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Temporal variability of reactive iron over the Gulf of Alaska shelf

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ABSTRACT

The Gulf of Alaska (GoA) shelf is a highly productive regime bordering the nitrate-rich, iron (Fe)-limited waters of the central GoA. The exchange between nitrate-limited, Fe-replete coastal waters and nitrate-rich, Fe-deplete offshore waters, amplified by mesoscale eddies, is key to the productivity of the region. Previous summer field studies have observed the partitioning of Fe in the coastal GoA as being heavily dominated by the particulate phase due to the high suspended particulate loads carried by glacial rivers into these coastal waters. Here we present new physico-chemical iron data and nutrient data from the continental shelf of the GoA during spring and late summer 2011. The late summer data along the Seward Line showed variable surface dissolved iron (DFe) concentrations (0.052 nM offshore to 4.87 nM inshore), within the range of previous observations. Relative to available surface nitrate, DFe was in excess (at Fe:C=50 µmol:mol) inshore, and deficient (at Fe:C=20 µmol:mol) offshore. Summer surface total dissolvable iron (TDFe, acidified unfiltered samples) was dominated by the acid-labile particulate fraction over the shelf (with a median contribution of only 3% by DFe), supporting previously observed Fe partitioning in the GoA. In contrast, our spring data from southeast GoA showed TDFe differently partitioned, with surface DFe (0.28–4.91 nM) accounting on average for a much higher fraction (~25%) of the TDFe pool. Spring surface DFe was insufficient relative to available nitrate over much of the surveyed region (at Fe:C=50 µmol:mol). Organic Fe-binding ligand data reveal excess concentrations of ligands in both spring and summer, indicating incomplete titration by Fe. Excess concentrations of an especially strong-binding ligand class in spring surface waters may reflect in-situ ligand production. Due to anomalous spring conditions in 2011, river flow and phytoplankton biomass during our spring sampling were lower than the expected May average. We argue our samples are likely more representative of early spring pre-bloom conditions, providing an idea of the possible physico-chemical partitioning of Fe in coastal GoA waters relevant to initial spring bloom dynamics.

1. Introduction

The essential micro-nutrient iron (Fe) regulates primary productivity over large areas of the open ocean including the Gulf of Alaska (GoA) high-nutrient, lower than expected chlorophyll (HNLC) region (e.g. Martin et al., 1989; Boyd et al., 2004). Additionally, Fe availability influences algal community composition, which transitions from a diatom-dominated community at high concentrations of Fe to a system dominated by small phytoplankton at low Fe concentrations (Morel et al., 1991; Landry et al., 1997). The biological regulatory effect of Fe can also influence coastal waters (Hutchins et al., 1998; Johnson et al., 2001). As a consequence, it is of interest to understand the factors that affect the distribution of biologically accessible Fe in surface waters. Physical, chemical, and biological processes transform Fe in seawater by altering its distribution within various pools, and thus its biological availability. Truly soluble (< 0.02 µm) inorganic Fe, although it appears to be easily accessible to phytoplankton (Maldonado and Price, 2000), is found at exceedingly low concentrations due to its extreme low solubility in oxygenated seawater. Organic complexation increases the solubility of Fe in seawater (Liu and Millero, 2002), and > 99% of dissolved (< 0.4 µm) Fe (DFe) is organically complexed by strong Fe-binding ligands that can allow for elevated DFe concentrations ([DFe]) (Buck et al., 2007; Bundy et al., 2014). However, the biological availability of these complexes has been shown to be

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variable (e.g. Maldonado and Price, 1999; Rijkenberg et al., 2006). In addition, a fraction of the suspended particulate Fe pool may be mobilized into dissolved or soluble phases over short time scales, rendering this labile fraction potentially available to phytoplankton (Johnson et al., 1999). Together DFe and suspended labile particulate Fe represent reactive species that are potentially significant to biological uptake.

Surface waters exhibit pronounced inshore–offshore gradients in DFe and suspended particulate Fe, with inshore Fe concentrations enhanced by up to 2–3 orders of magnitude (or greater), as has been observed in the GoA (Wu et al., 2009; Lippiatt et al., 2010a). The gradients result from the proximity of inshore waters to terrestrial Fe sources (aeolian, fluvial and sedimentary). Atmospheric deposition, via episodic dust events from Asia and North America, has been traditionally thought as the main mechanism for transporting Fe to the central GoA (Boyd et al., 1998; Moore et al., 2002). Recent studies (Johnson et al., 2005, Lam et al., 2006, Cullen et al., 2009; Lippiatt et al., 2011; Brown et al., 2012) suggest fluxes of Fe from coastal waters to the central GoA could be as important as atmospheric deposition. For example, anticyclonic mesoscale eddies in the GoA that propagate from the inner shelf westward into the basin (Ladd et al., 2005) are able to transport Fe-rich waters offshore (Johnson et al., 2005; Lippiatt et al., 2011; Brown et al., 2012), and it has been calculated that the flux of reactive Fe from mesoscale eddy activity in the GoA is in the same order of magnitude as atmospheric flux (Brown et al., 2012). Lam et al. (2006) presented evidence of lateral advection of suspended particulate Fe from the continental shelf into the remote HNLC region at depths of 0–300 m, and Lam and Bishop (2008) calculated the flux of biologically available Fe to be within the same order of magnitude for these two sources by assuming higher lability for sedimentary Fe as compared to dust. Additional cross-shelf Fe transport via the California Undercurrent, downwelling, and/or tidal currents could enhance the importance of coastal input relative to atmospheric deposition, as suggested by Cullen et al. (2009).

Input of Fe to the GoA is highly seasonal. In the northern GoA prevailing winds stimulate downwelling from fall through spring (Stabeno et al., 2004; Weingartner et al., 2005), and likely contribute to episodic offshore flow of Fe in bottom layers. During May–October, weaker and variable winds induce intermittent upwelling along the coast (Stabeno et al., 2004). Fresh water runoff is at its peak between June and September, and higher concentrations of Fe have been observed in July as compared to May in the inner GoA shelf (Wu et al., 2009). The various glaciers along the mountainous GoA coastline cause rapid erosion and contribute to the high suspended sediment (Christensen et al., 2000) and Fe loads (Lippiatt et al., 2010a) carried by rivers. The rapid physical weathering of glaciers produces particles with a low labile Fe component (Lippiatt et al., 2010a) as compared to more labile Fe-coatings on resuspended particles that have been exposed to chemical reduction and re-oxidation processes at the sediment–water interface (e.g. Hurst et al., 2010). Dust storms generated by episodic gap wind events (Ladd and Cheng, 2016; Ladd et al., 2016) can deposit glacial flour with high Fe loadings (Crusius et al., 2011) over the shelf and offshore waters from exposed river beds of glacial rivers. These events occur most frequently in mid-autumn (Ladd and Cheng, 2016; Ladd et al., 2016) when low river levels and snow cover expose the riverbed sediment (Crusius et al., 2011 and references therein). The concentration of dissolved organic Fe-binding ligands likely caps the amount of Fe from various inputs that contribute to the DFe pool, as observed in other river influenced coastal systems (Buck et al., 2007), but inorganic colloidal Fe is potentially an important component of the dissolved Fe pool in the high particle regime of the inner GoA shelf during summer. Most fluvial input of Fe is confined within the buoyancy driven Alaska Coastal Current (ACC) (Fig. 1), and although the ACC can be discontinuous particularly between Cross Sound and Yakutat Bay (Stabeno et al., 2016), it has the potential to act as Fe reservoir, and a vehicle for alongshore transport (Wu et al., 2009).

We present Fe and ligand data from the continental shelf of southeast GoA during spring, and the western GoA during late summer, 2011 (Fig. 1), collected as part of the Gulf of Alaska Integrated Ecosystem Research Program (GOA-IERP). Dissolved and particulate samples were collected from surface waters and

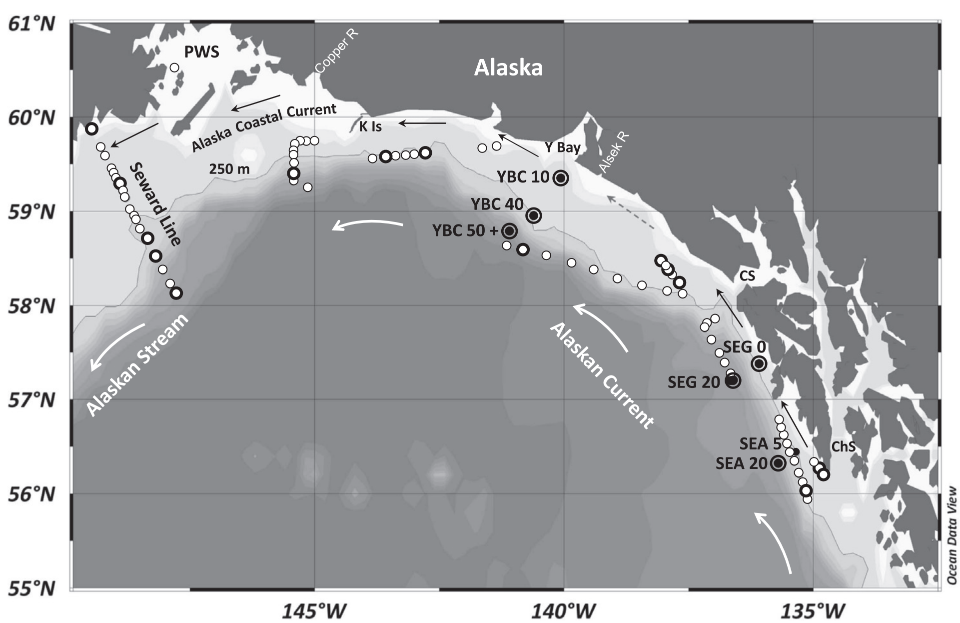

Fig. 1. Map showing the general surface circulation of the Gulf of Alaska, and locations sampled for Fe and related parameters. White circles indicate locations where surface transects were sampled. Black circles show stations where Fe profiles were collected. Heavy outlines on circles denote locations where Fe-binding organic ligand samples were collected. Also labeled are Prince William Sound (PWS), Kayak Island (K Is), Yakutat Bay (Y Bay), Cross Sound (CS), Chatham Strait (ChS), the mouths of the Copper River (Copper R) and Alsek River (Alsek R). The Alaska Coastal Current is indicated by thin black arrows, and a dashed grey arrow where it might not exist. The 250 m contour line denotes the shelf break.