GEOSCIENCES

Exploratory evaluation of iron and its speciation in surface waters of Admiralty Bay, King George Island, Antarctica

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Abstract: The determination of dissolved iron concentrations and speciation was conducted for the first time in surface seawater coastline samples collected during the austral summer of 2020 in Admiralty Bay, King George Island, Antarctica. The technique of competitive ligand exchange/adsorptive cathodic stripping voltammetry with 2,3-dihydroxynaphthalene as the competing ligand was evaluated, showing a sensitivity between 14.25 and 21.05 nA nmol L^{-1} min^{-1}, with an LOD of 14 pmol L^{-1} and a mean blank contribution of 0.248 nmol L^{-1}. Physicochemical parameters such as pH (7.85 ± 0.2), salinity (32.7 ± 0.8) and dissolved oxygen (51.3 ± 26.6%) were compatible with those of the literature; however, the average temperature (4.2 ± 0.8 °C) was higher, possibly as a reflection of global warming. The dissolved iron mean value was 18.9 ± 6.1 nmol L^{-1}, with a total ligand concentration of 23.6 ± 12.2 nmol L^{-1} and a conditional stability complex constant of 12.2 ± 0.2, indicating humic substances as possible ligands. On average, the calculated free iron concentrations were 0.7 ± 0.3 pmol L^{-1}. Relatively high concentrations of iron indicate a possible local source of Fe, likely predominantly from upwelling sediments and secondarily from ice-melting waters, which does not limit the growth of the phytoplankton.

Key words: Ads-CSV, coastal waters, dissolved iron, iron biogeochemistry.

INTRODUCTION

Iron is an essential element for life in the ocean once it participates in many physiological processes, such as nitrate uptake, nitrogen fixation and phytoplankton photosynthesis (Geider & La Roche 1994, Hogle et al. 2014). In regions with high nutrients and low chlorophyll (HNLC), such as most of the Southern Ocean, iron has been recognized as a limiting nutrient of primary productivity (Boyd & Law 2001, Kuma et al. 1998, Martin 1990).

Iron concentration in oceanic waters is reduced to levels from nanomole to picomole per litre due to a combination of factors, including its low solubility, its biological uptake and its partition to suspended particulate matter and consequent removal from the water column by scavenging (Liu & Millero 2002). Despite its low solubility, dissolved iron (DFe) concentrations are higher than expected, varying widely in the water column and ocean surfaces due to the tendency of iron to form organic complexes (Waite & March 2001). This occurs because DFe concentrations are controlled by dissolved organic ligands that bind trace metals, increasing the solubility of Fe, and maintaining DFe at levels higher than expected for low solubility oxygenated seawater. This concentration usually varies from < 0.1 to 1 nmol L^{-1} Fe depending on pH, salinity, depth and temperature (Liu & Millero 2002).

The presence of natural ligands regulates the bioavailability and photoreaction process, as organic complexation sustains DFe on the surface for longer and higher concentrations than its solubility, consequently resulting in a larger supply of iron for phytoplankton (Shaked & Lis 2012) and increasing the rate of Fe(II) oxidation (Rose & Waite 2002). Despite being mostly a HNLC region, the Southern Ocean has an important role in iron biogeochemistry and subsequently in the carbon cycle (Henkel et al. 2018, Raiswell et al. 2008). In this region, there is intense primary productivity during austral spring and summer, including high gas exchange, intense winds, formation of bottom water and extensive winter ice cover, which makes Antarctic shelf waters a net sink for atmospheric carbon dioxide (Arrigo et al. 2008, Frölicher et al. 2015, Jones et al. 2015). According to Arrigo et al. (2000, 2003), light availability determines phytoplankton species distribution, whereas the availability of Fe controls the magnitude of annual primary productivity.

Reports involving the quantification of iron around the Antarctic continent have examined different matrices. Henkel et al. (2018) investigated the iron cycling and the Fe isotope fractionation in shelf sediments of Potter Cove, a bay located on King George Island, which is affected by rapid glacier retreat due to atmospheric warming. At the Amundsen Sea Polynya, experiments that simulated biological activity and DFe uptake demonstrated that glacial meltwater and sediments are the main contributors of DFe to primary productivity at depths up to 100 m (St-Laurent et al. 2017). In addition, the "melt water pump", which is the circulation driven by the melting of the ice shelf within its cavities (Greisman 1979), plays an important role in providing DFe (St-Laurent et al. 2017). According to Sherrell et al. (2015), meltwater-enriched seawater flowing from the Dotson ice shelf cavity contributed 0.7 nmol kg^{-1} of biologically available iron to the Amundsen Sea Polynya over a three-week period between 2010 and 2011.

Concentrations of DFe were up to 700 μmol L^{-1} in sediment pore waters from Potter Cove (Monien et al. 2014), representing a substantial source of iron to coastal waters in Antarctica. Raiswell et al. (2016) observed the presence of iron in atmospheric dust delivered to sea ice, where exposure to melting/refreezing cycles may enhance fractional solubility and thus result in fluxes of iron to surface sea water. Moreover, in the western Weddell Sea, sediment resuspension in areas characterized by high turbulence due to rugged bottom topography represented an important source of iron in enriching the water column near the Antarctic continent, potentially fertilizing coastal and open ocean waters of the region (De Jong et al. 2012).

Several analytical techniques have been applied to determine DFe in natural waters. Among them are chemiluminescence, spectrophotometry, mass spectrometry with inductively coupled plasma (ICP–MS), and voltammetry (Lin et al. 2018). Voltammetric techniques such as adsorptive cathodic stripping voltammetry (Ads-CSV) are highly adequate for the determination and speciation of iron in ocean waters due to their low limits of detection and quantification, high sensitivity, and repeatability. Another advantageous aspect of the technique is the elimination of pretreatment and reduction of sample volume (Laglera & Monticelli 2017).

The high sensitivity and advances in voltammetric techniques make this method advantageous for the study of iron biogeochemistry, as it also allows the evaluation of the presence of natural organic ligands by competing ligand exchange with the detection of a labile fraction by cathodic stripping

voltammetry (CLE/CSV) (Gledhill & Van den Berg 1994, Rue & Bruland 1995, Wu & Luther 1995). Fe(III) speciation in oceanic waters has been resolved after iron titration, in which a part of iron is dissociated from its complex with the natural ligand, forming complexes with an added ligand that are detected by Ads-CSV (Abualhaija & Van den Berg 2014). As the metal concentration increases, the free natural ligand is gradually saturated so that the titration curve results in a linear range that is often used to calculate the sensitivity of the method (Hudson et al. 2003, Kogut & Voelker 2001, Laglera et al. 2013a, Turoczy & Sherwood 1997, Voelker & Kogut 2001, Wu & Jin 2009).

With CLE-Ads-CSV, using an artificial ligand and an oxidant to catalytically increase the sensitivity of the signal, it is possible to obtain information on the complexation capacities and conditional stability constants of iron at trace levels. In addition, it is possible to obtain information about the complexation properties of iron with humic substances (HS) in seawater using 2,3-Dihydroxynaphthalene (DHN) as a ligand in the absence of bromate (Laglera et al. 2011). More recently, it has been demonstrated by Laglera et al. (2020) that advances in the method allows for quantification of the individual contributions of the different types of natural ligands present in ocean waters, which until then was hypothetically estimated.

Considering all of these factors, this work aims to provide an exploratory analysis with novel results related to the concentration of iron and its speciation in subsurface water samples from Admiralty Bay, an Antarctica Specially Managed Area located on King George Island that has experienced one of the highest warming rates in the Southern Hemisphere (Dauner et al. 2021). The enhanced iron fluxes into coastal and ocean regions of the Southern Ocean through glacial weathering and meltwater runoff may affect phytoplankton growth. Then, the establishment of a robust analytical method for the determination of iron concentrations and speciation in Antarctic waters will contribute to understanding the recent environmental changes in the region.

MATERIALS AND METHODS

Study Area and Sample Collection

Admiralty Bay is situated on King George Island, is 131 km wide and opens to the Bransfield Strait south-southeast. The temperatures in the region are low, with an annual average varying around -10 °C, and it is one of the largest bays in the South Shetland Islands (Figure 1) (Ferreira Júnior et al. 2016). It is geomorphologically divided into three main inlets where three permanent research stations are now operating: the Brazilian "Comandante Ferraz" station is located in Martel Inlet; the Peruvian "Machu Picchu" station is near Crepin Point in Macklar inlet; and the Polish "Henryk Arctowski" established near Thomas Point in Ezcurra Inlet (Gheller & Corbisier 2022, Montone et al. 2016).

The central basin is the deepest point of the bay, reaching 550 m in depth (Campos et al. 2013, Siciński et al. 2012). Hydrological conditions in Admiralty Bay are determined by the exchange of waters of the bay with the deep oceanic waters from the Bellingshausen and Weddell Seas, freshwater runoff and local processes such as tidal variations in the fjord (Pruszak 1980, Rakusa-Suszczewski 1980).

The surface layer from 0 to 100 m presents current velocities from 0.3 to 1.0 m s^{-1}, with deep currents generated by tides that produce a daily vertical mixing of the entire water column (Pruszak 1980, Rakusa-Suszczewski 1980). Moreover, Admiralty Bay has heterogeneous fjord topography, where wind interactions with the surface layer influence circulation
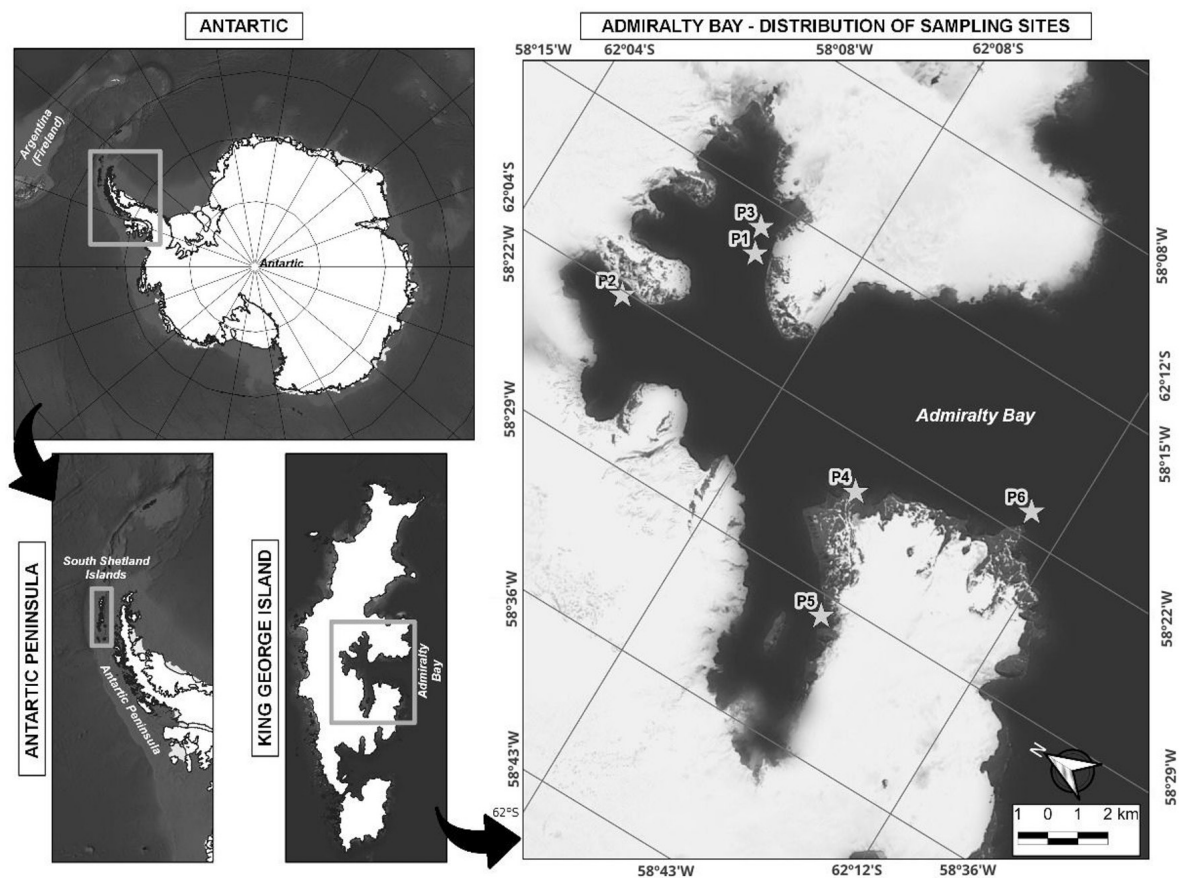
Figure 1. Location of sampling stations in Admiralty Bay, King George Island, Maritime Antarctica.

and create water column mixing (Campos et al. 2013, Siciński et al. 2012), playing a key role as a primary production regulator (Brandini & Rebello 1994). Freshwater runoff influences column turbidity through the suspension of soft sediments (Pichlmaier et al. 2004).

During Brazilian Antarctic Expedition XXXVIII (2019/2020), subsurface water samples (0 to 1 m deep) were collected in a Zodiac inflatable boat at six sites chosen in different environments at the bay with goal of making this study as representative as possible. P1 and P3 are in Martel inlet; P2 is in Mackellar inlet, P4 and P5 are in Ezcurra inlet and P6 is just off Admiralty Bay to Bransfield Strait. Clean techniques were used during all processes of collection, transport and preparation of the samples (adapted from Caprara et al. 2015). The

depth of the sampling points was 150 m in P1, 80 m in P2, 10 m for P3, P4, and P5, and 30 m for P6. At each point, 2 liter sample was manually collected using nitrile gloves against the current at low tide events except for P3 and P6, when high tide events occurred. Then, the collected samples were kept in high density polyethylene bottles (HDPE), which were previously washed, decontaminated and conditioned with the sample. At the laboratory, the total volume was divided into three 500 mL subsamples in HDPE bottles and frozen (-20 °C) until all analyses were carried out, which lasted approximately 7 months. Water samples were thawed to room temperature inside a laminar flow hood and then filtered by gravity using 0.22 μm pore cellulose acetate membranes (Filtrilo©) in a closed polysulfone system (Merck Millipore®).

Aliquots reserved for the determination of total dissolved iron (DFe) were acidified to pH 2 with purified HCl. For speciation analyses, samples filtered in polytetrafluoroethylene (PTFE) vials were kept frozen for up to 2 h before analysis.

Ancillary seawater parameters such as temperature, pH, dissolved oxygen, and salinity were measured *in situ* at each site. All sensors were purchased from Hanna Instruments, USA. Portable pH/EC/TDS/Temperature Metre, model HI9811-5; accuracy at 20 °C: pH from 0.0 to 14.0 ± 0.1. Portable dissolved oxygen metre, model HI9146; accuracy at 25 °C from 0.0 to 300.0 ± 1.5% of saturation. Marine salinity tester, model HI98319; from 0.0 to 70.0 ± 1.0. Temperature from 0.0 to 50.0 ± 0.5 °C.

Equipment and reagents

A Computrace Control 797 VA instrument (Metrohm, Switzerland) was used for the determination of total DFe concentration and organic speciation. The cell consists of a hanging mercury drop electrode (HMDE, Metrohm Model 797 VA, Switzerland) as the working electrode, a Ag/AgCl double junction reference electrode with a 3 mol L^{-1} KCl-filled salt bridge (Metrohm, Switzerland) and a Pt auxiliary electrode. The solutions (10 mL) were placed in a glass voltammetric cell that was rinsed five times using Milli-Q$^®$ type water plus HCl 1.0% and then ten times with Milli-Q$^®$ water between the analyses to avoid adsorption onto the cell wall. To evaluate losses of Fe by adsorption onto the cell walls or iron enrichment by permeable KCl through the reference electrode frit, 15 voltammetric readings of the same 0.7 mol L^{-1} NaCl solution with 1.0 nmol L^{-1} Fe were performed in sequence at 2 min intervals. The voltammetric cell was fitted with a rotating PTFE rod for solution stirring, and the oxygen was removed by purging with water-saturated nitrogen. The instrumental parameters used for

the determination were based on Obata & Van den Berg (2001) and are listed in Table I:

The differences in relation to the Obata & Van den Berg (2001) parameters are 7 s instead of 10 s for the equilibrium time, a final potential of -1.2 V rather than -0.8 V, and scan rate of 15 mV s^{-1} instead of 24 mV s^{-1}.

UV-digested Seawater (UVSW) was prepared using a home-built system with a 125 W high-pressure mercury vapour lamp (Philips, HPL-N) (Figure 2).

The water used to prepare the solutions, rinse the electrodes and glassware was purified using a Milli-Q$^®$ system (Simplicity, FRA) with 18.2 MΩ resistivities. Hydrochloric acid (Merck IQ grade) was purified using a PTFE distiller (Berghof), and ammonia was prepared by vapour-phase transfer of the reagent-grade concentrated ammonium hydroxide into Milli-Q$^®$ water. Stock solutions of iron were prepared by diluting a standard atomic absorption spectrometry solution (Tritisol, Merck, 1000 mg L^{-1}) in ultrapure acid medium (HCl pH 2.0) at concentrations of 0.3, 3.0 and 10 µmol L^{-1}. 2,3-Dihydroxynaphthalene competing ligand (DHN; ≥ 98%, Sigma–Aldrich) was prepared in acidified ultrapure water (pH ± 1.8) at a concentration of 1.0 mmol L^{-1}. A combined solution of the buffers

Table I. Electrochemical parameters used to determine the total dissolved iron and organic Fe-binding ligand concentrations.

Parameters	Settings
Purging time (s)	300
Scan	Sample Direct Current
Deposition potential (V)	-0.1
Equilibration time (s)	7
Deposition time (s)	60
Start potential (V)	-0.1
End potential (V)	-1.2
Scan rate (mV s^{-1})	15

piperazine-N,N'-bis-(2-hydroxypropanesulfonic acid) (POPSO, Sigma–Aldrich) and potassium bromate (Sigma–Aldrich) was prepared to obtain the catalytic effect with sufficient ammonia to reach pH = 8.2. A 0.7 mol L^{-1} sodium chloride (NaCl) solution was prepared in Milli-Q® water.

Iron contamination of buffer/bromate and NaCl solutions was removed by sorption onto a suspension of MnO_2 0.01 mol L^{-1} and subsequent removal by gravity filtration (0.2 μm) (Obata & Van den Berg 2001).

The quartz tubes used for digestion of the sample as well as the reagent containers (HDPE, Nalgene) were cleaned first by soaking in 2.0% neutral detergent (Extran® MA 02) for 1 week and then rinsed exhaustively in tap water followed by distilled water and then acidification for a week in HCl (10%) (adapted from Caprara et al. 2015). Containers were then rinsed with Milli-Q® water, dried in a laminar flow hood, and stored in double plastic bags until use.

Analytical procedure for the determination of the total concentration of dissolved iron

To determine the total DFe concentrations, the method described by Laglera et al. (2013b) was
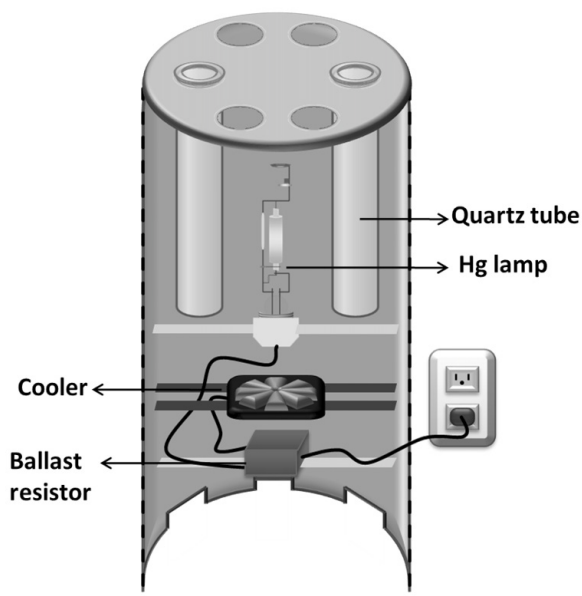

Figure 2. Representation of the home-built digestor.

employed with slight modifications. First, 15 mL of each filtered sample (0.2 μm) was acidified (with ultrapure HCl to pH 2.0), transferred to a quartz tube and placed inside the reactor around the UV lamp for a 6 h irradiation period, instead of the 2 h used by Laglera et al. (2013b), for the photochemical digestion of the organic matter.

To reduce seawater matrix interferences related to the presence of vanadium and the higher iron concentrations, digested samples were diluted four times in 0.7 mol L^{-1} sodium chloride solution. An aliquot of 10.0 mL of the diluted digested sample was pipetted into the voltammetric cell. Then, 500 μL of BrO_3^-/POPSO solution (concentrations of 20 mmol L^{-1} and 5 mmol L^{-1}, respectively) and 30 μL of 1.0 mmol L^{-1} DHN solution were added, and an appropriate volume of a 50% ammonium hydroxide solution was required to raise the pH to ~8.7 (the exact volume used depended on the ageing of the ammonia solution). Finally, the samples were submitted to voltammetric analysis with the parameters described in Table 1.

The iron reagent blanks of BrO_3^-/POPSO and DHN solutions were determined using analysis of ultrapure water, tripling the concentrations of the following individual solutions and subtracting from each seawater measurement.

The limit of detection (LOD) was determined in Milli-Q® water according to the IUPAC recommendation as 3.3 s_{blank}/sensitivity, where "s_{blank}" is the standard deviation of the blank signal. The accuracy and precision of the analytical protocol were confirmed by recovery tests. For this, 10 mL of the 0.7 mol L^{-1} NaCl solution was fortified with 5.0 nmol L^{-1} of iron and submitted to the same procedure to determine the total DFe.

Determination of iron speciation

The CLE-CSV using DHN, POPSO, and BrO_3^- was applied to perform iron speciation (a detailed description of the analytical protocol can be found in Laglera et al. (2011) and in Van den Berg (2006)). After the sample was thawed at room temperature, 120 mL was mixed with DHN (final concentration 1.0 µmol L^{-1}, log $\alpha_{Fe'-DHN}$ = 2.81 (Van den Berg 2006)) in a PTFE bottle. The mixture was left aside to reach equilibrium for 30 min. Then, aliquots of this solution (10.0 mL) were pipetted into a series of 12 PTFE cups previously conditioned with iron solution of the same concentration (Buck et al. 2012, Thuróczy et al. 2011). To run the batch titration, nine containers with sample plus DHN were spiked with iron in increasing concentrations up to 60.0 nmol L^{-1} and left to equilibrate from 12 to 17 h. The first two aliquots were used only to condition the electrochemical cell. In sequence, each aliquot was consecutively transferred to the voltammetric cell; then, 500 µL of the BrO_3^-/POPSO mix solution for a pH of 8.05 ± 0.05 was added.

Concentrations of the ligands (L_t) and the conditional stability constant (log K'_{FeL}) were calculated using a Ruzic/Van den Berg linearization plot as described previously (Ruzic 1982, Van den Berg 1982).

For the recovery test, 120 mL of the 0.7 mol L^{-1} NaCl solution was fortified with 5.0 nmol L^{-1} of iron and 10.0 nmol L^{-1} of deferoxamine mesilate (DFO) (Sigma–Aldrich) as a ligand (Van den Berg 2006). Then, this solution was submitted to the same titration and voltammetric procedure described earlier in this section.

RESULTS

Quality Assurance and Quality Control (QA/QC)

To evaluate the iron contribution from the analytical blank, Fe levels in the reagents were determined daily by measuring their individual concentrations in triplicate during the analysis of Milli-Q® water. For the POPSO/BrO_3^- mixed solution, the mean iron contribution for each 500 µL added was 0.178 ± 0.016 nmol L^{-1} (Table II), while for each 30 µmol L^{-1} DHN, the iron contribution was 70 pmol L^{-1}.

Figure 3 shows the Ads-CSV scans resulting from the determination of a blank followed by 3 additions of 0.5 nmol L^{-1} iron for internal calibration.

The LOD obtained was 0.014 nmol L^{-1} using 60 s of preconcentration. This value was calculated according to the IUPAC recommendation, using 3.3 times the standard deviation of 15 scans (1.44 ± 0.09 nA) and dividing it by the sensitivity after internal calibration (21.05 nA $nmol^{-1}$ L).

To evaluate the possible sorption of iron into the cell walls, including the enrichment from the reference electrode solution, successive readings using the same solution were performed. Aleatory peak intensities varying from 5.33 to 5.54 nA were recorded with no tendency of increase or decrease in the signal.

Table II. Results of iron concentration in blank and sensitivities by the Adsorptive Cathodic Stripping Voltammetry (Ads-CSV) Analysis with DHN and POPSO/BrO_3^-.

DFe (nmol L^{-1})	Sensitivity (nA $nmol^{-1}$ L^{-1})	DFe (nmol L^{-1})	Sensitivity (nA $nmol^{-1}$ L^{-1})
0.16	15.55	0.15	15.00
0.19	14.55	0.19	14.25
0.19	14.40	0.19	15.50

The recovery test for DFe determination resulted in 5.5 nmol L^{-1} of iron, which corresponds to 110.6 ± 2.3%. For the titration, the DFO concentration was determined to be 11.3 nmol L^{-1}, corresponding to 112.7 ± 3.1%, with a log K′$_{FeL}$ of 11.83.

Physicochemical parameters of the surface water samples

The temperature, pH, dissolved oxygen, and salinity results determined for each sample collected in Admiralty Bay are shown in Table III.

The temperature of the surface water ranged from 3.4 (P2) to 5.6 °C (P5). The lowest observed salinity value was 31.8 in P3, and the maximum value was 34.0 in P4. The pH ranged from 7.6 (P6) to 8.1 (P1 and P2). The percentage of dissolved oxygen saturation ranged from 27.7 (P2) to 101.1% (P6).

Iron speciation in admiralty bay surface waters

The dissolved iron (DFe) concentrations, the concentration of iron ligands and their conditional stability constants are presented in Table IV as average values (n = 3).

The DFe fraction was found in a narrow range, 16.5 ± 1.2 nmol L^{-1}, except for Station P2 with 31.1 nmol L^{-1} of DFe. The L$_T$ concentration ranged from 11.9 (P6) to 43.9 nmol L^{-1} (P2), while Fe′ ranged from 0.14 (P4) to 0.92 nmol L^{-1} (P1). The conditional stability constants of organic iron
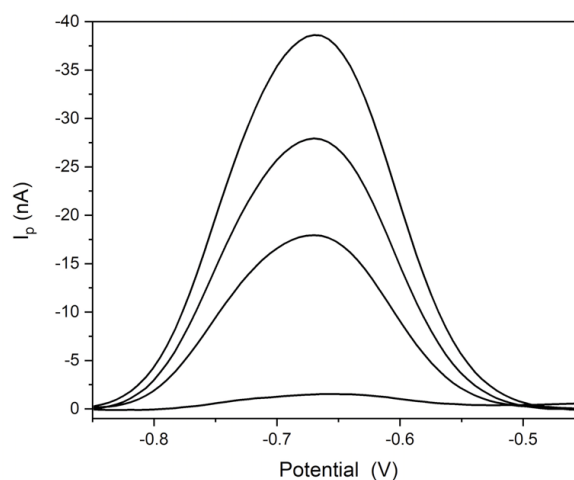

Figure 3. Determination of dissolved iron in the blank in the presence of 30 mmol L^{-1} DHN after neutralization with ammonia. Internal calibration with 3 consecutive 0.5 nmol L^{-1} additions of Fe (deposition potential of -0.1 V, equilibration time of 7 s, deposition time of 60 s, initial potential of -0.1 V, final potential of -1.2 V and scan rate of 15 mV s^{-1}).

complexes (log K′$_{FeL}$) presented values between 11.8 (P1) and 12.8 (P4).

DISCUSSION
QA/QC

The systematic evaluation of the contribution of iron in the reagents throughout the analytical process is essential for the acquisition of reliable data. The concentration of iron in seawater is usually small enough that reagent blanks and contamination make the analysis difficult (Boyle et al. 2007).

Table III. Physicochemical data (temperature, pH, salinity and dissolved oxygen - DO) for the surface seawater samples of Admiralty Bay, King George Island (Antarctica). SD: standard deviation.

Sample Station	P1	P2	P3	P4	P5	P6	Mean ± SD
Water Temperature (°C)	4.2	3.4	4.0	3.6	5.6	4.5	4.2 ± 0.7
Air Temperature (°C)	4.0	2.5	4.0	5.5	7.4	3.0	4.4 ± 1.8
pH	8.1	8.1	7.8	7.8	7.7	7.6	7.9 ± 0.2
Salinity (PSU)	33.1	32.4	31.8	34.0	32.2	33.0	32.8 ± 0.7
DO (% of saturation)	31.4	27.7	49.0	56.6	42.1	101.1	51.3 ± 24.3

The concentration levels obtained for the blank in this work are in agreement with values reported from the literature, which range from negligible values below the LOD up to 230 pmol L^{-1} (Abualhaija & Van den Berg 2014, Caprara et al. 2015, Laglera et al. 2013b, 2016). Moreover, our data present excellent repeatability concerning iron concentration and sensitivity.

Comparative measurements showed that the limit of detection obtained in this work is compatible with those reported by other studies. Laglera et al. (2013b) reported an LOD of 5 pmol L^{-1}, while Obata and Van den Berg (2001) determined an LOD of 13 pmol L^{-1}. The LOD reported by Su et al. (2015) was 210 pmol L^{-1}. In our case, the LOD makes the method well suited for the detection of DFe at the low concentrations expected for ocean waters.

The results obtained in the recovery tests were satisfactory and are within the limits recommended by IUPAC for the concentration levels evaluated in this study, including for the stability constant obtained by the DFO, which theoretically is 11.54 (Van den Berg 2006). Overall, these results ensured the control and quality of the results obtained in the determination of dissolved iron and its speciation.

Physicochemical parameters in surface waters

The physicochemical parameter analyses provide information on water characteristics and might directly influence the assessment of metal speciation. In particular, pH and salinity alter the ionic strength of the medium and the partition of iron, while biological processes and temperature may affect DO levels (Brandini & Rebello 1994).

The ocean waters of Admiralty Bay presented temperatures, DO, pH and salinity expected for the sub-Antarctic marine environments. The results obtained in the present study for pH and DO are in agreement with the results reported by Cascaes et al. (2012), which obtained pH values from 7.66 to 8.01 and DO from 5.11 to 8.13 mg L^{-1}, resulting in 35.8 to 56.9% DO saturation based on a mean temperature of 0.84 °C during the austral summer from 2009 and 2012 in the same study area.

The data for DO obtained in this work agree with those reported in previous studies (e.g., Lange et al. 2007); however, the DO levels were shown to be relatively low compared to open ocean waters. The variation in DO levels may reflect the rates of production and degradation of organic matter in the water column, which are highly influenced by sediment resuspension, sea ice melting and meteorological events.

Table IV. Results of iron speciation (dissolved iron, ligand concentration, free iron and conditional stability constant of ligands with Fe (III)) for the surface seawater samples of Admiralty Bay, King George Island (Antarctica). SD: standard deviation.

Sample Station	DFe (nmol L^{-1})	L_T (nmol L^{-1})	Fe' (pmol L^{-1})	Log K'$_{FeL}$	$[L_T]/[DFe]$
P1	18.3 ± 0.6	30.7 ± 0.9	0.92	11.8 ± 0.1	1.7
P2	31.1 ± 0.5	43.9 ± 1.4	0.86	11.9 ± 0.1	1.4
P3	15.6 ± 0.3	24.3 ± 0.6	0.75	11.9 ± 0.1	1.6
P4	17.2 ± 0.9	17.5 ± 0.4	0.14	12.8 ± 0.4	1.0
P5	16.4 ± 0.4	13.2 ± 0.4	0.68	12.3 ± 0.3	0.8
P6	15.2 ± 0.3	11.9 ± 1.1	0.65	12.3 ± 0.5	0.8
Mean ± SD	18.9 ± 0.5	23.6 ± 0.8	0.7 ± 0.3	12.2 ± 0.3	1.2 ± 0.4

The temperature of surface waters obtained during our sampling ranged from 3.4 to 5.6 °C, while it ranged from -0.52 to 1.77 °C during 2009 and 2012 (Cascaes et al. 2012) and from 1.1 to 2.1 °C during late summer 2003 (Lange et al. 2007). This increase in surface water temperature during the last decades may result from the increase in temperatures that have been registered in recent years in the Antarctic continent (Turner et al. 2020, Wachter et al. 2020). In particular, the sampling was marked by a high mean air temperature in agreement with the temperature record of 20.75 °C on the Antarctic continent, registered in February 2020 (Turner et al. 2020, Wachter et al. 2020).

According to Cascaes et al. (2012), the salinity in Admiralty Bay varies from 33.89 to 34.35, but in this study, the range was slightly lower, from 31.8 to 34.0. A small increase in temperature reflects a decrease in salinity, especially in surface water, due to the inflow of freshwater from melting glaciers in Antarctic coastal areas (Gerringa et al. 2015). This effect has also been verified by Lange et al. (2007) and Cascaes et al. (2012), who analysed these parameters in surface water collected in early (high salinity, low temperature) and late summer (low salinity, high temperature).

Dissolved iron and its speciation

To the best of our knowledge, this study is the first one related to Fe speciation at Admiralty Bay on King George Island. The results obtained in this study show higher Fe contents in the surface water than the iron concentrations reported in other locations of Antarctica, as shown in Table V.

All the studies cited in Table V report a decrease in DFe with the distance from the coast. De Jong et al. (2015) found 8.49 nmol L^{-1} of DFe at 9 km from the coast, while at 230 km, the concentration was 0.35 nmol L^{-1}. Kim et al. (2015) measured 3.76 nmol L^{-1} at the beach and 0.09 nmol L^{-1} at bay seawater. Finally, Annett et al. (2017) determined 7.82 nmol L^{-1} at the coastline and < 0.1 nmol L^{-1} at 25 km from the coast. In this study, the distance of the coast ranged from 70 to 500 m, so the proximity of the collection points to the coastline may be one of the factors influencing the increases in DFe concentrations.

The main sources of DFe in surface waters include upwelling and vertical mixing of deeper Fe-rich waters (Klunder et al. 2011), atmospheric dust (Raiswell et al. 2016), seasonal melting of seasonal sea ice (De Jong et al. 2012), and partial dissolution of sediment carried along Antarctic ice sheets with calving and melting icebergs (Gerringa et al. 2012) or from Antarctic continental margin sediments (Gerringa et al.

Table V. Dissolved iron in different locations of maritime Antarctica.

Location	DFe (nmol L^{-1})	Depth (m)	Distance of coast	Reference
Southern Ocean (Atlantic sector)	0.10 - 0.34	Surface	not reported	Klunder et al. (2011)
Ross Sea Polynya	0.02 - 0.18	5.0	not reported	Gerringa et al. (2015)
Bellingshausen Sea	0.18 - 8.49	10.0	9 to 230 km	De Jong et al. (2015)
Marina Cover	0.09 - 3.76	4.0	beach to bay seawater	Kim et al. (2015)
Charcot Island	0.02 - 7.82	Surface	coastline to 25km	Annett et al. (2017)
Admiralty Bay	15.2 - 31.1	Surface	70 to 500 m	This study

2015). Thus, the iron content found in Admiralty Bay may be from different sources.

For example, the concentration of total iron in the flowing water at the western shore of Admiralty Bay was quantified between 1.5 and 28.0 nmol L^{-1} (Szopińska et al. 2018). Additionally, Admiralty Bay presents upwelling currents (Pruszak 1980), which cause vertical mixing that could be a potential source of nutrients and iron. Furthermore, the proximity of the sampling location to the coastline may present an increase in DFe concentrations.

Gerringa et al. (2012) observed an increase of 0.57 nmol L^{-1} in DFe concentrations and heterogeneous temporal and spatial profiles in surface water near glaciers due to the different rates of upwelling and subsequent mixing with glacier melt water, which can also be observed in Admiralty Bay.

Another possibility is that the low DO levels in the innermost locations might have increased iron solubility specifically at P2 and P1. In seawater, DFe is present as Fe(II) and Fe(III). Trivalent iron is the main form of iron in oxic seawater; however, Fe(II) is more soluble, and under hypoxic conditions its formation can be favoured (Croot et al. 2001, Johnson et al. 1994).

Sediments can be considered the main source among the possible sources of DFe in Admiralty Bay. The predominant winds in the region move surface waters to the Bransfield Strait, originating a flux of deep waters to Admiralty Bay, so the vertical mixing is very intense (Pruszak 1980), resulting in upwelling and deeper Fe-rich waters and increasing the presence of sediments from the continental Antarctic margin. Cascaes et al. (2012) observed an increase in silicate levels due to upwelling in Admiralty Bay, while Lange et al. (2007) observed the same for diatom species, indicating that this process contributes to nutrients in the bay. In Pine Island Bay, Amundsen polynyas, the DFe

concentrations were attributed to turbulence caused by downslope currents that resuspended sediment particles and thus increased DFe concentrations (Gerringa et al. 2012).

Moreover, during spring and summer in Admiralty Bay, ice melt is a significant source of nutrients and many chemical elements in near-shore seawater (Siciński et al. 2011). According to Kim et al. (2015), in Marian Cove (King George Island), the iron concentrations in seawater vary from 0.09 to 3.76 nmol L^{-1}, in snow melt it varies from 2.6 to 29.2 nmol L^{-1} and in floating icebergs this variation is from 2.1 to 38.1 nmol L^{-1}. Thus, it is possible to infer that the ice-melt waters may be a relevant source of DFe in surface waters from Admiralty Bay in cases where a decline in salinity is observed. Nevertheless, studies to quantify DFe in these different sources are necessary to assert this possibility confidently.

The concentration of ligands varied considerably. The highest concentrations coincided with the innermost region of the bay in P1, P2 and P3 in the Martel and Mackellar inlets. These points also presented the lowest values of the conditional stability constant (log K'_{FeL}) of the complexes formed and the highest values in the ratio of $[L_T]/[DFe]$. The ratio $[L_T]/[DFe]$ is a practical concept used to highlight spatial and temporal differences in ligand saturation (Thuróczy et al. 2011). If $[L_T]/[DFe] \geq 1$, the ligand sites are fully saturated with Fe. Thus, in the inner portion of Admiralty Bay, we observed a small excess of ligands compared to DFe but ligands that form weaker complexes.

Saturation of the ligands is an indication that the DFe concentrations were likely to be maximum values beyond which DFe would precipitate (Gerringa et al. 2015). Moreover, the concentration of the ligand might represent the difference between the production of ligands and/or iron absorption by phytoplankton in the euphotic layer, the degradation of nonresistant

ligands by microbial activity (Gerringa et al. 2015, Thuróczy et al. 2011) and photodegradation (Laglera et al. 2020).

On the other hand, sites P5 and P6 located in the Ezcurra Inlet and just off Admiralty Bay to the Bransfield Strait, respectively, presented [L_t]/[DFe] ≤ 1.0. In these locations, the excess DFe may exist as colloidal Fe (inorganic), which may be due to iron sources in the surface water, as previously discussed.

According to Campos et al. (2013), Admiralty Bay can be compared to an estuarine region since the freshwater output from terrestrial ice melt induces variations in salinity during austral summer. Nutrient concentrations inside the inlets can be high, even though concentrations of chlorophyll-*a* are low (Lange et al. 2007). During summer, wind velocity and solar radiation increase the seawater temperature and nitrite and ammonium concentrations; however, silicate, phosphate and nitrate concentrations decrease. The nitrate, phosphate and silicate concentrations are even higher at the entrance of the bay than at the three main inlets, which are consumed by microphytoplankton in shallow waters near the shore. Both nutrients show considerable spatial and temporal variation depending on sea and terrestrial ice formation over the winter and its melt rate during spring and summer (Lange et al. 2018) affect the dissolved iron and ligand concentrations and stability constant of organic complexes.

According to Lipski (1987) in Admiralty Bay, the concentration of silicate varies from 74.8 to 90.0 µmol L^{-1}, nitrates from 11.3 to 33.2 µmol L^{-1}, and nitrite from 0.015 to 0.370 µmol L^{-1}, while phosphate ranged from 1.26 to 2.40 µmol L^{-1} and chlorophyll-*a* from 0.07 to 1.97 µg L^{-1}. These values confirmed the presence of high nutrient concentrations, and according to the author, they did not limit phytoplankton growth.

In this study, log K'_{FeL} presents low values when compared to other studies in Antarctic waters. According to Thuróczy et al. (2011), log K'_{FeL} varies from 21.60 to 22.56 in the sub-Antarctic region, and Lannuzel et al. (2015) reported values ranging from 21.6 to 21.9 in the East Antarctic sector. Natural organic compounds that complex with Fe in seawater range from low molecular weight substances produced by heterotrophic bacteria and cyanobacteria, such as siderophores (Gledhill et al. 2004), to macromolecular complexes represented by humic (Laglera & Van den Berg 2009) and exopolymeric substances (Hassler et al. 2015). Humic substances (HS) are important dissolved Fe chelators that are found in large concentrations in estuarine and coastal environments (Laglera et al. 2011) and can also be found in sea ice and icebergs (Hassler et al. 2017, Van der Merwe et al. 2009). Although we did not determine the HS concentrations (Laglera & Van den Berg 2009), it can be presupposed that surface seawater from Admiralty Bay may have a considerable amount of HS. On the western coast of Admiralty Bay, the total organic carbon concentration in surface water varied from 0.02 to 4.09 mg L^{-1} during summer 2016, indicating the presence of a relatively large amount of organic matter (Potapowicz et al. 2020), which indicates the possible presence of humic substances.

According to Laglera & Van den Berg (2009), the stability constants of humic complexes with Fe (log K'_{FeHS} values) are 10.6 for FA and 11.1 for HA and coastal HS. The same assumption was made by Velasquez et al. (2011).

In the present study, more than 99% of the DFe is complexed, so the levels obtained for Fe' are very low. Our results are similar to those reported in other studies. At sites sampled close to Antarctica, Boye et al. (2001) found concentrations ranging from 0.04 to 3.29 pmol L^{-1} at depths of 20 and 2500 m, respectively. From sites located south of the Pacific Ocean,

Kondo et al. (2012) found concentrations between 0.56 and 5.72 pmol L^{-1} at 100 and 2950 m depths, respectively. These low free Fe levels suggest that the organically complexed iron fraction must become biologically accessible for phytoplankton growth (Rue & Bruland 1995), and the main route to iron absorption is likely to be through direct uptake of the organic fraction (Boye et al. 2001).

CONCLUSIONS

The analytical method studied can be considered satisfactory for the determination of dissolved iron and the evaluation of iron speciation in surface waters of Admiralty Bay. The values obtained for the limit of detection, sensitivity and contribution of iron to the blank were suited for the low levels of iron generally found in Antarctic waters, in addition to being compatible with other studies. The application of the method to samples in this study allowed the evaluation of a variety of results for DFe, L_T and log K'_{FeL}, which are important for the biogeochemistry study of this metal.

Furthermore, a spatial variation in DFe and L_T concentrations was observed. There was a relatively low excess of organic ligand concentrations (ratio $[L_T]/[DFe] \geq 1$) and a lower log K'_{FeL}, indicating weaker complexes at Martel and Mackellar inlets. In contrast, in the Ezcurra Inlet and just off Admiralty Bay to Brasnfield Strait, the ratio $[L_T]/[DFe] \leq 1.0$ indicated excess DFe, probably colloidal Fe (inorganic). These results are corroborated by the low concentrations of free iron, indicating that more than 99% of DFe is bound to ligands. This phenomenon may be a result of iron sources to the upper water column. Considering the values obtained for log K'_{FeL}, humic substances are the potential ligand present in Admiralty Bay.

The use of adsorptive cathodic stripping voltammetry with DHN as a ligand and BrO_3^-/POPSO as an oxidizing agent in the catalytic effect of the signal for iron to determine iron and its speciation by ligand exchange as proposed in this study opened a low-cost and fast method to evaluate DFe in Antarctic samples.

The results of this study, combined with the analysis of nutrients such as phosphates and nitrates and the determination of chlorophyll-*a* concentrations, among other physicochemical parameters, will allow the evaluation of iron biogeochemistry and its implications for the environment of Admiralty Bay and may motivate the development of similar studies on a larger spatial scale, including the open Antarctic Ocean sector.

The results obtained for the physicochemical parameters of the samples showed little variation and agree with other studies carried out in Admiralty Bay, King George Island, except for temperature, which was higher than values previously recorded in the area. However, the average dissolved Fe in the surface water was higher than that observed in other studies in Antarctic water as well as the concentrations of natural ligands, probably, in greater proportion, from vertical mixed layer upwelling but also by local and temporal input events of ice melt.

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