2014-09-02

Determination of dissolved iron in seawater: A historical review

Worsfold, Paul

<http://hdl.handle.net/10026.1/4346>

10.1016/j.marchem.2014.08.009

MARINE CHEMISTRY

Elsevier BV

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

1 Disclaimer: This is a pre-publication version. Readers are recommended to consult the full
2 published version for accuracy and citation. Published in Marine Chemistry, 166, 25-35 (2014)
3 doi: 10.1016/j.marchem.2014.08.009.
4

5 Determination of dissolved iron in seawater: A historical review

6
7 Paul Worsfold^{1*}, Maeve Lohan¹, Simon Ussher¹ and Andrew Bowie^{2,3}
8

9 ¹ Biogeochemistry Research Centre, Plymouth University, Plymouth, Devon PL4 8AA, UK
10

11 ² Antarctic Climate & Ecosystems CRC, Private Bag 80, Hobart, TAS 7001, Australia
12

13 ³ Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, TAS 7001, Australia
14
15

16 Abstract
17

18 This paper overviews the evolution of suitable analytical approaches for the determination of
19 dissolved iron in seawater. The focus is on sampling and sample treatment, detection methods
20 and quality assurance of the data. Iron is a vital trace element for the growth of marine
21 organisms and is the limiting micronutrient for primary production in many parts of the world's
22 oceans. The concentration of dissolved iron in seawater therefore influences the past and
23 present day global carbon cycle and consequently Earth's climate. Hence it is important to
24 understand the marine biogeochemistry of iron and quantify the spatial and temporal distribution
25 of the element. In order to do this, it is essential that robust and validated methods with
26 appropriate detection limits, precision and accuracy are available for the determination of iron
27 species in seawater.
28

29 Keywords: iron biogeochemistry; sampling; sample treatment; iron determination; data quality
30

31 *Biogeochemistry Research Centre, School of Geography, Earth and Environmental Sciences,
32 Plymouth University, Plymouth, PL4 8AA, United Kingdom.

33 Email: pworsfold@plymouth.ac.uk

34 Tel: +44 1752 584579.
35

1. Iron biogeochemistry

Iron has a relative atomic mass of 55.847 a.m.u. and six known isotopes, of which ^{54}Fe (5.82 %), ^{56}Fe (91.66 %) and ^{57}Fe (2.19 %) are the most abundant (Taylor, 1964). The element has a high crustal abundance (~5.6 %) and its compounds make up a significant proportion of the Earth's rocks and soils but its low solubility dictates that dissolved iron concentrations in oceanic waters are typically sub-nanomolar (Liu and Millero, 2002). Iron exists predominantly as oxides and carbonates but forms salts with most inorganic anions in the solid phase. The most commonly occurring compounds in iron ores, all of which are highly stable, are haematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), siderite (FeCO_3) and pyrite (FeS_2) (Greenwood and Earnshaw, 1984).

The marine biogeochemistry of iron is influenced by low solubility, redox speciation and the role that it plays in biological cycles. The major inputs of iron to the oceans are from the atmosphere, continental shelf sediments, hydrothermal vents, rivers and glacial melt in polar regions. The main removal pathways are biological uptake, scavenging, precipitation and sedimentation. In the remote surface waters of the open-ocean (and some enclosed basins) the main source of iron is atmospheric dust deposition (Jickells and Spokes, 2001; Séguet et al., 2011). A summary of ambient dissolved iron concentrations in the major reservoirs and annual flux estimates between the reservoirs is shown in **Fig. 1** and an inventory of >13,000 oceanic dissolved iron measurements can be found in Tagliabue *et al.* (Tagliabue et al., 2012). Using the mean off-shelf dissolved iron concentrations (± 1 s.d.) from this inventory for surface (0 – 100 m) and deep (2000 – 6000 m) waters and a total ocean volume of $1.35 \times 10^9 \text{ km}^3$ gives estimates for standing stocks of dissolved iron of $2.34 \times 10^{13} \pm 3.40 \times 10^{13} \text{ g}$ for surface waters and $4.08 \times 10^{13} \pm 1.97 \times 10^{13} \text{ g}$ for deep waters.

In most oceanic regions, primary production is limited by the availability of light and macro-nutrients (nitrate, phosphate and silicate) but approximately 40 % of the world's surface waters are replete with major nutrients but have relatively low phytoplankton biomass (Boyd et al., 2007; Moore et al., 2002). These regions are termed high-nutrient, low chlorophyll (HNLC), the most important being the Southern Ocean, the Equatorial Pacific and the Subarctic Pacific. The first reliable iron determinations in an HNLC region were made in the late 1980's in the Pacific Ocean as part of the VERTEX programme (Landing and Bruland, 1987; Martin and Gordon, 1988; Martin et al., 1989) using sampling and analytical techniques developed by Bruland *et al.* (Bruland et al., 1979).

71 John Martin then published the 'Iron Hypothesis' in 1991 (Martin, 1990) based on an inverse
72 correlation between carbon dioxide and iron (inferred from aluminium data) in Vostok ice cores
73 linked with glacial and interglacial transitions. Martin proposed that increased Fe input to HNLC
74 oceanic regions as a result of higher dust loading could stimulate primary production. It was
75 further proposed that this effect could potentially cause intense drawdown of carbon dioxide,
76 reduce atmospheric temperatures and hence be an important driver of global climate change. A
77 recent study using a sediment core from the Subantarctic Atlantic Ocean has shown that during
78 glacial times an increase in dust flux resulted in higher productivity and nitrate consumption
79 which is consistent with Subantarctic iron fertilisation (Martinez-Garcia et al., 2014).

80

81 This iron limitation hypothesis has been tested in the under-productive waters of the Equatorial
82 Pacific (e.g. IronEx; Coale et al., 1996), Subarctic Northeast Pacific (Boyd et al., 2005) and
83 Southern Ocean (SOIREE; Boyd and Law, 2001) by seeding surface ocean waters with low
84 concentrations of dissolved iron. These *in situ* experiments triggered large phytoplankton
85 blooms that resulted in a significant drawdown of atmospheric carbon dioxide and surface water
86 nitrate. More recently it has been shown that iron also plays an important role in nutrient cycling
87 processes such as nitrogen fixation in the North and South Atlantic (Schlosser et al., 2014) and
88 can limit growth in non-HNLC regions and coastal upwelling areas (Bruland et al., 2001;
89 Capone and Hutchins, 2013; Chase et al., 2005). These observations highlight the need for
90 robust conceptual and numerical models of ocean biogeochemistry to include iron as a limiting
91 component (Moore and Doney, 2007; Tagliabue and Völker, 2011).

92

93 In order to provide accurate measurements of dissolved iron for the modelling community and to
94 understand the processes that control iron marine biogeochemistry, the species to be
95 determined must be clearly and operationally defined. Size fractionation is particularly important
96 due to the broad variety of Fe species thought to exist in seawater, including nanoparticles,
97 colloidal phases and macromolecules. Historically, dissolved iron has been defined as that
98 which passes through a 0.45, 0.4 or 0.2 μm filter membrane (Cutter et al., 2010; de Baar and de
99 Jong, 2001), but the development of trace metal clean ultra-filtration techniques (Gobler et al.,
100 2002; Nishioka et al., 2001; Wu et al., 2001) now allows improved characterisation of different
101 size fractions. For example, the total dissolved (dFe), (truly) soluble (sFe) and colloidal (cFe)
102 iron pools can be operationally defined by the pore size of the filtration membrane used, i.e. dFe
103 $<0.2 \mu\text{m}$; sFe $<0.02 \mu\text{m}$; cFe $0.02 - 0.2 \mu\text{m}$ (Ussher et al., 2010a), with the total dissolvable
104 (TDFe) iron pool being operationally defined as the fraction detected after acidification and long

term (> 6 months) storage without prior filtration (Ussher et al., 2013). A surface water profile of sFe, dFe and TDFe in the Atlantic Ocean on the AMT 16 transect is shown in **Fig. 2**.

Iron usually has a nutrient-type vertical distribution in open ocean HNLC waters, with depleted dFe concentrations of < 0.2 nM in surface waters (Boyd and Ellwood, 2010; de Baar and de Jong, 2001), increasing to 0.4 – 0.7 nM below 500 m. Dissolved (defined as < 0.4 µm) iron measurements from 354 samples at 30 stations in the North and South Pacific, Southern Ocean and North Atlantic gave a mean dFe concentration of $0.76 \pm 0.25 \text{ nmol kg}^{-1}$ (n = 117) at depths below 500 m with minimal inter-ocean variability (Johnson et al., 1997) in spite of variable sources of iron and relatively short residence times in deep waters of ~ 70 – 200 yr. The presence of strong iron binding organic ligands and/or equilibrium between dissolved and suspended particulate iron were the most likely controlling factors. In the mixed layer, mean dFe concentrations were $0.07 \pm 0.04 \text{ nmol kg}^{-1}$ (n = 112). More recently a study of > 13,000 global measurements of dissolved iron found that in shelf waters the mean surface water dFe concentration was $0.61 \pm 1.14 \text{ nM}$ (n = 382) and in deeper waters was $0.53 \pm 0.17 \text{ nM}$ (n = 20) (Tagliabue et al., 2012). Open ocean (off-shelf) data showed a much clearer nutrient/scavenged element profile, with a surface water dFe minimum of 0.31 ± 0.45 (n = 999) that increased with depth to $0.54 \pm 0.26 \text{ nM}$ (n = 301) (Tagliabue et al., 2012). A summary of this dataset is shown in **Fig. 3**. Dissolved iron residence times in the upper water column are very short, e.g. ~ 250 days in the Sargasso Sea (Jickells, 1999), due to biological uptake and physical mixing processes (Hutchins et al., 1993).

The concentrations of the different physico-chemical species of iron in seawater are dependent on the equilibrium between various particulate and dissolved phases (see **Fig. 4**), the rate of each of the processes shown and the physical composition and condition of the seawater. Under most natural conditions, iron is found in the +2 and +3 oxidation states and forms salts with the majority of common anions. Redox transitions between the two oxidation states are dependent on pH and electron activity (pE) (Morel and Hering, 1993). In aerated aqueous solutions at circumneutral pH, the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ cation is hydrolysed to form polynuclear oxyhydroxides. A solubility of $\sim 10^{-11} \text{ M}$ has been reported for iron(III) hydroxide in 0.7 M NaCl (pH 8.1, 25 °C) where soluble iron was defined as the fraction which passed through a 0.02 µm filter (Liu and Millero, 1999) and in seawater (Liu and Millero, 2002).

The solubility of Fe(II) greatly exceeds that of Fe(III). Under anoxic conditions, Fe(II) can be found at mM concentrations but under oxic conditions at pH >5 it becomes unstable and

oxidizes rapidly. Hence oxic aqueous solutions at seawater pH are predicted to contain negligible Fe(II) at equilibrium (Stumm and Morgan, 1996) although significant Fe(II) concentrations can be found near sources such as hydrothermal plumes and in low oxygen waters (Breitbarth et al., 2010). However, > 99 % of the dissolved iron pool is complexed by organic iron-binding ligands (siderophores) (Gledhill and Buck, 2012) which means that iron redox speciation in seawater is strongly linked with the concentrations and physico-chemical properties of the iron complexes present. Two classes of strong iron binding ligands (L_1 and L_2) have been characterised and determined in open ocean seawater, and their complexing ability is expressed using conditional stability constants (K_{Fe3+L}), i.e. $K_{Fe3+L} = [FeL] / [Fe^{3+}] [L]$, where $[Fe^{3+}]$ is the sum of the inorganic Fe(III) species (including hydroxide complexes). A range of siderophores (generally low molecular mass hydroxamates, ferrioxamines and amphibactins) in seawater have been identified using mass spectrometric techniques (Boiteau et al., 2013; Mawji et al., 2008; Mawji et al., 2011; Velasquez et al., 2011).

2. Sampling and sample treatment

The quality of analytical data for iron concentrations in seawater is dependent on the acquisition and storage of clean and stable samples and the availability of suitable detection methods. It is therefore important that well documented protocols that reflect best practice are used for sample collection and treatment in order to minimise contamination. Open discussion within the community is also an essential part of this process. A good starting point for reliable sample collection is the GEOTRACES 'cookbook' for micronutrient sampling and sample-handling (Cutter et al., 2010). This has a specific section (section VI) dealing with sampling and handling protocols for trace elements, including iron.

The first step is to ensure that trace metal-clean sampling apparatus and sample collection bottles are used. For surface water sampling a clean surface pump sipper/tow fish system is recommended (Cutter et al., 2010) such as the device reported by Vink *et al.* (Vink et al., 2000). The key components of any surface sampling system are a clean pump (a PTFE diaphragm pump is preferred but a peristaltic pump can also be used), clean plastic tubing on all lines and a tow fish of suitable hydrodynamic design, material and density.

Several clean sampling systems have been reported for obtaining depth profiles. Since the earliest reliable design of a discrete sampler for obtaining open ocean depth profiles (Bruland et al., 1979) various devices and modifications have been reported (Bell et al., 2002; Cutter and Bruland, 2012; de Baar et al., 2008; Fitzsimmons and Boyle, 2012; Measures et al., 2008;

Sedwick et al., 2005). Measures *et al.* described a commercially available rosette-based system for trace metal-clean sampling (Measures et al., 2008) that was successfully deployed on several CLIVAR cruises for high-resolution trace element sampling. De Baar *et al.* described a fast and ultraclean system for sampling deep ocean waters for trace metals (de Baar et al., 2008) constructed with a titanium frame and having 8000 m of Kevlar wire with internal power and signal cables. Cutter and Bruland reported a system for the rapid and non-contaminating sampling of trace elements with volumes of up to 36 L per depth for both dissolved and particulate phases (Cutter and Bruland, 2012). Based on the use of this system on three major cruises, the launch-sample-recover time for the carousel (2 bottles triggered per depth) was 1 h per 1000 m, and dissolved and particulate sampling time averages were 6 h per hydrocast. In all cases, the collected samples were then handled in a trace metal-clean laboratory on board the ship, which should conform to ISO Class 5 specifications (ISO, 2010).

The next step in the process is sample storage, which requires the use of appropriate containers and rigorous cleaning protocols for those containers. The GEOTRACES cookbook (Cutter et al., 2010) recommends low density polyethylene (LDPE) or high density polyethylene (HDPE) bottles for both the total dissolvable (unfiltered) and total dissolved (filtered) fractions for most trace metal determinations, including iron. Rigorous sample bottle cleaning is essential and in addition to the recommended protocol in the GEOTRACES guide there are several other similar and effective strategies (e.g. Achterberg et al., 2001). For the determination of dissolved iron ($< 0.2 \mu\text{m}$) it is necessary to filter the sample, for which a cartridge (capsule) type filter, with $0.8/0.2 \mu\text{m}$ pore sizes, is recommended (Cutter et al., 2010). Polycarbonate membrane filters have also been successfully used for smaller sample volumes (Bowie et al., 2010). To obtain the soluble ($< 0.02 \mu\text{m}$) fraction an ultrafiltration membrane can be used (Schlosser et al., 2013), usually in a cross flow configuration (Schlosser and Croot, 2008). Aluminium oxide membranes have also been used (Wu et al., 2001).

For the determination of total dissolved iron, samples should be acidified using concentrated hydrochloric acid to pH 1.7 - 1.8 (0.024 M) (Johnson et al., 2007). The acid should be as pure as possible, with acidification blanks collected and analysed on a regular basis, and handling must conform to the required standards of cleanliness. Acidification can be done at sea or when samples are returned to the laboratory. For speciation analysis, e.g. the direct determination of Fe(II), the analysis must be carried out immediately after sampling, and hence on-board ship, because of its high reactivity. In this case two strategies are to buffer the sample to pH ≤ 7.2 or to cool it to 2 – 4 °C (Cutter et al., 2010).

3. Analytical methods

One of the earliest reported attempts to determine iron in seawater was in 1935 (Cooper, 1935). A spectrophotometric method was used, with tripyridyl as the selective reagent; Fe(II), “reducible” Fe (after treatment with HCl/sulphite) and “total” Fe (after treatment with HCl/bromine water) were determined on 100 mL volumes of filtered seawater samples. Since that time both laboratory and shipboard methods have evolved to a remarkable degree and there are a number of relatively recent overviews of methods for the determination of dissolved iron in seawater (Achterberg et al., 2001; Bowie and Lohan, 2009; Bruland and Rue, 2001).

The most common approach used to determine iron in seawater in the late 1970s and 1980s was preconcentration using solvent extraction (Danielsson et al., 1985; Gordon et al., 1982; Landing and Bruland, 1987; Spencer et al., 1970) or co-precipitation (Symes and Kester, 1985) coupled with detection by electrothermal (graphite furnace) atomic absorption spectrometry (ETAAS). Chelation with ammonium 1-pyrrolidinedithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC), double extraction into chloroform and back-extraction into nitric acid was the most popular solvent extraction approach (Bruland et al., 1979). A detection limit of 50 pM was reported by Landing and Bruland (Landing and Bruland, 1987), with high reagent blanks and contamination during sample handling being the main challenges at that time. On-line solid phase preconcentration became increasingly popular during the 1980s and 1990s with Saager *et al.* reporting a detection limit of 150 pM using Chelex-100 (Saager et al., 1989). In addition, these approaches typically required 250 mL - 4 L of sample (Bruland et al., 1979).

In recent times, high resolution (magnetic sector) ICP-MS has become the preferred atomic spectrometric method of detection, providing sensitive and time efficient iron determinations whilst excluding isobaric interferences. Isotope dilution is often used for quantification, either with co-precipitation or on-line solid phase preconcentration. An attraction of isotope dilution is that it is an absolute and hence traceable method that does not require external standards or standard additions. Hence matrix interferences and variations in recovery are not a significant problem. Magnesium hydroxide co-precipitation (Wu, 2007; Wu and Boyle, 1998) requires minimal use of reagents and hence gives a very low reagent blank, with reported detection limits of 50 pM (Wu and Boyle, 1998) and 2 pM (Wu, 2007). On-line solid phase chelation has reported detection limits of 15 pM with 8-hydroxyquinoline (8-HQ) immobilised on silica gel (Akatsuka et al., 1992), 21 pM with Toyopearl AF-Chelate-650M (iminodiacetic acid chelating

group) (Milne et al., 2010), 70 pM with nitrilotriacetic acid (NTA) SuperflowTM resin (Lee et al., 2011) and 14 pM with a “seaFAST” column (co-immobilised ethylenediaminetriacetic acid and iminodiacetic acid chelating groups immobilised on a hydrophilic methacrylate polymer) (Lagerstrom et al., 2013).

Quantitative recoveries can also be obtained using solid phase preconcentration and standard additions to the seawater matrix without the need for isotope dilution, with reported detection limits of 640 pM with 8-hydroxyquinoline immobilised on fluorinated metal alkoxide glass (Sohrin et al., 1998) and 14 pM (Biller and Bruland, 2012) and 2000 pM (Sohrin et al., 2008), both with the Nobias Chelate PA1 resin (co-immobilised ethylenediaminetriacetic acid and iminodiacetic acid chelating groups). Millilitre sample volumes are required for ICP-MS, e.g. 12 mL was used by Milne et al. with isotope dilution (Milne et al., 2010) and 40 mL by Biller and Bruland without isotope dilution (Biller and Bruland, 2012). These data show the significant improvements that have been made in recent years with regard to detection limits and sample volumes required for the determination of dissolved iron in seawater, as well as the greater emphasis on method validation using reference materials (see section 4 for further details).

ICP-MS and ETAAS can generate high quality data in a controlled laboratory environment but there is a requirement for portable methods that can be used at sea, thereby providing rapid analysis whilst minimising sample treatment and storage. In this context flow injection (FI) techniques provide an excellent platform for sample handling (Zagatto et al., 2012). There are two main detection systems used in conjunction with FI for the determination of dissolved iron, namely chemiluminescence (CL) and spectrophotometry (SP) and typical manifold diagrams are shown in **Fig. 5** (Bowie et al., 2004). With both systems preconcentration of iron onto a chelating resin is a necessary requirement to concentrate the iron and separate it from the bulk seawater matrix. The majority of FI techniques use 8-HQ as the functional chelating group immobilised on a chemically-resistant vinyl polymer resin such as Toyopearl TSK (Landing et al., 1986). More recent studies have used commercially available chelating resins such as NTA “Superflow” (Lohan et al., 2005) and Toyopearl AF-Chelate-650 (Hurst and Bruland, 2007), thereby eliminating the synthesis step involved in using 8-HQ. Due to the speciation of iron, a key consideration is the pH dependency on the recovery of Fe(III) and Fe(II) on the preconcentration column. For example, Fe(III) is recovered by 8-HQ at pH 3.0 - 4.2, while at pH 5.2 - 6.0 both Fe(III) and Fe(II) are quantitatively recovered (Obata et al., 1993). Therefore, FI may also allow the iron redox speciation measurements by careful selection of the pretreatment pH, reagent conditions and an appreciation of possible interferences (Bowie et al., 2002;

Hopkinson and Barbeau, 2007; Ussher et al., 2005). For “total” dissolved iron (Fe(II) + Fe(III)) measurements, either an oxidation step (addition of 10 μ M hydrogen peroxide (Lohan et al., 2006) or a reduction step (addition of 100 μ M sodium sulfite (Bowie et al., 1998) prior to preconcentration is required.

FI-CL methods are based on the catalytic effect of either Fe(II) or Fe(III) ions on the oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) to generate blue luminescence ($\lambda_{\text{max}} \sim 440$ nm) which is detected using a photomultiplier tube. FI-CL methods that determine Fe(II) require acidified samples to be reduced off-line using, e.g., sodium sulphite (e.g. Bowie et al., 1998). Reduced samples are then buffered in-line to pH 5 using ammonium acetate prior to preconcentration on a suitable resin such as 8-HQ. Iron(II) ions are eluted from the resin using HCl (e.g. 0.09 M) and merged with a luminol/carbonate buffer reagent stream. Bowie *et al.* achieved a detection limit of 40 pM and 3.2 % RSD (n=5) for 1 nM iron (Bowie et al., 1998). FI-CL methods that determine Fe(III) and total dissolved iron if acidified samples are first oxidised off-line using hydrogen peroxide (Johnson et al., 2007; Klunder et al., 2011). Acidified, oxidised samples are buffered in-line to pH 3 with ammonium acetate prior to preconcentration. Iron(III) ions are eluted from the resin using HCl (e.g. 0.3 M). A 2 m heated coil is required to efficiently mix the eluted Fe(III) with the luminol/carbonate buffer reagent and hydrogen peroxide streams prior to detection. A mean blank for this method has been reported as 32 ± 14 pM Fe (n=19) with a detection limit of 5.7 ± 2.9 pM Fe (n=4) (Klunder et al., 2011).

FI-SP involves the catalytic oxidation of DPD (N,N-dimethyl-p-phenylenediamine dihydrochloride) by Fe(III) cycled with hydrogen peroxide (Lohan et al., 2006; Measures et al., 1995). The catalysis increases the sensitivity of this method, as the amount of oxidised DPD is proportional to the concentration of iron. Hydrogen peroxide (10 μ M) is added to the sample to ensure complete oxidation of iron to Fe(III). In-line buffering of the sample is generally required and is dependent on the resin used for preconcentration. Iron is eluted from the resin and mixes with DPD/buffer and hydrogen peroxide, producing coloured semiquinone derivatives, which are detected spectrophotometrically at 514 nm. The average blank for this method was 60 ± 8 pM Fe (n=35) with a detection limit of 24 ± 4.9 pM Fe (n=9) (Lohan *et al.* 2006). SAFe surface samples gave a mean $\pm$ SD value of 0.10 ± 0.009 nM (n=14) and SAFe deep samples 0.93 ± 0.04 nM (n=18), in excellent agreement with the SAFe consensus values of 0.097 ± 0.007 nM and 0.91 ± 0.17 nM respectively (Lohan et al., 2006).

Voltammetric techniques provide an alternative strategy for both the shipboard and laboratory based determination of dissolved iron in seawater. The preferred variant of the technique is cathodic stripping voltammetry (CSV) in which an iron-binding ligand is added to the seawater sample to selectively form a complex with Fe(III). This complex is adsorbed onto the working electrode, typically a hanging mercury drop, followed by cathodic stripping as the Fe(III) is reduced. Detection limits are typically 80 – 100 pM (Croot and Johansson, 2000; Gledhill and van den Berg, 1995). However, to determine total dissolved iron, the seawater sample needs to be pre-treated to liberate iron from complexes with natural seawater ligands. The technique is also used to determine the complexation capacity of Fe(III) with natural ligands using a competitive ligand exchange approach (Buck et al., 2012; Croot and Johansson, 2000; Hassler et al., 2013; Hawkes et al., 2013; Town and Van Leeuwen, 2005; Wu and Jin, 2009). The most common ligands used for this purpose are 1-nitroso-2-naphthol (NN) (Gledhill and van den Berg, 1995), salicylaldoxime (SA) (Rue and Bruland, 1995), 2-(2-thiazolylazo)-p-cresol (TAC) (Croot and Johansson, 2000) and dihydroxynaphthalene (DHN) (Obata and Van den Berg, 2001).

Measurements of the stable isotopes of dissolved iron in seawater may help to answer important biogeochemical questions (e.g. Lacan et al., 2008). There are four naturally occurring stable iron isotopes: ^{54}Fe (5.84%), ^{56}Fe (91.76%), ^{57}Fe (2.12%), and ^{58}Fe (0.28%), and isotopic data are typically reported using a standard δ notation in units of per mil (‰) (deviations in parts per 1000 relative to a reference ratio), using either $^{56}\text{Fe}/^{54}\text{Fe}$ or $^{57}\text{Fe}/^{54}\text{Fe}$ ratios (Johnson et al., 2008). The investigation of natural mass-dependent isotopic fractionation of iron has been boosted by the recent development of multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; de Jong et al., 2007). Many natural marine processes fractionate iron isotopes, suggesting great promise for seawater $\delta^{56}\text{Fe}$ as a new tracer of the pathways, sources and sinks of iron in the ocean, and how iron is biologically cycled. The largest fractionation of iron isotopes occur during redox changes (e.g., microbial Fe^{3+} reduction), as well as differences in bonding, but these are expressed only in natural environments in which significant quantities of iron are mobilised and separated. In addition, since iron concentrations in seawater are very low (< 1 nM), there are significant challenges to separate and purify iron from seawater without introducing contamination and to accurately determine $\delta^{56}\text{Fe}$ on the small quantities of iron extracted (John and Adkins, 2010). Nonetheless, Conway et al. have simultaneously determined Fe, Zn and Cd stable isotopes ($\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$) in seawater using Nobias Chelate PA-1 chelating resin for extraction, followed by purification using anion exchange chromatography and detection by double spike MC-ICP-MS (Conway et al., 2013a; Conway et al., 2013b). The method was notable for the use of low sample volumes (only 1 litre)

and very low blanks compared with previously reported methods. In addition, iron isotopic data have been used in palaeo-reconstructions of ancient anoxic and early oxygenated marine environments (Rouxel et al., 2005).

In situ sensors, as distinct from shipboard techniques, are attractive because they are potentially low cost, low maintenance and suitable for long term remote deployments. They can also be interrogated remotely using wireless technologies and microwave transmitters (mobile phones) (Angove et al., 2011). There are however challenges with regard to long term stability/calibration, biofouling and sample conditioning, e.g. filtration. Ion-selective electrodes can now be miniaturised and manufactured as disposable devices (Zuliani and Diamond, 2012) and although they are suitable for monitoring freshwater systems they are often prone to matrix interferences in seawater. Optical sensors can potentially overcome these issues and a fluorescence quenching-based siderophore (parabactin) biosensor has been developed for the direct measurement of Fe(III) in oceanic waters (Lam et al., 2006). The LOD was 40 pM, with a reproducibility of 6% RSD (n = 10) for 1000 pM Fe(III) and a 50 – 1000 pM working range.

Roy *et al.* used changes in the infrared spectrum of the iron binding siderophore desferrioxamine B covalently immobilised on a mesoporous silica film when complexed with Fe(III) (Roy et al., 2008). The system had a detection limit of ~50 pM for a 1 L seawater sample at pH 1.7 and was used to determine dissolved iron in the Subarctic Pacific. The device is potentially deployable on autonomous research platforms for long term *in situ* monitoring.

In situ sensors have great potential for high resolution and low cost spatial and temporal mapping of dissolved iron (and other species) in seawater, including the remote open-ocean, but further development is still required, not least in sample presentation and treatment, in order to ensure reliable, long term operation.

4. Quality assurance of iron data

Method validation has been defined as *“the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled”* (ISO/IEC, 2005). In addition ISO/IEC 2005 states that *“the range and accuracy of the values obtainable from validated methods (e.g. the uncertainty of the results, detection limit, selectivity of the method, linearity, limit of repeatability and/or reproducibility, robustness against external influences and/or cross-sensitivity against interference from the matrix of the sample/test object), as assessed for the intended use, shall be relevant to the customer’s needs.”* It also proposes

five approaches to method validation that can be used individually or in combination: (i) calibration using reference standards or reference materials, (ii) inter-laboratory comparisons, (iii) comparison of results achieved with other methods, (iv) systematic assessment of the factors influencing the results and (v) assessment of the uncertainty of the results based on scientific understanding of the theoretical principles of the method and practical experience.

Early inter-laboratory comparisons for trace metals in seawater (Bewers et al., 1981; Landing et al., 1995) reported inconsistent results with up to one order of magnitude degree of variability in the quantification of the analytical blank and inaccuracies in system calibration. Two more recent intercomparison exercises that focussed on the determination of iron (both on board ship and in the laboratory) were IRONAGES, using Atlantic Ocean samples collected in 2000 (Bowie et al., 2003; Bowie et al., 2006), and SAFe (Sampling and Analysis of Fe), using Central North Pacific samples collected in 2004 (Johnson et al., 2006; Johnson et al., 2007). A summary of the analytical methods used by participating laboratories in the IRONAGES intercomparison exercise is shown in **Table 1**. Both of these exercises also produced “in-house” seawater reference materials with “consensus values” for the concentration of dissolved iron. These were made available to the marine biogeochemistry community in response to the unavailability of commercial seawater certified reference materials (CRMs) with suitably low certified concentrations for iron. As an example of the use of these reference materials, Ussher *et al.* compared the results obtained for the IRONAGES sample by FI-CL with isotope dilution ICP-MS and found good agreement over a concentration range of 0.15 - 2.1 nM iron (Ussher et al., 2010b) and any differences were attributed to random effects such as variable contamination rather than systematic effects.

The marine biogeochemistry community has now established GEOTRACES (<http://www.geotraces.org/>) to facilitate the study of the global marine biogeochemical cycles of a suite of trace elements and their isotopes (TEIs), including iron (SCOR Working Group, 2007). GEOTRACES conducted two intercalibration cruises, one in the North Atlantic Ocean at the BATS (Bermuda Atlantic Time Series) site in 2008 and one at the SAFe site in the oligotrophic North Pacific in 2009, and collected seawater for the preparation of ‘in-house’ reference samples at both sites. A summary of the analytical methods used by participating laboratories during analysis of the North Atlantic GEOTRACES reference sample to determine a consensus value for dissolved iron in the North Atlantic is shown in **Table 2**. The ultimate goal for the intercalibration component of GEOTRACES (Cutter, 2013) is to achieve the best possible accuracy (lowest random and systematic errors) for these TEIs by evaluating and developing

GEOTRACES sample acquisition, handling, and storage protocols (Cutter et al., 2010), identifying existing GEOTRACES primary standards and certified reference materials (CRMs) and, where needed, producing suitable reference materials (RMs) or primary standards.

In the last few years there has been a proliferation of both new methods and new laboratories reporting dissolved iron concentrations in seawater and rigorous quality assurance is therefore essential. The most common methods use commercially available chelating resins such as Nobias Chelate PA1 (e.g. Sohrin et al., 2008) and ICP-MS detection (e.g. Biller and Bruland, 2012; Lagerstrom et al., 2013; Milne et al., 2010). There are also commercially available preconcentration systems such as “seaFAST” that automate the sample handling steps (Hathorne et al., 2012; Lagerstrom et al., 2013), which should also improve precision. During the IRONAGES intercomparison exercise seven different analytical techniques were used (Bowie et al., 2006) whereas eighteen different methods have been used to date in the GEOTRACES programme to produce consensus values for dissolved iron in surface (GS) and deep (GD) seawater RMs

<http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html>. These RMs are available free of charge and allow laboratories to assess the accuracy and precision of their measurements and also facilitate the development of new analytical methods.

All of these intercalibration efforts have greatly improved the accuracy of dissolved iron measurements in seawater. This has enabled international programmes such as CLIVAR and GEOTRACES that engage in ocean basin scale mapping of dissolved iron concentrations to ensure that temporally and spatially variable data from different cruises, obtained by different researchers using different analytical methods, can be reliably intercompared. A key aspect of the sampling strategy is the use of cross-over stations whereby two or more cruises carrying out ocean scale mapping have at least one common station where they determine the concentration of dissolved iron, often using different sampling systems and, in some cases, different analytical techniques. Both sample concentrations and RM consensus values are compared to ensure that acceptable intercalibration is achieved. Deep water values are preferred because surface waters values are impacted by seasonal changes in productivity and inputs from atmospheric sources. The GEOTRACES programme has recently released an intermediate data product and an atlas of dissolved Fe measurements in seawater (<http://www.egeotraces.org/>) which is enabling a paradigm shift in our understanding of iron cycling in seawater. An example of the data product showing a screen shot of an animated 3D scene of reported dFe concentrations in the Atlantic Ocean is given in **Fig. 6**.

Uncertainty is one aspect of method validation and can be defined as the ‘parameter, associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand’ (JCGM, 2012). A simple statistical procedure is often used by chemical oceanographers to estimate the uncertainty of a measurement result, e.g. the internal instrumental precision obtained for analysis of a single sample is calculated to give the range within which the stated result is likely to lie. However, this may underestimate the uncertainty of a measurement, leading to over-interpretation of the significance of the result. Evaluation of uncertainty is more reliably done using a mathematical model coupled with some numerical method of differentiation that combines the individual uncertainties associated with each model parameter, i.e. each of the steps in the sample collection, pre-treatment, storage and measurement processes (Worsfold et al., 2013). Prior knowledge of the major sources of input to the measurement results, and their associated uncertainties, will indicate where to focus efforts to meet the target uncertainty. Further details of the approach can be found in “The Guide for Uncertainty in Measurements”, often abbreviated to “the GUM”, (JCGM, 2008) and, more specifically, in the Eurachem/CITAC Guide “Quantifying Uncertainty in Analytical Measurement” (Ellison and Williams, 2012).

5. Future perspectives

With regard to sampling, there are developments in autonomous samplers, gliders, buoys and Argo floats that offer great potential for the acquisition of long term time series samples, higher sampling frequency, greater spatial coverage and regular access to more remote locations. More use could also be made of ships (and submarines) of opportunity. However deployment of these devices needs to be accompanied by improved sample treatment at the point of collection and/or coupling with *in situ* measurement technologies. At present, laboratories are collecting samples at a faster rate than their capacity to analyse them.

There is also a need for new measurement technologies, with the emphasis on fast, selective methods with good accuracy and precision that need minimal sample treatment or can be used directly, i.e. *in situ* sensors. This requires greater collaboration between the Analytical Chemistry and Chemical Oceanography communities, supported by meetings such as that hosted in Hawaii in 2013 (COCA Working Group, 2013). It also requires community wide protocols for assessing and reporting data and for estimating uncertainty.

From a biogeochemistry perspective the same rigorous approach to sampling, analysis and data treatment needs to be applied to the determination of particulate iron (Cutter et al., 2010) and aerosol derived iron (Morton et al., 2013) and the GEOTRACES community is at present focussing on the intercalibration of these two important measurements. Methods for the determination of iron speciation also need to be critically evaluated and stable reference materials for speciation studies developed.

Acknowledgements

The authors thank Dr. Robert Clough for helpful discussions on the Quality Assurance section. Dr Clough is funded by the EMRP *via* JRP-ENV05-REG1 (Metrology for ocean salinity and acidity). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union. PW acknowledges funding from the Marine Institute, Plymouth University. SU acknowledges funding from the European Commission via a Marie Curie Career Integration Grant (PCIG-GA-2012-333143 DISCOSAT). ML acknowledges funding from the Natural Environment Research Council (NERC) grant NE/H0004475/1). ARB acknowledges funding from the Australian Research Council (FT130100037) and the Antarctic Climate and Ecosystems Cooperative Research Centre.

Table 1. Analytical methods used during the IRONAGES iron intercomparison (Bowie et al., 2006).

Acronym	Summary	Reference(s)
CSV-DHN	Competitive ligand equilibration - cathodic stripping voltammetry (ligand: 2,3-dihydroxynaphthalene)	(Obata and Van den Berg, 2001)
FI-CL Fe(II)	Flow injection – luminol chemiluminescence (using dissolved O ₂ , sulfite reduction to FeII); preconcentration on 8HQ resin	(Bowie et al., 1998; King et al., 1995)
FI-CL Fe(III)	Flow injection - luminol chemiluminescence (using H ₂ O ₂ , natural oxidation to FeIII); preconcentration on 8HQ resin	(de Jong et al., 1998; Obata et al., 1993)
FI-SP	Flow injection - catalytic spectrophotometry (reagent: <i>N,N</i> -dimethyl- <i>p</i> -phenylenediamine dihydrochloride); preconcentration on 8HQ resin	(Measures et al., 1995)
ID-ICP-MS	Mg(OH) ₂ co-precipitation, isotope dilution - inductively coupled plasma mass spectrometry	(Wu and Boyle, 1998)
SE-ETAAS	Chelation solvent extraction - electrothermal atomic absorption spectrometry (ligand: APDC/DDDC)	(Bruland et al., 1979)
SPE-ICP-MS	Solid phase extraction - inductively coupled plasma mass spectrometry (ligand: bis(2-hydroxyethyl) dithiocarbamate, C ₁₈ column)	(Fujishima et al., 2001; Wells and Bruland, 1998)

Table 2. Analytical methods used during the analysis of the North Atlantic GEOTRACES reference sample to determine a consensus value for dissolved iron (adapted from http://es.ucsc.edu/~kbruland/GeotracesSaFe/2012GeotracesSAFeValues/GEOTRACES_Ref_Fe.pdf).

Acronym	Summary	Reference(s)
ID-ICP-MS	Concentrated off-line with the $\text{Mg}(\text{OH})_2$ co-precipitation method and analysed by isotope dilution ICP-MS. Blanks were quantified using 50 μL of sample instead of 1.6 mL. A single co-precipitation step was carried out followed by dilution of the precipitate with 4% HNO_3 .	(Wu and Boyle, 2002)
ID-ICP-MS	Double co-precipitation with $\text{Mg}(\text{OH})_2$ and isotope dilution ICP-MS.	(Wu, 2007)
FI-SP	Flow injection using the NTA-type resin and DPD catalytic enhancement of the UV-visible absorption signal.	(Lohan et al., 2006)
SPE-ICP-MS	Off line concentration using an EDTriA-type chelating resin with subsequent analyses by ICP-MS.	(Sohrin et al., 2008)
SE-ICP-MS	Concentrated by solvent extraction and analysed by ICP-MS. 100 g seawater samples were buffered to a pH of 4.5 with purified ammonium acetate buffer. Purified ammonium pyrrolidinedithiocarbamate (PDC) and sodium diethyldithiocarbamate (DDC) were added to the samples which were then extracted twice by shaking following the addition of purified chloroform. The two chloroform extracts obtained were combined, acidified with nitric acid, shaken for 1 min and then diluted with purified water.	(Bruland et al., 1979)
SE-ETAAS	300–500 g portions of the samples were subjected to a dithiocarbamate–freon	(Danielsson et

	extraction modified from the procedure by implying maximum concentration factors of al., 1978; 500. The final extracts with the metals were measured by electrothermal atomic absorption spectrometry with Zeeman background correction (ETAAS; Perkin-Elmer Model 4100 ZL).	Kremling and Streu, 2001)
SPE-ICP-MS	Off-line concentrations using an EDTri-A-type chelating resin with subsequent analyses by ICP-MS. The method entailed an eight column manifold enabling eight separate 40 mL samples.	(Biller and Bruland, 2012; Sohrin et al., 2008)
ID-ICP-MS	Off-line extraction using IDA Toyopearl AF-Chelate-650 M resin followed by analysis using isotope dilution ICP-MS Prior to extraction the samples (12 mL) were buffered to pH ~6.2.	(Milne et al., 2010)
SPE-ICP-MS	On-line flow injection analysis of 4 mL of sea water using an EDTA-type chelating resin at pH 6 utilising purified ammonium acetate buffer and eluting analytes with 1.5 M HNO ₃ followed by detection with ICP-MS.	(Sohrin et al., 2008)
FI-CL	Flow Injection with chemiluminescence detection.	
ID-ICP-MS	100-bead NTA resin separation on small samples together with isotope dilution and ICP-MS detection.	(Lee et al., 2011)
FI-CL	Flow injection analysis with chemiluminescence detection.	(Sedwick et al., 2008)
FI-CL Fe(II)	Flow injection analysis with the Fe(II) luminol chemiluminescence method using sulfite reduction and NTA resin preconcentration.	(King and Barbeau, 2007)
CSV	Adsorptive cathodic stripping voltammetry of UV oxidised samples.	(Rue and

ETAAS	The final extracts were measured by electrothermal atomic absorption spectrometry.	Bruland, 1995) (Kremling and Streu, 2001)
FI-CL	Flow Injection with chemiluminescence detection using IDA Toyoparl AF-Chelate-650 M resin.	(Klunder et al., 2011)
ID-ICP-MS	Off-line batch preconcentration of 50 mL of acidified sample with NTA-type resin and analysed by isotope dilution MC-ICP-MS on a Nu Plasma instrument. Iron was analysed in low-resolution mode with a desolvating sample introduction system (Cetac Aridus 2). Concentrations calculated using the ratios between ^{57}Fe or ^{56}Fe and the added ^{54}Fe spike were internally consistent.	(de Jong et al., 2008)
ID-ICP-MS	On-line flow injection with a modified seaFAST system, the Nobias PA-1 resin, isotope dilution and ICP-MS detection.	
ID-ICP-MS	Off-line extraction with Nobias PA-1 chelating resin and analysis on an Element XR ICP-MS.	
SPE-ICP-MS	Off-line extraction using a WAKO chelating resin followed by analysis on an Element XR ICP-MS. Samples were UV digested for 3 h.	(Kagaya et al., 2009)
ID-ICP-MS	NTA resin bead preconcentration and MC-ICP-MS detection.	(Lee et al., 2011)

Figure captions

Figure 1

Approximations for annual global fluxes of dissolved iron (dFe) to the surface ocean (values are reported in or calculated from Bowers and Yeats, 1977; Chester and Jickells, 2012; Stallard and Edmond, 1983; Tagliabue et al., 2014). Riverine flux is estimated on the basis of 90% loss from estuarine mixing (Boyle et al., 1977). The sinking particulate flux (including scavenging) assumes a steady state and no other significant sinks.

Figure 2

Surface water iron size speciation profiles for the Atlantic Ocean on the Atlantic Meridional Transect (for AMT16), 20th May – 28th June 2005 showing soluble iron (sFe, <0.02 µm), dissolved iron (dFe, <0.2 µm), and total dissolvable iron (TDFe, unfiltered seawater). Reproduced with the permission of the authors from “Impact of atmospheric deposition on the contrasting iron biogeochemistry of the North and South Atlantic Ocean”, S. J. Ussher et al., *Global Biogeochemical Cycles*, 27 (2013) 1, doi: 10.1002/gbc.20056 (Ussher et al., 2013). The inset shows the cruise track for AMT16.

Figure 3

Box and whisker plots of dFe by (a) region and (b) basin. The size of the box represents the 1st to 3rd quartiles, with the vertical bar corresponding to the median and the whiskers representing 1.5 times the inter-quartile range. Reproduced with the permission of the authors from “A global compilation of dissolved iron measurements: Focus on distributions and processes in the Southern Ocean”, Tagliabue et al., *Biogeosciences*, 9 (2012), doi: 10.1029/2003GL017721 (Tagliabue et al., 2012).

Figure 4

Phase transfers of iron and related processes in seawater. This figure was originally published by CSIRO Publishing in *Environmental Chemistry* 1, 67-80. doi: 10.1071/EN04053 <http://www.publish.csiro.au/paper/EN04053.htm> and is reproduced with their permission (Ussher et al., 2004).

Figure 5

Two flow injection manifolds for the determination of dissolved iron in seawater: (A) with chemiluminescence detection (FI-CL), and (B) with spectrophotometric detection (FI-SP).

Reproduced with permission from A.R. Bowie, P.N. Sedwick and P.J. Worsfold, *Limnology and Oceanography: Methods* (Association for the Sciences of Limnology & Oceanography), 2004, 2, “Analytical intercomparison between flow injection – chemiluminescence and flow injection-spectrophotometry for the determination of picomolar concentrations of iron in seawater”, p 45. Copyright 2014 by the Association for the Sciences of Limnology and Oceanography, Inc. (Bowie et al., 2004).

Figure 6

Screen shot of the GEOTRACES animated 3D scene of reported dFe concentrations in the Atlantic Ocean. Reproduced with permission from Schlitzer, R., *eGEOTRACES - Electronic Atlas of GEOTRACES Sections and Animated 3D Scenes*, <http://www.egeotraces.org>, 2014. Original data supplied by Andrew Bowie, Ken Bruland, Tim Conway, Hein de Baar, Fanny Chever, Seth John, Maarten Klunder, Patrik Laan, Francois Lacan, Rob Middag, Abigail Noble, Micha Rijkenberg, Mak Saito, Geraldine Sarthou, Peter Sedwick and Jingfeng Wu (Schlitzer, 2014).

References

- Achterberg, E.P., Holland, T.W., Bowie, A.R., Mantoura, R.F.C. and Worsfold, P.J., 2001. Determination of iron in seawater. *Analytica Chimica Acta*, 442(1): 1-14.
- Akatsuka, K., McLaren, J.W., Lam, J.W. and Berman, S.S., 1992. Determination of iron and ten other trace elements in the open ocean seawater reference material NASS-3 by inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 7(6): 889-894.
- Angove, P. et al., 2011. A mobile gateway for remote interaction with wireless sensor networks. *IEEE Sensors Journal*, 11(12): 3309-3310.
- Bell, J., Betts, J. and Boyle, E., 2002. Mitess: A moored in situ trace element serial sampler for deep-sea moorings. *Deep-Sea Research Part I: Oceanographic Research Papers*, 49(11): 2103-2118.
- Bewers, J.M., Dalziel, J., Yeats, P.A. and Barron, J.L., 1981. An intercalibration for trace metals in seawater. *Marine Chemistry*, 10(3): 173-193.
- Bewers, J.M. and Yeats, P.A., 1977. Oceanic residence times of trace metals. *Nature*, 268(5621): 595-598.
- Biller, D.V. and Bruland, K.W., 2012. Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS). *Marine Chemistry*, 130-131: 12-20.
- Boiteau, R.M., Fitzsimmons, J.N., Repeta, D.J. and Boyle, E.A., 2013. Detection of iron ligands in seawater and marine cyanobacteria cultures by high-performance liquid chromatography-inductively coupled plasma-mass spectrometry. *Analytical Chemistry*, 85(9): 4357-4362.
- Bowie, A. and Lohan, M., 2009. Chapter 12: Analysis of Iron in Seawater. In: W. O (Editor), *Practical Guidelines for the Analysis of Seawater*. Taylor and Francis, Boca Raton, pp. 235-257.
- Bowie, A.R. et al., 2003. Shipboard analytical intercomparison of dissolved iron in surface waters along a north-south transect of the Atlantic Ocean. *Marine Chemistry*, 84(1-2): 19-34.
- Bowie, A.R. et al., 2006. A community-wide intercomparison exercise for the determination of dissolved iron in seawater. *Marine Chemistry*, 98(1): 81-99.
- Bowie, A.R., Achterberg, E.P., Mantoura, R.F.C. and Worsfold, P.J., 1998. Determination of sub-nanomolar levels of iron in seawater using flow injection with chemiluminescence detection. *Analytica Chimica Acta*, 361(3): 189-200.
- Bowie, A.R., Achterberg, E.P., Sedwick, P.N., Ussher, S. and Worsfold, P.J., 2002. Real-time monitoring of picomolar concentrations of iron(II) in marine waters using automated flow injection-chemiluminescence instrumentation. *Environmental Science and Technology*, 36(21): 4600-4607.
- Bowie, A.R., Sedwick, P.N. and Worsfold, P.J., 2004. Analytical intercomparison between flow injection-chemiluminescence and flow injection-spectrophotometry for the determination of picomolar concentrations of Iron in seawater. *Limnology and Oceanography: Methods*, 2(FEB.): 42-54.
- Bowie, A.R., Townsend, A.T., Lannuzel, D., Remenyi, T.A. and van der Merwe, P., 2010. Modern sampling and analytical methods for the determination of trace elements in marine particulate material using magnetic sector inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta*, 676(1-2): 15-27.
- Boyd, P.W. and Ellwood, M.J., 2010. The biogeochemical cycle of iron in the ocean. *Nature Geoscience*, 3(10): 675-682.
- Boyd, P.W. et al., 2007. Mesoscale iron enrichment experiments 1993-2005: Synthesis and future directions. *Science*, 315(5812): 612-617.

- Boyd, P.W. and Law, C.S., 2001. The Southern Ocean Iron RElease Experiment (SOIREE) - Introduction and summary. *Deep-Sea Research Part II: Topical Studies in Oceanography*, 48(11-12): 2425-2438.
- Boyd, P.W. et al., 2005. The evolution and termination of an iron-induced mesoscale bloom in the northeast subarctic Pacific. *Limnology and Oceanography*, 50(6): 1872-1886.
- Boyle, E.A., Edmond, J.M. and Sholkovitz, E.R., 1977. The mechanism of iron removal in estuaries. *Geochimica et Cosmochimica Acta*, 41(9): 1313-1324.
- Breitbarth, E. et al., 2010. Iron biogeochemistry across marine systems - progress from the past decade. *Biogeosciences*, 7(3): 1075-1097.
- Bruland, K.W., Franks, R.P., Knauer, G.A. and Martin, J.H., 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. *Analytica Chimica Acta*, Vol. 105: 233-245.
- Bruland, K.W. and Rue, E.L., 2001. Analytical methods for the determination of concentrations and speciation of iron. In: K.A.H. D. R. Turner (Editor), *The Biogeochemistry of Iron in Seawater*. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems. John Wiley, New York, pp. 255-290.
- Bruland, K.W., Rue, E.L. and Smith, G.J., 2001. Iron and macronutrients in California coastal upwelling regimes: Implications for diatom blooms. *Limnology and Oceanography*, 46(7): 1661-1674.
- Buck, K.N. et al., 2012. The organic complexation of iron and copper: An intercomparison of competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) techniques. *Limnology and Oceanography: Methods*, 10(JULY): 496-515.
- Capone, D.G. and Hutchins, D.A., 2013. Microbial biogeochemistry of coastal upwelling regimes in a changing ocean. *Nature Geoscience*, 6(9): 711-717.
- Chase, Z. et al., 2005. Manganese and iron distributions off central California influenced by upwelling and shelf width. *Marine Chemistry*, 95(3-4): 235-254.
- Chester, R. and Jickells, T., 2012. *Marine Geochemistry*.
- Coale, K.H. et al., 1996. A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature*, 383(6600): 495.
- COCA Working Group, 2013. The Collaborative on Oceanography and Chemical Analysis (COCA) and suggestions for future instrumental analysis methods in chemical oceanography
- Conway, T.M., Rosenberg, A.D., Adkins, J.F. and John, S.G., 2013a. Corrigendum to "A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry" [*Anal. Chim. Acta* 793 (2013) 44-52]. *Analytica Chimica Acta*, 801: 97.
- Conway, T.M., Rosenberg, A.D., Adkins, J.F. and John, S.G., 2013b. A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. *Analytica Chimica Acta*, 793: 44-52.
- Cooper, L.H.N., 1935. iron in the sea and in marine plankton. *Proceedings of the Royal Society of London*, 118B: 419-438.
- Croot, P.L. and Johansson, M., 2000. Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-thiazolylazo)-p-cresol (TAC). *Electroanalysis*, 12(8): 565-576.
- Cutter, G.A., 2013. Intercalibration in chemical oceanography-Getting the right number. *Limnology and Oceanography: Methods*, 11(JULY): 418-424.
- Cutter, G.A. et al., 2010. Sampling and Sample-handling Protocols for GEOTRACES Cruises (Cookbook)
- Cutter, G.A. and Bruland, K.W., 2012. Rapid and noncontaminating sampling system for trace elements in global ocean surveys. *Limnology and Oceanography: Methods*, 10(JUNE): 425-436.

- Danielsson, L.G., Magnusson, B. and Westerlund, S., 1978. An improved metal extraction procedure for the determination of trace metals in sea water by atomic absorption spectrometry with electrothermal atomization. *Analytica Chimica Acta*, 98(1): 47-57.
- Danielsson, L.G., Magnusson, B. and Westerlund, S., 1985. Cadmium, copper, iron, nickel and zinc in the north-east Atlantic Ocean. *Marine Chemistry*, 17(1): 23-41.
- de Baar, H.J.W. and de Jong, J.T.M., 2001. Distributions, Sources and Sinks of Iron in Seawater. In: K.A. Hunter and D.R. Turner (Editors), *The Biogeochemistry of Iron in Seawater*. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems. John Wiley, New York, pp. 123-153.
- de Baar, H.J.W. et al., 2008. Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program. *Marine Chemistry*, 111(1-2): 4-21.
- de Jong, J., Schoemann, V., Lannuzel, D., Tison, J.L. and Mattielli, N., 2008. High-accuracy determination of iron in seawater by isotope dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) using nitrilotriacetic acid chelating resin for pre-concentration and matrix separation. *Analytica Chimica Acta*, 623(2): 126-139.
- de Jong, J. et al., 2007. Precise measurement of Fe isotopes in marine samples by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). *Analytica Chimica Acta*, 589(1): 105-119.
- de Jong, J.T.M. et al., 1998. Dissolved iron at subnanomolar levels in the Southern Ocean as determined by ship-board analysis. *Analytica Chimica Acta*, 377(2-3): 113-124.
- Ellison, S.L.R. and Williams, A. (Editors), 2012. *Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement*. Eurachem.
- Fitzsimmons, J.N. and Boyle, E.A., 2012. MITESS/Vanes sampling systems for dissolved iron concentration analyses (and a closer look at adsorption effects). *Limnology and Oceanography: Methods*, 10(JUNE): 437-450.
- Fujishima, Y. et al., 2001. Distribution of trace bioelements in the subarctic North Pacific Ocean and the Bering Sea (the R/V Hakuho Maru Cruise KH-97-2). *Journal of Oceanography*, 57(3): 261-273.
- Gledhill, M. and Buck, K.N., 2012. The organic complexation of iron in the marine environment: A review. *Frontiers in Microbiology*, 3.
- Gledhill, M. and van den Berg, C.M.G., 1995. Measurement of the redox speciation of iron in seawater by catalytic cathodic stripping voltammetry. *Marine Chemistry*, 50(1-4): 51-61.
- Gobler, C.J., Donat, J.R., Consolvo, J.A. and Sanudo-Wilhelmy, S.A., 2002. Physicochemical speciation of iron during coastal algal blooms. *Marine Chemistry*, 77(1): 71-89.
- Gordon, R.M., Martin, J.H. and Knauer, G.A., 1982. Iron in Northeast Pacific Waters. *Nature*, 299(5884): 611-612.
- Greenwood, N.N. and Earnshaw, A., 1984. *Aquatic Chemistry*. Pergamon, New York, N.Y.
- Hassler, C.S., Legiret, F.E. and Butler, E.C.V., 2013. Measurement of iron chemical speciation in seawater at 4°C: The use of competitive ligand exchange-adsorptive cathodic stripping voltammetry. *Marine Chemistry*, 149: 63-73.
- Hathorne, E.C. et al., 2012. Online preconcentration ICP-MS analysis of rare earth elements in seawater. *Geochemistry, Geophysics, Geosystems*, 13(1).
- Hawkes, J.A., Gledhill, M., Connelly, D.P. and Achterberg, E.P., 2013. Characterisation of iron binding ligands in seawater by reverse titration. *Analytica Chimica Acta*, 766: 53-60.
- Hopkinson, B.M. and Barbeau, K.A., 2007. Organic and redox speciation of iron in the eastern tropical North Pacific suboxic zone. *Marine Chemistry*, 106(1-2): 2-17.
- Hurst, M.P. and Bruland, K.W., 2007. An investigation into the exchange of iron and zinc between soluble, colloidal, and particulate size-fractions in shelf waters using low-abundance isotopes as tracers in shipboard incubation experiments. *Marine Chemistry*, 103(3-4): 211-226.

- Hutchins, D.A., Ditullio, G.R. and Bruland, K.W., 1993. Iron and Regenerated Production - Evidence for Biological Iron Recycling in 2 Marine Environments. *Limnology and Oceanography*, 38(6): 1242-1255.
- ISO, 2010. Cleanrooms and associated controlled environments -- Part 1: Classification of air cleanliness by particle concentration.
- ISO/IEC, 2005. General requirements for the competence of testing and calibration laboratories, ISO/IEC 17025:2005. International Organization for Standardization/International Electrotechnical Commission, Geneva.
- JCGM, 2008. Evaluation of measurement data — Guide to the expression of uncertainty in measurement (GUM), JCGM 100:2008. Joint Committee for Guides in Metrology, Paris.
- JCGM, 2012. International vocabulary of metrology – Basic and general concepts and associated terms (VIM), JCGM 200:2012. Joint Committee for Guides in Metrology, Paris.
- Jickells, T.D., 1999. The inputs of dust derived elements to the Sargasso Sea; a synthesis. *Marine Chemistry*, 68(1-2): 5-14.
- Jickells, T.D. and Spokes, L.J., 2001. Atmospheric Iron Inputs to the Oceans. In: K.A.H. D. R. Turner (Editor), *The Biogeochemistry of Iron in Seawater*. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems. John Wiley, New York, pp. 85-121.
- John, S.G. and Adkins, J.F., 2010. Analysis of dissolved iron isotopes in seawater. *Marine Chemistry*, 119(1-4): 65-76.
- Johnson, C.M., Beard, B.L. and Roden, E.E., 2008. The iron isotope fingerprints of redox and biogeochemical cycling in modern and ancient earth, *Annual Review of Earth and Planetary Sciences*, pp. 457-493.
- Johnson, K. et al., 2006. Sampling and Analysis of Fe: The SAFE Iron Intercomparison Cruise, Ocean Sciences Meeting, Hawaii, US.
- Johnson, K.S. et al., 2007. Developing standards for dissolved iron in seawater. *Eos*, 88(11): 131-132.
- Johnson, K.S., Gordon, R.M. and Coale, K.H., 1997. What controls dissolved iron concentrations in the world ocean? *Marine Chemistry*, 57(3-4): 137-161.
- Kagaya, S. et al., 2009. A solid phase extraction using a chelate resin immobilizing carboxymethylated pentaethylenehexamine for separation and preconcentration of trace elements in water samples. *Talanta*, 79(2): 146-152.
- King, A.L. and Barbeau, K., 2007. Evidence for phytoplankton iron limitation in the southern California Current System. *Marine Ecology Progress Series*, 342: 91-103.
- King, D.W., Lounsbury, H.A. and Millero, F.J., 1995. Rates and Mechanism of Fe(II) Oxidation at Nanomolar Total Iron Concentrations. *Environmental Science & Technology*, 29(3): 818-824.
- Klunder, M.B., Laan, P., Middag, R., De Baar, H.J.W. and van Ooijen, J.C., 2011. Dissolved iron in the Southern Ocean (Atlantic sector). *Deep-Sea Research Part II: Topical Studies in Oceanography*, 58(25-26): 2678-2694.
- Kremling, K. and Streu, P., 2001. The behaviour of dissolved Cd, Co, Zn, and Pb in North Atlantic near-surface waters (30°N/60°W-60°N/2°W). *Deep-Sea Research Part I: Oceanographic Research Papers*, 48(12): 2541-2567.
- Lacan, F. et al., 2008. Measurement of the isotopic composition of dissolved iron in the open ocean. *Geophysical Research Letters*, 35(24).
- Lagerstrom, M.E. et al., 2013. Automated on-line flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open ocean seawater: Application to the GEOTRACES program. *Marine Chemistry*, 155: 71-80.
- Lam, C.K.S.C.C., Jickells, T.D., Richardson, D.J. and Russell, D.A., 2006. Fluorescence-based siderophore biosensor for the determination of bioavailable iron in oceanic waters. *Analytical Chemistry*, 78(14): 5040-5045.

- Landing, W.M. and Bruland, K.W., 1987. The Contrasting Biogeochemistry of Iron and Manganese in the Pacific-Ocean. *Geochimica et Cosmochimica Acta*, 51(1): 29-43.
- Landing, W.M. et al., 1995. Analytical Intercomparison Results from the 1990 Intergovernmental-Oceanographic-Commission Open-Ocean Base-Line Survey for Trace-Metals - Atlantic-Ocean. *Marine Chemistry*, 49(4): 253-265.
- Landing, W.M., Haraldsson, C. and Paxeus, N., 1986. Vinyl polymer agglomerate based transition metal cation chelating ion-exchange resin containing the 8-hydroxyquinoline functional group. *Analytical Chemistry*, 58(14): 3031-3035.
- Lee, J.M. et al., 2011. Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. *Analytica Chimica Acta*, 686(1-2): 93-101.
- Liu, X. and Millero, F.J., 1999. The solubility of iron hydroxide in sodium chloride solutions. *Geochimica et Cosmochimica Acta*, 63(19-20): 3487-3497.
- Liu, X. and Millero, F.J., 2002. The solubility of iron in seawater. *Marine Chemistry*, 77(1): 43-54.
- Lohan, M.C., Aguilar-Islas, A.M. and Bruland, K.W., 2006. Direct determination of iron in acidified (pH 1.7) seawater samples by flow injection analysis with catalytic spectrophotometric detection: Application and intercomparison. *Limnology and Oceanography: Methods*, 4(JUN.): 164-171.
- Lohan, M.C., Aguilar-Islas, A.M., Franks, R.P. and Bruland, K.W., 2005. Determination of iron and copper in seawater at pH 1.7 with a new commercially available chelating resin, NTA Superflow. *Analytica Chimica Acta*, 530(1): 121-129.
- Martin, J.H., 1990. Glacial-Interglacial CO₂ Change: The Iron Hypothesis. *Paleoceanography*, 5(1): 1-13.
- Martin, J.H. and Gordon, R.M., 1988. Northeast Pacific Iron Distributions in Relation to Phytoplankton Productivity. *Deep-Sea Research Part A-Oceanographic Research Papers*, 35(2): 177-196.
- Martin, J.H., Gordon, R.M., Fitzwater, S. and Broenkow, W.W., 1989. Vertex - Phytoplankton Iron Studies in the Gulf of Alaska. *Deep-Sea Research Part A-Oceanographic Research Papers*, 36(5): 649-680.
- Martinez-Garcia, A. et al., 2014. Iron fertilization of the subantarctic ocean during the last ice age. *Science*, 343(6177): 1347-1350.
- Mawji, E. et al., 2008. Hydroxamate siderophores: Occurrence and importance in the Atlantic Ocean. *Environmental Science and Technology*, 42(23): 8675-8680.
- Mawji, E. et al., 2011. Production of siderophore type chelates in Atlantic Ocean waters enriched with different carbon and nitrogen sources. *Marine Chemistry*, 124(1-4): 90-99.
- Measures, C.I., Landing, W.M., Brown, M.T. and Buck, C.S., 2008. A commercially available rosette system for trace metal-clean sampling. *Limnology and Oceanography: Methods*, 6(SEPTEMBER): 384-394.
- Measures, C.I., Yuan, J. and Resing, J.A., 1995. Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. *Marine Chemistry*, 50(1-4): 3-12.
- Milne, A., Landing, W., Bizimis, M. and Morton, P., 2010. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Analytica Chimica Acta*, 665(2): 200-207.
- Moore, J.K. and Doney, S.C., 2007. Iron availability limits the ocean nitrogen inventory stabilizing feedbacks between marine denitrification and nitrogen fixation. *Global Biogeochemical Cycles*, 21(2).
- Moore, J.K., Doney, S.C., Glover, D.M. and Fung, I.Y., 2002. Iron cycling and nutrient-limitation patterns in surface waters of the World Ocean. *Deep-Sea Research Part II-Topical Studies in Oceanography*, 49(1-3): 463-507.

- Morel, F.M.M. and Hering, J.G., 1993. Principles and Applications of Aquatic Chemistry. John Wiley, New York, N.Y.
- Morton, P.L. et al., 2013. Methods for the sampling and analysis of marine aerosols: Results from the 2008 GEOTRACES aerosol intercalibration experiment. *Limnology and Oceanography: Methods*, 11(FEB): 62-78.
- Nishioka, J., Takeda, S., Wong, C.S. and Johnson, W.K., 2001. Size-fractionated iron concentrations in the northeast Pacific Ocean: Distribution of soluble and small colloidal iron. *Marine Chemistry*, 74(2-3): 157-179.
- Obata, H., Karatani, H. and Nakayama, E., 1993. Automated-Determination of Iron in Seawater by Chelating Resin Concentration and Chemiluminescence Detection. *Analytical Chemistry*, 65(11): 1524-1528.
- Obata, H. and Van den Berg, C.M.G., 2001. Determination of picomolar levels of iron in seawater using catalytic cathodic stripping voltammetry. *Analytical Chemistry*, 73(11): 2522-2528.
- Rouxel, O.J., Bekker, A. and Edwards, K.J., 2005. Iron isotope constraints on the Archean and Paleoproterozoic ocean redox state. *Science*, 307(5712): 1088-1091.
- Roy, E.G., Jiang, C., Wells, M.L. and Tripp, C., 2008. Determining subnanomolar iron concentrations in oceanic seawater using a siderophore-modified film analyzed by infrared spectroscopy. *Analytical Chemistry*, 80(12): 4689-4695.
- Rue, E.L. and Bruland, K.W., 1995. Complexation of iron(III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. *Marine Chemistry*, 50(1-4): 117-138.
- Saager, P.M., De Baar, H.J.W. and Burkill, P.H., 1989. Manganese and iron in Indian Ocean waters. *Geochimica et Cosmochimica Acta*, 53(9): 2259-2267.
- Schlitzer, R., 2014. *eGEOTRACES* - Electronic Atlas of GEOTRACES Sections and Animated 3D Scenes, www.egeotraces.org.
- Schlosser, C. and Croot, P.L., 2008. Application of cross-flow filtration for determining the solubility of iron species in open ocean seawater. *Limnology and Oceanography: Methods*, 6(NOV.): 630-642.
- Schlosser, C. et al., 2014. Seasonal ITCZ migration dynamically controls the location of the (sub)tropical Atlantic biogeochemical divide. *Proceedings of the National Academy of Sciences of the United States of America*, 111(4): 1438-1442.
- Schlosser, C., Streu, P. and Croot, P.L., 2013. Vivaspin ultrafiltration: A new approach for high resolution measurements of colloidal and soluble iron species. *Limnology and Oceanography: Methods*, 11(APR): 187-201.
- SCOR Working Group, 2007. GEOTRACES - An international study of the global marine biogeochemical cycles of trace elements and their isotopes. *Chemie Der Erde-Geochemistry*, 67(2): 85-131.
- Sedwick, P.N., Bowie, A.R. and Trull, T.W., 2008. Dissolved iron in the Australian sector of the Southern Ocean (CLIVAR SR3 section): Meridional and seasonal trends. *Deep-Sea Research Part I: Oceanographic Research Papers*, 55(8): 911-925.
- Sedwick, P.N. et al., 2005. Iron in the Sargasso Sea (Bermuda Atlantic Time-series Study region) during summer: Eolian imprint, spatiotemporal variability, and ecological implications. *Global Biogeochemical Cycles*, 19(4).
- Séguret, M.J.M. et al., 2011. Iron solubility in crustal and anthropogenic aerosols: The Eastern Mediterranean as a case study. *Marine Chemistry*, 126(1-4): 229-238.
- Sohrin, Y. et al., 1998. Determination of trace elements in seawater by fluorinated metal alkoxide glass-immobilized 8-hydroxyquinoline concentration and high-resolution inductively coupled plasma mass spectrometry detection. *Analytica Chimica Acta*, 363(1): 11-19.

- Sohrin, Y. et al., 2008. Multielemental determination of GEOTRACES key trace metals in seawater by ICPMS after preconcentration using an ethylenediaminetriacetic acid chelating resin. *Analytical Chemistry*, 80(16): 6267-6273.
- Spencer, D.W., Robertson, D.E., Turekian, K.K. and Folsom, T.R., 1970. Trace element calibrations and profiles at the Geosecs test station in the Northeast Pacific Ocean. *J Geophys Res*, 75(36): 7688-7696.
- Stallard, R.F. and Edmond, J.M., 1983. Geochemistry of the Amazon 2. The influence of geology and weathering environment on the dissolved load. *Journal of Geophysical Research*, 88(C14): 9671-9688.
- Stumm, W. and Morgan, J.J., 1996. *Aquatic Chemistry*. John Wiley, New York, N.Y.
- Symes, J.L. and Kester, D.R., 1985. The distribution of iron in the Northwest Atlantic. *Marine Chemistry*, 17(1): 57-74.
- Tagliabue, A. et al., 2012. A global compilation of dissolved iron measurements: Focus on distributions and processes in the Southern Ocean. *Biogeosciences*, 9(6): 2333-2349.
- Tagliabue, A. et al., 2014. Surface-water iron supplies in the Southern Ocean sustained by deep winter mixing. *Nature Geoscience*, 7(4): 314-320.
- Tagliabue, A. and Völker, C., 2011. Towards accounting for dissolved iron speciation in global ocean models. *Biogeosciences*, 8(10): 3025-3039.
- Taylor, S.R., 1964. Trace element abundances and the chondritic Earth model. *Geochimica et Cosmochimica Acta*, 28(12): 1989-1998.
- Town, R.M. and Van Leeuwen, H.P., 2005. Measuring marine iron(III) complexes by CLE-AdSV. *Environmental Chemistry*, 2(2): 80-84.
- Ussher, S.J. et al., 2013. Impact of atmospheric deposition on the contrasting iron biogeochemistry of the North and South Atlantic Ocean. *Global Biogeochemical Cycles*, 27: 1-12.
- Ussher, S.J. et al., 2010a. Distribution of size fractionated dissolved iron in the Canary Basin. *Marine Environmental Research*, 70(1): 46-55.
- Ussher, S.J., Achterberg, E.P. and Worsfold, P.J., 2004. Marine biogeochemistry of iron. *Environmental Chemistry*, 1(2): 67-80.
- Ussher, S.J., Petrov, I., Quétel, C.R. and Worsfold, P.J., 2010b. Validation of a portable flow injection–chemiluminescence (FI-CL) method for the determination of dissolved iron in Atlantic open ocean and shelf waters by comparison with isotope dilution–inductively coupled plasma mass spectrometry (ID-ICPMS). *Environmental Chemistry*, 7(2): 139-145.
- Ussher, S.J., Yaqoob, M., Achterberg, E.P., Nabi, A. and Worsfold, P.J., 2005. Effect of Model ligands on iron redox speciation in natural waters using flow injection with luminol chemiluminescence detection. *Analytical Chemistry*, 77(7): 1971-1978.
- Velasquez, I. et al., 2011. Detection of hydroxamate siderophores in coastal and Sub-Antarctic waters off the South Eastern Coast of New Zealand. *Marine Chemistry*, 126(1-4): 97-107.
- Vink, S., Boyle, E.A., Measures, C.I. and Yuan, J., 2000. Automated high resolution determination of the trace elements iron and aluminium in the surface ocean using a towed fish coupled to flow injection analysis. *Deep-Sea Research Part I: Oceanographic Research Papers*, 47(6): 1141-1156.
- Wells, M.L. and Bruland, K.W., 1998. An improved method for rapid preconcentration and determination of bioactive trace metals in seawater using solid phase extraction and high resolution inductively coupled plasma mass spectrometry. *Marine Chemistry*, 63(1-2): 145-153.
- Worsfold, P.J. et al., 2013. Flow injection analysis as a tool for enhancing oceanographic nutrient measurements-A review. *Analytica Chimica Acta*, 803: 15-40.
- Wu, J.F., 2007. Determination of picomolar iron in seawater by double $Mg(OH)_2$ precipitation isotope dilution high-resolution ICPMS. *Marine Chemistry*, 103(3-4): 370-381.

- Wu, J.F. and Boyle, E., 2002. Iron in the Sargasso Sea: Implications for the processes controlling dissolved Fe distribution in the ocean. *Global Biogeochemical Cycles*, 16(4): art. no.-1086.
- Wu, J.F., Boyle, E., Sunda, W. and Wen, L.S., 2001. Soluble and colloidal iron in the oligotrophic North Atlantic and North Pacific. *Science*, 293(5531): 847-849.
- Wu, J.F. and Boyle, E.A., 1998. Determination of iron in seawater by high-resolution isotope dilution inductively coupled plasma mass spectrometry after $\text{Mg}(\text{OH})_2$ coprecipitation. *Analytica Chimica Acta*, 367(1-3): 183-191.
- Wu, J.F. and Jin, M., 2009. Competitive ligand exchange voltammetric determination of iron organic complexation in seawater in two-ligand case: Examination of accuracy using computer simulation and elimination of artifacts using iterative non-linear multiple regression. *Marine Chemistry*, 114(1-2): 1-10.
- Zagatto, E.A.G., Oliveira, C., Townshend, A. and Worsfold, P., 2012. Flow Analysis with Spectrophotometric and Luminometric Detection. *Flow Analysis with Spectrophotometric and Luminometric Detection*.
- Zuliani, C. and Diamond, D., 2012. Opportunities and challenges of using ion-selective electrodes in environmental monitoring and wearable sensors. *Electrochimica Acta*, 84: 29-34.

a)

b)