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SANTA CRUZ

THE DISTRIBUTION OF REACTIVE IRON ALONG THE NORTHEAST PACIFIC MARGIN AND THE DELIVERY OF THIS COASTAL IRON TO THE OPEN OCEAN

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ABSTRACT

Sherry M. Lippiatt

THE DISTRIBUTION OF REACTIVE IRON ALONG THE NORTHEAST PACIFIC MARGIN AND THE DELIVERY OF THIS COASTAL IRON TO THE OPEN OCEAN

The objective of this dissertation is to characterize the distribution of reactive iron in the near-field Columbia River plume, the coastal Gulf of Alaska, and a Kenai eddy in the Gulf of Alaska (GoA). The research conducted for this dissertation presents a substantial contribution to the continuing effort to characterize the continental source of reactive iron and the delivery of that iron to the coastal ocean. Reactive iron is defined here as the sum of the leachable particulate and dissolved iron phases, and is an estimate of the total potentially bioavailable iron concentration. In the near-field Columbia River plume (Chapter 1), tidal amplitude and river flow were found to be the primary factors influencing the estuary leachable particulate Fe concentrations, with greater values during high flow and/or spring tides; resuspended shelf sediment was an additional source to the plume during coastal upwelling and spring tides. Leachable particulate iron concentrations in both the river/estuary and near-field plume were consistently one to two orders of magnitude greater than dissolved iron concentrations. Chapter 2 characterizes reactive iron
concentrations in the Alaska Coastal Current. Coastal waters in the northern GoA are considered iron-rich and nitrate-poor, in contrast to the iron-poor, high-nitrate, low chlorophyll (HNLC) waters of the central GoA. The degree of mixing between these two regimes, is essential to maintain high productivity. Surface water leachable particulate iron concentrations were more variable and at least an order of magnitude higher than dissolved iron concentrations; the data suggests that the system’s ability to solubilize this large concentration of leachable particulate iron is overwhelmed by the massive input of glacial-derived particulate iron. Chapter 3 discusses the delivery of this coastal iron to HNLC waters via a Kenai eddy. In the subsurface core of the eddy there was nearly nine times more reactive iron at inside eddy stations compared to the basin waters. Deep mixing can bring iron enriched eddy core waters to the surface and promote primary production. Furthermore, anticyclonic GoA eddies can be a source of iron to HNLC waters when they propagate into the central GoA and eventually relax or rebound.
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The chapters of this dissertation include reprints of the following previously published manuscripts, and one submitted manuscript:


My contribution to this chapter was the interpretation and synthesis of all data presented in the publication. Matthew Brown provided particulate metal data from the 2006 cruises, Maeve Lohan provided dissolved iron data, and Carolyn Berger provided particulate metal data from the 2004 and 2005 cruises. Kenneth Bruland directed and supervised the research.


My contribution to this chapter was a) the analysis of all particulate metal data presented in the publication and b) interpretation and synthesis of all data presented in the publication. Maeve Lohan provided shipboard dissolved iron data and Kenneth Bruland directed and supervised the research.


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INTRODUCTION

Marine phytoplankton require nutrients to grow and reproduce. Compared to the principal macronutrients carbon, nitrogen, phosphorus, and silicon, iron is required in trace amounts. Iron (Fe) is an essential micronutrient required in biochemical electron transfer processes such as the light reactions of photosynthesis, respiration, and the reduction of nitrate prior to assimilation. Furthermore, iron has been shown to limit primary productivity in portions of the world ocean (e.g. Martin and Gordon, 1988; Boyd et al., 2007). Due to the biological requirements for iron, it can indirectly influence the biogeochemical cycles of carbon, nitrogen, phosphorus, and silicon (e.g. Falkowski, 1997; Morel et al., 2003). In light of increasing impetus to better understand the oceanic carbon cycle, it is important to investigate the sources and distribution of iron available for phytoplankton uptake.

Not all forms of iron in seawater are bioavailable. Dissolved iron (defined as < 0.4 µm or < 0.2 µm) is traditionally considered the most biologically accessible phase (Wells et al., 1995). However, particulate matter (defined as either > 0.2 µm or > 0.4 µm) contains another important reservoir of iron that can be solubilized and therefore made available to phytoplankton on timescales of days. Figure 1 is a schematic
of the size spectrum of iron phases in the marine environment. The bioavailability of particulate iron is dependent on the solubility and/or remineralization of the solid phase.

Various mechanisms result in the dissolution of particulate metals in seawater, for example reductive solubilization of iron and manganese oxides under sub- or anoxic conditions (Trefry and Presley, 1982; Canfield, 1989). These oxide (or oxyhydroxide) particulate iron phases are subsequently released into solution during reductive dissolution of the iron (Warren and Zimmerman, 1994). Aeolian dust offers another source of reactive particulate iron; aerosol iron oxyhydroxides can be solubilized via photochemical dissolution in the presence of siderophores and other efficient electron donors (Sunda et al., 1983; Barbeau et al., 2001; Borer et al., 2005). Finally, the biogenic phase contains another source of reactive particulate iron; remineralization of organic matter via grazing and respiration releases biogenic iron (i.e. iron associated with ferritin, porphyrins, etc.) into solution in concert with carbon, nitrogen and phosphorus (Castruita et al., 2008; Hutchins et al., 1993; Hutchins and Bruland, 1994). In growout experiments in the Bering Sea, Hurst and Bruland (2007) used stable isotopes of iron and zinc to demonstrate that solubilization of reactive particulate iron would be the major source of iron to the phytoplankton community in this region.
These reactive particulate iron phases (that can become solubilized by the mechanisms discussed above) are operationally defined by a chemical leach method and referred to as “leachable particulate” iron; the remainder of the particulate phase is referred to as “refractory” iron. Refractory particulate iron is insoluble and unavailable to phytoplankton even on long timescales. This iron exists in a refractory fraction locked within mineral lattices, such as alumino-silicate minerals and crystalline iron oxyhydroxides (Jenne, 1977). In this dissertation the total particulate iron concentration is reported as the sum of the leachable and refractory phases, where only the leachable phase is considered to be bioavailable on a timescale of days. Furthermore, the sum of the dissolved and leachable iron phases, which is considered the total potentially bioavailable iron concentration, is referred to as “reactive” iron.

The partitioning of iron between the dissolved, leachable particulate, and refractory particulate phases (Figure 1) is important to understanding the bioavailability and biogeochemical cycling of this essential micronutrient. Dissolved iron can exist in two different oxidation states in seawater, Fe(II) and Fe(III). However, Fe(II) is thermodynamically unstable in oxygenated seawaters and is rapidly oxidized to Fe(III). The solubility limit for inorganic Fe(III) hydrolysis species in purely inorganic seawater is ~ 0.08 nM (Wu et al., 2001), but
the presence of natural, organic, Fe(III)-binding ligands allows dissolved iron concentrations in seawater to exceed this limit. In fact, Rue and Bruland (1995) demonstrated that greater than 99.9% of dissolved Fe(III) in seawater is chelated by natural organic ligands in surface waters.

Weakly bound, readily leachable particulate iron can become dissolved via a variety of mechanisms, as discussed above. Buck et al. (2007) have suggested that the concentration of strong L₁-type Fe(III)-binding organic ligands dictates the dissolved iron concentration in the presence of an excess of readily leachable particulate iron (Figure 2). Therefore, as dissolved iron is consumed by phytoplankton a small fraction of the leachable particulate iron may become solubilized, maintaining saturation of the low concentration of strong organic ligands.

Rivers are an important source of trace metals to coastal regions (Gibbs, 1973; Martin and Meybeck, 1979). Non-conservative behavior of dissolved metals can lead to the removal of a major part of the riverine-derived dissolved metal pool to the particulate phase during estuarine mixing (Mackenzie and Garrels, 1966). For example, the majority of the dissolved iron found in rivers associated with dissolved humic acids flocculates within estuaries (Sholkovitz, 1978) and is transferred to the particulate phase. In coastal waters, particularly within river plumes or the benthic boundary layers over continental shelf regions, the
particulate concentrations of trace metals such as iron and aluminum can greatly exceed the dissolved concentrations (e.g. Johnson et al., 1997, 1999, 2001; Bruland et al., 2001; Fitzwater et al., 2003). Further evidence of the importance of the particulate trace metal phase in coastal waters is provided in Chapters 1 and 2 of this dissertation, with an emphasis on an estimation of the potentially biologically available leachable particulate iron fraction (Lippiatt et al., 2010a,b).

Review articles and modeling papers dealing with iron sources have stated that there is a paucity of reliable iron data from the world’s rivers, estuaries, and coastal regions (Fung et al., 2000). Particulate iron concentrations dominate associated dissolved iron concentrations in the surface ocean, but particulate iron has received relatively little attention from researchers and modelers (Boyd et al., 2010). Fung et al. (2000), in a landmark paper compiling available iron data into a global ocean iron budget, state “Coastal oceans (depth <200 m or <800 km from a coastline) have been excluded from the analysis because there is little information about inputs from rivers and shallow continental margin sediments...” Eight years later, in another noteworthy iron modeling paper (using only dissolved iron data), Moore and Braucher (2008) state, “One uncertainty in our sedimentary source is missing offshore transport in the model due to eddies and other mesoscale physical processes, which likely play an
important role (Johnson et al., 2005; Lam et al., 2006). Similarly, the model advects only dissolved iron offshore, even though small particulates are also likely to contribute (Lam et al., 2006).” More recently, Boyd et al. (2010) revealed that the relative proportions of different types of particulate iron (lithogenic versus biogenic) present in the water column can influence the rate of remineralization of dissolved iron and significantly impact the biogeochemical cycling of iron. Thus, understanding the magnitude and form of iron delivered from coastal zones to the open ocean is essential to understanding the drivers of primary productivity in nearshore waters, particularly in iron-limited regions (Bruland et al., 2001). This dissertation contributes to the dearth of near-shore reactive iron data as interest in constraining the input of bioavailable iron to the coastal zone and ultimately offshore waters continues to grow.

Due to the extremely low concentration of iron in seawater and the prevalence of iron onboard ships (e.g., rust) and in ambient air (e.g., dust), extreme measures must be taken to avoid contamination and ensure accuracy. Thus, analytical techniques for measurement of dissolved and particulate iron that require minimum sample handling under clean conditions are essential. In this dissertation, dissolved iron was measured onboard ship by flow injection analysis (FIA) following the
method of Lohan et al. (2006). Samples were filtered in-line through acid-cleaned 0.45 µm Teflon membrane polypropylene cartridge filters (that have been shown to be effectively equivalent to a 0.2 um Nuclepore filter; Hurst et al., 2010), acidified with sub-boiled quartz distilled 6 N hydrochloric acid (Q-HCl) to the equivalent of 4 mL of acid per liter of seawater (pH ~ 1.7 – 1.8), and spiked with hydrogen peroxide to convert all Fe(II) to Fe(III). The FIA method preconcentrates Fe(III) in-line on a commercially-available nitrilo-triacetic acid-type resin, followed by elution of the Fe(III) off the column, subsequent Fe-catalyzed production of a colored end product and spectrophotometric detection.

Operationally defining the bioavailable particulate trace metal fraction is not straightforward, and researchers have used various methods for estimating the reactive particulate iron phase in suspended matter. In order to try to mimic natural processes, some researchers have used multiple sequential leaches of particulate samples to characterize specific portions of the labile trace metal pool. For example, Tessier et al. (1979) developed a sequential leach that attempted to divide the particulate trace metal pool into five fractions: exchangeable, bound to carbonates, bound to manganese and iron oxides, bound to organic matter, and residual or refractory. Sequential leaches can be useful for understanding trace metal partitioning in particles and geochemical
cycles (Koschinsky et al., 2001; Turner and Millward, 2002), but there are drawbacks to using these methods for quantifying reactive or potentially bioavailable trace metals in suspended particulate matter. The selectivity of a given extraction step for a specific metal phase is not absolute (Shannon and White, 1991). In addition, these methods are labor intensive, costly, and increase the opportunity for contamination and/or loss of the sample. On the other hand, single-step leach methods reduce experimental error and save substantial time and expense in sample processing and analyses.

I am the second author (and the corresponding author) on a new single-step leach methods paper “Application of a chemical leach technique for estimating labile particulate aluminum, iron, and manganese in the Columbia River plume and coastal waters off Oregon and Washington” (Berger et al., 2008), which presents an improvement on existing single step leach methods in order to estimate the portion of the particulate trace metal pool that is potentially bioavailable on the timescale of phytoplankton generations (days). The method is a modification of the traditional 25% acetic acid (HAc) leach described by Chester and Hughes (1967). Martin et al. (1989) recognized that the Chester and Hughes (1967) leach would not account for the portion of the particulate iron associated with biogenic material. Furthermore, Hurst
and Bruland (2007) performed grow out experiments using stable isotopes of iron and zinc as tracers and detected a portion of their iron and zinc isotope amendments in the operationally “refractory” particulate iron pool, which was defined as the particulate metals that are not solubilized by the 25% HAc leach. The authors suggested that the room temperature, weak acetic acid leach (pH 2) did not release a portion of the more tightly bound biogenic metals associated with phytoplankton. Iron storage proteins, such as ferritin (Marchetti et al. 2008), contain a portion of the particulate iron pool that is available to phytoplankton and should be solubilized by a leach designed to measure the reactive particulate iron phase. Therefore, the leach method presented in Berger et al. (2008), and used for analysis of samples in this dissertation, incorporates a reducing agent (0.02 M hydroxylamine hydrochloride) and a short 10 minute heating step (90 – 95 °C) into the traditional two hour, room temperature HAc leach. The reducing agent is intended to mimic suboxic conditions that can result in the solubilization of particulate iron (as described above), and the heating step was added to denature Fe-containing proteins and solubilize biogenic cellular iron. Although it is operationally defined, this method is thought to solubilize that portion of the particulate iron that is accessible to phytoplankton on a timescale of days. Berger et al. (2008) provides evidence based on analysis of a
plankton/clay standard reference material (BCR 414) that the modified leach accesses a greater portion of the biogenic particulate iron phase than the traditional room temperature HAc leach.

The application of the above leach method to samples collected in the Columbia River, estuary, and near-field plume is described in Chapter 1 of this dissertation. Chapter 1 is published in *Estuarine, Coastal and Shelf Science* (Lippiatt et al., 2010a). This study was part of a major field effort “River Influence on Shelf Ecosystems” (RISE), which consisted of five cruises during spring/summer of 2004, 2005, and 2006. The main objective of the RISE program was to examine how the Columbia River plume influences biological productivity on the Washington and Oregon continental shelves. The Columbia River plume is directed offshore and toward the southwest during upwelling-favorable winds, northward and toward the coast during downwelling-favorable winds, or bi-directionally, with branches both north and south of the river mouth (Hickey et al., 2005). Oregon coastal waters experience greater upwelling stress compared to the waters off of the Washington coast, yet there is higher productivity off of Washington (Landry et al., 1989; Hickey et al., 2009); it has been suggested that the observed difference in productivity is related to the increased presence of the plume off the coast.
of Washington and greater iron availability in this region (Hickey and Banas, 2003; Banas et al., 2009).

The focus of this study was to characterize the source and variability of summertime delivery of leachable and total particulate iron from the Columbia River and estuary to the near-field plume, and to compare the delivery of particulate iron to that of dissolved iron. Summertime concentrations of dissolved iron were previously shown to be most dependent on wind direction; upwelling-favorable winds result in elevated dissolved iron in the plume from an iron enriched coastal seawater endmember (Bruland et al., 2008). Furthermore, data presented in Berger et al. (2008) showed that leachable particulate iron in the Columbia River plume is present in concentrations orders of magnitude higher than associated dissolved iron concentrations.

Analysis of five near-field transects under varying tidal, river flow, and wind conditions indicated that river flow and tidal amplitude are the main drivers of leachable particulate iron concentrations in the near-field plume during the summer months. In particular, the suspended sediment load of the river and the degree of interaction between the plume and estuarine and shelf sediments dictate leachable particulate iron concentrations in the near-field plume, with upwelling during low river flow conditions providing an additional source of reactive iron from the
bottom boundary layer. Near-field plume leachable particulate iron concentrations (normalized to a salinity of 20) averaged 660 nM during either spring tide or high flow compared to 300 nM during neap tide, low flow conditions. In contrast, dissolved iron concentrations in the near-field plume (at a salinity of 20) were orders of magnitude lower, ranging from 2 – 20 nM (Bruland et al., 2008). The results of Chapter 1 indicate that the availability of leachable particulate iron delivered by the Columbia River supplements the much lower concentration dissolved iron and helps to prevent iron limitation in this productive eastern boundary region. Furthermore, this study highlights the importance of considering the leachable particulate iron phase, in addition to the dissolved phase, when quantifying the potentially bioavailable iron concentration in coastal zones.

The second and third chapters of this dissertation are from a major field effort in the Gulf of Alaska during August – September 2007. The major objective of this cruise was to characterize the delivery of iron from the high iron coastal waters to the high-nutrient, lower than expected chlorophyll (HNLC) waters of the central Gulf of Alaska (GoA) via mesoscale anticyclonic eddies. A necessary precursor to examining the impact of eddy-derived iron was to examine the distribution of iron in the coastal waters, which are entrained in these eddies during formation.
Thus, Chapter 2 of this dissertation, which is published in *Marine Chemistry* (Lippiatt et al., 2010b), is a thorough description of the reactive (dissolved + leachable) and total (dissolved + leachable + refractory) iron concentrations in the northern GoA coastal waters.

Coastal northern GoA waters are iron-rich and nitrate poor, in contrast to the nitrate-rich, iron poor HNLC waters of the central GoA. Thus, mixing between these two regimes promotes primary productivity in the region (Stabeno et al., 2004; Ladd et al, 2005; Strom et al., 2006). The mountainous coastline of the northern GoA contains numerous glaciers that erode the underlying bedrock and supply a large amount of sediment to glacial rivers and streams and the wind and buoyancy driven Alaska Coastal Current (ACC). Dissolved iron concentrations in surface transects along the coast between Yakutat and the Kenai Peninsula ranged from 0.5 to 4.1 nM, with an average of about 2 nM. Dissolved iron concentrations were remarkably consistent, regardless of dramatic decreases in salinity (down to ~ 7 in the Alsek River plume). On the other hand, leachable particulate iron concentrations were much higher and more variable, ranging from over 1 µM in the Alsek River plume to less than 5 nM at the base of Cook Inlet. In general, leachable particulate iron values were at least an order of magnitude greater than dissolved iron in these coastal waters. This order of magnitude difference is attributed to
the low dissolved organic carbon concentrations in glacial meltwater (Lafreniere and Sharp, 2004) and the low concentrations of Fe(III)-binding organic ligands in these waters. Dissolved organic carbon is a major source of iron-binding organic ligands and acts to keep iron in solution. As a result of low ligand concentrations, the system’s ability to solubilize the readily available leachable particulate iron is overwhelmed by riverine input. However, the suspended leachable particulate iron remains available for exchange to the dissolved phase and acts as a buffer to maintain a relatively constant (~ 2 nM) source of dissolved iron.

Chapter 3 of this dissertation is titled “Reactive iron delivery to the Gulf of Alaska via a Kenai eddy” and has been submitted for publication in Deep Sea Research Part I (Lippiatt et al., submitted). The Kenai eddy formed in January 2007 near the Kennedy Entrance to Cook Inlet (Rovegno et al., 2009) and was sampled eight months after formation just off the shelf break to the southwest of Kodiak Island, Alaska. Mesoscale anticyclonic eddies in the GoA are an important mechanism for cross-shelf exchange of coastal and offshore waters. Eddies entrain high iron coastal water during formation and generally propagate along the shelf break, interacting with shelf-slope circulation and enhancing cross-shelf exchange (Okkonen et al., 2003). In addition, eventual relaxation of the
eddy can lead to isopycnal rebound, injecting iron and nutrients into the euphotic zone (Crawford et al., 2007).

The Kenai eddy vertical structure was divided into the surface layer ($\sigma_\theta \leq 25.4$), the subsurface core layer ($25.4 \leq \sigma_\theta \leq 25.8$), and the deeper core layer ($25.8 \leq \sigma_\theta \leq 27.0$). These layers correspond to different timescales of delivery to the photic zone. The subsurface core layer is seasonally important as these waters can be brought to the surface with storm-induced mixing, particularly during the winter. The deeper core layer can act as a source of iron to HNLC waters on a longer timescale, due to isopycnal mixing and eventual eddy relaxation and rebound. It is useful to consider the eddy iron inventory in order to compare to other sources of iron in the GoA. Dissolved and reactive iron inventories in the subsurface core were estimated to be $0.46 \times 10^6$ and $2.4 \times 10^6$ mols, respectively. Both the subsurface and deeper cores are shown to be important reservoirs of iron that can promote and sustain primary productivity over the lifetime of the Kenai eddy.

This dissertation is largely focused on the delivery of potentially bioavailable iron, or reactive iron, from freshwater sources to the coastal ocean. In particular, the importance of leachable particulate iron to the
reactive iron phase is emphasized, and the biological implications of the delivery of reactive iron to potentially iron limited waters are discussed.
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Figure 1. Conceptual diagram of the size spectrum of iron phases in the marine environment. All species less than 0.2 µm are considered dissolved, including the truly soluble and colloidal species. Everything larger than 0.2 µm is considered particulate, including biogenic and inorganic iron particles.
Figure 2. From Buck et al. (2007). Dissolved iron versus leachable particulate iron concentrations (open circles) and total iron-binding ligand concentrations (short black bars) for A) the San Francisco Bay system and B) the Columbia River system. Despite large concentrations of leachable particulate iron, dissolved iron concentrations level off as they approach ligand concentrations.
CHAPTER 1:

LEACHABLE PARTICULATE IRON IN THE COLUMBIA RIVER, ESTUARY, AND NEAR-FIELD PLUME


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Leachable particulate iron in the Columbia River, estuary, and near-field plume

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\textbf{ABSTRACT}

This study examines the distribution of leachable particulate iron (Fe) in the Columbia River, estuary, and near-field plume. Surface samples were collected during late spring and summer of 2004–2006 as part of a four River Influence on Shelf Ecosystems (FIESTE) cruise. Tidal amplitude and river flow are the primary factors influencing the estuary-leachable particulate Fe concentrations, with greater values during high flow and/or spring tides. Near the mouth of the estuary, leachable particulate Fe (defined as the particulate Fe solubilized with a 25% acetic acid (pH 2) leach containing a weak reducing agent to reduce Fe oxyhydroxides and a short heating step to access intracrystalline Fe) averaged 770 nM during either spring tide or high flow, compared to 220 nM during neap tide, low flow conditions. In the near-field Columbia River plume, elevated leachable particulate Fe concentrations occur during spring tides and/or higher river flow, with suspended shelf sediment as an additional source to the plume during periods of coastal upwelling and spring tides. Near-field plume concentrations of leachable particulate Fe (as a salinity of 20) averaged 160 nM during either spring tide or high flow, compared to 380 nM during neap tide, low flow conditions. Regardless of tidal amplitude and river flow, leachable particulate Fe concentrations in both the river/estuary and near-field plume are consistently one to two orders of magnitude greater than dissolved Fe concentrations. The Columbia River is an important source of reactive Fe to the productive coastal waters off Oregon and Washington, and leachable particulate Fe is available for solubilization following biological remineralization of the dissolved phase. Elevated leachable Fe concentrations allow coastal waters influenced by the Columbia River plume to remain Fe-reactive and support phytoplankton production during the spring and summer seasons.

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1. Introduction

Sources of iron (Fe) to productive eastern boundary upwelling regimes include rivers (Wetzel et al., 2006; Buck et al., 2007; Bruland et al., 2008), windblown dust (Gao et al., 2003), bottom sediments (Ellard et al., 2004; Lohan and Bruland, 2008), and upwelling of nutrient-rich water along the continental shelf (Bruine et al., 2001; Chase et al., 2002, 2005). In the coastal waters off Oregon and Washington, the Columbia River is an important source of dissolved Fe (Bruland et al., 2008). The Columbia River is the largest river on the west coast of North America, accounting for 77% of the drainage north of San Francisco (Barnes et al., 1972; Thomas and Weatherbee, 2005) and discharging 8 × 10\textsuperscript{6} tons of sediment per year (Buck et al., 2004). The Columbia River plume can be divided southwest and offshore during periods of upwelling-favorable winds, northward along the Washington shelf during downwelling-favorable winds or bi-directionally with branches both north and south of the river mouth (Barnes et al., 1972; Landry et al., 1989; Hickey et al., 2005). Despite greater upwelling stress off the coast of Oregon, there is higher productivity in coastal Washington waters (Landry et al., 1989; Hickey et al., 2009). This difference in productivity between the Oregon and Washington coasts has been suggested to be linked to both the increased presence of the Columbia River plume off the coast of Washington and greater Fe availability in this region (Hickey and Banas, 2003; Banas et al., 2009).

The near-field Columbia River plume forms near the mouth of the estuary as a result of tidal mixing between coastal seawater and river water. The chemical characteristics of the near-field plume vary with upwelling/downwelling conditions, river flow, and tidal phase (Bruland et al., 2008). Summertime concentrations of dissolved Fe are most dependent on wind direction; upwelling-favorable winds result in elevated dissolved Fe in the plume from this enriched coastal seawater source of upwelled water (Bruland et al., 2008). The partitioning of Fe between dissolved and
particulate phases is important to the bioavailability and biogeochemical cycling of this essential micronutrient. The concentration of dissolved Fe in rivers can be several orders of magnitude higher than open ocean concentrations, but within an estuary up to 5% of the dissolved Fe can be lost to the particulate phase (Boyle et al., 1977; Sholl and Vitz, 1978). Rivers, however, can overwhelm the coastal ocean with leachable particulate Fe. During a study in the Columbia River estuary and near-field plume, Buck et al. (1990) have shown that the concentration of strong Li⁺-type Fe(III)-binding organic ligands dictates dissolved Fe concentrations, regardless of the availability of readily leachable particulate Fe. At any moment in time a small fraction of the leachable particulate Fe may become solubilized, maintaining saturation of the low concentration of strong Li⁺-type organic ligands (Buck et al., 2007). Furthermore, Chase et al. (2005), in a study off the Oregon coast during summer, observed nitrate and silicate uptake beyond what the ambient dissolved Fe concentrations should have allowed, indicating that Fe from the particulate phase had become available on a timescale of days. As dissolved Fe is consumed, suspended leachable particulate Fe can become available via a variety of mechanisms, including photochemical processes (Stunda et al., 1983; Barbeaux et al., 2001; Borer et al., 2005), ligand-assisted dissolution (Buck et al., 2007), direct utilization of the particulate phase (Nodwell and Price, 2001), and/or reducing conditions (Landing and Bruland, 1987). Using stable isotopes of Fe and zinc as tracers, Hurst and Bruland (2002) performed grow out experiments that demonstrated active solubilization of particulate Fe and subsequent uptake of this solubilized Fe.

In the Columbia River plume, leachable particulate Fe is present at concentrations orders of magnitude higher than dissolved Fe (Berger et al., 2008). We suggest that the availability of leachable particulate Fe to supplement the much lower concentration of dissolved Fe helps prevent Fe limitation in this productive eastern boundary region influenced by the Columbia River. The focus of this study is to examine the source and variability of summertime leachable particulate Fe, total particulate Fe, and dissolved Fe concentrations in the Columbia River, estuary, and near-field plume under differing tidal and river discharge conditions.

2. Methods

2.1. Field work

Sampling of the Columbia River, estuary, and near-field plume off the California coast and Washington and Oregon was conducted during four cruises as part of the River Influence on Shelf Ecosystems (RISE) program. Pre-RISE was conducted aboard the RV Point Sur from 27 June to 2 July 2004; the remaining cruises were aboard the RV Wenona: RISE-2W from 29 May to 26 June 2005, RISE-3W from 4 to 26 August 2005, and RISE-4W from 21 May to 11 June 2006. Daily mean river discharge for the Columbia River was obtained from the U.S. Geological Survey site at Beaver Army Terminal at Quincy, Oregon (located 86 km upstream of the mouth of the river). Tidal data is from the National Weather Service at Astoria, Oregon. Tidal range (m) is defined as the daily maximum tidal height minus the daily minimum.

Surface mixed layer (from a depth of ~1 m) and benthic boundary layer (BBL) samples (depths less than 23 m) were pumped using a trace metal clean surface “fish” system with a YSI 600 OMS CTD sonde calibrated against the ship Sea-Bird Electronics SBE 911plus CTD system (Bruland et al., 2000; Hickey et al., 2006). Fluorescence and beam attenuation (BAT) data was acquired from the ship’s flow-through system at 4 m depth. Dissolved trace metal samples were filtered in-line through acid-cleaned 0.45 μm PTFE membrane polypropylene capsule filters (GE Osmonics) (Bruland et al., 2005, 2008). Unfiltered samples for particulate metals were pumped directly into a Class-100 clean area and collected in 2 L low-density polyethylene (LDPE) bottles for subsequent off-line filtration.

2.2. Analytical methods

Dissolved Fe was measured onboard by flow injection analysis (FIA); the method is described in detail elsewhere (Lohan et al., 2006). Briefly, samples were acidified with sub-boiled quartz distilled 6 N hydrochloric acid (HCl) to the equivalent of 4 mL of acid per liter of seawater (to pH ~1.7-18) and hydrogen peroxide was added to convert all Fe(II) to Fe(III). The FIA method involves in-line preconcentration of Fe(III) on a commercially available nitro-triacetic acid-type resin (Qiagen), followed by Fe-catalyzed production of a colored end product and spectrophotometric detection. Unfiltered samples for particulate trace metal analysis were filtered (under pressure with filtered nitrogen gas) within a few hours of collection. Seawater samples were filtered through 47 mm diameter 0.4 μm pore size Nuclepore polycarbonate track-etched membrane filters (Whatman) in polypropylene filter sandwiches (MilliporeTM). The 2 L LDPE sample bottles were routinely swirled to prevent particle settling during filtration. The total sample volume filtered ranged from 250 to 2140 mL. Filters were folded into eightths and stored frozen in 2 mL polystyrene acid-cleaned vials. The chemical leach technique applied to the filters follows the procedure of Berger et al. (2008). This two-hour leach applied a 2.5% acetic acid (HAc) 0.02 M hydroxyamine hydrochloride solution with a short (10 min) heating step to 95-95 °C. Prior to leaching, filters were aligned in the vials such that 1 mL of leach solution would not cover the top of the filter and cause undigested particles to float off of the filter and into solution. Following the 2-h leach, the leachate was transferred to a quartz beaker. The transfer of undissolved particulate matter from the filter into the quartz beaker was avoided by pipetting the leachate out of the vial from the outside of the filter. Leachates were then acidified with 100 μL of sub-boiled quartz distilled nitric acid (HNO₃) and brought to dryness. The residue was digested with another 100 μL of HNO₃, heated to dryness, and subsequently dissolved and transferred to a 15 mL LDPE bottle with 8 mL 1 N HNO₃.

It has been shown that the traditional 25% HAc room temperature leach does not completely solubilize the intracellular Fe within phytoplankton (e.g. Fertilin, Marchetti et al., 2008), whereas the modified leach technique used in this study addresses both the reactive Fe coatings on river-derived particles and the pool of intracellular Fe within phytoplankton (Hurst and Bruland, 2007; Berger et al., 2008). We suggest that this leach accesses a more representative portion of the reactive particulate Fe phase. Leachable particulate Fe is defined as the portion of the particulate Fe phase that is solubilized by the above leach, and is suggested to be a source of potentially bioavailable Fe, namely, the reactive fraction of the particulate phase which can become dissolved via various mechanisms on the timescale of phytoplankton blooms (1–10 days) (Berger et al., 2008). Total reactive Fe refers to the sum of dissolved and leachable particulate Fe.

Refractory particulate Fe concentrations were measured by microwave bomb-digestion of the leached filters. Filters were transferred to PFA Teflon bombs with pressure relief valves (Savilnex, Minnetonka, MN). The bombs were closed and sample concentrated trace metal grade (TMG) HNO₃, 2 mL concentrated HCl, and 100 μL concentrated TMG hydrofluoric acid. The bomb solutions were transferred to a 15 mL LDPE bottle and diluted with 8 mL 1 N TMG HNO₃.
Leachable and refractory Fe concentrations were measured using inductively coupled plasma-mass spectrometer (ICP-MS). Solutions were transferred to acid-cleaned 7 mL HDPE vials and spiked to an internal standard concentration of 1 ppb Ga. Multi-element standards were made from 1000 ppm stock solutions (SPI Supplies, NJ; Fisher Scientific) in 1 N (HNO₃) spiked with an internal standard concentration of 1 ppb Ga. The sample introduction system consisted of a PFA ST torch (Elemental Scientific, Omaha, NE) and PFA spray chamber (Hurst and Bruland, 2007, 2008; Burger et al., 2008). Leachable and refractory particulate Fe is reported as the sum of the concentrations in the 0.4 μm and 10 μm filters. Total particulate Fe indicates the sum of the leachable and refractory phases. Filter blanks were processed the same as samples except that no seawater passed through the filters. The average leach filter handling blank was 0.27 ± 0.25 nM for 1.4 μm filters and 0.30 ± 0.30 nM for 10 μm filters. Leach on replicate filters indicated a relative uncertainty of ±5%. Although there is no certified value for partial sediment digests, the analytical procedure has been verified by total digests of standard reference materials. Particulate Fe, Al, and Mn values were within the range of error of the certified values for river sediment (SRM 2704, National Institute of Standards and Technology, USA, percent recoveries: Al 98.9%, Fe 90.1%, Mn 99.2%) and marine sediment (BCSS-1, National Research Council of Canada, percent recoveries: Al 88.1%, Fe 94.0%, Mn 90.2%).

### 3. Results

Five surface transects (2004T10, 2005T4, 2005T8a, 2006T4, and 2006T11) across the near-field Columbia River plume were conducted (Fig. 1). All of the transects except for 2006T4 were during periods of upwelling-favorable winds. In order to characterize the estuary/river endmember, surface estuary and/or river samples (denoted as 2004F1, 2005F1, 2005F3, 2006F4, and 2006F5) were collected within a few days of each transect (with the exception of 2006T11, see below). In addition, BBL samples were collected at 15–22 m depth over the inner shelf on 21 August 2005. Estuary, river, and BBL station locations are shown on Fig. 1; salient features of the transects, estuary/river samples, and BBL samples are listed in Tables 1, 2, and 3, respectively. The following results are divided into low and high river flow conditions and subdivided based on tidal amplitude.

For each dataset, near-field plume leachable particulate and dissolved Fe values and surface estuary/river leachable particulate Fe concentrations are reported. Particulate size-fraction data is not reported, but in general the leachable particulate fraction was evenly distributed between the large and small size-fractions in both the estuary/river and near-field plumes. It is unknown whether this distribution is an artifact of filter loading, which may change the effective pore size of the filters.

For comparative purposes, the dissolved and leachable particulate Fe concentrations for the near-field transects are reported for a common salinity of 20 (Table 1). Excel’s linear regression tool was used to interpolate the plume Fe data to a salinity of 20. Regression $r^2$ values averaged 0.8 ± 0.1 for both dissolved and leachable Fe when plotted versus salinity.

#### 3.1. Low river flow (less than 6000 m$^3$ s$^{-1}$)

##### 3.1.1. Spring tide

Transact 2004T10 was sampled on the outgoing ebb of a spring tide. At a salinity of 20, the plume had 820 nM leachable particulate Fe and 2800 nM total particulate Fe, compared to 17 nM dissolved Fe. 26.6% of the total particulate Fe pool was leachable. Fluorescence and beam attenuation (BAT) were decoupled within the plume, indicating that the leachable particulate Fe phase was dominated by non biogenic suspended particulate matter (Fig. 2).

Two days prior, estuary samples were collected on the ebb tide (2004E1); leachable particulate Fe concentrations at stations 3–5 were all greater than 1000 nM and surface salinities increased towards the river mouth from 1.8 at station 3 to 27.9 at station 5 (Table 2).

The second low flow/spring tide near-field plume, 2005T8a, was sampled during the ebb of a strong spring tide. Plume leachable particulate Fe concentrations were 720 nM and dissolved Fe was 21 nM (Fig. 3). River samples were collected during the flood of a spring tide and estuary samples were collected at high tide (2005E3). River samples had leachable particulate Fe of 1000 and 1500 nM, while estuarine samples had leachable particulate Fe of

### Table 1

<table>
<thead>
<tr>
<th>Transect</th>
<th>Cruise</th>
<th>Date</th>
<th>River Flow (m$^3$ s$^{-1}$)</th>
<th>Total Suspended (μM)</th>
<th>Leachable Fe (nM)</th>
<th>Dissolved Fe (nM)</th>
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<td>pre-RE</td>
<td>4-7-04</td>
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<td>820 (841)</td>
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<td>4220</td>
<td>300 (8.95)</td>
<td>-</td>
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<td>RE-3W</td>
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<td>RE-4W</td>
<td>27-May-06</td>
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<td>2500 (0.72)</td>
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<td>11 648</td>
<td>490 (8.81)</td>
<td>2000 (0.84)</td>
<td>15 (0.87)</td>
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</table>

* Leachable particulate, total particulate, and dissolved Fe concentrations have been interpolated to plume salinity = 20 based on a linear regression of the plume samples. Regression $r^2$ values are given in parentheses. The dissolved Fe data for 2005T8a had too much scatter to provide a reliable correlation with salinity.
Table 2
Salient features of the estuary/river samples

<table>
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<th>Samples</th>
<th>Date</th>
<th>River Flow (m^3/s)</th>
<th>Tidal Amplitude (m)</th>
<th>Tidal Phase</th>
<th>Station</th>
<th>Salinity</th>
<th>Leachable Fe (nM)</th>
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950 and 690 nM at salinities of 10 and 9.3, respectively (Table 2). River flow was 5936 m^3/s during the 2004T1 tract versus 4284 m^3/s during 2005T8a; 2004T10 plume leachable particulate Fe was elevated compared to 2005T8a leachable particulate Fe, despite larger tidal amplitude during 2005T8a. Estuary 2004E1 samples had higher leachable particulate Fe concentrations than 2005E3, in accordance with higher river flow.

Samples were collected from two stations within the inner shelf BBL during upwelling conditions (Bruland et al., 2008), two days after 2005T8a; the samples had high salinity (33.8), low temperature (7.6–7.7 °C), and were oxygen depleted (52.2 µmol kg^-1). Dissolved and leachable particulate Fe concentrations were elevated at 28 ± 2 and 660 ± 8 nM, respectively (Table 3).

3.1.2. Neap tide

2005T4 was surveyed during neap tide, low river flow conditions (Fig. 4). Plume leachable particulate Fe was 300 nM, the lowest of the five transects. Nevertheless, leachable particulate Fe was extremely elevated compared to a dissolved Fe concentration of 5.5 nM 2005E2 samples were collected during the flood conditions of a neap tide. Samples from estuary stations 5 and 4 were fairly consistent, with surface salinities ranging from 2.9 to 4.0 and leachable particulate Fe ranging from 330 to 450 nM. Station 5, closer to the mouth of the estuary, had a comparatively higher average salinity of 12.6 and slightly lower average leachable particulate Fe concentration of 320 nM.

3.2. High flow (greater than 6000 m^3/s)

3.2.1. Spring tide

2006T4 was sampled during an intense spring tide. At a salinity of 20 leachable particulate Fe was 610 nM, though the maximum plume core leachable particulate Fe was the highest of all 5 near-field transects (1012 nM at a salinity of 16.8; Fig. 5): plume dissolved Fe was 14 nM and total particulate Fe was 2500 nM. The total particulate Fe phase was 24.3% leachable. 2006E4 estuary samples were collected during the flood and high tides, while 2006E4 river samples were collected during the ebb tide. Surface salinities at stations 1–4 were all <1.0 and leachable particulate Fe ranged from 820 to 1200 nM. At station 5, leachable particulate Fe was 750 nM at a surface salinity of 3.0. Total particulate Fe in the estuary/river ranged from 3100 to 6300 nM, and total particulate Fe was 22 ± 3 leachable (Table 2). Although the tidal amplitudes of 2005T8a and 2006T4 were about equal, river flow was much greater during 2006T4. However, river plume leachable particulate and dissolved Fe concentrations were greater during the low flow 2005T8a, which was surveyed during upwelling-favorable winds (Bruland et al., 2008). Estuarine samples had comparable leachable particulate Fe concentrations during the two transects.

3.2.2. Neap tide

Sampled during a neap tide, 2006T11 had 490 nM leachable particulate Fe, 2000 nM total particulate Fe, and 15 nM dissolved Fe (at a salinity of 20; Table 1, Fig. 6). The total particulate Fe phase was 23% leachable. Dissolved Fe and leachable particulate Fe concentrations in the neap tide, high flow plume core of 2006T11 were greater than those found in the neap tide, low flow 2006T4 plume. Unlike the other datasets, samples were not collected in conjunction with 2006T11. 2005E5 is a conservative estimate of leachable particulate Fe concentrations in the estuary endmember during 2006T11, as river flow in June 2005 was about half what it was in June 2006 (Table 1). 2005E5 samples were collected during both the rising and falling tides. At stations 3 and 4 conditions were fairly consistent: station 3 surface salinity and leachable particulate Fe
averaged 0.5 and 1000 nM, respectively, while salinity increased and leachable particulate Fe decreased at station 4 (average salinity was 1.7 and leachable particulate Fe 807 nM). At station 3, surface salinity was much higher on the rising tide (216 versus 3.1 on the falling tide) and leachable particulate Fe averaged 6-90 nM.

4. Discussion

The Columbia River plume is an important source of macro- and micronutrients to the coastal waters off Oregon and Washington, which leads to high primary and export production in this region. This river plume enhances cross-shelf transport of reactive Fe-rich waters (Franz et al., 2009) potentially exporting Fe offshore. Under downwelling-relaxation conditions, the Columbia River near-field plume may have 2.5-6 μM nitrate and 2-13 nM dissolved Fe (Bruland et al., 2008). Based on Redfield stoichiometry and luxury Fe uptake under Fe-replete conditions (an Fe:C uptake ratio of 100 μmol Fe: mol C; Sundal and Huntsman, 1995), a biological drawdown of about 4 nM Fe would be expected to complement the nitrate drawdown. Thus, we suggest that it is the additional large source of reactive particulate Fe that allows regions influenced by the Columbia River to remain Fe-replete. This study provides data

Fig. 3. Near-field transect 2005T8a: A) salinity (gray circles) and leachable particulate Fe (dark triangles), and B) temperature (gray circles) and dissolved Fe (dark diamonds).

to confirm the suggestion of Chase et al. (2005), on the basis of dissolved Fe and nutrient data, that phytoplankton blooms off Oregon must be utilizing a source of reactive particulate Fe. Results from this study in conjunction with others, such as Lam et al. (2006)
Fig. 5. Near-field transect 2006T4: A) salinity (gray circles) and leachable particulate Fe (dark triangles), and B) temperature (gray circles) and dissolved Fe (dark diamonds).

and Blain et al. (2008) that show offshore transport of reactive Fe, indicate that it is very important to consider the leachable particulate Fe source when investigating the biogeochemical cycling of Fe.

Depending on the local sediment source, the ambient concentration of leachable particulate Fe can be highly variable. Hurst and Bruland (2008) measured 150 nM leachable particulate Fe in the San Francisco Bay plume core in the summer and 740 nM in the winter, resulting in 2% and 57% leachable Fe, respectively; their study also used a traditional 25% HCl leach, which they suggested does not access all of the potentially bioavailable particulate intracellular Fe. In contrast, summertime Columbia River plume samples in this study had an average 590 nM leachable Fe and were about 26% leachable. Compared to the Columbia River watershed, San Francisco Bay is more influenced by tidal exchange of coastal water and winter runoff than spring snowmelt, which results in lower summertime leachable Fe concentrations in the San Francisco Bay plume entering the Gulf of the Farallons. Although there is seasonal variability in the flow of the Columbia River, its summertime flow is still substantial and has a strong influence on the Columbia River plume throughout the summer resulting in high concentrations of leachable particulate Fe. Additional estuarine studies have reported elevated leachable particulate Fe concentrations (i.e. Turner and Millward, 2000; Hage, 2003; Hinz et al., 2008; Lippert et al., submitted for publication). Although reactive particulate Fe concentrations are extremely variable across these studies, in each region the reactive particulate Fe concentrations overwhelm dissolved Fe concentrations and should be considered in Fe biogeochemical cycling.

4.1. Plume formation

The formation of the near-field Columbia River plume occurs as coastal seawater is mixed with river water at or near the mouth of the estuary (Barnes et al., 1972). Near-field plume salinity ranges from 10 to 25, varying with tidal amplitude and river flow (Nash et al., 2009). Depending on the direction and strength of wind forcing, the summertime coastal seawater endmember may be cold, high salinity, high nutrient, high Fe upwelled water, compared to warm, intermediate salinity, lower nutrient, lower Fe California Current surface seawater during downwelling conditions (Lohan and Bruland, 2006); Bruland et al., 2008). Dissolved Fe concentrations in the river (at surface salinities less than 1) ranged from 2 to 210 nM (Bruland et al., 2008); in the estuary (stations 3–5) dissolved Fe varies from 0.4 to 32 nM (Lohan and Bruland, 2006). Compared to rivers in eastern North America, the Columbia River has a lower concentration of humic substances which results in relatively low dissolved Fe concentrations (Boyle et al., 1977; Bruland et al., 2008).

However, the Columbia River provides a large source of leachable particulate Fe to the near-field plume, overwhelming the availability of strong L-type Fe-binding organic ligands. Fig. 7 shows dissolved Fe versus leachable particulate Fe for the five near-field plume transects. The dissolved Fe concentrations appear to be "capped" around 30–45 nM, which is in reasonable agreement with the leachable Fe concentrations for the near-field plume (Buck et al., 2007). Interestingly, the highest dissolved Fe values occurred during the 2006T11 transect, which was a time of intense upwelling and spring tides, where there was evidence of Fe(II) being mixed into the surface waters from the benthic boundary layer (Lohan and Bruland, 2008). In this case dissolved Fe(II) could exist in excess of the concentration of strong Fe(II)-binding organic ligands (Lohan and Bruland, 2008).

Unlike dissolved Fe which varies with wind stress, suspended sediment concentration, and the degree of interaction between the plume and estuarine shelf sediments, vary primarily with river
flow and tidal amplitude. It is these two factors that largely influence the plume leachable particulate Fe concentration.

4.1. Effect of river flow

Over three seasons of sampling, the highest river flow was observed in spring 2005. Suspended particulate loads generally increase with river flow (Spahr et al., 2009), and thus higher flows deliver more sediment from the river to the plume (for a given salinity). Transects 2005T4 and 2005T1 were both sampled under high flow conditions and resulted in leachable Fe concentrations of 610 nM and 490 nM respectively. Transect 2004T10 had a smaller tidal amplitude but 1.4 times greater river flow than 2005T8a resulting in a leachable particulate Fe concentration 100 nM greater than that in 2005T8a. In contrast, despite having similar tidal amplitudes, the low flow 2005T10 had higher leachable particulate Fe (720 nM) than the high flow 2005T4, indicating an additional source to the plume during this low river flow period. During high river flow, the elevated suspended sediment concentration in the freshwater plume exiting the mouth of the estuary is highly stratified, which reduces the interaction of the plume with the BBL (Spahr et al., 2009, Nash et al., 2009). As a result, resuspended shelf sediments are not appreciably entrained in the plume during high river flow (Spahr et al., 2009). On the other hand, low river flow conditions result in less stratified near-field plume allowing the potential entrainment of resuspended shelf sediments.

4.1.2. Effect of tides

In coastal regions tidal amplitude can have a large effect on suspended sediment concentration and thus leachable particulate Fe concentrations. Within the Columbia River estuary endmember, there is net sediment resuspension during spring tides and settling during neap tides (Jay and Smith, 1990). The incoming spring tide acts to mobilize periphery sediments, which are then delivered to the plume with the outgoing tide (Spahr et al., 2009) low flow, spring tide plumes result in a weakly stratified, partially-mixed estuary which leads to significant entrainment of resuspended shelf sediments into the plume (Spahr et al., 2009). Although river flow during 2003T4 was very similar to that during 2003T4a, leachable particulate Fe was more than 400 nM higher (about 2.5 times) in 2003T4a due to a strong spring tide. The mobilization of periphery sediments in the river and estuary is evidenced by high leachable particulate Fe in 2003T4a samples. Thus, it appears that during neap tides, high river flow conditions are necessary in order to create a plume with elevated leachable particulate Fe (i.e. 2006T11 versus 2005T4a).

Similar to dissolved Mn (Aguilar-Isla and Redford, 2006), both river flow and tidal amplitude have a great effect on leachable particulate Fe concentrations. There appear to be two different scenarios: lower leachable particulate Fe (>300 nM at a salinity of 20) during neap tide, low flow conditions (i.e. 2005T4, Figs. 4 and 8), and higher leachable particulate Fe (~600–730 nM at a salinity of 20) during higher flow or spring tide conditions (Fig. 8). Leachable particulate Fe concentrations are always one to two orders of magnitude greater than dissolved Fe, but there is about a factor of three variation in plume leachable particulate Fe concentrations (~280–630 nM) depending on tidal amplitudes and river flow. In the spring/early summer months (during high river flow), plume sediments and thus high plume leachable particulate Fe concentrations are primarily from the river, while later in the summer (during low flow) the seabed may become a significant leachable particulate Fe source, depending on the tidal phase. The plume sediment source (either the river, seabed, or both) does not appear to affect the percentage of the total particulate Fe phase that is leachable (see Section 4.1.3). The effects of river flow and tides act in concert resulting in high leachable particulate Fe in the plume throughout the spring and much of the summer period.

4.1.3. Upwelling-favourable winds and resuspended sediments

Although the combination of river flow and tidal amplitude appears to be the primary mechanism by which sediments are delivered to the near field plume, upwelling favourable winds can
provide an additional input of resuspended shelf sediments to the plume (see Schematic Fig. 5). The fieldwork completed in August 2005 by Spath et al. (2009) and Nash et al. (2009) was during a period of upwelling-favorable winds (this time period corresponds to 2005/3a: Bruland et al., 2008). The upwelling movement of cold, high salinity, high nutrient water contributes to the mix of BBL waters into the plume. The combination of upwelling and lower river flow results in a less stratified plume into which these resuspended sediments can be entrained (Spath et al., 2009; Nash et al., 2009) with BBL waters acting as a source of leachable particulate and dissolved Fe to the plume. Benthic boundary layer samples collected during upwelling conditions (Bruland et al., 2008) in conjunction with J00/01/03b had high salinity and were elevated in both dissolved and leachable particulate Fe (Table 3). Benthic boundary layer samples were not collected in conjunction with 2004/07/10, but upwelling, low flow, spring tide conditions most likely resulted in the entrainment of resuspended shelf sediments and contributed to the observed high leachable particulate and dissolved Fe concentrations in the plume. The possible entrainment of BBL sediments into the plume during higher flow or near tide conditions in conjunction with upwelling is uncertain based on the lack of available data. It is likely, however, that increased stratification associated with higher river flows effectively cuts off the source of resuspended BBL sediments. The effect of upwelling in combination with low flow and spring tide conditions resulted in elevated leachable particulate Fe concentrations within the near-field Columbia River plume as indicated in Figure 4B. Bruland et al. (2008) measured leachable particulate Fe in the mid-shelf BBL off the coast of Washington and Oregon during upwelling conditions (128 ± 54 and 84 ± 28 μM, respectively). Near-field BBL leachable particulate Fe concentrations over the inner shelf of the Columbia River plume reported in this study were 660 ± 8 μM, much higher than the values over the mid-shelf north and south of the river mouth. This suggests that the increased presence of the river plume over the BBL stations results in sediment deposits that act as a source of sediments back into the plume during upwelling and low flow, spring tide conditions.

Although total particulate Fe data was only measured on three near-field transects and in one estuary/river sampling, the percentage of the total particulate Fe that is leachable is fairly consistent at 26 ± 4% in the plumes (at a salinity of 20) and 22 ± 3% in estuary, 2004/07/10 samples. This consistency between the percent leachable in the plumes and river/estuary is likely due to the short residence time of river/estuary Fe in the near-field BBL (Spath et al., 2009), resulting in minimal chemical alteration of sediments that may eventually become entrained into the river plume. Leachable particulate Fe/Al ratios (molar ratio) averaged 1.2 ± 0.1 in the BBL samples, near the plume. Getting to the inner shelf BBL, resuspended sediments in the vicinity of the plume do not undergo significant chemical transformation (Fe data not reported, see Brown and Bruland, 2009). Total particulate Fe/Al ratios were consistent between the 2004/07/10, 2004/07/14, 2004/07/21 and 2004/07/28, averaging 0.29 ± 0.03 in the river/estuary and 0.33 ± 0.02 in the surface transects. Leachable Fe/Al ratios were lower and closer to the crustal average (0.33, Taylor, 1954), indicating the enrichment of Fe in reactive (oxy-)hydroxide coatings.

4.2. Riverine Fe delivery to coastal Oregon and Washington.

One of the main objectives of the RISE program was to examine the influence of the Columbia River plume on the chemistry of the coastal regions off Oregon and Washington. The delivery of macronutrients, dissolved Fe, dissolved Mn, and dissolved and leachable particulate Al has been detailed elsewhere (Aguilera-Terlan and Bruland, 2006; Loahan and Bruland, 2006; Bruland et al., 2009). This study shows that leachable particulate Fe in the near-field plume is an order of magnitude higher than dissolved Fe. Based on average river flow (1750 m³/s, USGS) and the average concentration at the mouth of the estuary (station 5), an annual flux of 0.8 × 10³ mol of leachable particulate Fe is delivered to the near-field plume. The delivery of this large source of reactive Fe to the Columbia River plume influences the productivity of the coastal ocean. The stratification, temperature, and macro- and micronutrient loading of the freshwater plume act to promote phytoplankton growth in the near-field plume (Hickey et al., in press). In addition, the Columbia River plume increases cross-swell transport of nutrient and Fe-rich waters (Fanan et al., 2009), potentially exporting reactive Fe out to the California Current system.

This study shows that tidal phase and river flow are the primary factors influencing reactive Fe concentrations in the near-field plume, with an additional source of reactive Fe from the plume, during upwelling conditions. During downwelling-favorable winds, the Columbia River plume is directed northward and towards the coast, delivering this Fe and nitrate-rich water to the near-shore waters off Washington. When winds shift to upwelling-favorable, the plume waters off Washington are advected farther offshore. During upwelling-favorable winds the plume is directed southwest and away from the Oregon coast. Furthermore, during downwelling-favorable winds, the plume does not influence the coastal waters off Oregon. Thus, the delivery of reactive Fe in plume waters to the Washington coast can potentially influence a larger area and have a greater overall impact than the presence of the plume off of Oregon during upwelling.

There is a definite lack of Fe data from the world’s rivers, estuaries, and coastal regions (Tang et al., 2003). This work contributes to the ongoing effort to characterize the riverine delivery of reactive Fe. In particular, it reveals the importance of considering the leachable and labile particulate Fe phase, in addition to dissolved Fe, when quantifying reactive or biologically available Fe in the coastal zone. Because of the requirement of Fe for photosynthesis, the biogeochemical cycling of Fe is coupled to that of carbon and nitrogen (Falkowski, 1997). Coastal zones cover approximately 1% of the global ocean’s surface area yet are estimated to account for as much as 40% of the global ocean export production (Muller-Karger...
et al., 2005; Hales et al., 2006). In particular, the eastern boundary of the North Pacific has been identified as a strong sink for $\text{P}_{\text{OC}}$, where organic carbon export may account for 5% of the annual uptake of $\text{P}_{\text{OC}}$ over the entire basin (Hales et al., 2005). The delivery of large quantities of reactive Fe from the Columbia River is arguably essential to sustaining the productivity required to support the carbon export observed in near-shore waters off Oregon and Washington. The data from this study indicate the significance of the input of reactive Fe from rivers to the coastal zone and ultimately offshore waters. In addition to riverine inputs, continental margin reactive Fe has been shown to be delivered to the open ocean (Lam et al., 2004; Lam et al., 2006; Lam and Bishon, 2008). This particulate Fe source has shown to have a long enough residence time to affect productivity hundreds of kilometers away from the source (Lam et al., 2006). In regions with large river plumes and those that are affected by upwelling there is the potential for a larger source of reactive Fe to be transported offshore. The residence time of continental-derived reactive particulate Fe versus dissolved Fe will ultimately determine the impact of the particulate Fe phase on open ocean productivity. The incorporation of the reactive particulate Fe phase into the Fe component of biogeochemical models has been largely neglected (Moore and Braucher, 2008), and should be addressed in future studies.

5. Conclusions

This study confirms the significance of the leachable particulate Fe phase to total biologically available Fe concentrations in the near-field Columbia River plume. Leachable particulate Fe varies primarily with tidal phase and river flow, with additional inputs to the plume during upwelling conditions. As depicted in Fig. 9, the plume acts as a source of sediments to the inner shelf, particularly during high flow conditions. Significant entrainment of resuspended shelf sediments has been documented during upwelling and low flow, spring tide conditions. The plume always has leachable Fe concentrations at least an order of magnitude higher than corresponding dissolved Fe concentrations, which appear to be limited by the availability of $\text{L}_{\text{Fe}}$ strong Fe-binding ligands (Fig. 7; Bicket et al., 2007). Leachable particulate Fe in the near-field plume is available for solubilization following biological breakdown of the dissolved phase. This study has shown that elevated leachable Fe concentrations allow coastal waters influenced by the Columbia River plume to remain Fe-replete and support phytoplankton production during the spring and summer seasons.

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References


CHAPTER 2:

THE DISTRIBUTION OF REACTIVE IRON IN NORTHERN GULF OF ALASKA COASTAL WATERS


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The distribution of reactive iron in northern Gulf of Alaska coastal waters

Sherry M. Lippiatt, Maeve C. Lohan, Kenneth W. Bruiland

1. Introduction

The central Gulf of Alaska (GoA) is a high-nutrient, lower than expected chlorophyll (HNLC) region, in which primary productivity is limited by the supply of iron (Fe) (Martinelli et al., 1999; Boyer et al., 2004). In contrast, the coastal GoA waters are fed by Fe-rich runoff from glacial rivers and streams. Stommel et al. (2006), in a study in the northern GoA, observed a cross-shelf gradient in phytoplankton biomass, cell size, species composition, macronutrient consumption, growth rate, and nitrogen limitation that they attributed to water P availability over the inner shelf. The high productivity observed over the shelf is suggested to be a result of the exchange and mixing of Fe-rich coastal waters with macronutrient-rich offshore waters (Sambrotto and Lorenzen, 1980; Stabeno et al., 2001). However, Fe data in coastal waters to support these ideas is scarce (e.g., Wu et al., 2000).

Circulation in the GoA is controlled by the cyclonic Alaska Gyre. This upwelling gyre is bordered by the West Wind Drift to the south, the Alaska Current to the east, and the Alaskan Stream to the north and west. Transport over the northern GoA shelf is dominated by the Alaska Coastal Current (ACC), which hugs the coast from the Bering Strait to the Aleutian Islands. The ACC is a narrow, swift current forced largely by coastal winds and freshwater runoff (Stabeno et al., 1995, 1999). Maximum freshwater discharge to the ACC generally occurs in late summer/early fall, with glacial melt and increased precipitation in the form of rain (Royer, 1982; Stabeno et al., 2004; Wernigarter et al., 2005). Maximum monthly-averaged downwelling favorable winds occur in January, resulting in Ekman-layer transport of macronutrient-rich, Fe-poor basin water onto the shelf (Ladd et al., 2005). Downwelling winds are relaxed during the summer months, and cross-shelf exchange is dominated by intermittent upwelling, tidal and topographically-induced mixing, and mesoscale eddies impinging on the shelf break (Ladd et al., 2005).

The mountainous coastline of the northern GoA contains numerous glacial rivers and streams that deliver a substantial amount of sediment to the ACC (Peey et al., 1979; Milliman and Syvitski, 1992). The buoyancy-driven ACC transports particulate material discharged from the coastal rivers westward alongshore (Stabeno et al., 2004). Sediment discharge to the ACC is dominated by the Copper River, estimated at 107 ± 107 km² yr⁻¹ (Battaglin 1984). Significant sediment discharge also occurs east of Kayak Island where drainage from the Bering, Conoco, and Malaspina glaciers and the Alsek River results in a distributed freshwater runoff that spills the northern GoA (Fecht and Cline, 1977; Molina and Carlson, 1976). Offshore transport of near-bottom suspended sediment can occur in deeper waters, augmented by downwelling-favorable winds forcing advection off the shelf (Fecht et al., 1975; Lam et al., 2006).

Poulton and Rainwell (2005) have shown that a significant fraction of the Fe (oxyhydr)oxide material in glacial runoff is contained in
potentially bioavailable surface-bound nanoparticles. Although dissolved Fe is considered more biologically accessible, reactive particulate Fe can dominate the total biologically available Fe pool in coastal waters (de Baar and de Jong, 2001; Berger et al., 2008). Raison et al. (2006) estimate a "highly reactive" Fe (oxyhydroxide) flux from ice sheets and glaciers to the coastal ocean (accounting for estuarine loss) of 0.2 to 2 Tg yr⁻¹, compared to estimates of riverine dissolved Fe input ranging from 0.2 to 2 Tg yr⁻¹ (Wollast and Mackenzie, 1985; Haese, 2000; de Baar and de Jong, 2001). Thus, particularly in coastal regions dominated by glacial input, it is essential to measure the reactive (leachable) particulate Fe phase in addition to dissolved Fe, as the solubilization of even a fraction of the reactive particulate Fe phase can dominate potentially bioavailable Fe concentrations (Lyons et al., 2010).

In the northern GoA, the buoyant freshwater discharge is rich in particulate Fe, yet nitrate poor due to its glacial origin (Reeburgh and Kipphat, 1986). As a result, the upper water column across the GoA shelf exhibits Fe-replete conditions but is nitrate depleted throughout the summer months (Childress et al., 2005). Evidence of this nearshore-offshore gradient in Fe availability along the GAK line (Fig. 1, T4) was hypothesized by Strom et al. (2006) and has recently been verified by Wu et al. (2009). Based on phytoplankton community structure and response to macronutrient addition, Strom et al. (2006) suggested that during spring and summer the outer-shelf region of the coastal GoA transitions into Fe-stressed HNLC waters, whereas the inner and mid-shelf phytoplankton communities become macronutrient (nitrate) limited. Thus, mixing between the ACC and HNLC waters is required to maintain the high productivity observed in this region of the GoA (Stabeno et al., 2004; Ladd et al., 2005; Strom et al., 2006).

The study presented here characterizes these two contrasting regimes; the high Fe, low nitrate coastal waters and the low Fe, high nitrate offshore waters. The emphasis is on characterizing the distribution of reactive Fe over a broad geographical region of the coastal waters of the GoA during the high discharge, late summer months of August and September, 2007.

2. Methods

2.1. Sample collection

Sampling took place aboard the R/V Thomas G. Thompson in the northern GoA from 15 August to 20 September 2007. Surface seawater was collected along five transects (Fig. 1) using a trace metal clean surface tow fish system pumped into a Class-100 clean area (Bruandet et al., 2005). Underway temperature and salinity data were obtained using a YSI 600 OMS CTD stow attached to the surface tow fish. Subsurface samples were collected at seven stations from GoFlo bottles tethered to a Kevlar line. All aspects of sample processing and analysis were completed following rigorous trace metal clean methods. Chlorophyll a (Chl-a) samples were collected on Whatman GF/F filters, extracted for ~24 h in 7 mL of 90% acetone (−20 °C) and analyzed with a Turner Designs 10-AU fluorometer calibrated with pure Chl a (Sigma) using the non-acidification technique (Weichumeyer, 1994).

2.2. Analytical Methods

2.2.1. Dissolved Fe analysis

Dissolved Fe samples were filtered in-line through acid-cleaned 0.45-μm Teflon™ membrane polypropylene capsule filters (GE Osmonics). Dissolved Fe was measured onboard ship by flow injection analysis (FIA): the method has been described in detail elsewhere (Johan et al., 2006). Briefly, samples were acidified (pH ~1.7-1.8) with sub-boiled quartz distilled 6% hydrochloric acid (HCl) and hydrogen peroxide was added to completely oxidize Fe(II) to Fe(III). The FIA method involves in-line preconcentration of Fe on a commercially-available nitro-triacetic acid-type resin (Qasen), followed by Fe-catalyzed production of a colored solution and spectrophotometric detection. Average blank values for samples above 1 nM were 0.038 ± 0.0024 nM Fe (n = 50), with a detection limit (defined as three times the standard deviation of the blank) of 0.072 nM while for samples with a concentration less than 1 nM the blank was 0.061-0.008 nM (n = 10) resulting in a detection limit of

![Fig. 1. Map of the study area. Depth profiles are indicated by open circles and Cooper River stations are indicated by black circles. The star indicates the division between T1a and T1b. Depth contours are 100 m to 500 m. Inset shows the major currents in the region.](image)

38
0.024 nM. To validate the system, SAF standards were measured regularly. The average value of SAF surface water was 0.002 ± 0.005 nM Fe (n = 13) and for deep water 0.02 ± 0.006 nM Fe (n = 13); these concentrations agree well with the original consensus values of 0.007 ± 0.043 nM and 0.01 ± 0.007 nM, respectively (Johnson et al., 2002), and the methods were validated using the GEOCAPS Program of 0.094 ± 0.008 nM and 0.093 ± 0.009 nM, respectively (GEOCAPS Website; www.geocaps.org).

2.2.2. Particulate Fe analysis
Unfiltered seawater was collected in 2 l acid cleaned low-density polyethylene (LDPE) bottles and filtered in-line under nitrogen gas pressure. Samples were filtered within 2 h of collection through 0.2 µm polycarbonate track-etched membrane filters (Nuclepore) mounted in polypropylene filter sandwiches. After filtration, filters were folded into eights and placed into acid cleaned 2 ml polypropylene vials and stored frozen. Filter blanks were processed using the same procedure except that no sample was filtered. We chose a 0.2 µm rather than 0.4 µm Nuclepore filter size for particulate analysis because previous filtration experiments (unpublished data) have shown that the Monosorbs 0.45 µm Teflon membrane capsule filter used for dissolved Fe analysis has an effective pore size similar to the 0.2 µm Nuclepore membrane filters. This is supported by data from the Bering Sea reported by Hurst et al. (2010). Thus, we do not expect there to be any significant overlap between the 0.2 µm particulate Fe and 0.45 µm dissolved Fe phases. Although it is possible that a portion of the colloidal Fe phase between 0.2 and 0.45 µm is represented in both dissolved and particulate samples, it is likely insignificant, especially compared to the leachable particulate Fe concentrations that are reported.

Filters were leached following the procedure of Berger et al. (2008). Briefly, the leach involved adding 1 ml of 0.2% acetic acid (HAc) with 0.02 M hydroxylamine hydrochloride to each 2 ml vial for 2 h, with a short 10 minute heating step to 90-95°C at the beginning of the leach step. The portion of the particulate Fe phase solubilized by this leach is herein referred to as “leachable particulate Fe”, and the sum of the dissolved and leachable particulate Fe concentrations is defined as “reactive Fe”. Leached filters were subsequently microwave bomb-digested to solubilize the remaining refractory metals. The bomb-digestion method is described elsewhere (Lippert et al., 2010).

Leach and bomb digestion solutions were analyzed using a Thermo-Finnigan high-resolution inductively coupled plasma-mass spectrometer (Lippert et al., 2010). Fe standards were made from a 1000 ppm stock solution (STX, Edenfield, NJ; Fisher Scientific) in 1 N TMG HNO₃ (with 1 ppm Ga as an internal standard). Leachable and refractory particulate Fe were reported as the sum of the concentrations on the 0.2 µm and 10 µm filters. Total particulate Fe indicates the sum of the leachable and refractory phases.

Standard reference materials were digested and analyzed to ensure that the refractory analyses of field samples were total digestions. Seven to twelve milligrams of soil sand (NIST 2704, National Institute of Standards and Technology, USA) and marine sediment (BCS-1, National Research Council of Canada) was deposited onto a 0.2 µm filter and digested with the above bomb-digestion method. Particulate Fe, Al, and manganese (Mn) values were within the range of error of the certified values (percent recoveries for SRM 2704: Al 58.9%, Fe 101.6%, Mn 90.2%; percent recoveries for BCS-1: Al 88.1%, Fe 94.0%, Mn 90.2%). Although there are no certified values for partial digests of marine sediment, the analytical procedures have been verified based on total digests of reference materials.

2.2.3. Macronutrient analysis
Macronutrient concentrations (nitrate+nitrite referred to as nitrate), phosphate, and silicate acid) were measured on a Lachat QuickChem 8000 Flow Injection Analysis system using standard colorimetric methods (Parsons et al., 1984). Filtered (0.45 µm) samples were taken every 2 km from the outflow of the low fish, and filtered vertical profile samples were collected from GoFo bottles.

3. Results
According to the NOAA ERK Rapid upwelling index near Seward, AK (the beginning of the GAK line at 60°N 149°W) winds were generally weakly downwelling-favorable over the course of the cruise with brief periods of upwelling winds on 21 and 5 September. Salient features of the surface transects are presented in Table 1 and 2.

3.1. Transect T (T1): Ahek River and glacial plumes along with Yukatat profiles
Transect T began near Cape Fairweather southeast of Yukatat, AK, crossed the Ahek River plume (near Dry Bay), and extended to the northwest past Yukatat Bay and Icy Bay with two excursions offshore (Fig. 1). During T1 (21 August), background surface water temperatures and salinities were 16–17°C and 30–31, respectively (Fig. 2). Temperature and salinity decreased to 9°C and ~7 within the Ahek River plume (59.72°N 142.00°W), which is warm and had cooled Fisher water properties than the first (59.72°N 141.35°W). Within the second low salinity plume, leachable particulate Fe increased to 325 nM, more than 2-fold greater than background concentrations. Chi a was elevated to 3.5 µg F⁻¹ in the second low-salinity plume, indicative of biological production (Fig. 3).

Cross shelf transport was investigated using depth profiles from three stations across the continental shelf near Yukatat on 21 August 2007 (Fig. 4). Moving from the inner to mid-shelf from YAK1–YAK2, significant increases in water column leachable and total particulate Fe were apparent. For example, at 50 m depth leachable particulate Fe decreased from 59 nM at YAK1 to only 1.9 nM at YAK2 (Fig. 4a,b). YAK3, at a water depth of 650 m, was located just off the shelf break. This station showed evidence of horizon (offshore) advection of a continental shelf Fe source, with the dissolved and leachable Fe profiles exhibiting maxima of 1.7 and 4.0 nM at 200 m (Fig. 4c).

3.2. Transect T (T3): Copper River plume and Kayak profile
Transect T (27 August 2007) began along the western shore of Kayak Island and ran northeast across the continental shelf, turned to the northwest continuing along the inner shelf, and crossed the mouth of the Copper River before cutting back away from shore. Two low salinity plumes were crossed at 60.18°N 145.31°W (salinity 19.0) and 60.20°N 146.08°W (salinity 19.3; Fig. 5). Slight increases in nitrate were observed in both plumes. Leachable and total particulate Fe concentrations were elevated in both plumes, with higher concentrations of 460 nM and 4.2 µM in the first plume (Fig. 5). Although the two plumes had similar salinities, the second low salinity plume was slightly warmer and had lower nitrate and particulate Fe concentrations, consistent with biological production, particle settling, and the second plume being a more aged water mass than the first.
Table 1
Upper portion: Salient features of the surface transects. The range of values measured for each parameter is given. Lower portion: Samples collected from the Copper River. CR1 was collected during the research cruise (August 2007). G1 and G2–4 were collected in August 2008.

<table>
<thead>
<tr>
<th>Transect</th>
<th>Salinity</th>
<th>Temp. (°C)</th>
<th>Nitrate (µM)</th>
<th>Silicate (µM)</th>
<th>Chl a (µg l⁻¹)</th>
<th>Dissolved Fe (nM)</th>
<th>Leachable Fe (nM)</th>
<th>Total Part. Fe (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>6.0–6.1</td>
<td>9.1–10.6</td>
<td>0–2.3</td>
<td>12.0–33.3</td>
<td>0.5–1.3</td>
<td>1.6–3.2</td>
<td>6.5–10.6</td>
<td>44–1090</td>
</tr>
<tr>
<td>T1b</td>
<td>10.1–10.7</td>
<td>9.1–15.8</td>
<td>0–0.7</td>
<td>11.3–14.8</td>
<td>0.5–3.5</td>
<td>0.3–3.0</td>
<td>1.2–33.0</td>
<td>10.3–3600</td>
</tr>
<tr>
<td>T1</td>
<td>15.1–30.0</td>
<td>13.1–14.5</td>
<td>0–0.9</td>
<td>8.6–22.4</td>
<td>–</td>
<td>0.7–3.3</td>
<td>14.6–450</td>
<td>4–500</td>
</tr>
<tr>
<td>T4</td>
<td>25.4–32.5</td>
<td>12.0–14.1</td>
<td>0–0.9</td>
<td>0.2–10.3</td>
<td>0.7–4.2</td>
<td>0.04–4.1</td>
<td>1.6–280</td>
<td>27–150</td>
</tr>
<tr>
<td>T5</td>
<td>28.1–31.8</td>
<td>8.6–13.2</td>
<td>0–12.0</td>
<td>0.4–30.4</td>
<td>10–31</td>
<td>0–1.3</td>
<td>2.3–187</td>
<td>10.6–150</td>
</tr>
<tr>
<td>T6</td>
<td>23.0–30.0</td>
<td>10.2–13.6</td>
<td>0–0.4</td>
<td>0.2–2.6</td>
<td>1.3–2.3</td>
<td>0.7–3.4</td>
<td>1.4–270</td>
<td>6–1400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dissolved Fe (nM)</th>
<th>Leachable Fe (nM)</th>
<th>Total Part. Fe (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR1</td>
<td>–</td>
<td>2.82 (12.25)</td>
<td>23.0</td>
</tr>
<tr>
<td>G1</td>
<td>109</td>
<td>–</td>
<td>131</td>
</tr>
<tr>
<td>CR2</td>
<td>35.0</td>
<td>–</td>
<td>380</td>
</tr>
<tr>
<td>CR3</td>
<td>49.8</td>
<td>–</td>
<td>348</td>
</tr>
<tr>
<td>CR4</td>
<td>83.5</td>
<td>11.5 (448)</td>
<td>202</td>
</tr>
</tbody>
</table>

Fe concentrations were again relatively less variable throughout the transect, ranging from 0.7 to 3.3 nM (Fig. 5). Data for total Chl a is not available for T3, but ~8 µM Chl a concentrations (data not shown) were slightly elevated in the second plume compared to the first, indicating additional biological production in the more aged plume.

A depth profile was collected west of Kayak Island on 29 August 2007 (at a bottom depth of 225 m; Fig. 1). At this station, leachable and total particulate Fe concentrations increased by an order of magnitude between 100 and 200 m depth, to 123 and 631 nM, respectively (Fig. 6).

3.3. Copper River samples

Five grab samples were collected from the Copper River. Table 1 lists the available dissolved, leachable, and total particulate Fe data. CR1 was collected near the mouth of the Copper River (60.41°N 145.56°W) on 28 August 2007. The remaining four samples for dissolved and particulate Fe analysis were collected further upstream in the Copper River during August 2008. G1 sampled glacial melt from Childs Glacier (60.66°N 144.77°W) and CR2 was collected from the Copper River just next to Childs Glacier. CR3 was collected downstream of the confluence of the Copper and Chilnna Rivers at
Fig. 3. Transect 1b: Top panel: temperature, salinity, dissolved Fe, and leachable particulate Fe. Lower panel: nitrate, silicate, Chl a, and total particulate Fe.

61.53°N 144.41°W and CR4 was collected just upstream of the Clatsina River. Based on these five samples, it appears that dissolved Fe concentrations decrease moving downstream while the percent of the total particulate Fe phase that is leachable increases.

3.4. Transect 4 (T4): GAK line and GAK depth profiles

Commonly referred to as the GAK or Seward line (as historically sampled by the University of Alaska and the GLOBEC program), T4

Fig. 4. Yakutat (YAK) depth profiles: a) YAK1 temperature (gray diamonds), salinity (black diamonds), dissolved Fe (white triangles), leachable Fe (gray circles), and total particulate Fe (black triangles). YAK2 profiles in plot b and YAK3 profiles in plot c.
was sampled on 20 August 2007. The transect began near Seward, AK, and extended to the southeast out into the subarctic Alaskan gyre (Fig. 1). Moving away from shore, an abrupt decrease in dissolved Fe (from 3–4 nM to ~0.2 nM) and leachable particulate Fe (from 28 nM to ~4 nM) was observed (Fig. 7). Elevated Chl a concentrations (~4.2 µg L⁻¹) were observed in the transitional waters over the mid-shelf region. Moving further offshore beyond the shelf break, true HNLC waters were encountered, where dissolved Fe decreased to <0.05 nM, leachable particulate Fe to about 1 nM, and surface nitrate increased to over 9 µM.

Three depth profiles were completed along 14 on 31 August–1 September 2007. Over the inner shelf near GAK1 (bottom depth was 240 m), dissolved, leachable and total particulate Fe and nitrate concentrations increased by an order of magnitude between the upper water column and 200 m, to 2.0 nM, 22 nM, 99 nM, and 2.5 µM (Fig. 8a,b). GAK6 was located farther offshore over a ridge with a bottom depth of 152 m. Similar trends were observed at GAK6, however, there were lower dissolved Fe concentrations and higher leachable and total particulate Fe concentrations in the deep waters at GAK6 compared to GAK1 (Fig. 8c,d). GAK10 was located within HNLC waters beyond the shelf break. Fe concentrations were depleted throughout the upper water column and increased with depth (150–200 m), but deep water concentrations were depleted compared to those observed at GAK1 and GAK6 (Fig. 8f).

3.5. Transect 5 (TS): Kennedy–Stevenson entrance

Transect 5 was sampled on 2 September 2007; the upwelling index switched from negative to positive on 1 September, and was slightly elevated to 6 m³ s⁻¹ (100 m coastline)⁻¹ on 2 September. The transect began at the southern end of Cook Inlet, extended south toward the Kennedy–Stevenson entrance, and continued northeast along the southern coast of the Kenai Peninsula ending just south of Gore Point. About 46 km into the transect, temperature reached a minimum of 8.6 °C with a salinity of 31.8 (Fig. 9), indicative of mixing of deeper waters. This temperature/salinity signature corresponds to water found at 50 m depth at GAK1 (Fig. 8a). The cooler, more saline waters appeared to be a source of elevated nitrate (Fig. 9), but the deeply mixed waters did not appear to be a major source of
particulate Fe, as leachable and total particulate Fe concentrations decreased approximately threefold within the cooler, more saline waters. Dissolved Fe concentrations were consistently about 0.5 nM over the first two-thirds of the transect (Fig. 9).

As the transect exited the Kennedy entrance and headed northeast towards Gore Point, temperatures increased to a maximum of 13°C and salinities decreased to 28.1, although the transect crossed narrow bands of cooler, more saline waters. Nitrates concentrations decreased to near zero in the warmer, fresher coastal waters (with locally elevated nitrate in the narrow bands of cooler water), while Fe concentrations were elevated within the coastal waters at the end of the transect.

3.6 Transect 6 (T6): Anvik Glacier

Transsect 6 began on 3 September 2007 at the foot of the Anvik Glacier in Anvik Bay southeast of Seward. AI and continued seaward before ending near the GAK1 depth profile station. Nearshore, relatively low salinities (23.3) indicated the influence of the Anvik Glacier meltwater directly flowing into the Bay (Fig. 10). Moving away from the glacier, dissolved Fe decreased from 2.4 nM to 0.75 nM and leachable particulate Fe decreased from 207 nM to 14 nM (Fig. 10).

4. Discussion

4.1 Glacial inputs of reactive iron to coastal waters

Although there is a paucity of Fe data from polar regions and glacial meltwaters in particular, it is important to consider the contribution of glacial meltwater to coastal ocean reactive Fe concentrations. Globally averaged, glacial runoff contains about 1.0 kg m⁻² of suspended sediment (Curnell, 1987) compared to an average of 0.5 kg m⁻² in non-glacial runoff (Holland, 1978; Rainbow et al., 2006). However, glacial runoff generally contains only one-fifth of the total dissolved load observed in average non-glacial runoff (Tranter et al., 2002; Rainbow et al., 2006). Thus, the leachable particulate Fe phase in glacial meltwater is expected to be much more significant than dissolved Fe, as is observed in this study.

In coastal surface waters between Cape Fairweather and the Kenai Peninsula, dissolved Fe concentrations were approximately 1 to 3 nM, with a maximum of about 4 nM in low salinity coastal waters of T4. However, leachable particulate Fe values were more variable and at least an order of magnitude higher than dissolved values. In surface waters between Cape Fairweather and Prince William Sound (T1 and T3), leachable particulate Fe concentrations exhibited close to three orders of magnitude variation, from 1.5 nM in the background waters of T1B to 100 nM in the low salinity (~7) Alek River plume of T1A. In general, leachable particulate Fe concentrations increased with decreasing salinity (Fig. 11). At the beginning of T4, low salinity coastal waters (~23.5) contained 28 nM leachable Fe, while 16 low salinity glacial meltwaters (~23) had 607 nM leachable Fe. Although the glacial meltwater was not a source of elevated dissolved Fe, it does appear to have been a source of elevated leachable particulate Fe. In contrast to glacial meltwater, the upwelled waters in the Kennedy Entrance near Cook Inlet (T5) did not appear to have been a source of dissolved Fe (which measured 0.5 nM) or significantly elevated leachable Fe, as leachable Fe concentrations in these cooler, high salinity waters were only 2.18 to 15.1 nM. It is worth noting, however, that the leachable particulate Fe concentrations in the upwelled water mass were still up to an order of magnitude greater than dissolved values.

Fig. 7. Transect 4 (GAI line): Top panel: temperature, salinity, dissolved Fe, and leachable particulate Fe. Lower panel: nitrate, silicate, Chl a, and total particulate Fe.
Although many of the dissolved Fe values observed in this study exceed the solubility of inorganic Fe in seawater (~0.08 nM; Wu et al., 2001), the maximum concentrations observed (~3 to 4 nM) are lower than expected based on the availability of readily exchangeable particulate Fe. It has been well documented that ~90% of dissolved Fe(III) is complexed by Fe(III)-binding organic ligands in seawater (Rue and Bruland, 1985; van den Berg, 1995). A recent study in the Columbia River estuary and near-field plume has shown that the concentration of strong L-type Fe(III)-binding organic ligands dictates dissolved Fe concentrations, regardless of the availability of readily exchangeable particulate Fe (Buck et al., 2007). In addition, Buck and Bruland (2007) demonstrated that dissolved Fe concentrations in the Bering Sea, AK are strongly correlated with L-ligand concentrations. Glacial runoff has very low dissolved organic carbon (DOC) concentrations, as meltwaters have had little exposure to soil and plant organic matter (Lafferty and Sharp, 2004). In North Dove Inlet, a glacial estuary in southeastern Alaska, Loder and Hood (1972) measured ~12 µM DOC in glacial runoff while downstream river waters contained ~12 to 40 µM DOC. These are relatively low DOC concentrations compared to an average river DOC concentration of 479 µM (Meybeck, 1982). In addition, in a study in situ near Juneau, Alaska, Hood and Scott (2008) found that watersheds with less glacial inputs yielded higher DOC concentrations. The loss of dissolved substances to the particulate phase due to flocculation of humic substances in estuaries is well documented (Sublette et al., 1977; Doyle et al., 1997), and DOC is an indicator of the presence of humic substances and other metal-binding ligands. Thus, although DOC concentrations are probably highly variable throughout the GoA, we suggest that low DOC concentrations in glacial meltwaters that feed the ACC result in the observed relatively low (~1-3 nM) dissolved Fe concentrations (yet high total reactive Fe concentrations) in the coastal transects. For comparisons, off the coast of Oregon/Washington, Columbia River plume dissolved Fe concentrations averaged ~13 nM at salinity of 20 (Lippert et al., 2010). Furthermore, Brown et al. (in press) have attributed the lack of a colloidal AI fraction to low DOC concentrations in the northern GoA (all of the dissolved Al was found in the soluble phase). The dissolved and particulate Fe data presented in this study supports the apparent disparity between dissolved and particulate loads in glacial runoff. Stahr et al. (2008) measured an average flow-weighted total dissolved Fe (<0.4 µm) concentration of 53 nM in Greenland Ice Sheet meltwaters. Their study did not sample downstream of the glacial terminus and thus could not determine the fate of meltwater reactive Fe in higher salinity waters. The authors suggest that because meltwater reaches the coastal ocean more rapidly than estuarine waters, less of the dissolved Fe phase would precipitate out and more of the finest particulate fraction would remain in suspension. We measured 198 nM dissolved Fe in glacial meltwater sample G1, and 35 nM dissolved Fe at G2, which was collected from the Copper River near the glacial sample. However, in the low salinity plumes of transects T1 and T3, the highest dissolved Fe concentration was 3.3 nM. Thus, it appears that a large portion of the dissolved Fe phase is precipitated with increasing salinity and distance from the glacial source. Fig. 11b shows dissolved Fe vs. salinity for the coastal transects. Even at low salinities, the dissolved Fe concentration appears to be capped around 3-4 nM, which would be consistent with
the theorized saturation of about the same concentration of strong Fe (III)-binding ligands. In contrast, there is a trend of increasing leachable particulate Fe with decreasing salinity (Fig. 11a), indicating that glacial meltwaters and rivers entering the northern GoA are a significant source of leachable particulate Fe. For example, along T1a at salinities less than 19 there was on average 896 nM leachable particulate Fe versus 2.8 nM dissolved Fe; over 300-fold more leachable particulate Fe than dissolved Fe. Between salinities of 19–29, there was 46.9 nM leachable particulate Fe and 2.5 nM dissolved Fe, about 20-fold more leachable particulate Fe.

4.2. Percent leachable particulate Fe in rivers and plumes

The sample collected just upstream of the confluence of the Copper and Chitina Rivers, C14, had 4.4% of the total particulate Fe phase in the leachable fraction, compared to 12.2% at C11, which was collected in the low-salinity waters near the mouth of the Copper River. Although leachable particulate Fe concentrations decrease with distance downstream, this downstream increase in the percentage of the total particulate Fe phase that is leachable is arguably due to redox chemistry and the interaction of Copper River waters with low dissolved oxygen pore- and groundwater. The solubility of Fe increases in low oxygen environments due to Fe(II) reduction and the formation of soluble Fe(II), and the subsequent exposure to oxygenated waters will result in the oxidation of Fe(II) and the subsequent precipitation of Fe(III) (oxyhydrous) oxide coatings which are included in the leachable particulate Fe pool. Similarly, percent leachable particulate Fe averaged 11.0% (n=4) in the Alek and Copper River plumes (T1a and T1). Samples collected along T14 had an average of 18.1% (n=5) leachable particulate Fe in the nearshore samples, increasing to 32.3% (n=5) offshore in the subarctic gyre waters. Brown et al. (in press) saw a similar increase in percent leachable Al moving offshore, which they attributed to the scavenging of dissolved Al onto particle surfaces. In the case of Fe, however, the dissolved Fe concentrations are much lower than leachable concentrations such that the precipitation of dissolved Fe would not appreciably change the percent leachable value. Thus, it is more likely that with distance from the source region more of the larger particles settle out of the water column. In C14 75% of the refractory particulate Fe was found in the larger size fraction (>10 µm), indicating that removal of the larger particles would potentially increase the percent leachable Fe in the remaining suspended particles.

In a study of the summertime near-field Columbia River plume, Lippard et al. (2010) measured on average 590 nM leachable particulate Fe with about 26% in the leachable phase. In the Alek and Copper River plumes, the comparatively lower percent leachable Fe value (11%) is probably a result of physical, rather than chemical, weathering of the source material. Glaciers in the northern GoA have been described as “buzzsaws” grinding on and eroding the mountainous region they cover (Spotila et al., 2004). This physical weathering introduces more refractory sedimentary material into the glacial meltwaters. On the other hand, chemical weathering, which becomes more significant with distance downstream in the drainage basin (Wadhams et al., 2001), releases mineral framework Fe into solution. Due to the low solubility of Fe(III), the chemically weathered dissolved Fe precipitates out as reactive Fe (oxyhydr)oxide coatings. Thus, in regions where chemical weathering dominates over physical weathering, such as the Columbia River, a larger fraction of the total particulate Fe phase is found in the leachable fraction.

4.3. Cross shelf transport

Reactive Fe concentrations decrease dramatically moving out of the ACC and into the subarctic gyre. Wu et al. (2009) have referred to
the ACC as an Fe reservoir that is continually recharged via Fe-rich freshwater discharge which is for the most part confined in nearshore waters. However, the cross-shelf transport of high Fe coastal waters maintains the elevated productivity over the shelf, as is demonstrated by the elevated Chl a concentrations in the mid-shelf region of T4.

YAK depth profiles show that there was 2.90 nM dissolved Fe at 50 m at YAK1 and only 0.61 nM dissolved Fe at 50 m at YAK3. This cross-shelf gradient reflects the coastal source region and a transition from high-Fe coastal waters over the inner-shelf to the lower Fe waters of the subarctic Alaskan gyre. A similar trend with lower dissolved Fe concentrations was observed further west over the broad shelf along the GAK line (Fig. 8) which is farther downstream from the major freshwater sources. At 50 m depth at GAK1 and GAK10 there was 0.54 and 0.02 nM dissolved Fe, respectively. Dissolved Fe values were elevated at GAK6 (0.63 nM at 50 m) presumably due to the influence of the topographic ridge at that station. The relatively low dissolved Fe and high nitrate concentrations beyond the shelf break at GAK10 (<0.1 nM Fe in the upper 100 m) are indicative of the HNLC waters of the subarctic gyre. The transition to HNLC waters beyond the shelf break was also apparent in surface waters along T4, where dissolved Fe concentrations rapidly decreased to <0.05 nM (Fig. 7).

Wu et al. (2009) sampled the GAK line (T4) in May and July 2004. GAK1 surface water dissolved Fe concentrations were 4.4 nM (May) and 8.5 nM (July). The authors attributed the elevated dissolved Fe in July to relaxation of downwelling, which allowed the ACC to extend farther offshore (out 100 km) and increased freshwater runoff as indicated by lower salinities (20.0 vs. 21.8). The May 2004 scenario was more similar to conditions experienced during the present study. On 30 August 2007 winds were downwelling favorable, which arguably kept the low salinity ACC waters confined against the coast nearshore T4 (GAK line) surface salinities were 25.6–26.7 with 2.9 nM dissolved Fe at the coastal-mid station and 4.1 nM at the second station, the highest dissolved Fe concentration measured on any of our northern GoA coastal transects (Fig. 7). While downwelling favorable winds resulted in a narrow ACC where Fe concentrations decreased dramatically with distance from shore, there appeared to be subsurface offshore export of dissolved Fe. At GAK10, dissolved Fe was 0.49 nM at 150 m compared to only 0.01 nM in the surface mixed layer (Fig. 8).

Cross-shelf gradients of leachable particulate Fe in the upper water column (top 50 m), as observed in depth profiles at YAK and GAK stations (Figs. 4 and 8), illustrate that the large input of this reactive Fe is trapped within coastal waters and does not generally reach the subarctic gyre. Low concentrations of leachable particulate Fe in the HNLC waters near GAK10 were also observed by Martin et al. (1987) in August 1987, with values increasing from 0.01 nM at 50 m to a maximum of 3.9 nM at 150 m. However, in the northern GoA, various mechanisms result in the cross-shelf flux of coastal and offshore HNLC waters. During the winter, the predominant downwelling-favorable winds result in onshelf Ekman transport of high nutrient offshore waters, acting as a source of nitrate to the nutrient-stressed coastal waters (Stabeno et al., 2004; Storm et al., 2006). These nutrients support the high productivity over the shelf during the spring bloom (Ladd et al., 2005). In addition, sporadic summertime upwelling-favorable winds and upwelling seaward of the coastal barrier jet (Stabeno et al., 2004) can supply macronutrients to surface waters over the shelf. Topographic steering and persistent tidally-induced deep mixing results in the delivery of subsurface nutrient-rich waters into the euphotic zone (Stabeno et al., 2004; Ladd et al., 2005). This was observed in T3, where upwelled waters were a source
of elevated silicate and nitrate (Fig. 9; Brown et al., in press). Finally, mesoscale eddies are an important mechanism of cross-shelf exchange of coastal and offshore waters. In the northern GoA, Yakutat, Slika, and more recently lensai eddies (e.g., Ladd et al., 2005; Boegman et al., 2008) have been shown to interact with shelf circulation as they propagate along the shelf break. The formation of these eddies over the shelf entrains high Fe coastal water, which can be delivered to offshore waters via propagation offshore and the eventual relaxation of the eddy (Ladd et al., 2005).

In addition to the mixing of surface shelf and HNLC waters, subsurface transport of high Fe continental margin waters can supply Fe to the subarctic gyre (Lam et al., 2005; Cullen et al., 2005). Subsurface reactive Fe is less susceptible to biological uptake and thus may have a longer residence time in the water column. Lam et al. (2005) have suggested that continental margin particulate Fe can be laterally transported up to 1000 km from the shelf to Ocean Station Papa in the central subarctic gyre. Subsequent upwelling of this subsurface (100-150 m) Fe source can support phytoplankton blooms in these shelf-limited waters. Our depth profiles at YAK-1 and YAK-2 showed evidence of a subsurface reactive Fe source, as there were increased concentrations of both dissolved and labile particulate Fe at 150-250 m. Furthermore, the primary source of continental shelf sedimentary Fe is likely the Fe-rich glacial runoff that feeds the ACC. The relative importance of the surface versus subsurface source of Fe to the HNLC waters will vary seasonally with changes in runoff, wind forcing, and mesoscale eddy activity.

4.4. Macronutrients in the northern GoA coastal waters

Predominantly downwelling conditions along the northern GoA shelf in conjunction with nutrient-poor runoff beg the question of how the region supports such high phytoplankton productivity. Data presented here in conjunction with historical data (e.g., Cullen et al., 2005) indicate that nitrate concentrations are generally depleted in the ACC in late summer. Deep tidal mixing or rare upwelling events can supply nitrate to the ACC in late summer (e.g., ~12 µM nitrate in deeply mixed waters encountered during T5). In addition, mixing of nitrate-rich HNLC waters onto the shelf via mesoscale eddies is a mechanism for nitrate introduction into the ACC in late summer.

Fig. 12 shows nutrient-salinity plots for the freshwater plumes from transects T1a, T1b, T3, T4, and T6. Based on the silicate-salinity relationships (Fig. 12a), T1a (the Alek River) and T3 (the Copper River) appear to have different freshwater sources than T1b and T6. The theoretical zero-salinity endmember silicate concentration for T1a and T3 is ~44 µM while that for T1b and T6 is ~25 µM. The higher silicate endmember concentration for T1a and T3 is suggested to be due to chemical weathering of glacial meltwaters in the drainage basins of the Alek and Copper Rivers, while Transects T1b and T6 sampled fresh glacial meltwaters from the Bering, Guyot, and Malaspina glaciers (T1b) and Aialik glacier (T6) which have lower silicate concentrations (Brown et al., in press).

Nitrate-salinity relationships (Fig. 12b) indicate that the plumes of T1a and T3 had theoretical zero-salinity endmember nitrate concentrations of ~2.5 µM. USGS data from the Alek River station near Yakutat (USGS station 1512900) indicates an average nitrate concentration of 4.5 µM during late summer months (n = 3); data from the Copper River station at million dollar bridge (USGS station 15214500) near the mouth of the river) average 9.9 µM (n = 4) in late summer. The nitrate-salinity relationship for T1b indicates nitrogen...
drawdown, suggestive of biological consumption (Fig. 12b). In fact, Chl a concentrations were elevated to 3.5 pg µL⁻¹ in the T1b low salinity plume (Fig. 3). However, it is hard to discern any dissolved Fe drawdown from Fig. 11b. Based on the previous discussion of Fe(III)-binding organic ligands, we argue that the dissolved Fe concentration in these coastal waters is buffered by the availability of a large source of readily-leachable particulate Fe and saturation of a low but consistent Fe(III)-binding ligand concentration.

4.5. Biological impact of glacial meltwaters

Leachable particulate Fe is a potential source of bioavailable Fe to marine phytoplankton. Laboratory studies have shown that Fe(III)-oxo (oxy-)phosphates can act as an Fe source for diatom growth (Weis et al., 1985; Rich and Morel, 1986). In a study off the coast of Oregon, Chae et al. (2005) have shown that a portion of the particulate Fe phase can become available to phytoplankton on the timescale of days. Furthermore, Hurd and Bruland (2007), using stable isotopes of Fe and zinc as tracers, performed growth out experiments in the Bering Sea that demonstrated active solubilization of particulate iron and subsequent uptake of this solubilized Fe. Thus, we argue that in the northern GoA the leachable particulate Fe phase is present at concentrations at least an order of magnitude higher than dissolved Fe. It is available for solubilization and maintains a low and consistent (2 nm) dissolved Fe concentration in the coastal shelf waters of the northern GoA.

Strom et al. (2006) have shown that during the spring and summer months, there is a significant difference in Fe concentration between T1 and T3 compared to T5, the late summer freshwater discharge appears to be a much more significant source of reactive Fe to the surface waters over the shelf as well as mixing. Dissolved Fe concentrations are a possible source of Fe to these surface waters. However, the strong pycnocline that exists from spring through fall may reduce the probability of this subsurface reactive Fe making it to the euphotic zone. During the winter months, deep mixing associated with storms may deliver bottom sediments to the surface zone (Royer, 1975; Stabeno et al., 2004), recharging reactive Fe concentrations in the euphotic zone prior to the spring bloom (Liddell et al., 2005).

5. Conclusions

The ACC receives a massive input of reactive Fe, primarily in the leachable particulate form, from glacial rivers and streams. This coastal input creates a strong cross-shelf gradient of reactive Fe, with concentrations decreasing to <1 nm in subarctic gyre surface waters. Dissolved Fe concentrations were consistently low (~1-3 nm) in the ACC, indicating that the region has a low availability of Fe(III)-binding organic ligands to maintain dissolved Fe in solution. Leachable particulate Fe, on the other hand, was present in much higher and more variable concentrations. This leachable particulate Fe is available for solubilization to sustain saturation of the organic ligands and acts as a capacitor that prevents depletion of dissolved Fe. The glacial runoff contains a substantial source of nitrate to coastal waters, which in combination with prevailing downwelling conditions creates an Fe-rich but nitrate-poor ACC mixing between the ACC and HNIC waters of the subarctic Alaskan gyre, along with sporadic vertical mixing of nitrate-rich subarctic waters, results in high productivity in the transitional waters over the shelf.

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References


CHAPTER 3:

REACTIVE IRON DELIVERY TO THE GULF OF ALASKA VIA A KENAI EDDY

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ABSTRACT

Mesoscale anticyclonic eddies in the Gulf of Alaska are an important mechanism for cross-shelf exchange of high iron, low nitrate coastal waters and low iron, high nitrate offshore waters. A Kenai eddy was sampled in September 2007, eight months after formation. The subsurface eddy core layer contained reactive iron concentrations more than eight times greater than waters at the same depths outside the eddy. The subsurface core of the Kenai eddy (25.4 \leq \sigma \theta \leq 25.8) is seasonally important as these waters can be brought to the surface with deep winter mixing. The deeper core layer (25.8 \leq \sigma \theta \leq 27.0) is a source of iron to HNLC waters on a longer timescale, due to isopycnal mixing and eventual eddy relaxation. The subsurface and deeper core layers are shown to be important reservoirs of iron that can promote and sustain primary productivity over the lifetime of the Kenai eddy. In addition, dissolved and leachable particulate manganese are shown to be excellent tracers of eddy surface and subsurface waters, respectively.

1. INTRODUCTION

Transport over the northern Gulf of Alaska (GoA) shelf is dominated by the Alaska Coastal Current (ACC) (Stabeno et al., 2004). The ACC is fed by iron (Fe)-rich but nitrate-poor runoff from glacial rivers
and streams (Lippiatt et al., 2010a), whereas the central GoA is a high-nutrient, lower than expected chlorophyll (HNLC) region in which primary productivity is limited by the low supply of Fe (Martin et al. 1989; Boyd et al., 2004). In the Alaskan Stream corridor in the southwestern coastal GoA, the transition from low nitrate coastal waters to the HNLC waters of the GoA occurs just beyond the continental shelf (Figure 1a). Mixing between the coastal and offshore regimes can result in the high productivity observed over the GoA shelf and along the shelf break (Sambrotto and Lorenzen, 1986; Stabeno et al., 2004) and can occur via relaxation of downwelling winds, tidal mixing, and mesoscale eddies (Ladd et al., 2005a).

Large anticyclonic eddies are suggested to play a significant role in the cross-shelf exchange of both coastal and HNLC waters in the GoA (Stabeno et al., 2004). These eddies form on or near the shelf and thus exhibit distinct hydrographic, biological, and chemical water properties as they propagate away from the source region. At any given time there are usually several of these mesoscale eddies in the offshore regions of the GoA (~ 13 per year; Henson and Thomas, 2008).

Mesoscale eddies can enhance cross-shelf exchange by interacting with shelf-slope circulation during their propagation and entraining shelf water during their formation and propagating offshore (Whitney and
Robert, 2002; Ladd et al., 2005b). The leading edge of an eddy propagating along the shelf break entrains macronutrient-rich central GoA water while the trailing edge entrains Fe-rich shelf waters (Okkonen et al., 2003). Thus, eddies result in the net exchange of macronutrients, Fe, and biological populations between the ACC and central GoA (Stabeno et al., 2004; Peterson et al., 2005; Johnson et al., 2005; Ladd et al., 2005b). Using satellite imagery, Okkonen et al. (2003) have observed regions of high chlorophyll along the edges of eddies, presumably the result of mixing between these two regimes. The cross-shelf transport of macro- and micronutrients by eddies into the central GoA (Whitney and Robert, 2002; Johnson et al., 2005) makes them an important factor influencing primary productivity in the offshore region of the GoA.

Crawford et al. (2007) have shown that mesoscale eddies contain the majority of surface chlorophyll in the northern GoA. They showed that, on average, more than half of all surface chlorophyll was inside the 4 cm contours of anticyclonic mesoscale eddies (approaching 80% in spring months), yet these contours enclosed only 10% of the total surface area of pelagic waters in the GoA.

Four different types of anti-cyclonic mesoscale eddies in the GoA have been identified, and are named based on their formation region: Haida, Sitka, Yakutat, and Kenai eddies. Haida eddies form during
winter off the southern tip of Queen Charlotte Island and tend to propagate directly west into the interior of the basin (Johnson et al., 2005). Sitka eddies form farther north near Baranof Island (Tabata 1982) and propagate either westward towards the central GoA or towards the northwest within in the Alaskan Stream (Matthews et al., 1992; Crawford et al., 2000). Yakutat eddies form near Yakutat, close to the head of the GoA, propagate west/northwest along the shelf-break, and can turn southwestward with the Alaskan Stream, remaining in close proximity to the shelf (within ~ 200 km, Crawford et al., 2000; Okkonen et al., 2001; Ladd et al., 2005b; Henson and Thomas, 2008). Finally, a recently documented fourth type of eddy, the Kenai eddy, forms adjacent to the Kenai peninsula to the southeast of the Kennedy and Stevenson entrance to Cook Inlet (Rovegno et al., 2009) and propagates southwestward along the shelf break with the Alaskan Stream.

This study investigated the hydrography, trace metal concentrations, macronutrient (nitrate and silicate) content, and chlorophyll in a Kenai eddy during September 2007 (Figure 1b). During the same field effort, nearshore Fe and aluminum (Al) concentrations were characterized (Lippiatt et al., 2010a; Brown et al., 2010). In addition, core waters of a Sitka eddy and surrounding basin waters were sampled; Fe, Al, and manganese (Mn) data from this eddy is described in
Brown et al. (in prep). The delivery of coastal-derived reactive Fe to the Fe-limited central GoA via the Kenai eddy is discussed here. Additionally, dissolved and leachable Mn will be discussed in terms of their use as tracers of coastal source water in the eddy core.

2. METHODS

2.1. Sample collection

Fieldwork took place aboard the *R/V Thomas G. Thompson* in the northern GoA from 1 – 18 September 2007. The location of the core of the eddy was tracked using real time altimetry data as described by Rovegno et al. (2009) (Figure 1b). Surface seawater was collected along a transect across the eddy (Figure 2) using a trace metal clean surface tow fish system (Bruland et al., 2005) that was plumbed into a Class-100 clean area. Underway temperature and salinity data were obtained using a YSI 600 OMS CTD sonde attached to the surface tow fish. Sub-surface trace metal samples were collected from GO-Flo bottles tethered to a Kevlar line, and triggered by Teflon-coated messengers. CTD casts were completed in conjunction with every GO-Flo cast. All aspects of sample processing and analysis followed rigorous trace metal clean methods (Bruland et al., 1979).
A series of CTD casts were conducted on transects from the east to west (stations K1 to K10 from 6 – 7 September) and north to south (stations K11 to K18 from 8 – 9 September; Figure 2). Based upon the characterization of the Kenai eddy using the CTD transects, GO-Flo trace metal profiles were obtained from nine stations along two transects across the eddy. Stations K18 – K21 crossed the eddy approximately north – south (9 – 11 September), and stations K22 – K26 crossed from northeast – southwest (11 – 14 September). A CTD cast was performed along with each GO-Flo cast. Additional GO-Flo profiles were collected on 1 September at the predicted eddy source water location outside of the Kennedy Entrance to Cook Inlet (SW2) and on 15 September at a basin reference station located to the southwest of the eddy (K27) (Figure 2). Finally, surface transect 7 (T7) was sampled on 16 – 17 September from south – north across the eddy from HNLC waters to the shelf break (Figure 2).

2.2. Analytical methods

2.2.1. Dissolved metals analysis

Dissolved Fe samples were filtered through acid-cleaned 0.45 µm Teflon™ membrane polypropylene capsule filters (GE Osmonics). These
capsules have been shown to be effectively similar to a 0.2 µm Nuclepore membrane filter (Aguilar-Islas et al. 2007). Dissolved Fe was measured onboard ship by flow injection analysis (FIA); the method has been described in detail elsewhere (Lohan et al., 2006). Briefly, samples are acidified (pH ~ 1.7 – 1.8) with sub-boiled quartz distilled 6 N hydrochloric acid (Q-HCl) and hydrogen peroxide is added to completely oxidize Fe(II) to Fe(III). The FIA method involves in-line preconcentration of Fe on a commercially-available nitrilo-triacetic acid-type resin (Qiagen), followed by Fe-catalyzed production of a colored solution and spectrophotometric detection. For this study, average blank values for samples above 1 nM were $0.058 \pm 0.024$ nM Fe (n=50), with a detection limit (defined as three times the standard deviation of blank) of 0.072 nM. For samples with a concentration less than 1 nM the blank was $0.06 \pm 0.008$ nM Fe (n=10), resulting in a detection limit of 0.024 nM. The differences in blank values and detection limits results from differences in column loading time, with longer loading times used to quantify samples with lower concentrations. To validate the system, SAFe standards were measured regularly. The average value of SAFe surface water was $0.092 \pm 0.005$ nM Fe (n=13) and for deep water $0.92 \pm 0.006$ nM Fe (n=13); these concentrations agree well with the original consensus values of $0.097 \pm 0.043$ nM and $0.91 \pm 0.07$
nM, respectively (Johnson et al., 2007), and the recent consensus values provided by the GEOTRACES Program of 0.094 ± 0.008 nM and 0.923 ± 0.029 nM, respectively (www.geotraces.org and www.es.ucsc.edu/~kbruland/).

Dissolved Mn was measured on archived samples following the method of Aguilar-Islas et al. (2006). The FIA method requires pre-concentration of Mn on an iminodiacetate resin (Toyopearl AF-Chelate 650M) followed by spectrophotometric detection of a Mn-catalyzed end-product (leuchomalachite green). When preconcentrating 1.6 mL of sample, the method has a detection limit of 0.03 nM and a precision of 3.2%.

2.2.2. Particulate metals analysis

Unfiltered seawater was collected in 2 L acid cleaned low-density polyethylene (LDPE) bottles and filtered in-line under nitrogen gas pressure. Samples were filtered sequentially within 2 hours of collection through acid cleaned 10 µm and 0.2 µm 47 mm polycarbonate track-etched membrane filters (Nuclepore™) mounted in polypropylene filter sandwiches. After filtration, filters were folded into eighths and placed into acid cleaned 2 mL polypropylene vials and stored frozen. Filter
blanks were processed using the same procedure except that no sample was filtered.

Filters were leached following the procedure of Berger et al. (2008). The leach method involves adding 1 mL of 25% acetic acid (HAc) with 0.02 M hydroxylamine hydrochloride to each 2 mL vial for 2 hours, with a short 10 minute heating step to 90 – 95 °C. After the 2-hour leach, leachates are transferred to a quartz beaker and the filters are rinsed with milliQ water. These rinses are also transferred to the quartz beakers, and the solution is acidified with 100 µL of trace-metal grade nitric acid (TMG HNO₃) and heated to dryness. The residue is taken down to dryness a second time with 100 µL TMG HNO₃, dissolved in 8 mL 1 N TMG HNO₃ (with 1 ppb Ga as an internal standard), and transferred to acid cleaned 15 mL LDPE bottles. The portion of the particulate phase solubilized by this leach is herein referred to as “leachable particulate” Fe or Mn. Further explanation of the phases solubilized by this leach is provided in Berger et al. (2008). The sum of the dissolved and leachable particulate Fe concentrations is defined as “reactive Fe.” Leached filters were subsequently microwave bomb-digested to solubilize the remaining refractory metals. Filters are placed in PFA Teflon bombs (Savillex, Minnetonka, MN) with 3.5 mL TMG
HNO$_3$ and 500 µL TMG hydrofluoric acid (HF). The bomb solutions are heated to dryness and the dry residue was dissolved in 8 mL 1 N TMG HNO$_3$ (with 1 ppb Ga) and transferred to acid cleaned 15 mL LDPE bottles.

Leach and bomb digestion solutions were analyzed using a ThermoFinnigan Element 1 high-resolution inductively coupled plasma-mass spectrometer (ICP-MS). Fe and Mn standards were made from a 1000 ppm stock solution (SPEX, Edison, NJ; Fisher Scientific) in 1 N TMG HNO$_3$ (with 1ppb Ga as an internal standard). The sample introduction system consisted of a PFA-ST nebulizer (Elemental Scientific, Omaha, NE) and PFA spray chamber. Leachable and refractory particulate metals are reported as the sum of the concentrations on the 0.2 µm and 10 µm filters. Total particulate Fe or Mn indicates the sum of the leachable and refractory phases.

Standard reference materials were digested and analyzed to ensure that the refractory analyses of field samples are total digestions. Seven to twelve milligrams of river sediment (SRM 2704, National Institute of Standards and Technology, USA) and marine sediment (BCSS-1, National Research Council of Canada) were deposited onto a 0.2 µm filter and digested with the above bomb-digestion method. Particulate Fe, Al,
and Mn values were within the range of error of the certified values (percent recoveries for SRM 2704: Al 98.9%, Fe 101.6%, Mn 99.2%; percent recoveries for BCSS-1: Al 88.1%, Fe 94.0%, Mn 90.2%). Although there are no certified values for partial digests of marine sediment, the analytical procedures have been verified based on total digests of reference materials.

2.2.3. Macronutrients and chlorophyll analysis

Macronutrient concentrations (nitrate+nitrite [referred to as nitrate], phosphate, and silicic acid) were measured on a Lachat QuikChem 8000 Flow Injection Analysis system using standard colorimetric methods (Parsons et al., 1984). Filtered (0.45 µm) samples were taken every two minutes from the outflow of the tow fish, and filtered vertical profile samples were collected from CTD and GO-Flo bottles.

Chlorophyll a (Chl a) samples were collected on Whatman GF/F filters, extracted for ~ 24 h in 7 mL of 90% acetone (−20°C) and analyzed with a Turner Designs 10-AU fluorometer calibrated with pure Chl a (Sigma) using the non-acidification technique (Welschmeyer, 1994).

3. RESULTS
Rovegno et al. (2009) developed an algorithm using satellite altimetry data to identify and track eddy features in water deeper than 200 m in the GoA. The algorithm first located the Kenai eddy on 10 January 2007 within the Alaskan Stream just off the shelf break to the southeast of station SW2 (at 57.7 °N 147.8 °W; Figure 2). At the time of sampling, this eddy was eight months old and had a sea surface height anomaly (SSHa) at its core of 30 – 40 cm (Rovegno et al., 2009; Figure 1b). Based on the area within the 10 cm SSHa contour on September 12, 2007, the total surface area of the eddy was approximately 2.1x10^4 km^2, which gives an approximate diameter of 164 km (Rovegno, pers. comm.).

Assuming that the eddy is cylindrical and extends to a depth of 500 m (the approximate depth of the 27.0 kg m^3 isopycnal), we calculate an approximate eddy volume of 1x10^4 km^3. Subsequent analysis by Ueno et al. (2010) shows that the Kenai eddy remained in the Alaskan Stream moving west/southwest just off the shelf break until February 2009 when it split into two; one eddy continued to propagate westward along the Aleutian Islands and the other propagated south. Both eddies were still apparent as of August 2010.

3.1. Hydrographic properties
The temperature and salinity structure of the Kenai eddy reflected its coastal origin; core waters were warmer and fresher than surrounding waters (Figure 3). Based on hydrographic data, stations K20, K21, K23 and K24 were within the eddy core, K18, K19, K25, and K26 were transitional or edge stations, and stations K22 and K27 were outside the eddy (K27 is used here to represent the GoA HNLC end member; Figures 2, 3). The hydrographic structure at station SW2, the proposed formation region, is remarkably similar to the eddy core water properties (Rovegno et al., 2009, see their Figure 9) and is used to represent the coastal endmember. We define three eddy layers based on hydrography: the surface layer, the subsurface core layer, and the deeper core layer. Salient features of these layers are provided in Table 1. The temperature and density ($\sigma_\theta$) structure of the eddy during the north – south CTD transect (K11 – 18) are shown in Figure 4.

3.1.1. Surface layer

Within the core of the eddy, the surface mixed layer depth was on the order of 20 meters and had markedly warmed (to 11°C) and become slightly lower in salinity (to 32.22) over the course of the summer. The 1% light level was between 30 and 50 m depth, with an average of about 40 meters. A temperature gradient existed between 20 and 40 meters.
We define the surface layer of the eddy as depths where \( \sigma_b \leq 25.4 \) (and salinity is less than 32.43, average depth of 0 – 30 m). This layer includes the entire surface mixed layer and an upper portion of the thermocline (equivalent to the depth of the photic zone). For a given density, the eddy surface layer had cooler and fresher waters compared to basin waters (Figure 3). For example, at \( \sigma_b = 25.0 \) temperature and salinity at basin station K27 were 10.3 °C and 32.65 (at 24 m depth) compared to 8.8 °C and 32.31 at core station K20 (at 18 m depth). Isotherms were bowed up within the surface layer of the eddy and isopycnals and isohalines were bowed up from the surface down to about 150 m (Figure 4).

Surface transect T7 (Figure 2) extended from the continental shelf north of the eddy through the eastern part of the eddy core and into the HNLC waters to the south. Over the shelf, temperature and salinity were 9.1 °C and 31.8 (Figure 5), indicative of upwelled waters in this area. Within the eddy, surface waters were warmer and more saline, about 10 – 11 °C and 32.1. To the south of the eddy temperature and salinity were about 12 °C and 32.5, indicative of the HNLC waters of the northern GoA (Figure 5). The relatively low salinities observed within the eddy core were also observed in the surface mixed layer at K23, and are indicative
of the eddy pulling lower-salinity coastal water from riverine/glacial discharge off the shelf, as observed in previous studies (Okkonen et al., 2003; Crawford et al., 2005, 2007; Ladd et al., 2005b; Ladd et al., 2009).

3.1.2 Subsurface core layer

We define the subsurface core of the eddy as $25.4 \leq \sigma_\theta \leq 25.8$. The subsurface core includes the thermocline down to the “crossover point” in temperature salinity profiles, where the core station profiles first cross the basin station profile (at ~ 5 °C and salinity 32.69; Figure 3). On average, the subsurface layer at core stations was found between depths of 30 and 96 m. For a given density, the eddy subsurface core waters were cooler and fresher than basin waters (Figure 3). For comparison, Brown et al. (in prep) define a Sitka eddy shallow subsurface eddy core as $25.0 \leq \sigma_\theta \leq 25.7$.

3.1.3. Deeper core layer

The deeper core layer is defined as $25.8 \leq \sigma_\theta \leq 27.0$, and was found between average depths of 96 to 504 m at core stations. The deeper core is the water mass between the crossover point at the upper boundary and the merging of temperature and salinity in the deeper waters as seen in the T/S diagram (Figure 3). The designation of this deeper core is similar to the eddy cores defined by Ladd et al. (2005b; 2009). For comparison,
Ladd et al. (2009) define their Haida, Sitka, and Yakutat eddy cores as \(25.8 \leq \sigma_\theta \leq 26.8\), \(25.4 \leq \sigma_\theta \leq 26.8\), and \(25.3 \leq \sigma_\theta \leq 26.7\), respectively. Brown et al. (in prep) define a Sitka eddy deeper subsurface eddy core as \(25.8 \leq \sigma_\theta \leq 26.9\). Isopycnals and isohalines were depressed throughout the deeper core down to at least 1000 m depth (Rovegno et al., 2009). For example, the 26.4 isopycnal was at 200 m in the core of the eddy and 75 m outside of the eddy (Figure 4). It was 111 m deeper at K20 compared to K27 (55 °N and 53.7 °N, respectively; Figure 4). Deeper eddy core waters were warmer and fresher than waters at the same depth outside the eddy. At 170 m at K20 temperature and salinity were 6.1 °C and 33.41 compared to 4.1 °C and 33.92 at the K27 basin reference station. A pronounced temperature inversion was present in the deeper eddy core from about 100 to 350 m; the inversion was most pronounced at station K20 at 170 m (Figure 4). Such temperature inversions are typical of Sitka and Yakutat eddies (Ladd et al., 2005b; Ladd et al., 2009) and appear to also exist in Kenai eddies (Rovegno et al., 2009).

### 3.2 Macronutrients

Surface waters within the eddy along T7 had about 2 – 5 µM nitrate compared to >10 µM nitrate outside the eddy in the Alaskan
Stream and shelf waters (Figure 5). In the inside eddy stations, surface layer nitrate averaged 3.7 µM and silicate averaged 14.6 µM. In the upper 30 m of the water column at basin station K27, both nitrate and silicate were higher than the eddy stations (9.5 and 15.8 µM, respectively; Figure 6), indicative of the HNLC nature of the central GoA. The Si:N ratio in the surface layer within the eddy was 3.9 compared to 1.7 at K27, reflective of the eddy’s silicate-rich coastal source water (Brown et al., 2010; Lippiatt et al., 2010a). The average nitrate and silicate concentrations in subsurface core layer waters (25.4 ≤ σθ ≤ 25.8) were 18.3 µM and 25.9 µM, respectively, compared to 24.4 µM nitrate and 42 µM silicate over the same average depth range (30 to 96 m) at K27 (Figure 6).

Throughout the deeper core, inside eddy stations had lower macronutrient concentrations compared to the same depth outside the eddy. For example, at K20 at 250 m (the core of the temperature inversion where σθ = 26.5), nitrate and silicate were 34.6 µM and 58.7 µM, respectively, compared to K27 with nitrate and silicate concentrations of 44.1 µM and 104 µM at 250 m (Figure 6).

When nutrient concentrations are plotted against density rather than depth, values within the eddy core are more similar to values outside the eddy, with the exception of two low nitrate values at K27 at σθ
= 26.0 and \( \sigma_\theta = 26.1 \) (80 and 100 m depth). For example, at \( \sigma_\theta = 26.5 \) (within the deeper core layer), interpolated average nitrate and silicate at eddy core stations were 32.6\( \pm 1.0 \) and 54.6\( \pm 1.8 \) compared to 32.1\( \pm 1.1 \) and 53.3\( \pm 1.9 \) at basin stations.

### 3.3 Dissolved and leachable particulate (reactive) iron

#### 3.3.1 Source water station

At SW2, the proposed eddy formation region, dissolved Fe increased from 0.06 nM at 10 m to 2.1 nM at 205 m (near the bottom). Leachable particulate Fe increased from 0.94 nM at 10 m to almost 200 nM at 205 m (Figure 7). These surface water leachable Fe concentrations were elevated compared to the surface leachable Fe of eddy surface waters.

#### 3.3.2 Surface layer

In surface waters along T7, reactive Fe within the eddy was depleted compared to values over the shelf. Surface dissolved Fe concentrations were about 1.0 nM in the upwelled waters over the continental shelf and decreased to about 0.1 nM within the eddy. Leachable particulate Fe followed a similar trend; surface concentrations measured 0.2 – 0.3 nM within the eddy and 5.4 nM in the upwelled water
over the shelf (Figure 5). GO-Flo depth profiles for dissolved and reactive Fe are shown in Figure 8. Although this discussion largely focuses on Fe within eddy layers defined by density, data is plotted against depth rather than density for a clearer physical interpretation of the data. In the GO-Flo depth profiles, dissolved Fe was consistently ~ 0.1 nM at 10 m depth within the eddy, similar to values measured along T7 and slightly elevated compared to K22 and K27 surface waters (Figure 8a). The average dissolved and leachable Fe concentrations within the surface layer at inside eddy stations were 0.07 and 0.89 nM, respectively, compared to 0.02 and 0.12 nM over the same density layer at outside eddy stations (Figure 8). Surface water dissolved Fe values measured during this study in HNLC waters (0.02 nM) are similar to those reported for the open GoA in other studies (e.g. Martin et al., 1989; Nishioka et al., 2001; Wu et al., 2009). The dissolved Fe concentrations within the eddy, together with the nitrate concentrations of 2 to 5 µM, suggest that the Kenai Eddy surface waters were Fe-limited at the time of sampling.

3.3.3 Subsurface core layer

Dissolved and leachable particulate Fe concentrations within the eddy core subsurface layer were markedly elevated compared to the same average depth range (30 to 96 m) at basin stations K22 and K27 (Figure 8). The average dissolved and leachable Fe concentrations within the
subsurface core at inside eddy stations were 0.30 and 1.36 nM, respectively, compared to 0.04 and 0.15 nM over the same depths at outside eddy stations (Figure 8). Thus, on average, within the subsurface core there was over eight times more reactive Fe (the sum of the dissolved and leachable phases) inside the eddy compared to the same densities outside the eddy. This elevated reactive Fe in the subsurface core existed along with 18.3 µM nitrate and 25.9 µM silicate. Brown et al. (in prep) also measured about eight times greater reactive Fe within their Sitka eddy shallow subsurface core compared to their basin reference station.

Furthermore, at a given density, dissolved and reactive Fe concentrations were elevated within the eddy compared to the basin stations. For example, at $\sigma_\theta = 25.7$, within the subsurface core of the eddy, interpolated dissolved and reactive Fe concentrations within the eddy core were $0.32 \pm 0.1$ and $1.72 \pm 0.43$ compared to $0.03 \pm 0.0$ and $0.19 \pm 0.12$ at basin stations. At $\sigma_\theta = 26.5$, within the deeper core of the eddy, interpolated dissolved and reactive Fe concentrations within the eddy core were $0.74 \pm 0.12$ and $2.70 \pm 0.82$ compared to $0.11 \pm 0.07$ and $0.28 \pm 0.26$ at basin stations.

3.3.4 Deeper core layer
The average dissolved and leachable particulate Fe concentrations within the deeper core at inside eddy stations were 0.74 and 2.63 nM, respectively, compared to 0.32 and 0.38 nM over the same average depth range (96 to 504 m) at outside eddy stations (Figure 8). Thus, on average, within the deeper core there was four times more reactive Fe inside the eddy compared to the same depths outside the eddy. At $\sigma_\theta = 26.5$ (about 200 m depth, Figure 4) within the core of the eddy, the average reactive Fe concentration was 2.7 nM. Comparatively, at K27 $\sigma_\theta = 26.5$ at 80 m depth, and the interpolated reactive Fe concentration is 0.08 nM. Thus, isopycnal mixing will supply Fe to shallower depths outside the eddy.

### 3.4 Manganese

Along T7, dissolved Mn was 1 nM in the HNLC waters to the south of the eddy, increased to about 4 nM in the eddy core, and then increased to 8 nM in the upwelled water over the shelf (Figure 5). In contrast to dissolved Fe, there is a distinct decrease in dissolved Mn along T7 at the transition from eddy core waters to HNLC waters (Figure 5). Similarly, in vertical profiles, dissolved Mn was elevated in the surface waters of the eddy core compared to surface waters at outside eddy stations (Figure 9). Dissolved Mn decreased with depth at eddy core stations, exhibiting a
scavenged-type profile (Figure 9a). These results are similar to what Brown et al. (in prep) report for a Sitka eddy sampled during the same field effort. This trend is consistent with photodissolution in surface waters and precipitation of Mn oxides beneath the photic zone (e.g. Sunda and Huntsman, 1994), and a relatively low biological requirement for Mn by phytoplankton, relative to its dissolved concentration. Leachable particulate Mn values were lower than associated dissolved Mn concentrations. Leachable particulate Mn was depleted at the surface within the eddy (< 1 nM) and increased to 1 – 2 nM at 50 m; in contrast, at basin stations leachable Mn was consistently < 0.1 nM throughout the water column (Figure 9b). Leachable particulate Mn appears to be a strong tracer of eddy core waters, particularly the subsurface eddy core. At the source water station near the Kennedy Entrance (SW2), surface dissolved Mn was 4.5 nM, about 1 nM greater than surface eddy values, but lower than values in the upwelled waters over the shelf during T7. Leachable particulate Mn was only 0.5 nM at 10 m at SW2 and increased to about 1 nM at 100 m (Figure 7). In deeper waters at SW2, leachable particulate Mn increased to 8.7 nM near the bottom at SW2 (205 m; Figure 7).

3.5 Chlorophyll

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Chl a concentration was 3-fold higher within the eddy core surface layer compared to the basin reference station. In the upper 10 m at stations K20, K21, K23, and K24, Chl a averaged 2.4 µg/L compared to 0.77 µg/L at K27 (Figure 10). The highest Chl a value (3.9 µ/L) was observed at the surface at K21, within the core of the eddy. Chl a was also elevated at 5 m depth at K22 (3.5 µg/L), behind the trailing edge of the eddy within its wake. Okkonen et al. (2003) have shown that chlorophyll is often elevated around the edges of an eddy due to upwelling and the entrainment of high chlorophyll shelf water. Salinity at the surface at K22 was 32.18 indicating that the elevated Chl a at this station was not likely due to entrainment of shelf water (K22 is located beyond the trailing edge of the eddy). Thus, the elevated Chl a at K22 may have been due to localized upwelling at the eddy edge (Okkonen et al., 2003; Peterson et al., 2011).

Underway fluorescence is used as a proxy for chlorophyll along T7. Spikes in fluorescence were observed in conjunction with decreases in temperature, presumably due to recent storm-induced mixing (Figure 5). A NOAA buoy off of Kodiak Island (station 46078, 56.07 °N 152.57 °W) reported wind speeds greater than 30 knots and wave heights of about 3.5 m during the day prior to sampling along T7. The storm-induced vertical
mixing causing the decreased surface temperature would have mixed subsurface reactive Fe into the surface waters along with nitrate and silicate resulting in relaxation of Fe-limitation and the observed spikes in fluorescence (Figure 5).

4. DISCUSSION

4.1 Eddy layers

We define three layers within the core of the Kenai eddy stratified by density: the warm surface layer, the subsurface core layer, and the deeper core layer. These eddy layers are associated with different timescales of Fe delivery to the surface layer (i.e. synoptic, seasonal and interannual). We suggest that subsurface core waters (found at depths between 30 and 96 m) will be mixed to the euphotic zone during storm events throughout the year in the GoA. Evidence of storm mixing of subsurface water into the surface mixed layer is apparent in T7 hydrographic, macronutrient, and fluorescence data (Figure 5). In addition, a portion of the deeper core layer will most likely be mixed to the surface over the course of the winter; Freeland et al. (1997) show that in the Alaska Gyre winter storms can mix the water column down to 100 – 125 m. Furthermore, Crawford et al. (2007) note that in March 2002 an Argo profiler measured a $\sigma_t$ of 26.3 at 10 m depth in the Alaska Gyre. For

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comparison, at K27 $\sigma_t = 26.3$ was found at about 75 m depth. Deep mixing to density surfaces within the deeper core suggests that winter mixing should impact the entire subsurface core layer in addition to a portion of the deeper core layer of the Kenai eddy.

The deeper core layer waters can also be ventilated on interannual timescales. Because isopycnals are depressed within the core of the eddy, “leakage” of deeper core layer waters along isopycnal surfaces can result in the delivery of core waters to shallower depths outside the eddy (Peterson et al., 2005). As discussed above, the deeper core waters at $\sigma_o = 26.5$ (about 200 – 220 m) contain similar macronutrient concentrations and elevated reactive Fe compared to shallower waters at the same density at K27 (about 80 – 90 m).

As an eddy ages, frictional decay and “eddy spin-down” will cause depressed isopycnals to relax and inject core water to shallower depths (Crawford et al., 2005). The timescale of isopycnal relaxation will depend on the lifespan of the eddy. Studies have estimated isopycnal rebound rates of 0.1 to 0.9 m day$^{-1}$ for Haida eddies (Peterson et al., 2005; Johnson et al., 2005).

4.2 Macronutrients
The macronutrient signature in eddy surface waters is a function of source water concentrations, biological uptake since formation in January 2007, export via the biological pump, and mixing with surrounding waters. Coastal waters in the northern GoA have been shown to be nitrate-poor and silicate-rich due to glacial meltwater inputs (Brown et al., 2010; Lippiatt et al., 2010a). This nutrient signature is reflected in the eddy core waters, where surface water Si:N ratios were more than twice the Si:N ratio outside the eddy. Similarly, there was lower nitrate (but similar silicate) in surface eddy waters compared to K27, the HNLC basin reference station (Figure 6). Eddy surface waters were Fe-deplete, but there was about 2 – 5 µM residual nitrate (Figures 6, 8). This is indicative of Fe-limitation within the surface waters of the Kenai eddy. In contrast, nitrate concentrations were near zero with about 0.05 nM reactive Fe in a Sitka eddy studied on the same cruise (Brown et al., in prep), likely indicative that a bloom had already occurred in the Sitka eddy surface waters.

Macronutrient concentrations were elevated at basin stations compared to similar depths at eddy core stations (Figure 6). However, due to the depression of isopycnals within the core, macronutrient concentrations in the eddy and at basin stations were similar for a given density. In contrast, Ladd et al. (2009) observed elevated nitrate within
their eddy Haidas, Sitka, and Yakutat eddy cores compared to the same densities at their Haida reference station and at Ocean Station Papa.

4.3. Reactive Fe

4.3.1. Previous data

There are relatively few studies on trace metals in mesoscale eddies in the GoA. Johnson et al. (2005) published the first study of Fe transport by a Haida eddy in the GoA. The study followed the eddy for almost two years; after four months they observed surface depletion and subsurface enrichment of labile Fe (an unfiltered sample acidified to pH 3.2 and analyzed within 1 – 2 hours), attributed primarily to biological uptake. At an age of 16 months the Haida eddy still contained about twice as much Fe compared to basin waters, with the majority of the Fe in the particulate phase, especially in surface waters.

Ladd et al. (2009) sampled three young eddies (a Haida, Sitka, and Yakutat eddy) in spring 2005. The Yakutat eddy was sampled in May 2005, only 1.5 months after it was first observed in altimetry data. Younger eddies are hypothesized to carry more of the water properties of the coastal formation region compared to older eddies. Thus, this young Yakutat eddy is useful for comparison to the eight-month-old Kenai eddy we sampled. Ladd et al. (2009) report “total Fe” (an unfiltered sample
acidified to pH 1.5 with HCl, microwaved, and analyzed back on shore), which is analogous to our reactive Fe (dissolved Fe + leachable particulate Fe), but likely accessing a greater portion of the particulate phase although not the entire refractory particulate Fe pool. The subsurface core of their young Yakutat eddy (110 – 335 m) had 30 nM “total Fe”, which the authors attributed to both the young age of the eddy and the shallow source region (200 m deep over the Yakutat shelf). Furthermore, the Ladd et al. (2009)’s 4.5-month-old Sitka eddy subsurface core (110 – 550 m) contained 11.5 nM “total Fe”. In contrast, our older Kenai eddy deeper core layer waters (96 – 504 m) had 2.9 nM reactive Fe and 10.8 nM total Fe (total being the sum of the reactive and refractory phases which reflects the actual total Fe concentration). Based on this comparison and observations by Johnson et al. (2005), it appears that much of the particulate Fe in young eddies spawned from the high particulate Fe coastal GoA waters (Lippiatt et al., 2010a) settles out of the water column fairly rapidly following formation. The lifetime of the reactive particulate Fe phase in GoA eddies is an important question that will determine the impact of eddy-Fe (particularly the particulate fraction) upon dissipation and relaxation.

4.3.2. Kenai eddy reactive Fe
As observed in previous studies (e.g. Lippiatt et al., 2010a, b), the leachable particulate Fe phase can be orders of magnitude greater than dissolved Fe and is essential to consider in assessing the potentially bioavailable Fe pool. Within the eddy core, reactive Fe that can be delivered from the subsurface core into the surface layer due to storm induced mixing would be almost nine times greater than concentrations outside the eddy. Deep mixing within the eddy can deliver a significant amount of dissolved and reactive Fe to surface waters in addition to abundant macronutrients.

Comparison of the source water Fe profiles (sampled eight months after eddy formation) to eddy core waters can provide an estimate of Fe loss over the lifetime of the eddy. Dissolved Fe between 50 – 100 m depth at our source water station SW2 averaged 0.54 nM, slightly elevated compared to an average of 0.3 nM in the subsurface core layer. Reactive Fe measured 4.9 nM at 100 m depth at SW2 compared to 1.66 nM within the subsurface core of the eddy. As an eddy ages, a combination of particle settling, biological uptake, export via the biological pump, and dilution with basin waters is expected to decrease the eddy core water Fe signal.

Depth-integrating and averaging reactive Fe over the subsurface core layers at each core station and using an eddy radius of 82 km, we
estimate an Fe inventory of $2.4 \times 10^6$ mols of reactive Fe in the subsurface core of the eddy (dissolved Fe inventory in the subsurface core was $0.46 \times 10^6$ mols). Similarly, we estimate $25 \times 10^6$ mols of reactive Fe in the deeper core of the eddy (dissolved Fe inventory in the subsurface core was $6.7 \times 10^6$ mols). Brown et al. (in prep) estimate that an average mesoscale eddy in the GoA contains about $0.8 \times 10^6$ mols of reactive Fe in the subsurface core. In a four-month-old Haida eddy with a radius of 56 km to a depth of 600 m (the average depth of our deeper core is 504 m), Johnson et al. (2005) reported $8.7 \times 10^6$ mols of labile Fe (an unfiltered sample acidified to pH 3.2; our leach method probably solubilizes a greater portion of the particulate phase than Johnson’s labile method), and $21 \times 10^6$ mols of “total” Fe (an unfiltered sample acidified to pH 1.5, stored for > 7 months and microwaved). Furthermore, based on estimates of the area influenced by Haida eddies and aerosol Fe deposition and solubility over the same area (an annual atmospheric flux on the order of 1 to $10 \times 10^6$ mols of soluble Fe based on Jickells and Spokes, 2001), Johnson et al. (2005) conclude that Haida eddies may be responsible for 5 – 50% of the dissolved Fe that is introduced to the upper 1000 m of the water column in that region. More recently, Crusius et al. (in press) examined the delivery of Fe from northern GoA riverbeds during late fall dust events. They used an aerosol optical thickness satellite product and an Fe
solubility of 2 – 5% to estimate that one November 2006 dust event transported $1 \times 10^6$ to $7 \times 10^6$ mols of soluble Fe to the GoA. These dust events can potentially deliver a significant amount of Fe hundreds of km past the shelf break, but the resulting impact on primary productivity is unclear as they appear to occur most often in late fall, when light levels are low. Further work is needed to determine the relative contributions of Fe sources to the GoA, but it is clear that mesoscale anticyclonic eddies are a significant means of Fe delivery from coastal waters to the central GoA.

4.4 Manganese

Manganese concentrations in coastal surface waters (T7; Figure 5) indicate that glacial meltwaters are a greater source of dissolved than leachable particulate Mn or that glacial leachable particulate Mn is solubilized readily in coastal waters. Furthermore, dissolved Mn appears to be an excellent tracer of eddy surface waters. Similar high surface water dissolved Mn surface concentrations are observed by Brown et al. (in prep) for a Sitka eddy. Below the photic zone, dissolved Mn is oxidized or adsorbed to particles and precipitates as Mn oxide coatings on particle surfaces, which are present in the leachable phase. As an eddy ages, dissolved Mn concentrations are expected to decrease due to biological
uptake. However, there is much less of a biological requirement for Mn than Fe (on a mol:mol basis; Bruland et al., 1991). Using the assumption that Mn concentrations in subsurface waters at the source water stations during eddy formation in January 2007 were similar to September 2007 values reported here, eddy subsurface water dissolved Mn concentrations decreased approximately 1 nM (to 2 nM). Unfortunately no 50 m particulate sample was collected at SW2; leachable particulate Mn was about 1 nM at 100 m depth both within the eddy core and at SW2. A decrease in subsurface dissolved Mn concentrations as the eddy ages is expected due to a combination of precipitation and particle settling.

4.5 Biological impact

Elevated dissolved and reactive Fe in the subsurface and deeper core waters that are mixed to the surface layer during deep winter mixing will drive a spring bloom within the eddy. In contrast, outside the eddy, deep winter mixing will bring almost nine times less reactive Fe to the surface resulting in Fe-limited HNLC waters. Crawford et al. (2007) observed that in the spring up to 80% of the surface chlorophyll in the GoA is associated with mesoscale eddies which occupied only 10% of the study region; the authors also show that eddy chlorophyll typically peaks in the spring and that eddies promote a stronger spring bloom compared
to surrounding waters. In the late summer / early fall in the GoA (the time period of this study), stratification begins to decrease, mixing of reactive Fe and macronutrients to the euphotic zone increases, and there is still enough sunlight for a fall bloom. In this study, there was clearly higher Chl $a$ at the surface within the eddy compared to stations outside the eddy (e.g. K27, Figure 10). A MODIS composite image from 29 August to 5 September, 2007 shows elevated surface chlorophyll within the eddy, particularly around the eddy edges and in the wake of the eddy (Figure 11). The elevated Chl $a$ at inside eddy station K21 may be due to proximity to the shelf break and mixing between high Fe, low nitrate shelf waters and the Fe-limited eddy surface waters (Lippiatt et al 2010a). Furthermore, Fiechter and Moore (in review) predict with a coupled physical-biological model for the coastal GoA that two-thirds of total primary production in the “eddy corridor” off the shelf break between Kenai Peninsula and the Shumagin Islands is associated with eddy-induced mixing.

Ribalet et al. (2010) describe a phytoplankton hotspot at the transition zone between iron-rich, nitrate-poor coastal waters and nitrate-rich, iron-poor offshore waters in the Northeast Pacific Ocean. The authors observed a succession of phytoplankton blooms of various size classes along a gradient in Fe availability across the transition zone,
which they suggest is an ecotone with elevated primary productivity and biological diversity. Furthermore, Peterson et al. (2011) conducted a mixing experiment with surface eddy core and outside basin waters and observed a higher rate of primary productivity and greater phytoplankton diversity in the mixed water. We suggest that eddy edges are analogous to the transition zone discussed by Ribalet et al. (2010) and are thus important regions of enhanced primary productivity in the GoA.

Peterson et al. (2005) show that during the first year of a Haida eddy, there was a spring bloom with ten times more silicic acid drawdown compared to the second year of the eddy life, when the bloom occurred later in the summer. The eddy Fe inventory may play a role in the observed shift from diatom-dominated to non diatom-dominated assemblages. As Fe becomes depleted in the eddy surface layer, phytoplankton blooms are expected to be smaller and occur later in the season at deeper depths (e.g. Whitney and Robert, 2002). As the Kenai eddy ages, the subsurface core and deeper core layers will become important reservoirs of Fe that can sustain primary productivity over the lifetime of an eddy.

Using an Fe:C uptake ratio of 10 µmol : mol (a rough estimate for phytoplankton in the GoA: Bruland et al., 2001), 1.2 nM Fe would be required to draw down the nitrate in the Kenai eddy subsurface core
layer (~ 18 μM). The subsurface core contained 1.66 nM reactive Fe compared to only 0.19 nM outside the eddy. Thus, deep mixing bringing the subsurface core waters to the surface will deliver enough Fe to promote a bloom within the eddy but non-eddy waters will be Fe-limited.

Average summertime surface nitrate concentrations in the GoA clearly show the HNLC region of the central GoA just off the shelf break near the Alaskan Stream corridor (Figure 1a). Alaskan Stream eddies, such as the Kenai eddy described here, propagate along this distinct boundary between high iron, low nitrate coastal waters and low iron, high nitrate offshore waters. Thus, eddies in the Alaskan Stream contribute to shelf/slope exchange between these two adjacent water masses and lead to elevated chlorophyll in the transitional waters, as is apparent in satellite-derived chlorophyll images (Figure 11).

5. CONCLUSIONS

The Kenai eddy sampled during this study contained elevated reactive Fe compared to regions outside the eddy. The three eddy layers defined here correspond to different timescales of delivery of Fe to the photic zone. The subsurface core eddy water can be mixed up with storm events and during deep winter mixing. The deep core water can mix along isopycnals to shallower depths at the eddy edges. Also, as the eddy
eventually propagates into the basin and relaxes, the deeper core layer will be a source of deep Fe to the HNLC waters of the central GoA. As noted by Ueno et al. (2010), as of August 2010, the Kenai eddy was still “alive” and propagating along the Aleutian Island chain. Any additional distance traveled by a GoA eddy along the shelf break creates more opportunity for cross-shelf exchange of coastal and HNLC waters via interaction with shelf-slope circulation (Okkonen et al., 2003). Thus, we argue that the long-lived Kenai eddy (a lifespan of at least 3.5 years) has clearly promoted mixing between the Fe-enriched shelf waters and offshore waters and thus enhanced primary productivity in the GoA. Interannual variability in eddy formation (Crawford et al., 2007; Henson and Thomas, 2008; Ladd, 2007; Rovegno et al., 2009) can drive the overall impact of GoA eddies on productivity.
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*Does not reflect the temperature inversion in the deeper core.

**Table 1.** Salient properties of the eddy layers.
Figure 1. Average summertime surface nitrate in the GoA (A). Data from the NODC World Ocean Atlas. Contours are 1 µM. The star marks the location of the Kenai eddy described here. The area inside the box is the region showed in (B), which depicts the sea surface height anomaly on 5 September, 2007. The Kenai eddy core is clearly shown in red with a 30 cm sea surface height anomaly. Figure credit: P. Rovegno.
Figure 2. Map of the study area and sample locations. GO-Flo stations are marked by black circles and CTD stations (K11 – K18 from north to south) are indicated by white diamonds (CTD stations K1 – K10 from east to west across the eddy are not plotted). A CTD cast was also completed at each GO-Flo station. The eddy was first detected by Rovegno et al. (2009) on 10 January 2007 at the location of the black diamond (57.7 °N 147.8 °W). Depth contours are 100 m up to 500 m.
**Figure 3.** Temperature - salinity structure at eddy core (shaded symbols), basin (open symbols), and transitional/edge stations. Dashed lines indicate the isopycnal layer divisions with densities ($\sigma_\theta$ marked at the upper right).
Figure 4. Density (upper panel) and temperature (lower panel) sections based on the north to south CTD transect (stations K11 – K18 on 8 – 9 September). The bold vertical lines indicate the locations of CTD casts.
Figure 5. Transect 7 temperature, salinity, dissolved and leachable Fe, and dissolved and leachable Mn (upper panel). Total particulate Fe, nitrate, silicate, and fluorescence are shown in the lower panel. Note that the transect was completed from south to north; for clarity the x-axis has been flipped and the shelf waters are located at the right side of the figure.
Figure 6. Nitrate (a) and silicate (b) depth profiles at the eddy core (shaded symbols) and basin stations (open symbols).
Figure 7. Source water station (SW2) dissolved and leachable Fe and dissolved and leachable Mn profiles.
Figure 8. Dissolved Fe (a) and reactive Fe (b) at eddy core (shaded symbols) and basin stations (open symbols).
Figure 9. Dissolved Mn (a) and leachable Mn (b) at eddy core (shaded symbols) and basin stations (closed symbols).
Figure 10. Chl $a$ at eddy core (shaded symbols) and basin stations (open symbols).
Figure 11. MODIS chlorophyll concentration composite image from 29 Aug – 5 Sept 2007. The eddy is circled. Higher chlorophyll concentrations appear as red/orange and lower chlorophyll concentrations appear blue/green. Image downloaded from NASA Ocean Color website (http://oceancolor.gsfc.nasa.gov/).
CONCLUSION

This dissertation described the distribution and delivery of reactive iron to the North Pacific Margin, in particular the coastal waters offshore of Washington and Oregon and the northern Gulf of Alaska (GoA). Coastal regions cover approximately 1% of the global ocean’s surface area yet are estimated to account for as much as 40% of the global ocean export production (Muller-Karger et al., 2005; Hales et al., 2006). Thus, it is essential to understand the availability of iron in coastal zones in order to better constrain the oceanic carbon cycle. The scarcity of available iron data limits modeling efforts and the ability to ground truth model results.

This dissertation presented and discussed new reactive iron data and suggested the drivers of variability in reactive iron concentrations in the summertime in two coastal regions. However, for a more complete understanding of the seasonal variability in iron supply, further studies should be conducted, particularly prior to the spring bloom.

In Chapter 1, the distribution of leachable particulate iron in the Columbia River, estuary, and near-field plume was examined. The Columbia River was shown to be an important source of reactive iron to the productive coastal waters off Oregon and Washington. It was found that tidal amplitude and river flow are the primary factors influencing the near-field leachable particulate iron concentrations, with additional
inputs to the plume during upwelling conditions. Leachable particulate iron was shown to be abundant (concentrations up to 900 nM) and suggested to be available for solubilization following drawdown of the dissolved iron phase in the near-field plume. Furthermore, the Columbia River plume, which increases cross-shelf transport of nutrient- and iron-rich waters, has the potential to export reactive iron to the California Current system.

Chapter 2 examined the distribution of dissolved and leachable particulate iron along the northern GoA coast. In general, leachable particulate iron concentrations varied as a function of salinity, with extremely elevated concentrations (over 1000 nM) within low salinity glacial meltwater plumes. In contrast, dissolved iron concentrations were relatively low (2 – 3 nM) and consistent, and did not show elevated concentrations in freshwater plumes. There was an obvious transition from low nitrate, high iron coastal waters to low iron, high nitrate offshore waters along a transect from Seward, Alaska out to the HNLC waters of the central GoA. Elevated chlorophyll was observed in the vicinity of the shelf break, indicating that mixing between these two regimes promotes primary productivity in the transitional waters. This set the stage for Chapter 3, which discussed enhanced availability of iron to offshore HNLC waters via mesoscale anticyclonic eddies.
In Chapter 3, the reactive iron content within an eight-month-old Kenai eddy propagating along the shelfbreak southwest of Kodiak Island was discussed. It was shown that reactive iron concentrations within the subsurface core were more than eight times higher inside the eddy core compared to outside the eddy. The subsurface core \(25.4 \leq \sigma_\theta \leq 25.8\), average depths within the eddy of 30 – 96 m) was argued to be seasonally important as these waters can be brought to the surface with deep winter mixing. Reactive iron concentrations within the deeper core layer \(25.8 \leq \sigma_\theta \leq 27.0\), average depths within the eddy of 96 – 504 m) were four times greater than outside the eddy; the deeper core was argued to be a source of iron to HNLC waters on a longer timescale, due to isopycnal mixing and eventual eddy relaxation.

A unifying trend in this dissertation was the dominance of the leachable particulate iron phase in the reactive iron pool. Leachable particulate iron concentrations were consistently at least an order of magnitude greater than dissolved iron concentrations, such that solubilization of even a fraction of the reactive particulate phase can dominate the bioavailable iron pool. In Chapter 1, dissolved iron concentrations in the near-field plume appeared to be “capped” around 20 – 25 nM, which is a reasonable upper limit for strong iron-binding ligand
concentrations (Buck et al., 2007). Although the Columbia River has a lower concentration of humic substances than rivers on the east coast of North America (Boyle et al., 1997; Bruland et al., 2008), it appears to contain about ten times more iron-binding ligands than the glacial meltwaters of the northern GoA. The low and remarkably consistent dissolved iron concentrations in the coastal waters of the northern GoA (about 2 – 3 nM) reflect the relative scarcity of iron binding ligands in these glacial meltwaters. The availability of leachable particulate iron in these coastal waters effectively buffers the dissolved iron concentration at 2 – 3 nM. Iron-binding ligands have a significant impact on the biogeochemistry of iron in the marine environment. Although the exact structures and identities of iron-binding ligands in seawater are unknown, they are understood to have a biological source, whether active (e.g. siderophore production) or passive (e.g. cell lysis products) (Hunter and Boyd, 2007). Thus, an understanding of iron-binding ligand dynamics is fundamental to interpreting dissolved and leachable particulate iron concentrations in the marine environment.

Depending on the nature of the freshwater source, the percent of the total particulate iron phase that is leachable varies. The percentage leachable particulate iron provides information on the residence time and composition of suspended particulate material. For example, Hurst and
Bruland (2008) found that 6% and 37% of the total particulate iron phase was leachable in the San Francisco Bay plume in the summer and winter, respectively. The seasonal difference in the percent leachable iron was attributed to the influence of winter rains on the residence time of sediment in the bay; winter flooding delivers fresh suspended particles to the plume in the winter whereas in the summer suspended particulate material has a longer residence time in the bay and much of the leachable iron coatings are solubilized before reaching the coastal ocean. As discussed in Chapter 2, summertime Columbia River near-field plume samples were on average about 26% leachable; in the Columbia River, particulate iron concentrations are influenced by high flow conditions due to spring snowmelt rather than precipitation (Lippiatt et al., 2010a). Furthermore, in the GoA, where physical glacial weathering dominates over chemical weathering, percent leachable particulate iron values were lower (~ 11%) nearshore and increased with distance from the source (~ 32% in offshore samples; Lippiatt et al., 2010b). Thus, in coastal regions it is essential to consider the source of the suspended particulate material, as it can have dramatic consequences on the percent of the particulate iron that is leachable and thus the availability of reactive particulate iron.
A major question that remains to be addressed in future studies is the residence time of reactive particulate iron, particularly within mesoscale anticyclonic eddies that mix this reactive iron out into the HNLC waters of the central GoA. Particulate iron derived from the GoA coastal margin has been shown to promote primary productivity hundreds of kilometers away from the source (Lam et al., 2006), but the degree of removal of particulate iron in the water column is not very well constrained (e.g. Boyd et al., 2010). Ueno et al. (2010) followed the trajectory of the Kenai eddy discussed in Chapter 3 and showed that although the eddy split into two in February 2009, both eddies were still propagating as of August 2010, more than 3.5 years since formation. One eddy continued to propagate westward along the Aleutian Islands while the other propagated south. Recent work has examined the relative contribution of eddy-derived iron compared to other sources of iron in the GoA (e.g. local dust storms, Crusius et al., 2011) and has highlighted the importance of mesoscale eddies. Thus, the residence time of particulate iron is especially important in considering the impact of eddy-iron on primary productivity in iron-deplete regions following the decay and isopycnal relaxation of long-lived mesoscale eddies.

This dissertation adds to growing evidence that although dissolved iron is the most biologically active phase, the readily leachable
particulate iron phase is an important reservoir of reactive iron that is available for solubilization and can maintain saturation of iron-binding organic ligands as dissolved iron is consumed. A shift in the partitioning of iron between the dissolved and particulate phases (and a change in the portion of the dissolved iron phase bound by organic ligands) with changes in ocean chemistry due to ocean acidification (Shi et al., 2010) highlights the importance of understanding the biogeochemical cycling of this essential micronutrient.
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