A Compilation of Iron Speciation Data for Open Oceanic Waters

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A Compilation of Iron Speciation Data for Open Oceanic Waters

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INTRODUCTION

Iron has been demonstrated to play a major role in limiting primary productivity in large areas of the ocean since the first formulation of the iron hypothesis (Martin, 1990). Efforts and papers devoted to this complex and multidisciplinary research topic (Jickells et al., 2005) saw an exponential increase over the last 25 years (Boyd and Ellwood, 2010). As a consequence, the latest available count (Tagliabue et al., 2016) tells us that the concentration of iron has been determined in around 20,000 oceanic water samples up to 2014. After the noteworthy achievement of reliable iron concentration profiles, the interest of the scientific community moved on to try and understand the fast dynamic of this metal in oceanic waters. However, one of the main factors that determine the concentration of Fe in the oceans is its complexation to organic Fe-binding ligands: this is the reason why Fe speciation measurement made its way in the topic early (Gledhill and van den Berg, 1994; Rue and Bruland, 1995): research aims at establishing the role played by ligands in iron solubility, bioavailability and, as a whole, in its biogeochemical cycle (Hiemstra and van Riemsdijk, 2006; Hunter and Boyd, 2007; Boyd and Ellwood, 2010; Gledhill and Buck, 2012; Boyd and Tagliabue, 2015; Völker and Tagliabue, 2015). A higher iron solubility has since long been connected to the presence of strong binding ligands (Johnson et al., 1997; Liu and Millero, 2002): whether this implies a higher productivity, i.e., an increase in the bioavailable fraction, is still a matter of investigation and strongly depends on the nature of the ligands (Chen and Wang, 2008; Boyd and Ellwood, 2010; Gledhill and Buck, 2012; Shaked and Lis, 2012). An attempt to directly model the dynamics of iron binding ligands in oceanic waters has been recently presented (Völker and Tagliabue, 2015).

The possibility to understand and correctly account for the biogeochemistry of iron in the oceans relies on the quality of the data. Robust analytical methods are clearly needed in speciation studies: the best performances in term of detection capabilities, selectivity, matrix tolerance and clean techniques are mandatory to achieve reliable results. In particular, competitive ligand equilibration coupled to adsorptive cathodic stripping voltammetry (CLE-AdCSV) has been invariably used to characterize iron complexing species, i.e., the concentration of the ligand and the conditional stability constant for the formation of the iron-ligand complex (structural characterization is outside the aim of this data report: the interested reader is referred to recent papers on this topic Gledhill and Buck, 2012; Boiteau et al., 2013). Four different artificial ligands have been used for the CLE-AdCSV procedure: 1-nitroso-2-napthol, NN (Gledhill and van den Berg, 1994); salicylaldoxime, SA, originally developed in 1995 (Rue and Bruland, 1995) and revised in 2014 (Abualhaia and van den Berg, 2014); 2-(2-thiazolylazo)-p-cresol, TAC (Croft and Johannson, 2000) and dihydroxynaphthalene, DHN (van den Berg, 2006). The importance of a correct analysis of the resulting CLE-CSV titration data and the assessment of its errors is the final critical step in this procedure (Monticelli et al., 2010; Laglera et al., 2013; Gerringa et al., 2014; Pižeta et al., 2015).
The present data report aims at making published data on ligand concentration in open oceanic waters available to the scientific community to foster the understanding of the role played by natural ligand in iron biogeochemical cycle. As per the nature of the data report paper, only a preliminary discussion of the data is presented in the form of possible uses of the dataset.

DESCRIPTION OF THE DATASET

The dataset “Iron speciation dataset.xlsx” can be found following this permanent link https://figshare.com/s/6572ca173695fa03738. Data were collected from published papers: pre-2012 papers were obtained from a recent review on the subject (Gledhill and Buck, 2012), whereas literature searches were employed for post-2012 research articles. The dataset covers the 1994–2015 timespan (papers published in 2016 are not included). Source papers are reported in Table 1 together with the investigated region, the filter cutoff employed, the nature of the added ligand and the data treatment.

The dataset includes observations for open oceanic waters only, i.e., off-shelf sampling locations. Open ocean data were selected and in-shelf, costal, estuarine and closed basin data (Mediterranean Sea, Black Sea, etc.) were excluded. Data obtained during fertilization experiments were also excluded: only off-patch or pre-fertilization data were included from those studies. Analogously, data from waters sampled in areas close to hydrothermal vents or thawing ice were not included. The idea is to create a consistent dataset, trying and collecting a tentatively homogeneous set of data. Most of the data were directly available as electronic datasets, whereas a few, mainly the oldest ones, had to be digitized from figures.

The iron speciation dataset includes around 1732 iron speciation data, organized by chronological order. In particular, we reported for each data point (whenever available): the reference in the form author-year, the sampling date, depth, and characteristics. In the following sections, we present different cuts through the data showing different possible uses of the dataset. A detailed discussion of the data is nevertheless outside the aim of the present data report: only general trends (or their absence) will be presented.

A first evidence from the dataset is the strongly uneven distribution of the data: 1185 out of 1732 data are from Atlantic Ocean waters, 232 from the Pacific, 214 from the Indian Ocean and the remaining ones from Polar regions, 51 from the Arctic (N of the Arctic Circle) and 50 from the Southern Ocean (south of 60°S). Accordingly, any discussion of this dataset is necessarily biased and reflects the features of the basins where the samples were collected.

Checking for consistency in the procedure or for the presence of bias is a possible way to extract information from the data. Figure 1A shows the measured side reaction coefficient $\alpha_{FeL}$ (defined as the product of the conditional stability constant $K_{cond}$ and the free ligand concentration $[L^+]$) as a function of the side reaction coefficient $\alpha_{FeAL}$, the alpha coefficient for the complexation of iron by the added ligand as obtained from the relevant papers ($[L^+]$ was calculated from the data by standard thermodynamic calculations van den Berg and Donat, 1992). The lowest and the two highest $\alpha_{FeAL}$ employed show very good agreement between the experimental data and their expected detection windows defined as the range 0.1–10 $\alpha_{FeAL}$ (van den Berg et al., 1990). The four central competition strengths with $1.86 < \log \alpha_{FeAL} < 2.5$ show most of their data outside the traditionally suggested upper limit for the detection window. This apparent discrepancy should be discussed in light of different factors: (1) the definition of the detection window as the range 0.1–10 $\alpha_{FeAL}$ is an approximate estimation defining the optimal range for the CLE methods; several studies demonstrated that a three orders of magnitude window is a more realistic estimate (Apte et al., 1988); (2) the choice of the method to treat/transform the data obtained from the titrations impacts the results, distinctively when more than one ligand class is considered (Laglera et al., 2013; Pižeta et al., 2015) and may alter the traditionally agreed idea about the position and width of the detection window. This point is anyhow worth of future investigation. Conversely, figures lower than the expected lowest limit of the detection window may be easily explained by the saturation of the natural ligands at ambient iron concentrations.

A further interesting point is the possibility that the difference in the data is due to the authors employing different analytical procedures, including different data treatment. The lack of standardization and validation protocols in this field, caused by the absence of reference material and the shortage of routine interlaboratory exercises, makes this risk sensible (see also the Conclusion section). Analysis of variance (ANOVA) conducted...
Table 1: Data sources for the iron speciation database listed in chronological order.

<table>
<thead>
<tr>
<th>Region</th>
<th>AL</th>
<th>AL conc (µM)</th>
<th>log alpha _Fe^′_AL</th>
<th>Fraction (pore size, µm)</th>
<th>Data treatment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlantic Ocean</td>
<td>NN</td>
<td>1; 5</td>
<td>1.9; 2.5</td>
<td>0.45</td>
<td>van den Berg</td>
<td>Gledhill and van den Berg, 1994</td>
</tr>
<tr>
<td>Central N Pacific</td>
<td>SA</td>
<td>27.5</td>
<td>1.86</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rue and Bruland, 1995</td>
</tr>
<tr>
<td>Pacific Southern Ocean</td>
<td>NN</td>
<td>1</td>
<td>1.9</td>
<td>0.45</td>
<td>non-linear</td>
<td>Gerringa et al., 1998</td>
</tr>
<tr>
<td>NW Atlantic</td>
<td>NN</td>
<td>20</td>
<td>3.04</td>
<td>0.2</td>
<td>van den Berg</td>
<td>and non-linear Gerringa</td>
</tr>
<tr>
<td>NE Indian</td>
<td>NN</td>
<td>20</td>
<td>3.04</td>
<td>0.4</td>
<td>van den Berg</td>
<td>Witter and Luther, 1998</td>
</tr>
<tr>
<td>Atlantic Southern Ocean</td>
<td>NN</td>
<td>5</td>
<td>2.5</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić and non-linear Gerringa</td>
</tr>
<tr>
<td>S and Equatorial Atlantic</td>
<td>SA</td>
<td>30</td>
<td>1.94</td>
<td>0.22</td>
<td>Non-linear</td>
<td>Gerringa et al., 2001</td>
</tr>
<tr>
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<td>NN</td>
<td>5</td>
<td>2.5</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić and non-linear Gerringa</td>
</tr>
<tr>
<td>Atlantic Southern Ocean</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.4</td>
<td>Non-linear</td>
<td>Gerringa et al., 2004</td>
</tr>
<tr>
<td>NE Atlantic</td>
<td>NN</td>
<td>5</td>
<td>2.4; 3.4; 4.3</td>
<td>0.4</td>
<td>van den Berg</td>
<td>Boye et al., 2005</td>
</tr>
<tr>
<td>Atlantic Southern Ocean</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2005</td>
</tr>
<tr>
<td>NE Atlantic</td>
<td>NN</td>
<td>5</td>
<td>2.5</td>
<td>0.2</td>
<td>Cullen et al., 2006</td>
<td></td>
</tr>
<tr>
<td>Pacific Ocean</td>
<td>DHN</td>
<td>0.5; 1</td>
<td>2.22; 2.56</td>
<td>0.1</td>
<td>van den Berg</td>
<td>Gerringa et al., 2005</td>
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<tr>
<td>Tropical North Pacific</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2007</td>
</tr>
<tr>
<td>Sulu Sea (Tropical N Pacific)</td>
<td>TAC</td>
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<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Boye et al., 2008</td>
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<td>TAC</td>
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<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
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<tr>
<td>Tropical N Atlantic</td>
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<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
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<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
</tr>
<tr>
<td>NE Atlantic</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
</tr>
<tr>
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<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.4</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
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<tr>
<td>N Atlantic</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
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<td>TAC</td>
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<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
</tr>
<tr>
<td>Atlantic Southern Ocean</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
</tr>
<tr>
<td>Central Pacific</td>
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<td>10</td>
<td>2.4</td>
<td>0.22</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
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<tr>
<td>Atlantic Southern Ocean</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
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<td>Rüžić et al., 2010</td>
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<tr>
<td>Atlantic Southern Ocean</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.2</td>
<td>van den Berg</td>
<td>Rüžić et al., 2010</td>
</tr>
<tr>
<td>N Atlantic</td>
<td>SA</td>
<td>27.5</td>
<td>1.86</td>
<td>0.2</td>
<td>van den Berg   and Scatchard</td>
<td></td>
</tr>
<tr>
<td>Atlantic Ocean</td>
<td>SA</td>
<td>25; 32.5</td>
<td>1.78; 2.00</td>
<td>0.2</td>
<td>van den Berg   and Scatchard</td>
<td></td>
</tr>
<tr>
<td>Pacific Ocean</td>
<td>SA</td>
<td>25</td>
<td>1.77</td>
<td>0.4</td>
<td>van den Berg   and Scatchard</td>
<td></td>
</tr>
<tr>
<td>W Atlantic</td>
<td>TAC</td>
<td>10</td>
<td>2.4</td>
<td>0.2</td>
<td>Non-linear</td>
<td>Gerringa et al., 2015</td>
</tr>
</tbody>
</table>


The relationship between iron and ligand concentrations is presented in Figure 1B. Beside the presence of some outliers, the linear correlation is significant (n = 1727, r = 0.445, p < 0.01): the intercept (0.87 ± 0.033) and the slope (0.92 ± 0.044) point to an average excess of 0.9 nM ligand with respect to total iron concentration, irrespective of total Fe as evidenced by the almost 1:1 increase of ligand with iron concentration. This linear model does not imply any cause/effect relationship between the two parameters and it is intended to be descriptive rather than predictive.
Figure 1C depicts the concentration of ligands for oceanic waters as a function of depth (note the log scale on the y-axis used to show possible trends in the upper part of the water column). No clear global trend emerges from open ocean data reported in the literature. The averaged data (see inset) shows a very uniform value down to a depth of 500 m, an enrichment in mid depth waters (<500 m to around 2000 m), possibly due to the remineralization of organic matter at these depths, and a decrease thereafter down to values similar to the ones determined in the upper part of the water column. This trend is anyhow hardly significant standing the variability in the data evidenced by their standard deviation (error bars in the graph represent the standard deviation of the mean): any strong depth trend on the global scale seems to be absent, although a higher variability of ligand concentrations in mid depth waters emerges.

As a final example of possible global trends, data for ligand concentrations on the entire water column as a function of sampling latitude are reported in Figure 1D (data averaged on a 5 degree base in the right section of the figure). Notwithstanding the high variability in the data, northern hemisphere waters are on average richer in ligands than the Austral ones, as already observed for Atlantic water samples (Gerringa et al., 2015). More detailed, northern hemisphere waters seem to show alternating minima and maxima in ligand concentrations: a minimum right North of the Equator (0–10 degrees), an enriched area extending up to mid latitudes (10–50 degrees), another minimum around 60° and again higher concentrations in the Arctic Ocean. A similar trend is observed for the excess ligand concentrations. Depleted and enriched areas are also present in the Austral hemisphere waters, although the limited number of data calls for caution in stating any trend.

CONCLUSIONS

The collection of published data on iron ligand concentrations is a first mandatory step in understanding the role played by iron ligands in the biogeochemical oceanic cycle of this element. The overall picture emerging from the data is the ubiquitous presence of ligands in open oceanic waters, with an average ∼0.9 nM excess with respect to dissolved iron concentration. Depth profiles show little to no tendency on a global averaged scale, whereas latitudinal trends are clearly visible, with northern hemisphere waters enriched in iron ligands (samples from the Atlantic Ocean mainly). As far as the Atlantic is concerned, ligands contributed to the Arctic by tributary rivers have been recently put forward as an explanation for this latitudinal trend (Gerringa et al., 2015).

Several points should be addressed before an exhaustive and reliable picture of the topic may be achieved and data used for the understanding of the iron cycle or its modeling. The first issue is that available data are strongly biased: around 70% of the samples were collected in the Atlantic Ocean and any conclusion is accordingly strongly biased by the provenance...
of the samples. Accordingly, representative sampling of world oceanic waters is the major gap to be filled: the GEOTRACES program (www.geotraces.org) is expected to contribute much to this aim. A second class of fundamental issues is related to the analytical procedures, their validation and reliability. Analytical procedures are cumbersome at the moment, requiring large volume of samples (120–150 mL) and 3–5 h of analysis time. Recent advancement in methods for total iron determination including reduction in sample size and analysis time (Caprara et al., 2015) may strongly contribute in the definition of higher performance speciation procedures, although at the moment the method was only validated for dissolved iron determination and not for the CLE-CSV procedure. Standing the difficulties in validating the employed analytical methods as standard reference materials are not available, calibration of the procedures may be achieved by intercomparison exercises, i.e., analyzing real or simulated samples distributed among participating laboratories. Data treatment should be included in this calibration procedure because of its value in achieving reliable results (Hudson et al., 2003; Laglera et al., 2013; Gerringa et al., 2014; Laglera and Filella, 2015; Pižeta et al., 2015). This process would ensure that results obtained by different laboratories are traceable to a common set of interlaboratory samples. Unfortunately, this procedure is not common practice at present, although intercalibration cruises have been organized (Buck et al., 2012) and results of a GEOTRACES cross-over station for ligands is submitted together with this paper (Buck et al., unpublished). A further related issue is the correlation between sampling areas and authors; any bias among the procedures used by different authors is at risk of resulting in erroneous evaluations of spatial trends.

**AUTHOR CONTRIBUTIONS**

All the authors contributed to this study. SC: Built the database; KB, LG, and MR: Contributed to the writing and correction of the manuscript; DM: Devised the data report, did the bibliographic research and drafted the manuscript. All the five authors reviewed the final version of the manuscript and contributed to the discussion of the data.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.