Iron BREW: Iron Beyond River Etive Water (Grant Award CPDSG3)

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The importance of Fe as an essential micronutrient in marine biogeochemistry is undisputed [1], and has driven many of the recent efforts to refine knowledge of Fe sources and fluxes to the ocean [e.g. 2]. Riverine transport is typically considered to be a relatively unimportant source of dissolved Fe because estuarine processes are observed to remove ≥95% [3]. However, complexation to dissolved organic carbon (DOC) is gaining attention as a mechanism for Fe to survive flocculation (salt coagulation) across estuarine salinity gradients [4, 5].

Recent efforts to characterise and quantify the riverine flux of Fe have identified humic substances (HS) as the dominant transport vector [5], specifically fulvic acids [4], with observations of substantially increased HS-bound Fe fluxes (~4 times greater) in northern European rivers over the last 20 to 40 years [6] mirroring the general increase in DOC observed in Northern Hemisphere rivers [7]. Given the important role Fe plays within marine ecosystems [8], identification of Fe transport vectors, their efficiency at maintaining Fe in suspension across estuarine salinity gradients, and the main factors instigating change in DOC-bound Fe, are timely research goals within the context of current changes in climate and land-use in the UK.

In this study, we focused on the behaviour of dissolved Fe in Loch Etive (Fig. 1), a sea loch on the West Coast of Scotland supplied with river waters that drain peat-dominated catchments. We carried out direct measurements and mixing experiments of dissolved trace metals and DOC to identify how dissolved Fe concentration varies across the salinity gradient, and how the dominant carrier phase varied with salinity.

Fig. 1: Location of sampling stations in Loch Etive (RE1-7) and the Rivers Etive and Awe. Each station was sampled at 3 depths (1, 5, 10 m).

Waters were collected from the two main rivers feeding into Loch Etive, the Rivers Awe and Etive, and along a salinity transect in January and August 2016 (Fig. 1). Temperature and salinity were recorded by CTD, and chemical parameters (DOC, dissolved metals) were analysed in the laboratory. The dissolved metals were measured for Fe concentration in two size fractions (0.4 µm, 5 kDa). The total dissolved fraction is operationally defined as <0.4 µm (or similar), and spans dissolved metals in their free ionic form and complexed to larger molecules, e.g. DOC. To isolate the "truly" dissolved fraction, ultrafiltration (<5 kDa) is used. This collects metals in their free ionic form and small inorganic and organic compounds (e.g. Fe-FA where FA is fulvic acid). To span the full salinity range, we carried out mixing experiments using 0.4 µm filtered River Awe and local coastal seawater, which were filtered again (0.4 µm, 5 kDa) prior to analysis. This reflects the behaviour of the purely dissolved fraction in the absence of particulates. Measurement by combined SeaFAST and ICP-MS generated reproducibility of 9% (1RSD) and accuracy of 7% relative to coastal seawater certified reference material (CRM) NASS-6 (National Research Council Canada). Total procedural blanks were <5% and <10% of the smallest sample concentration for the two size fractions respectively.

How much dissolved Fe is maintained in suspension across the salinity gradient? The Fe concentrations in samples collected from the salinity transects show similar behaviour to the mixing experiment data (Fig. 2a, b). On that basis, we calculate Fe concentrations using regression equations from both size fractions to make generalisations about the behaviour of dissolved Fe with
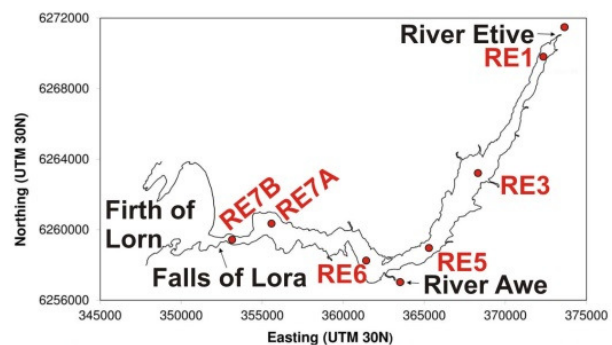
salinity. The dissolved Fe concentrations in both fractions do not show conservative behaviour (Fig. 2a,b). By 35 psu (practical salinity units) total dissolved Fe concentrations represent ~2% of the initial riverine Fe, supporting observations of significant Fe loss across the salinity gradient. Within the dissolved fraction, colloids (<0.4 μm >5 kDa) dominate absolute Fe export, holding 70% of the dissolved Fe by 35 psu. The <5 kDa Fe concentrations deviate least from conservative mixing (Fig. 2b), which is reflected by the greater Fe transport capacity of this fraction (18% at 35 psu; Fig. 2c). The estimated concentrations of both size fractions at 35 psu, based on regression lines through the mixing data, are 28 and 8 nmol/kg respectively. For comparison to typical coastal waters, CRM NASS-6 has 8.6 nmol/kg Fe (total dissolved).
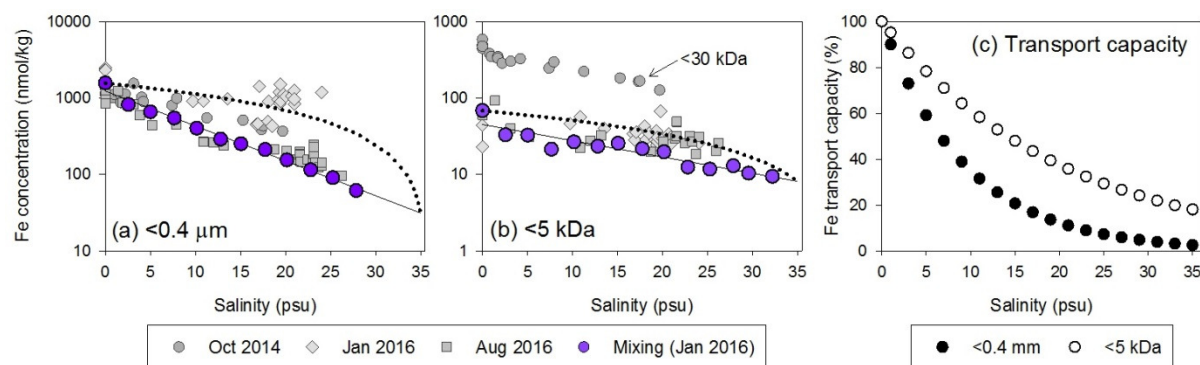

Fig. 2: Iron (nmol/kg) vs. salinity in (a) the <0.4 μm fraction, and (b) the <5 kDa fraction (October 2014 is <30 kDa). Unbroken regression lines are drawn through the mixing data, and conservative mixing trends are indicated by dotted lines. (c) The Fe transport capacity, i.e. [sample/river Fe concentrations x 100], based on regression-derived data.

What is the dominant carrier phase of dissolved Fe? The Fe/DOC ratio differentiates between the two main carrier phases of dissolved Fe, inorganic Fe oxyhydroxides (high Fe/DOC) vs. DOC (low Fe/DOC). Ultrafiltration further discriminates between humics and fulvics (generally > and <5 kDa
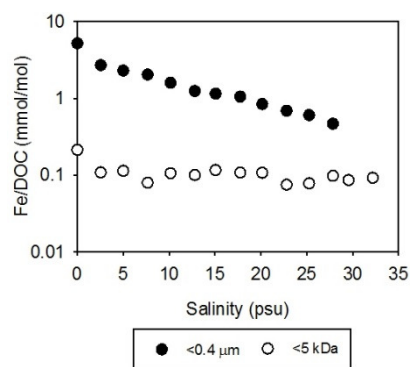

respectively). The <0.4 μm fraction has decreasing Fe/DOC with increasing salinity (Fig. 3) and points to loss of inorganic Fe, whereas the Fe/DOC in the <5 kDa fraction is relatively invariant and suggests it is mainly complexed to DOC throughout the salinity gradient. To note, the DOC was measured in the 0.7 μm fraction (GF filter). Tests to measure DOC in trace metal-matched pore size fractions revealed significant DOC contamination, and will require further development to overcome DOC contributions from the filter membrane and housing materials.

Fig. 3: The Fe/DOC (mmol/mol) in <0.4 μm and <5 kDa fractions of the mixing experiments (DOC is <0.7 μm).

Conclusions and future work. Removal of dissolved Fe (<0.4 μm) in Loch Etive occurs throughout the salinity gradient resulting in low Fe concentrations at high salinities (~2% of initial riverine Fe at 35 psu). The transport capacity of Fe is greatest in the <5 kDa fraction (18% at 35 psu). We tentatively suggest this supports the electrostatic neutrality and enhanced Fe export by fulvic acids, although further work is required to conclusively identify the nature and concentration of these substances. Further work should focus on the Fe bioavailability and fluxes to constrain the impact on Scottish coastal environments.

References: **[1]** Tagliabue, A., et al. Nature, 2017. **543**(7643): p. 51. **[2]** Conway, T.M. and S.G. John. Nature, 2014. **511**(7508): p. 212. **[3]** Sholkovitz, E.R. and D. Copland. Geochimica et Cosmochimica Acta, 1981. **45**(2): p. 181. **[4]** Krachler, R., et al. Marine Chemistry, 2015. **174**: p. 85. **[5]** Laglera, L.M. and C.M.G. van den Berg. Limnology and Oceanography, 2009. **54**(2): p. 610. **[6]** Neal, C., et al. Aquatic Geochemistry, 2008. **14**(3): p. 263. **[7]** Clark, J.M., et al. Science of The Total Environment, 2010. **408**(13): p. 2768. **[8]** Moore, C.M., et al. Nature Geoscience, 2013. **6**(9): p. 701.