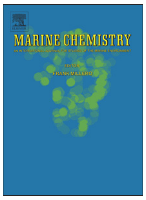
Marine Chemistry xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem



A review of colloidal iron partitioning and distribution in the open ocean

B.P. von der Heyden *, A.N. Roychoudhury

Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa

ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form 21 May 2015
Accepted 27 May 2015
Available online xxxx

Keywords:
Iron
Colloids
Colloidal iron
Size-fractionation
Euphotic zone
Concentration
Soluble iron
Dissolved iron
Seasonality

ABSTRACT

In many parts of the global ocean, iron bioavailability is a critical factor controlling primary productivity. Because colloidal Fe (cFe) makes up a substantial proportion of the surface water Fe inventory, it is critical to evaluate the biogeochemical behaviour and availability of this quantitatively important Fe pool. Here we present and review a compilation of over 1300 soluble and corresponding dissolved Fe concentration measurements from which operationally-defined colloidal Fe data have been determined. Partitioning between cFe and the smaller soluble Fe (sFe) size fraction shows a high degree of variability in the surface ocean caused by the range of factors affecting size fractionation (e.g., Fe sources, ligand controls, thermodynamic controls, biological utilisation). Evaluation of the seasonality of sFe and cFe partitioning indicates that a strong decoupling between their respective biogeochemical cycling occurs in the spring time. This suggests that a seasonal component (e.g., seasonal biological growth, seasonal changes in Fe supply) is responsible for a proportion of the observed surface ocean variability. Below depths of 200 m, the partitioning becomes more constant (49 ± 17%). To better understand the bioavailability of the cFe pool, future work should complement traditional size-fractionated data with molecular level investigation into the functional group chemistry of organic Fe colloids and the mineralogy and surface chemistry of inorganic Fe colloids.

1. Introduction

Despite the ubiquity of iron in terrestrial systems, its low supply to the open ocean, a high biological demand for Fe and its exceedingly low solubility are some of the factors that limit its concentrations to between pico-molar levels and 2–3 $\text{nmol} \cdot \text{L}^{-1}$ in the open ocean. Because marine biological growth and functioning rely on Fe as an essential nutrient (Boyd and Ellwood, 2010), these low Fe concentrations can limit optimal primary productivity and thus, biologically-mediated air-sea CO_2 exchange. To better understand the impact of Fe on ocean biogeochemistry, Fe concentration measurements are therefore becoming a routine component of oceanographic investigation. Recent advances in trace-metal clean sampling techniques (Cutter and Bruland, 2012), ultrafiltration techniques (Schlosser and Croot, 2008) and the enhanced detection limits of modern Fe analytical methods (Bowie et al., 2003) have enabled focused studies into the distribution, profiling and size fractionation of marine Fe (e.g. the GEOTRACES campaign). Although the number of published Fe measurements is steadily increasing (Tagliabue et al., 2012), their spatial and temporal resolution is still sparse relative to marine data measurements for major nutrients such as nitrate and silicate (Louanchi and Najjar, 2000).

Our understanding of marine Fe is further complicated by its complex cycling between various chemical and biological Fe pools. The size-fractionated approach to Fe speciation is commonly used as a proxy to investigate the dynamics and inter-conversions of the different Fe pools. These studies typically distinguish between "particulate" (PFe) and "dissolved" (dFe) size fractions, using either a 0.2 μm or 0.4 μm filter pore size as the nominal size cut-off. The advent of ultra-filtration techniques has resulted in the determination of "soluble" iron (sFe), constituting the smallest size fraction of Fe passing through a 0.02 μm, 200 kDa or 1000 kDa filter (Wu et al., 2001; Nishioka et al., 2001; Thuróczy et al., 2010). Furthermore, sFe measurements allow for the empirical determination of the "colloidal" Fe pool (cFe), given as the concentration difference between dFe and sFe. Despite there being a significant overlap in the physico-chemical speciation of both the inorganic and organic Fe species found in these four size classes (Fig. 1), a number of broad observations have been made with regard to their respective behaviours.

The availability of lithogenic PFe to marine primary productivity is limited by the large size and density of individual particles, which typically lead to rapid sinking to depth and a role in ballasting processes (Croot et al., 2004). The work by Frew et al. (2006) has however indicated a more dynamic PFe cycle in the upper water column, involving efficient conversions of lithogenic PFe to the biogenic PFe pool. Biogenic PFe can further be converted to smaller size classes and made available by recycling processes such as cell lysis and grazing (Strzepek et al., 2005; Sarthou et al., 2008). In comparison, dFe commonly displays a nutrient-like profile in most areas of the open ocean indicative of biological uptake and scavenging in the upper water column and remineralisation at depth (Johnson et al., 1997). The dFe behaviour and depth profile should however, be understood as the summation of

---

* Corresponding author.
E-mail address: bjornvdheyden@gmail.com (B.P. von der Heyden).

http://dx.doi.org/10.1016/j.marchem.2015.05.010

Please cite this article as: von der Heyden, B.P., Roychoudhury, A.N., A review of colloidal iron partitioning and distribution in the open ocean, Mar. Chem. (2015), http://dx.doi.org/10.1016/j.marchem.2015.05.010

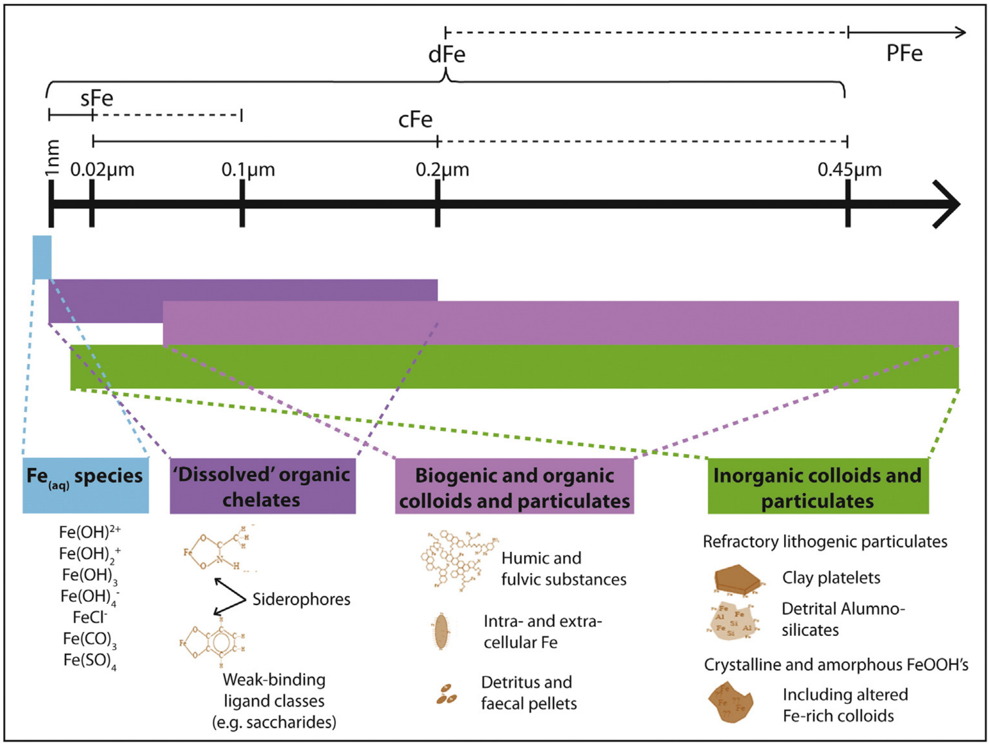


Fig. 1. Operationally-defined Fe size classes (sFe, dFe, cFe, PFe) compared to the range of chemical forms potentially present within each size fraction. Each chemical form behaves differently in the biogeochemical system, and this is one major limitation associated with size-fractionated Fe study.
Adapted from Bruland and Rue (2001).

their constituent sFe and cFe components, which can be strongly decoupled (Wu et al., 2001). This work focuses on the cFe pool which has long been identified as a quantitatively dominant size class of particles in the ocean (Wells, 1998) and has previously been shown to play an important role in controlling dFe variability (Bergquist et al., 2007). Its importance to marine photosynthetic biology has further been suggested through direct experimentation (Chen et al., 2003; Nodwell and Price, 2001) and a host of indirect evidence derived from size-fractionated oceanographic data (Hurst and Bruland, 2007; Chever et al., 2010; Ussher et al., 2010; Thuróczy et al., 2011).

To our knowledge, there has not yet been a global compilation of sFe, and thus cFe measurements, which can be used to broaden our understanding of these important Fe pools in the context of the world ocean. Here we review the current understanding of the cFe pool and evaluate its importance and significance in the context of the marine biogeochemical system. We present an up-to-date compilation of over 1300 sFe and cFe measurements, which is made available to the scientific community and will augment the current global dFe database (Tagliabue et al., 2012). The majority of our analyses focus on the upper 200 m of the water column, representing the euphotic zone where light penetration can facilitate the growth of photosynthetic organisms; and concentration variations are compared between different ocean basins. We further assess the controls on sFe and cFe partitioning across seasonal timescales and with depth down the water column.

2. Methods

We have assimilated a Microsoft Excel database of 1348 sFe measurements (Fig. 2; Appendix A) collected from 29 size-fractionated ocean studies. In these studies, the sFe ultra-filtration pore-size cutoffs ranged between 1 nm and 1000 kDa (Table 1). The depth and concentration values for each data point were collected from published tables or, in cases where only profiles were presented, accessed through direct communication with the corresponding author. For two datasets (Wu et al., 2001; Boyle et al., 2005), the corresponding authors could not be accessed and data was attained by digitising the published figures using the graphics program GIMP2. The error introduced through this manual derivation of the concentration values is smaller (±0.008 nM) than the average standard deviations reported in other datasets (±0.019 nM). All sFe measurements were collected along with any available corresponding dFe, total Fe, salinity and temperature datasets (Table 1). At each data point, cFe concentrations were calculated by subtracting the Fe concentration measured in the sFe fraction (all Fe passing through a 0.02 µm, 200 kDa or 1000 kDa filter) from the concentration in the dFe size fraction (Fe that passes through a 0.2, 0.4 or 0.45 µm filter). A number of artefacts are associated with this difference method for calculating cFe and these are discussed in Wells (2003) and in Section 4.1 below.

Our analyses of the cFe dataset focus predominantly on the euphotic zone of the water column, where light penetration and Fe bioavailability are two factors affecting photosynthetic productivity. Because transmittance data were not provided with each dataset, this study assumes a depth limit of 200 m for the base of the euphotic zone. For this operationally-defined boundary, no allowance is made for geographically variable light penetration (e.g., low light penetration at high latitudes and at sites with high particle loading). The averaged Fe concentration used in the analyses is defined as the 0–200 m mean of all cFe measurements and does not take into account any potential sampling depth biases or the structure of the Fe concentration profile in the upper 200 m. Biological activity is often strongly seasonal (Behrenfeld et al., 2005) and for the purposes of this study, the year is divided into quarters accordingly: Dec, Jan, Feb (austral summer/boreal winter); Mar, Apr, May (austral autumn/boreal spring); June, July, Aug (austral winter/boreal summer) and Sept, Oct, Nov (austral spring/boreal autumn).

Our analyses are further focussed on sampling sites that occur in the most remote regions of the respective oceans ('open ocean' sites). Because of the distal proximity of such sites to continental land masses, there is a much smaller likelihood that supply of excessive Fe inputs (e.g. from circulation dynamics or terrestrial sources (notably aeolian

Please cite this article as: von der Heyden, B.P., Roychoudhury, A.N., A review of colloidal iron partitioning and distribution in the open ocean, Mar. Chem. (2015), http://dx.doi.org/10.1016/j.marchem.2015.05.010