronger sea ice production to be maintained throughout the winter. The subsequent salinification of the upper ocean led to much deeper convective overturn in 2007. The behaviour of the sea ice largely reflects wind-driven variability, and it is noted that 2006/7 was an El Niño period. Water column properties (particularly winter mixed layer depth) at the RaTS site have been demonstrated to be especially susceptible to such planetary-scale forcing, with the direction/persistence of winds along the Antarctic Peninsula, and their impacts on sea ice production and mixed layer depths, being key (Meredith et al., 2004).

Biological parameters such as chlorophyll-a concentration (Fig. 3B) also showed seasonality and interannual variability as expected for the site. There was a dense algal bloom in both summer 2005/06 and 2006/07, with chlorophyll-a concentrations at 15 m reaching nearly 30 and 20 μg l$^{-1}$ respectively. The summer bloom of 2007/08 was much less intense, with chlorophyll-a concentrations averaging only 1.3 μg l$^{-1}$ from December to March. Deeper mixing in winter 2007 might be expected to produce a more intense algal bloom the following summer, however in this case the year-on-year variation in chlorophyll levels is thought to be the result of top-down changes in grazing pressure.

### 4.2. Seasonal and interannual variation in dissolved iodine speciation

Changes in iodide and iodate concentrations at 15 m depth show marked seasonality, albeit with high interannual variability superposed (Fig. 3C and D). Lowest iodide levels (10 to 20 nM) were observed at the beginning and end of the ice-free summer periods. Iodide concentrations rose steadily during the summer periods, reaching about 35 nM in 2005/06 (days 413 to 432) and 82 nM in 2007/08 (day 1151). During summer 2006/07, a much larger increase of about 150 nM iodide was observed (days 711 to 772). There was no significant positive correlation between iodide and chlorophyll-a, and only very weak negative correlations were found between iodide and

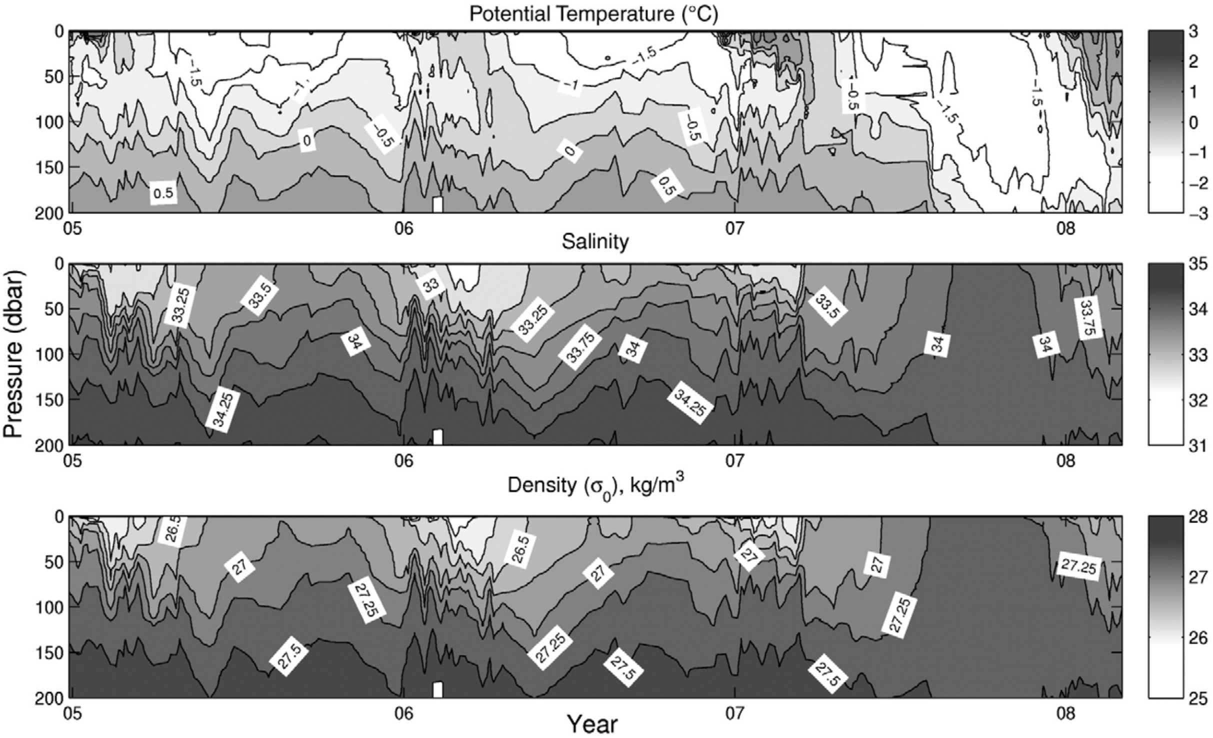

**Fig. 2.** Vertical sections of potential temperature, salinity and density in the upper 200 m of the water column for the time period of this study.

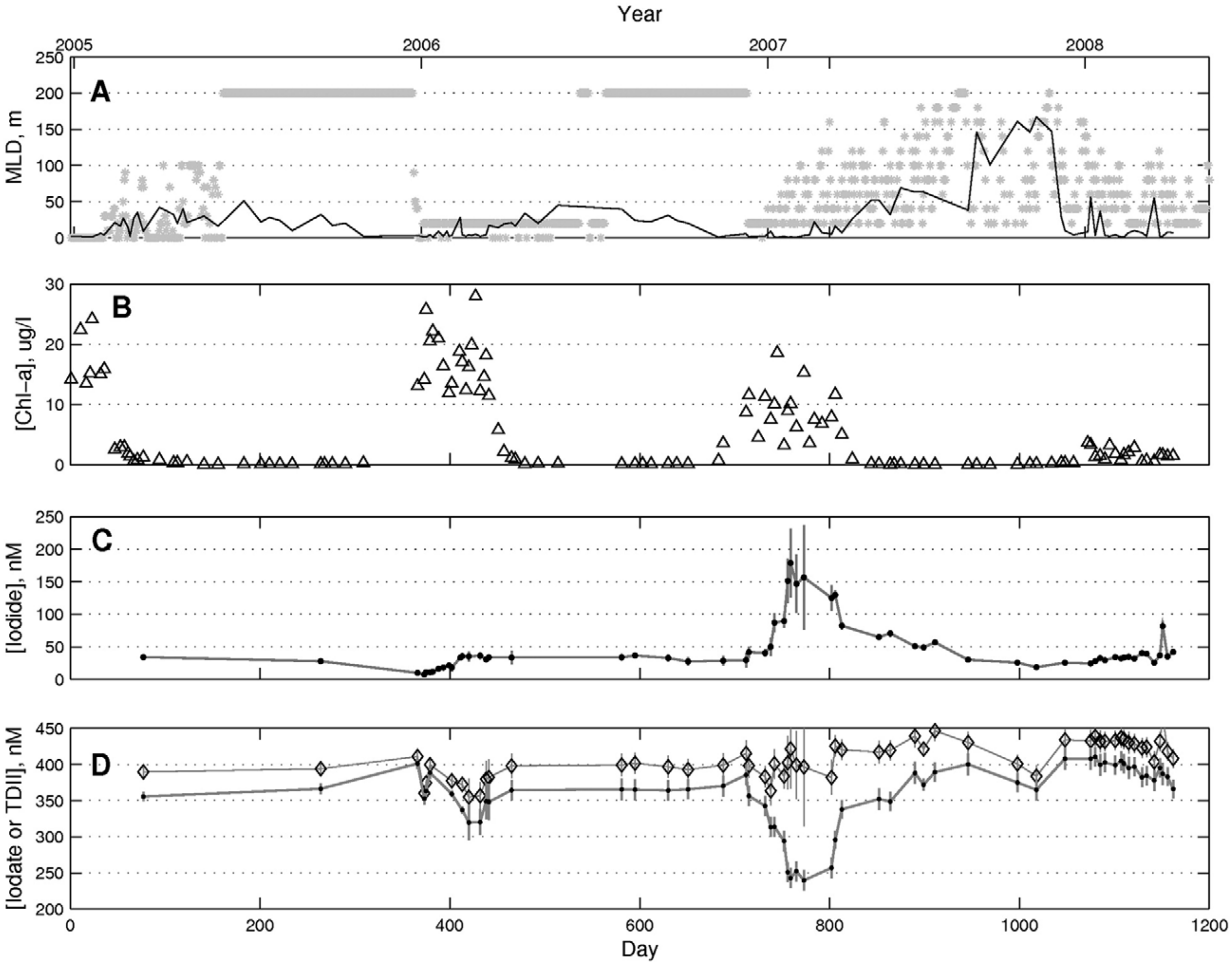

**Fig. 3.** Seasonal variation of selected parameters at the RaTS sampling site between 28/12/04 (day 1) and 03/03/08 (day 1162): A. Mixed layer depth (black line) and ice index (*; a value of 200 implies complete fast ice in Ryder Bay and a value of 0 implies no ice present); B. Total extractable chlorophyll-a at 15 m depth (△); C. Iodide concentrations at 15 m depth (◆); D. Iodate (◆) and total dissolved inorganic iodine (TDII; ◇) concentrations at 15 m depth. Iodide and iodate error bars show ± analytical standard deviation, TDII error bars calculated using propagation of error formulae.

nitrate or phosphate (Table 1). Each summer, there was a time lag of at least 60 days between the onset of the algal bloom, marked by a sharp increase in chlorophyll concentration, and the iodide maximum.

The summertime increases in iodide concentration appear to be accompanied by concurrent decreases in iodate concentration (Fig. 3D). This is most evident during summer 2006/07, when the increase in iodide levels is mirrored by a comparable decrease in iodate of ~140 nM. Correlation of iodate and iodide concentrations yields a line with a slope of −0.99 ± 0.08 (Fig. 4). Within the errors, total dissolved inorganic iodine (TDII) remains constant at about 410 nM throughout the year (Fig. 3D). Only weak correlations were found between iodate or TDII and chlorophyll-a, nitrate, nitrite and phosphate (Table 1). No statistically significant correlations were found between iodate or TDII and silicate. Normalising iodide, iodate

**Table 1**
Pearson correlation coefficients ($r^2$) for regressions of chlorophyll-a and nutrient concentrations against iodine species and total dissolved inorganic iodine (TDII). All values are significant at the 1% level except those marked * which are significant at the 5% level, ns indicates the correlation was not significant.

| | Iodide | n | Iodate | n | TDII | n |
|---|---|---|---|---|---|---|
| *15 m depth, 2005-08* | | | | | | |
| Chlorophyll-a | ns | 61 | 0.17 | 56 | 0.34 | 56 |
| Nitrate | 0.21 | 59 | 0.44 | 55 | 0.13 | 55 |
| Nitrite | ns | 59 | 0.36 | 55 | 0.51 | 55 |
| Phosphate | 0.14 | 59 | 0.38 | 55 | 0.14 | 55 |
| Silicate | ns | 59 | ns | 55 | ns | 55 |
| *0–100 m, 2006* | | | | | | |
| Chlorophyll-a | ns | 84 | 0.07* | 84 | ns | 84 |
| Nitrate | 0.26 | 32 | ns | 31 | ns | 31 |
| Phosphate | ns | 30 | ns | 29 | ns | 29 |
| Silicate | 0.15* | 32 | ns | 31 | ns | 31 |
| Ammonium | ns | 39 | ns | 38 | ns | 38 |

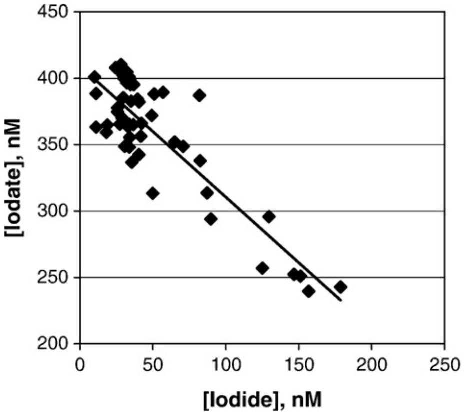

**Fig. 4.** Correlation of iodide and iodate concentrations at 15 m depth for entire sampling period.

and TDII concentrations to the average salinity of the sample set made only very small changes to the concentrations and the patterns observed. The average concentration changes for iodide, iodate and TDII were 0.5, 4 and 5 nM, respectively, and the maximum changes were 2, 10 and 11 nM.

### *4.3. Development of an iodide surface maximum during summer 2006*

During austral summer 2005/06, regular sampling at several depths throughout the productive period allowed the development of the bloom and iodine biogeochemistry to be considered in greater detail. There was a small but steady increase in iodide concentrations within the upper 100 m of the water column (Fig. 5). At the beginning of the sampling season (04/01/06, day 372), iodide was very low throughout the water column, at between 5 and 10 nM. Concentrations gradually increased to reach around 35 nM in surface waters by March. These changes in iodide concentration are readily detectable against the very low background concentrations prevalent in the winter. At each depth, the increase in iodide concentration with time was approximately linear. The net rate of increase was different at each depth, with the fastest rate (0.55 nM day$^{-1}$) occurring at 10 m depth, coincident with the average chlorophyll-a maximum for the period (Table 2).

These small changes in iodide concentration are comparable in size to the absolute precision of the iodate measurements, so the corresponding changes in iodate are expected to be at or below the limit of detection. In general iodate concentrations tended to decrease during summer 2005/06, but the trends were less clear (Fig. 5) and correlation of iodate concentrations against time did not show significant linear relationships at any depth except 50 m.

Deeper depth profiles of iodide and iodate collected from the RaTS site and the deep mooring site on the same day were very similar (Fig. 6). Iodide shows a surface maximum of 35 nM at both sites. Below 100 m, iodide maintained close to constant concentrations, with average values of 9 ± 2 and 13 ± 2 nM at the deep and shallow mooring sites respectively. Iodate did not show any clear trends with depth and the average iodate concentration was 330 ± 30 nM (9% RSD).

Considering the data from the 2005/06 summer sampling season alone, no strong relationships were observed between levels of iodine species and either chlorophyll-a or nutrient concentrations. There was no significant relationship between iodide and chlorophyll-a concentrations, though a weak negative correlation was found between iodate and chlorophyll-a (Table 1). Statistically significant negative correlations were only found between concentrations of iodide and nitrate, no relationships were found between iodide and ammonium or phosphate, or between iodate and any of the nutrients measured (Table 1). Normalising the data to the salinity of the samples did not change the outcome of this analysis.

### *4.4. Iodide concentration and primary productivity*

During the intensive 2005/06 sampling season, depth resolved measurements of both iodide concentration and biological primary productivity were made. A strong correlation between these variables was revealed when a model similar to that proposed by Campos et al. (1996) was applied to the data (Fig. 7). In the model, the rate of iodide accumulation is considered to be a function of primary productivity (P) alone (Eq. (1)):

$$dI^{-} / dt = FP. \qquad (1)$$

The parameter F represents the molar ratio of carbon fixation by primary production to iodide production and is assumed to be constant. It is assumed that iodide losses by oxidation and mixing are negligible, which seems reasonable given that oxidation rates are slow (several months or more) relative to the timescale of this study (Luther et al., 1995; Campos et al., 1996; Truesdale, 2007), and the water column is strongly stratified in the summer (Figs. 2 and 3A).

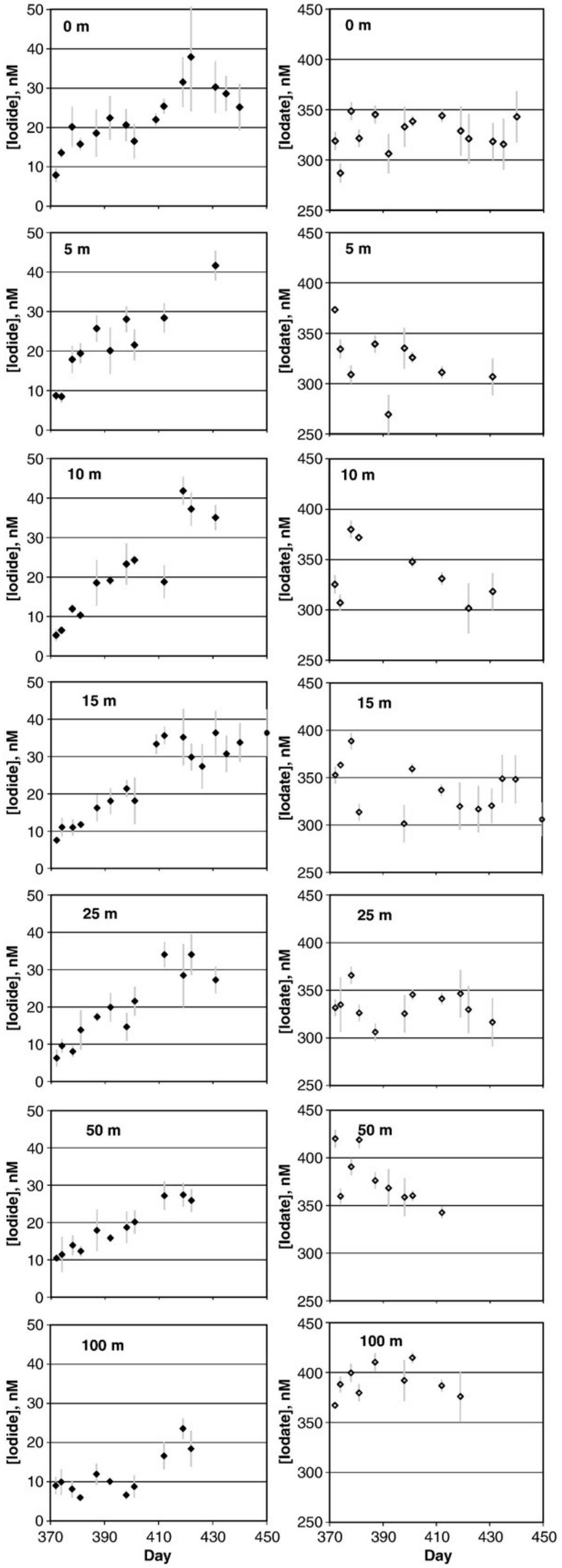

**Fig. 5.** Depth resolved changes in iodide and iodate concentrations at the RaTS site during the summer 2005/06 sampling season from 04/01/06 (day 372) to 23/03/06 (day 450). Error bars show ± analytical standard deviation.

**Table 2**
Rates of increase in iodide concentration over time at sampled depths, in relation to chlorophyll-a concentrations, for RaTS site during summer 2005/06 sampling season. All relationships are statistically significant at the 0.1% level, except for 100 m which is significant at the 1% level. Average chlorophyll-a concentrations over the same period also shown.

| Depth, m | Slope, nM $I^-$ $day^{-1}$ | Intercept, nM | $r^2$ | n | Chl-a, µg $l^{-1}$ |
|---|---|---|---|---|---|
| 0 | 0.27 | 13 | 0.65 | 15 | 4.2 |
| 5 | 0.48 | 10 | 0.84 | 10 | 11.3 |
| 10 | 0.55 | 5 | 0.85 | 12 | 13.6 |
| 15 | 0.38 | 9 | 0.82 | 17 | 13.2 |
| 25 | 0.44 | 7 | 0.82 | 12 | 11.8 |
| 50 | 0.34 | 9 | 0.94 | 11 | 6.8 |
| 100 | 0.24 | 5 | 0.60 | 11 | 0.8 |

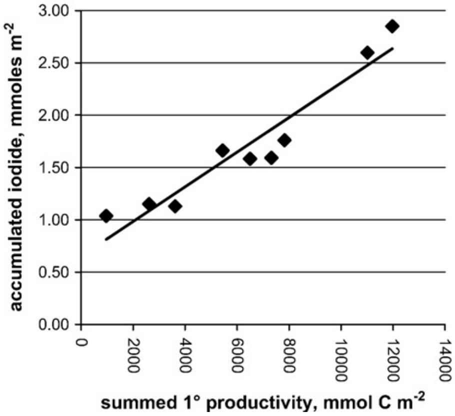

**Fig. 7.** Correlation of iodide standing stock against the summed primary productivity, from 04/01/06 to date of sample, for samples collected from the RaTS site during summer 2005/06. The observed relationship is described by the line $y = 0.00016x + 0.65$; $r^2 = 0.91$; $p = 0.005\%$.

Eq. (1) can be integrated to yield a linear relationship between iodide standing stock and the sum of the productivity over a given interval of time (t):

$$I_t^- - I_0^- = F\int_0^t Pdt \qquad (2)$$

To fit the data to this model, standing stock of iodide in the upper water column (in nmol m$^{-2}$) was calculated for each time point by integrating iodide concentrations over the upper 100 m of the water column. While it may have been preferable to integrate iodide concentration over the entire water column, sampling to this depth at regular intervals was not possible. The integration depth was chosen because iodide concentrations decreased with depth to 100 m, but below this appeared invariant (Fig. 6). Moreover, concentrations were found to increase over time through all depths sampled to 100 m (Table 1), while towards the end of the season (15/02/06) iodide concentrations below 100 m remained low, having values similar to winter surface concentrations (Fig. 6). Therefore, considering only the upper 100 m in this modelling exercise is believed to include essentially all iodide produced in the upper water column through the season. Standing stock of iodide was plotted against the cumulative primary production that had taken place to the depth of the NPI (~10 m) between the chosen time point ($t = t$) and 04/01/06 ($t = 0$). As shown in Fig. 7, the observed data fitted this simple model well and there was a strong correlation between iodide accumulation and total production.

Assuming negligible iodide losses, the parameter F is equivalent to the amount of iodide produced in nanomoles, per millimole of carbon fixed. From the slope of the line in Fig. 7, a value of $1.6 \times 10^{-4}$ is obtained for F, which is in good agreement with the particulate I/C ratio of $1 \times 10^{-4}$ of Pacific plankton (Elderfield and Truesdale, 1980). This is consistent with a scenario in which all iodine assimilated into the cell is released again as iodide within surface waters.

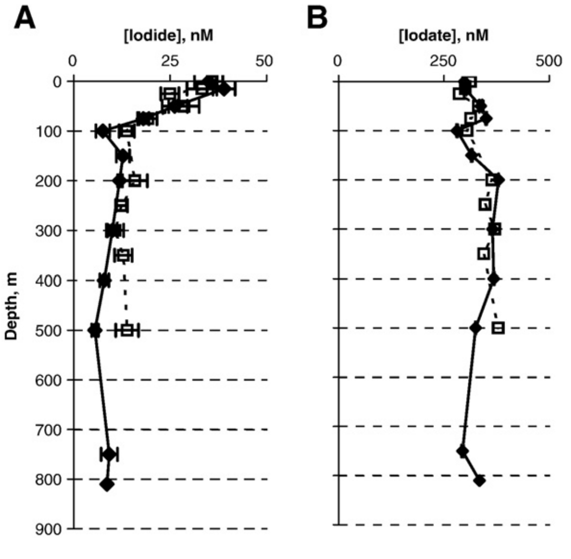

**Fig. 6.** Iodide (A) and iodate (B) depth profiles at the RaTS site (□) and the MT deep mooring site (◆) on 15/02/06. Error bars show ± analytical standard deviation.

## 5. Discussion

### 5.1. Seasonal and interannual variation in iodine speciation in Ryder Bay

The RaTS site is subject to pronounced seasonal changes in temperature, mixing depth, ice cover, freshwater run off and day length. The results shown in Fig. 3 suggest that surface concentrations of dissolved iodine species also follow a seasonal cycle at the site. During the austral summer, iodate appears to be converted to iodide in an approximately 1:1 ratio. The approximately constant concentration of TDII (~410 nM) suggests that there is little organic iodine present. Given the good agreement between iodide and iodate depth profiles taken at the RaTS site and a deeper mooring site approximately 35 km away (Fig. 6), the seasonality in iodine speciation is thought to be representative of the wider Marguerite Bay. Only a few time series studies of dissolved iodine speciation in seawater have been reported in the literature; these have found evidence for seasonal variation in dissolved iodine speciation in the tropics (Jickells et al., 1988; Campos et al., 1996) but not temperate coastal regions (Truesdale, 1978; Truesdale and Jones, 2000; Truesdale and Upstill-Goddard, 2003) or polar waters (Waite et al., 2006). Consequently this work is believed to be the first demonstration of seasonality in inorganic iodine speciation in high latitude coastal waters.

The apparent seasonality of iodide and iodate concentrations in Ryder Bay was subject to considerable interannual variation. During most of the study, iodide concentrations were low, at less than 50 nM, consistent with other measurements made at high latitudes (Campos et al., 1999; Waite et al., 2006). However, levels of more than 150 nM were observed during summer 2006/07. These are thought to be the highest iodide concentrations so far recorded for polar waters. These large year-on-year differences in iodine speciation observed at the RaTS site occur in the context of pronounced interannual variability in many other physical, biological and geochemical parameters at the site, and in the wider western Antarctic Peninsula region (Smith et al., 1998; Meredith et al., 2004; Ducklow et al., 2006; Clarke et al., 2008; Hughes et al., 2009).

### 5.2. Influence of vertical mixing

Although some diapyncal mixing will occur year-round on the western Peninsula shelf, the mixing process most likely to impact strongly on iodine speciation at the RaTS site is the seasonal deepening of the mixed layer during sea ice production, and the subsequent restratification the following spring. The mixed layer deepening excavates downward into the CDW layer, thereby entraining waters with very different physical properties (warmer, more saline), and lower iodide and higher iodate concentrations (Fig. 6).

The impact that mixed layer deepening will have on near-surface iodide and iodate concentrations depends on the vertical gradient in these parameters and the level to which the mixed layer changes. While these are difficult to assess quantitatively in a definitive way, the order of magnitude of the impact can be judged from sample calculations. For example, following the 2006/07 summertime peak of iodide (around day 800 onwards), the mixed layer deepened by around 80 m in 100 days. Relative to a starting mixed layer depth of ~15 m, and using the approximate iodide values for CDW shown in Fig. 6, this equates to a near-surface decrease in iodide concentrations from the observed peak of ~150 nM to around 45 nM in the absence of any other process. This is not dissimilar to the observed iodide concentration after 100 days of ~50–55 nM. For iodate, the same calculation predicts an increase in concentration from the observed minimum of ~250 nM around day 800 to around 360 nM 100 days later, which is again not very different from the observed iodate concentration of ~370–380 nM at day 900. This suggests mixed layer deepening may be an important process in controlling iodide and iodate concentrations near the surface.

Earlier in the season, springtime stratification is likely to have a different impact on iodine speciation in the upper water column. If there is a source of iodide to surface waters, the shoaling of the mixed layer will facilitate iodide accumulation thereby reducing dilution by vertical mixing with lower iodide waters below. The higher iodide and lower iodate concentrations seen in summer develop after the mixed layer has become stratified to its maximum level (Fig. 3), indicating that this process is likely to be important in setting the correct conditions for the extreme seasonal iodide/iodate levels to develop.

While it has been established that seasonal changes in vertical mixing are an important control on near-surface iodide and iodate concentrations, interannual changes in mixing also shed light on whether physical or non-physical processes are controlling iodine speciation. In particular, the strong peak of iodide in summer 2006/07 (and the coincident minimum in iodate) does not correspond to features in the physical fields (Fig. 2). Mixed layer depths in winter 2006 were not significantly different to those observed during the preceding winters, and the summer mixed layer was well-stratified in both 2005/06 and 2006/07. Consequently, it is concluded that the large differences in both iodide and iodate concentrations between summer 2005/6 and 2006/7 were not the consequence of vertical mixing processes.

### *5.3. External sources of iodide to Ryder Bay*

#### *5.3.1. Lateral transport*

The extent and variability of horizontal advection to the RaTS site from elsewhere in the western Peninsula circulation is hard to assess. As noted in Section 2, there are indications that northern Marguerite Bay is part of a general circulation whereby water flows southward close to the western side of Adelaide Island, then cyclonically around Marguerite Bay before exiting to the south near Alexander Island. The APCC is likely to be an important transport mechanism within this circulation, and there are some indications that it may be seasonal in intensity (e.g. Moffat et al., 2008). The possibility that some variability in iodide and iodate concentrations may be induced via advective throughflow of waters of differing iodide/iodate signature cannot be excluded. However, there are no known sources of relatively high iodide waters upstream in the general circulation of the western Peninsula shelf — where measurements are available iodide concentrations have been very low and iodate concentrations correspondingly high (Truesdale et al., 2003a). Furthermore, it is noted that anomalies generated relatively locally in northern Marguerite Bay (e.g. very deep WW observed in 1998; Meredith et al., 2004) tend to persist in situ for many months, suggesting that advective throughflow of anomalies is likely to be slow compared with other relevant biological and physical processes (e.g. mixed layer processes) that occur locally. While further investigation is required, it is currently thought that lateral transport is likely to be only a second-order contributor to the observed variability in iodine speciation.

#### *5.3.2. Glacial run off*

The Sheldon Glacier enters Ryder Bay to the north and numerous other glaciers feed the wider Marguerite Bay area with freshwater. Warming temperatures lead to increased glacial run off entering Marguerite Bay between around December and May, with a maximum typically around February or March (Meredith et al., 2008). Direct measurements of iodine speciation in glacial run off were not made as part of this study, but a sample of glacial ice from Port Lockroy, further north on the Antarctic Peninsula was found to contain 70 nM iodide and no detectable iodate (Chance, 2007). Similarly, glacial ice cores from the Swiss Alps have been found to only contain iodide, and iodide is the dominant inorganic iodine anion in snow (Gilfedder et al., 2008). Thus glacial run off is a possible source of water with a high iodide/iodate ratio to the surface waters of Ryder Bay in the austral summer. It has also been suggested that iodate-reducing substances might be present in terrestrial run off (Truesdale, 1978) and it is possible that similar reducing substances might be present in glacial run off. This is currently unknown, but it is noted that, since the Antarctic Peninsula has low vegetation cover and immature soils, terrestrial input of plant-derived organic matter is likely to be minimal.

Salinity data reflect freshening due to glacial melt input, but are also impacted by sea ice formation and melt, so an additional tracer is needed to decompose the freshwater budget and assess potential glacial melt contribution to iodide and iodate concentrations. Here, the ratio of stable oxygen isotopes in seawater ($\delta^{18}O$) from samples collected at 15 m is used to distinguish sea ice melt from meteoric water. This decomposition is possible since glacial melt and precipitation are strongly depleted in the heavier $H_2{}^{18}O$ molecule, whereas sea ice melt reflects the isotopic characteristics of the seawater from which it formed, and so is much isotopically heavier (see Meredith et al., 2008, for a full discussion). Applying the three-endmember mass balance given in Meredith et al. (2008), salinity and $\delta^{18}O$ have been used to quantify the percentages of meteoric water and sea ice melt in the upper ocean at the RaTS site as a function of time (Fig. 8; note data is currently only available up to mid-March 2007). Seasonality is present in both series, with meteoric water peaking around March in both 2005 and 2006, and showing minimum values during winter, and sea ice melt peaking about a month earlier in both years and also exhibiting minimum values during winter. The meteoric water prevalence varies between around 4 and 6%, while the sea ice melt varies between around −1 and 2%. (Note that negative values for sea ice melt denote net sea ice formation at the time of sampling, i.e. brine rejection had salinified the upper ocean rather than sea ice melt freshening it). While the meteoric water series shown in Fig. 8 will include freshwater inputs from direct precipitation, it has been shown previously that this term is small in the freshwater budget at the RaTS site, and that meteoric water as calculated strongly reflects glacial melt (Meredith et al., 2008).

Although the freshwater budget has only been calculated until March 2007 (Fig. 8), there is no evidence for a large pulse of glacial melt up to this point, while very high iodide and low iodate levels are present (iodide and iodate reached maximum and minimum values respectively by February 2007; Fig. 3C and D). In Jan 2007, the meteoric water prevalence was around 4–5%, slightly higher than it was in Jan 2006 (around 4%), but this difference (~1%) is too small to plausibly

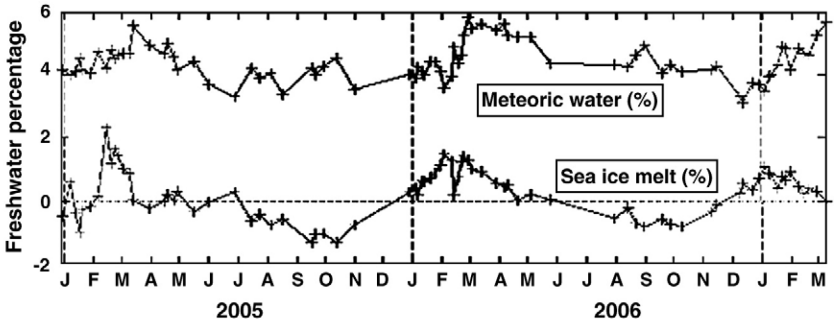

**Fig. 8.** Percentage contributions of sea ice melt and meteoric water to the water column at the RaTS site, calculated using $\delta^{18}O$ and salinity measurements.

explain the differences in iodide and iodate concentration; were a 150 nM increase in iodide concentration to be caused by a 1% increase in glacial melt, this would require the glacial melt to have an iodide concentration of several thousand nM. Therefore it is concluded that interannual changes in glacial melt are, at most, secondary contributors to the variation in iodide and iodate concentration.

## 5.4. Abiotic mechanisms for the reduction of iodate to iodide

### 5.4.1. Photochemistry

Because of its location at 67°S, diurnal light cycles at Rothera move from extremes of complete darkness around mid-winter to 24 h daylight around midsummer. Some experiments have demonstrated the reduction of iodate to iodide under natural light (Spokes and Liss, 1996), so the possibility that the summertime formation of iodide is photochemical must be considered. Such a process would not be inconsistent with the observed correlation between accumulated iodide and biological productivity, because both photochemical iodide formation and photosynthetic carbon fixation share a common driver, light. However, if photochemistry was the dominant iodide generating process, iodide concentrations might be expected to decline exponentially with distance from the sea surface, following the pattern of light attenuation in the water column. Instead, observed iodide profiles show elevated iodide levels to a depth of 100 m, and typically exhibit sub-surface maxima in absolute iodide concentration (Figs. 5 and 6).

### 5.4.2. Sediment interactions

It has also been suggested that interactions with sediments at the sea floor might cause reduction of iodate to iodide (Nakayama et al., 1989; Truesdale et al., 2003b). However, this seems unlikely to be important in surface waters at the RaTS site for two reasons. Firstly, such a mechanism would be expected to result in an increase in iodide concentrations toward the sediment–water interface, which is not observed (Fig. 6). Secondly, sediment interactions might be expected to result in enhanced iodide levels following deep mixing, as this would bring waters into contact with the sediments, while again the reverse is observed. Organic matter decomposition in the water column and underlying sediments can also alter the deep water concentrations of iodide species (Edwards and Truesdale, 1997), but rates of change are thought to be slower than observed here and would be expected to cause changes at depth rather than the surface.

### 5.4.3. Dissolved oxygen

Iodine speciation may be influenced by dissolved oxygen concentration, as this affects redox potential, and iodide has been identified as the dominant iodine species in oxygen minimum zones (Farrenkopf and Luther, 2002). However, in the upper layers of Ryder Bay, where iodide formation is observed, oxygen is thought to be saturated (see Section 2). Oxygen saturation may drop below about 100 m, but at these depths iodate is the dominant form (Fig. 6). Therefore, dissolved oxygen levels are not thought to impact iodine speciation at the RaTS site.

### 5.4.4. Sea ice processes

Perhaps the most conspicuous seasonal variable in Ryder Bay is the presence and extent of sea ice. Little is known about the influence of sea ice processes on inorganic iodine speciation, so possible scenarios are considered briefly here. If iodide and iodate are expelled from freezing seawater without fractionation, both will increase in concentration in the underlying seawater as ice forms between June/July and October. However, neither iodide nor iodate concentrations show enhancement during this period (Fig. 3). Furthermore, higher amplitude (negative) values for sea ice freshwater contribution were observed in 2005 than in 2006, reflecting slightly more sea ice formation that year (Fig. 8), but there was no difference in iodide or iodate concentrations between the two years for this period. Similarly, iodide and iodate would be expected to decrease in concentration as surface waters are diluted by fresh sea ice melt in spring but this does not match the observations reported here. The sea ice melt input in Jan/Feb 2007 was actually lower than that input in Jan/Feb 2006 (Fig. 8), suggesting the large rise iodide levels in early 2007 was not related to sea ice processes. If iodate were preferentially expelled over iodide during sea ice formation, it would show a stronger seasonal signal, but the data suggests a 1:1 relationship between iodide and iodate (Fig. 4). Furthermore, if brine expulsion were the dominant control on iodate, normalising concentrations to salinity would be expected to dampen the seasonal signal, but this is not observed (Section 3.2). The above considerations suggest that brine rejection upon sea ice formation is not a first order process in controlling iodine speciation at the RaTS site.

Alternatively, iodate might be reduced to iodide within the ice. Measurements made on ice brines collected at Rothera found the iodide/iodate ratio to be elevated relative to the underlying seawater but that total dissolved inorganic iodine was conservative (Chance, 2007). This would result in an influx of high iodide/low iodate water upon breakup of the sea ice in spring. However, this is inconsistent with the steady increase in iodide concentration in the water column observed following departure of the sea ice, so is not thought to be the dominant control on iodine speciation at the RaTS site.

## 5.5. Biological influences on iodine speciation

The seasonal increase in iodide levels in Ryder Bay is broadly concurrent with the high rates of algal growth that occur during the summer (Fig. 3). Furthermore, during summer 2005/06, the fastest rate of increase in iodide concentration was found at the same depth as the time averaged chlorophyll-a maxima (Table 1). Combining the observed net rate of iodide increase at the RaTS site for summer 2005/06 and the average chlorophyll-a concentration at 10 m (15 $\mu g\ l^{-1}$) gives an iodide production rate of 0.04 nmol $day^{-1}$ $\mu g$ chl-a $l^{-1}$. This is very similar to the iodide production rate of 0.03 nmol $day^{-1}$ $\mu g$

chl-a $l^{-1}$ observed in cold-water diatom cultures (Chance et al., 2007). This suggests that the reduction of iodate to iodide at the RaTS site could be accounted for by a biologically mediated reaction. The strong correlation between iodide concentration and biological carbon fixation during the summer 2005/06 season (Fig. 7) further supports this view, especially given the agreement between the observed F value and the I/C ratio of $10^{-4}$ given by Elderfield and Truesdale (1980). However, the possibility that the observed correlation between iodide and primary production is merely coincidental, arising from shared controlling factors (e.g. mixing depth, light), cannot be entirely excluded. Furthermore, iodide production may not be directly coupled to photosynthesis, but instead occur by a bacterial or zooplankton mediated process, as the activities of these groups are in themselves closely linked to primary production. Further research into the actual mechanism or mechanisms that cycle iodine species within the euphotic zone is still required.

If the summertime reduction of iodate to iodide observed at the RaTS site is biologically mediated, there are a number of apparent paradoxes that require explanation. Firstly, there is an approximately 60 day lag between the onset of the summer bloom and the peak in iodide concentrations, and correlations between iodine species and chlorophyll-a concentrations are weak or non-existent for both the three year time series at 15 m and the depth resolved samples taken during summer 2005/06 (Table 1). This lack of a direct relationship between the two may occur because the controls on each are different. Chlorophyll-a levels represent the standing stock of biomass at any given time and are controlled not just by biological production but also by grazing. Meanwhile, removal of iodide by oxidation is slow (Luther et al., 1995; Campos et al., 1996) so it is able to accumulate in the water column. Alternatively, the 60-day time lag may arise because iodide production is driven by a process that also lags behind new algal production, such as zooplankton grazing or regenerated production (rather than new, nitrate driven primary production). The relationships between iodide production and both 'new' and regenerated primary production were investigated as described for total production (Section 4.4). However, the fraction of total production that was driven by nitrate did not vary substantially during summer 2005/06 and so good correlations were achieved in both cases (data not shown). Consequently it was not possible to elucidate whether iodide production was linked to a particular type of nitrogen metabolism in this study.

Secondly, iodide concentrations at 15 m were highest in 2006/07 but chlorophyll-a was lower than the previous year. As chlorophyll concentration is a function of both biological productivity and grazing pressure, the lower chlorophyll-a levels in 2006/07 do not necessarily imply lower productivity. Primary productivity was not measured during summer 2006/07, so it was not possible to test whether it was correlated with accumulated iodide that year. However, although biological productivity on the western Antarctic Peninsula shows marked interannual variation (Smith et al., 1998; Ducklow et al., 2006), it seems unlikely that productivity in summer 2006/07 was an order of magnitude larger than that in 2005/06 or 2007/08. Differences in vertical mixing may account for some of the interannual variability in concentrations at 15 m depth (Section 4.2). The slightly higher input of meteoric water in summer 2006/07 may also have contributed some extra iodide, although this is likely to have been at most only a small contributor to the change (Section 5.3.2). It is also possible there was some lateral advection of high iodide waters, perhaps produced by an algal bloom upstream (Section 5.3.1). A further factor that may contribute to the observed variation in iodine speciation is interannual variation in the phytoplankton (and perhaps also the associated bacteria and zooplankton) assemblages present. Year on year differences in the relative dominance of phytoplankton groups in surface waters at the RaTS site have been documented (Annett et al., 2010), and there is pronounced variation in the ability of microalgal species to produce iodide (Chance et al., 2007). Further investigation is required to determine whether the relationship between iodide accumulation and biological production holds, albeit with different slopes, when different plankton assemblages are present.

Differences in phytoplankton composition may also explain the discrepancy between our results and those of a mesocosm study conducted at a similar location on the western Antarctic Peninsula (Livingston Island, 62° 39.576′S, 60° 22.408′W; Truesdale et al., 2003a), in which no significant change in iodine speciation was observed during 25 days of dense algal growth. The mesocosm blooms were dominated by *Thalassiosira antarctica* (Truesdale et al., 2003a), a centric diatom of a genus that did not produce iodide in algal culture experiments (Chance et al., 2007). Centric diatoms, of which *T. antarctica* was a main species, constituted 20% of the diatom biomass at the RaTS site in late December 2005, but this fell to less than 5% through January 2006 (Annett et al., 2010), the period for which iodide was increasing. During January and February 2006, the bloom was overwhelmingly dominated by the pennate diatom Proboscia inermis (Annett et al., 2010). The influence of this alga on iodine speciation has not been studied, but other cold-water pennate diatoms (*Navicula* sp., *Nitzschia* sp.) have been identified as prolific iodide producers (Chance et al., 2007).

## 6. Concluding remarks

Observations made at a coastal Antarctic site over three years show a seasonal cycle in dissolved iodine speciation in surface waters. Specifically, an increase in iodide concentrations and concurrent decrease in iodate accompanies a dense summertime algal bloom, demonstrating iodide production within Antarctic waters. In common with many other oceanographic parameters studied in the western Antarctic Peninsula region, there was considerable interannual variability in the magnitude of these changes. During two of the three summers studied, the increases in iodide and decreases in iodate concentration were only a few tens of nM while in the third summer a larger change of around 160 nM was observed.

A number of factors are thought to influence iodine speciation at the site and identifying the contribution of each is complex. Vertical mixing dilutes higher iodide surface waters with lower iodide deep waters and may account for at least some of the decline in iodide concentrations at 15 m observed during autumn and winter. Glacial run-off (and/or sea ice melt) may supply the high iodide/low iodate waters to the surface layers and account for some of the summer time iodide increase, but neither are thought to be dominant contributors. During summer 2005/06, the iodide increase was strongly correlated with the integrated biological production, with an implied I/C assimilation ratio in good agreement with that reported in the literature for marine phytoplankton. Furthermore, the in situ rate of iodide production was comparable with experimentally measured rates of iodide formation by cold-water algal cultures. These findings suggest that the observed iodide production could be explained by biologically mediated in situ reduction of iodate, though such a mechanism is not demonstrated explicitly in this work. However, the high levels of interannual variability observed are not satisfactorily explained by variations in biological productivity alone. A longer time series is required to definitively identify parameters that co-vary with iodide and iodate concentrations on an interannual scale and thus elucidate the controls on iodine speciation in these waters.

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