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Examining the dispersion and fate of terrestrially-derived, organically-bound dissolved Fe from source to sea

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A MASTS small grant (£500) was used to part-fund the collection of water samples from Loch Etive and the measurement of iron concentrations in different size fractions. The results of these analyses, together with their wider implications for the export of terrigenous dissolved Fe to coastal environments, are to be **presented as the MASTS 2015 Annual Science Meeting**.

Introduction

Iron is known to be essential micronutrient that enables algal productivity. Areas of the world's oceans that exhibit high macro-inorganic nutrients such as nitrate but exhibit low primary productivity and hence chlorophyll (High Nitrate Low Chlorophyll) have been shown to be artificially stimulated by the large scale addition of dissolved iron (Boyd et al., 2000; Coale et al., 1996). The natural flux of iron into the world oceans is largely atmospherically driven (Jickells et al., 2005; Jickells et al., 1998) with minor supplies coming from rivers (Meybeck, 2003) and hydrothermal vents (Bruland and Lohan, 2003). Classically, work that has looked at fluvial inputs into the marine environment has largely drawn the conclusion that many of the dissolved and particulate constituents of river water precipitate and flocculate due to the changing pH and ion strength and consequently sediment within the estuaries and deltas (Sholkovitz et al., 1978).

More recently, however, this notion has been challenged by the realisation that some dissolved and colloidal iron and other metal binding constituents are not prone to flocculation but instead can survive the electrostatic attractive forcing of increased salinity and are transported to sea (Laglera and van den Berg, 2009). This work has shown that terrigenous derived humic and fulvic compounds are in large part responsible for this transfer. These organic acids represent a very large number of compounds and attempts to chemically classify them have been limited due to their heterogeneity (Stevenson, 1994). They form the dominant organic component of many soil horizons and are particularly rich in peat horizons. Because of the molecular structure they are able to bind with a variety of transition metals, although the origin of the metal association (biological uptake and/or biogeochemical scavenging within the soil horizon) is less well known as is their long term fate in the marine environment.

Work at SAMS (unpublished data from NERC thematic programme Autosub Science Missions, grant no GST/02/2145, 1999) has demonstrated the clear link between the fresh water runoff entering Loch Etive and the associated high concentration of dissolved iron. The values obtained, which were of the order of $1\mu\text{M}$, are approximately 3 orders of magnitude greater than those measured in the UK shelf sea regions (Nedelec et al., 2007). The fluvial catchment of Loch Etive is the largest of all the sea lochs in Scotland (Edwards and Sharples, 1986) and includes a large areal coverage of land that contains a dominantly peat pedosphere with very high organic content. This forms part of the NW highlands of Scotland, which together with northern Scotland, parts of Ireland and Scandinavia, form the principle areas of Europe that are known to be dominated by this soil type (Montanarella et al., 2006). Loch Etive, therefore, provides an excellent location to examine the association of terrestrially

derived humic and fulvic compounds with iron and the fate of these compounds from their freshwater source to the marine environment.

Methods and results

In October 2014, the pilot project mapped the water column depth distribution of dissolved and particulate organic matter and associated iron fractions along a linear transect of Loch Etive (Fig. 1), presenting a single snapshot in time. The timing of the sampling coincided with the start of the autumnal rains which, from the previous work in 1999, are the time of highest concentrations of dissolved iron. This linear transect encompassed a salinity range of approaching 1-5psu at the headwaters of Glen Etive to 20 just before the Falls of Lora (far end of Loch Etive). Analyses of the two major rivers entering the Loch, the Etive and the Awe, were included.

Water was filtered through 0.4 μm filter membranes (total dissolved), followed by microfiltration (30 kDa) of a subsample ("truly" dissolved). Both fractions were acidified to pH 1.7 prior to measurement of Fe concentrations by combined SeaFAST+ICP-MS. The particulate fraction ($>0.4 \mu\text{m}$) underwent total microwave digestion before measurement by ICP-MS. The colloidal fraction represents the difference in Fe concentration between the total and "truly" dissolved fractions. External reproducibility of dissolved Fe, gauged by repeat measurement of NRC NASS-6 ($0.61 \pm 0.06 \mu\text{g}/\text{kg}$), is 10% (1RSD) with 27% deviation from the certified value ($0.483 \mu\text{g}/\text{kg}$). The largest total procedural blank represents $<5\%$ of the smallest total dissolved Fe sample, and 41% of the smallest "truly" dissolved sample ($<7\%$ of the mean sample concentration).

All fractions show some degree of linearity over the salinity range sampled (0 – 20 psu; Fig. 2), and thus suggest at first glance conservation of Fe. The size difference between humic and fulvic acids means the total dissolved fraction should contain relatively more of the larger humic acids, and the "truly" dissolved fraction more of the smaller fulvic acids. Excluding one outlier, the Loch Etive "truly" dissolved data show the greatest linear correlation with salinity ($R^2 = 0.92$). The high variability of the particulate fraction at low salinity is attributed to later inflow of River Awe water (between RE5 and RE6) with higher particulate Fe concentrations.

Conclusions

Linear projections fitted to each Fe fraction, with comparison to reference coastal water (NRC NASS-6), tests the behaviour of dissolved Fe in Loch Etive (Fig. 3). None approximates coastal (NASS-6) dissolved Fe concentrations, and none can realistically be forced through the coastal data while also replicating the trends in Loch Etive Fe data. Crucially, the "truly" dissolved fraction displays very different behaviour to the other Fe fractions (i.e. shallower gradient and less scatter). This is most likely due to dominance of aggregating Fe oxyhydroxides and larger humics in the larger size fractions and, by comparison, distinctly different behaviour of the small humic molecules in the "truly" dissolved fraction.

We suspect that use of a 30 kDa filter for the "truly" dissolved fraction was not entirely successful at isolating the fulvic acid fraction, which mostly occupies the $<10 \text{ kDa}$ size range (peak size $\sim 1 \text{ kDa}$). The slope of "truly" dissolved Fe vs. salinity and DOC may in fact be shallower when a $\leq 10 \text{ kDa}$ filter is applied, thus more closely approximating coastal water dissolved Fe concentrations.

We plan to repeat the sampling exercise in Loch Etive under drier conditions to span the full salinity gradient. We will also sample another sea loch to test whether the conclusions from Loch Etive are applicable to other West Coast locations.

Figures

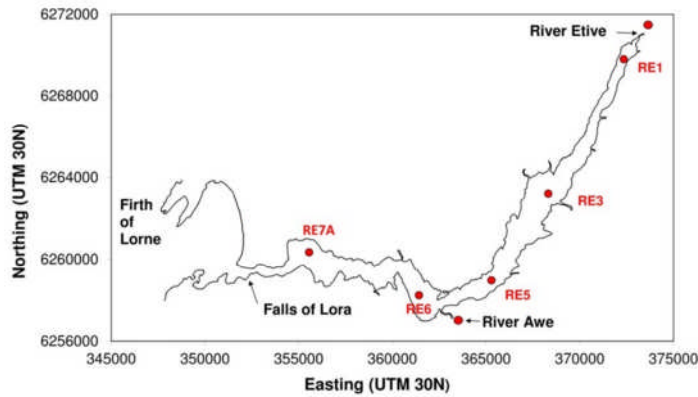


Figure 1: Location of sampling stations and the inflow of Rivers Etive and Awe in Loch Etive.

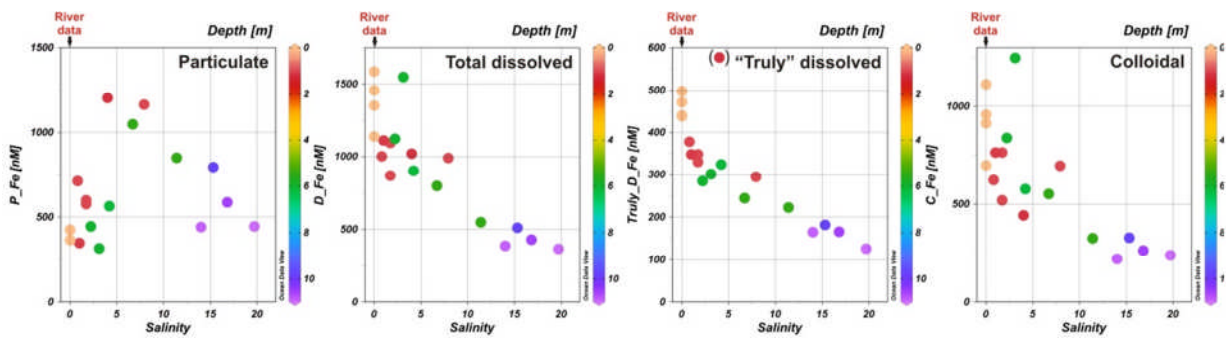


Figure 2: Variation of Fe concentration (nM) in different fractions vs. salinity. Colour coding represents depth of sample (m). River samples are zero depth. In the particulate Fe panel, only River Etive data is shown as River Awe particulate Fe is $\gg 2000$ nM. The brackets in the "truly" dissolved Fe panel represent an outlier data point.

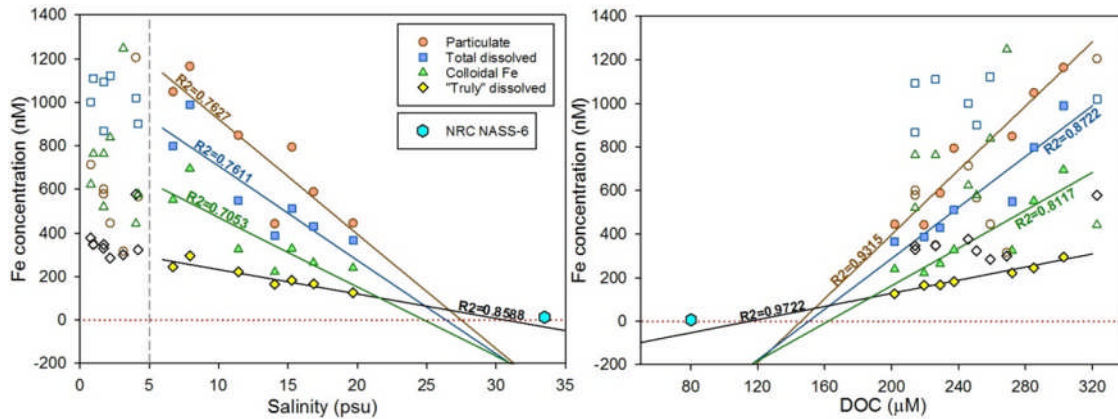


Figure 3: Variation of the Fe concentration (nM) in all fractions vs. (i) salinity (psu), and (ii) DOC (μM) in the total dissolved fraction. Linear projections are drawn through each fraction, with the R^2 value indicated. The closed symbols represent data with salinity >5 psu (grey dashed line in (i) Fe vs. salinity), and the open symbols represent data at salinity <5 psu. NRC NASS-6 data is shown for comparison, the DOC value of which was estimated from typical coastal water DOC (i.e. ~ 80 μM).

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