

Quantification of dissolved metals in samples and reference seawater was performed for total dissolved Fe, Ni, Cu, Zn, and Cd using isotope dilution. 15mL of acidified seawater sample was spiked with 50 μ L of a stable isotope spike solution artificially enriched in ^{57}Fe , ^{61}Ni , ^{65}Cu , ^{67}Zn , and ^{110}Cd . All stable isotopes were received in solid form (Oak Ridge National Laboratory). Initial dissolution and all subsequent dilutions were made using concentrated nitric acid (Optima, Fisher Scientific). Concentrations and spike ratios were verified by ICP-MS using a multi-element standard curve (SPEX CertiPrep). The composition of the isotope spike was made such that the 15mL spiked sample contained the following ratios: $^{57}\text{Fe}/^{56}\text{Fe} = 0.7$, $^{61}\text{Ni}/^{60}\text{Ni} = 0.5$, $^{65}\text{Cu}/^{63}\text{Cu} = 1$, $^{67}\text{Zn}/^{66}\text{Zn} = 0.7$, and $^{110}\text{Cd}/^{114}\text{Cd} = 1$ and were verified with ICP-MS. These ratios were chosen to minimize the uncertainty introduced by error propagation through the isotope dilution equation (Wu and Boyle 1998; Rudge et al. 2009; Tan et al. 2020). Because it is monoisotopic, total dissolved Mn was calculated using a modified isotope dilution equation:

$$\text{Mn (nM)} = \frac{{}^{55}\text{Mn}_{\text{spl}} \text{ (cps)}}{{}^{57}\text{Fe}_{\text{spl}} \text{ (cps)}} * {}^{57}\text{Fe}_{\text{spike}} \text{ (nM)} * {}^{57}\text{Fe}_{\text{slope}} \text{ (cps/ppb)} * \frac{1}{({}^{55}\text{Mn}_{\text{slope}}) \text{ (cps/ppb)}} \quad (1)$$

in which ${}^{55}\text{Mn}_{\text{spl}}$ and ${}^{57}\text{Fe}_{\text{spl}}$ refer to the blank corrected counts per second (cps) of ${}^{55}\text{Mn}$ and ${}^{57}\text{Fe}$ in the spiked sample, ${}^{57}\text{Fe}_{\text{spike}}$ is the concentration of ${}^{57}\text{Fe}$ spike, ${}^{57}\text{Fe}_{\text{slope}}$ is the slope of the external standard calibration curve (SPEX curve) relating ${}^{57}\text{Fe}$ cps to ppb, and ${}^{55}\text{Mn}_{\text{slope}}$ is the slope of the external calibration curve (SPEX curve) relating ${}^{55}\text{Mn}$ cps to ppb. Due to the acidification of seawater prior to ICP-MS analysis, Mn ICP-MS measurements do not include contributions from humic-type Mn(III)-ligand complexes (Oldham et al. 2021). Until the inclusion of Mn(III) is resolved and intercalibrated, we report these Mn values as Mn(II) and note that they are consistent with prior studies employing the same acidification technique (Sedwick et al. 2000; Noble et al. 2013; Gerringa et al. 2020).