The physico-chemical speciation of iron over an oxic shelf margin

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Due to the extremely low solubility of iron (Fe) in oxic seawater the concentration of dissolved Fe (dFe; < 0.2 μm) is typically sub-nanomolar. Consequently, Fe availability regulates phytoplankton growth over 20-40 % of the world's ocean. In order to alleviate the conditions for Fe limitation external sources of Fe are required. A picture is emerging that transport of Fe from oxic shelf margins is an important aspect of the marine Fe cycle[1-3], though less is currently known about the physico-chemical speciation of Fe derived from these regions.

In this study the aim was to determine the physico-chemical speciation of Fe over the shelf slope of the Celtic Sea. The distribution of soluble (sFe; < 0.02 μm), colloidal (cFe; 0.02-0.2 μm), dFe and total dissolvable Fe (TdFe; unfiltered) concentrations are presented for 3 cross slope transects sampled in November 2014, April 2015 and July 2015. In this region both particle resuspension and remineralisation influence the distribution of dFe. We show that particle rich intermediate nepheloid layers, which are enriched in dFe (~ 1-4 nM) and TdFe (~ 30-400 nM), are persistant features of the Celtic Sea shelf slope, indicating their importance as conduits of Fe supply to the ocean interior. Using radium isotopes we estimate the flux of dFe to be 16-170 μmol dFe m^{-2} d^{-1}. We also demonstrate that dFe supplied from the resuspension of oxic shelf margin sediments is predominantly (60-90 %) in the colloidal form. Therefore, the fate of dFe supplied from oxic margins is likely to be inexorably linked to that of colloidal material.

In the surface mixed layer (SML), summer concentrations of dFe and TdFe were < 0.15 nM and < 1.00 nM respectively. When considered together with the presence of residual nitrate in the SML, our results indicate that, despite proximity to the shelf slope, these waters are not Fe replete year round.

1 Conway & John, *Nature* **511**, 212-215 (2014). 2 Homocky *et al.Nature Communications* **4** (2013). 3 Radic *et al*. *Earth and Planetary Science Letters* **306**, 1-10 (2011).