Coastal iron fluxes to surface waters of the northern NE Pacific:
A driver of the marine ecosystem and carbon cycle

A USGS white paper

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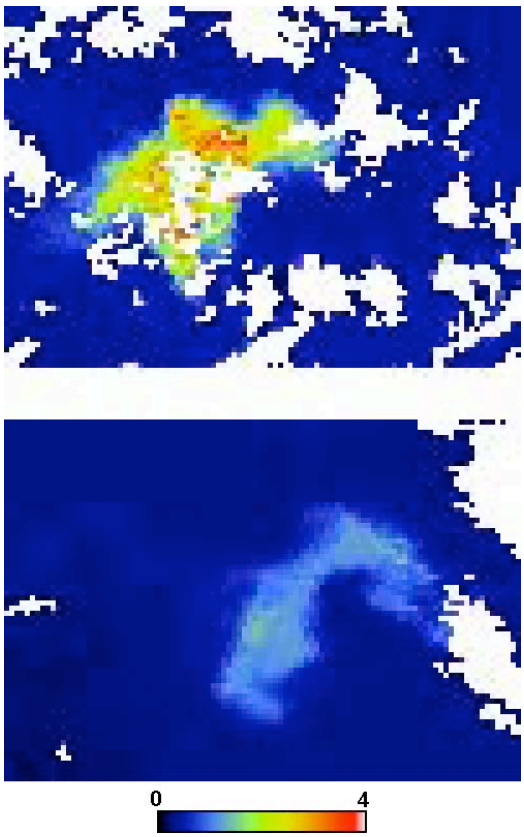

Cover image: *SeaWiFS Ocean Color images showing the rapid decline of a bloom induced by iron addition in the NE Pacific in 2004. The upper panel represents day 19 following addition while the bottom panel is day 24 (linear scale bar – mg chl m^{-3}). The bloom areal extent was ~1000 km^2 and the maximum chlorophyll concentration was 4.5 mg chl m^{-3}. Both panels are framed by the same latitudes and longitudes. White pixels denote cloud contamination. From Boyd et al., 2004.*

Executive Summary

Dissolved iron is a micronutrient that limits biological productivity in roughly 30-40% of the ocean surface, including much of the northern North Pacific (Moore et al., 2002). In these iron-limited regions, the iron supply profoundly influences biogeochemical processes. Iron addition in the northern North Pacific has been shown to stimulate the growth of phytoplankton (mostly large diatoms; Boyd et al., 2004). In this manner iron supply to surface waters may lead to a transfer of carbon from surface-waters to the deep sea, and has the potential to contribute to a reduction in atmospheric CO_2 (Martin, 1990; Buesseler and Boyd, 2003). Iron supply may also impact the fish yield in iron-limited regions, if bottom-up control of fisheries predominates (Ware and Thomson, 2005). All of these topics are active areas of exciting, interdisciplinary research.

Iron must be delivered to surface waters in order to be used by phytoplankton. Aeolian transport has long been thought to be the dominant transport mechanism. Recent research, however, suggests that other sources of dissolved iron may also be important, including rivers (Chase et al., 2002), diagenetic remobilization from sediments (Elrod et al., 2004), sediment resuspension (Chase et al., 2002; C. Measures, personal communication, 2005), and groundwater (Charette and Sholkovitz, 2002; Windom, Moore and Jahnke, unpublished data, 2005). Indeed diagenetic remobilization from sediments alone has recently been suggested to be at least as important as atmospheric inputs (Elrod et al., 2004).

The time is ripe to initiate an interdisciplinary USGS program examining these coastal sources of iron to the North Pacific, their impacts on the carbon cycle and on fisheries. This represents a unique opportunity, both because the importance of iron inputs to the ocean demands that we develop our understanding of iron sources and because there are several upcoming national and international oceanographic initiatives from which this effort can benefit (GEOTRACES, IMBER, OCCC, BEST (each discussed later)). In each case, a research emphasis on coastal processes would allow the USGS to carve out a niche within much larger oceanographic programs.

Compelling locations for focused studies include the Bering Sea and the Gulf of Alaska. One reason is that dissolved O_2 levels are low at reasonably shallow depths in both locations, which may enhance diagenetic remobilization of iron, creating a dissolved iron pool that could be readily transported to the surface for uptake by phytoplankton. In addition, the Bering Sea has a broad continental shelf where sediment resuspension is likely to be important. Furthermore, the Yukon River discharges into the Bering Sea, probably delivering considerable riverine iron. The Gulf of Alaska has a much narrower shelf, yet riverine iron and coastal iron transported offshore in eddies are likely to be important there (Stabeno et al., 2004; Whitney et al., 2005; Johnson et al., 2005). Studies in any of these locations will need to evaluate the physical transport processes which drive upwelling and exchange between nearshore and offshore waters. In the Gulf of Alaska, for example, these include processes that lead to elevated productivity and phytoplankton biomass in nearshore waters south of Alaska, despite wind-driven downwelling during most of the year (Ware and Thomson, 2005).

1. Introduction

Throughout most of the ocean the productivity of phytoplankton[1] is limited by the availability of one or more essential nutrients. In recent years we have come to realize that dissolved iron is one such limiting nutrient. Indeed, it is now thought that the availability of dissolved iron limits productivity in 30-40% of the ocean surface (Moore et al., 2002), including the vast majority of the northern North Pacific (Figure 1). Because of its impact on phytoplankton, the supply of iron to North Pacific surface waters is a driver of processes of enormous regional and global significance. Iron addition in the northern North Pacific has been shown to stimulate the growth of phytoplankton (mostly large diatoms; Boyd et al., 2004). In this manner iron supply to surface waters may lead to a transfer of carbon from surface-waters to the deep sea, and has the potential to contribute to a reduction in atmospheric CO_2 (Martin, 1990; Buesseler and Boyd, 2003). Iron supply may also impact the fish yields in iron-limited regions where they feed, if bottom-up control of fisheries predominates (Ware and Thomson, 2005). All of these topics are active areas of exciting, interdisciplinary research.

Recent work suggests that much of the dissolved iron delivered to the ocean may be derived from coastal sources. Diagenetic remobilization from sediments alone has recently been suggested to be at least as important as atmospheric inputs (Elrod et al., 2004). Sediment resuspension (Chase et al., 2002; C. Measures, personal communication, 2005), rivers (Chase et al., 2002) and groundwater (Charette and Sholkovitz., 2002; Windom, Moore and Jahnke, unpublished data, 2005) have also been suggested to play an important role supplying iron to the ocean. Given the important influences of iron on the marine ecosystem and carbon cycle, the USGS has a tremendous opportunity to develop an interdisciplinary research program aimed at understanding and quantifying these coastal sources of iron, and their biogeochemical impacts.

[1] Phytoplankton are microscopic plants that live in the ocean, forming the base of the marine food chain.

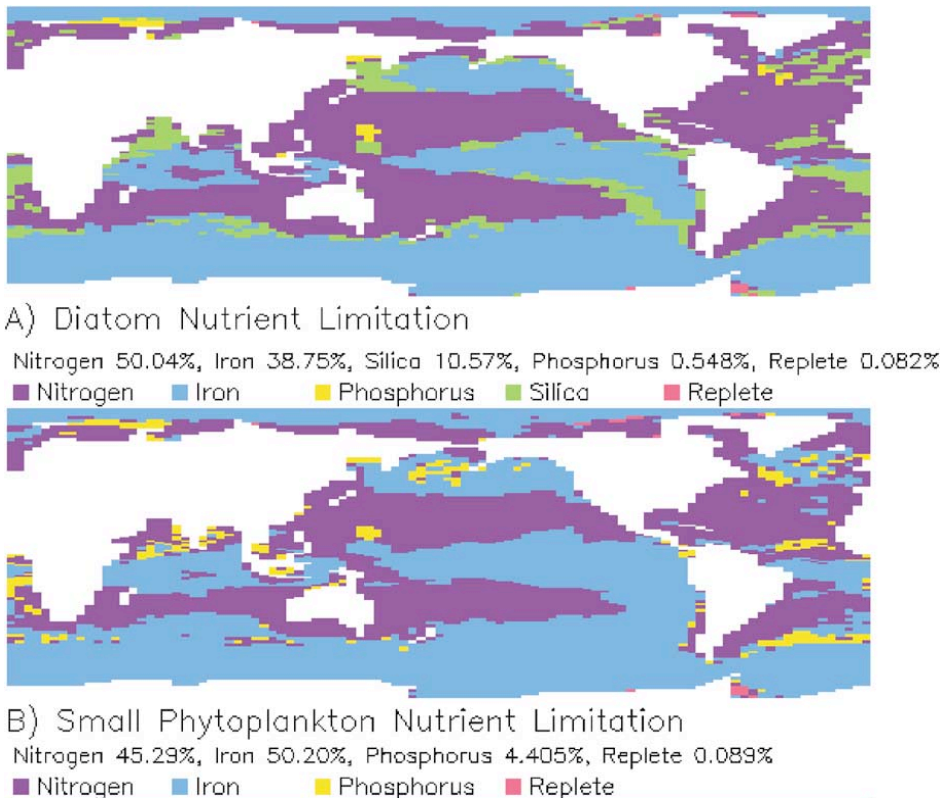

Figure 1: Global map showing the nutrient that limits biological productivity in various parts of the ocean. Note that iron is the limiting nutrient throughout most of the northern North Pacific Ocean for both diatoms and small phytoplankton. Note also how common iron limitation is in the ocean as a whole (although not in the Atlantic). (From Moore et al., 2002).

The most compelling location within U.S. waters in which to carry out research examining coastal iron sources and their impacts is the Northeast Pacific Ocean, in Alaskan waters. The fundamental reason is that this represents the largest region of iron-limited waters (Figure 1), hence the supply of iron has a profound influence on biogeochemical processes. Within the NE Pacific, the Gulf of Alaska and the Bering Sea are compelling regions in which to focus "process studies" examining iron sources, for several reasons. One reason is that dissolved O_2 levels are low at reasonably shallow depths in both locations, which may enhance diagenetic remobilization of iron, creating a dissolved iron pool that could be readily transported to the surface for uptake by phytoplankton. In the Gulf of Alaska, iron transport from the shelf to the open ocean via eddies has been documented to be important (Johnson et al., 2005). However, the Gulf of Alaska has a narrower shelf than the Bering Sea, hence resuspension may prove a less important iron source than in the Bering Sea. Significant riverine iron input could be provided to the Gulf of Alaska by several rivers, the largest of which is the Columbia River (although the Columbia is located some distance south of Alaska, the California undercurrent could transport considerable iron northward (Chase et al., 2002; Whitney et al., 2005)).The Bering Sea has been shown to be iron-limited seaward of the shelf break (Peers et al., 2005). The Bering Sea has a broad continental shelf (henceforth referred to simply as shelf) (Figure 2), hence resuspension may generate a significant dissolved iron

source there. In addition, the Yukon River discharges into the Bering Sea. The Yukon is one of the largest rivers in North America and may supply significant dissolved and particulate iron to the shelf.

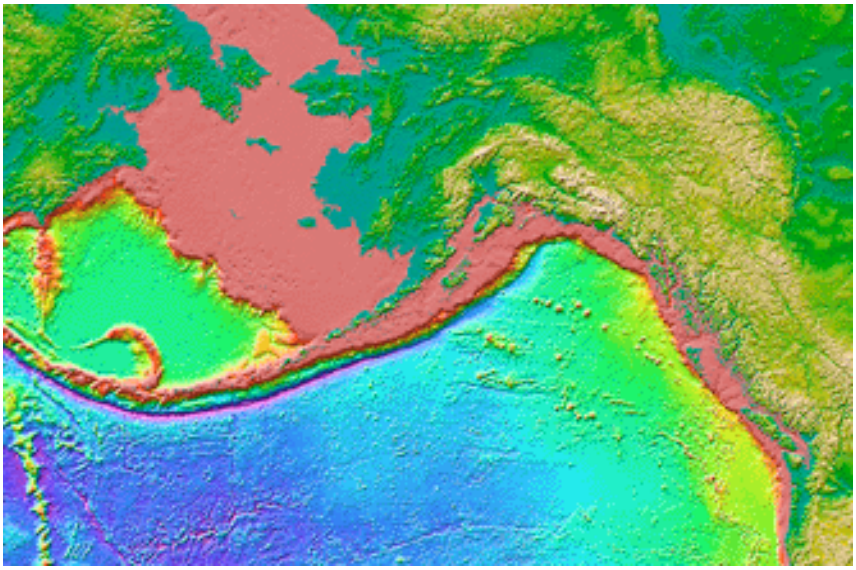

Figure 2: Bathymetry of the region near the Gulf of Alaska. The orange-colored regions represent continental shelf (from Smith and Sandwell, 1997).

The time is ripe to initiate a USGS program examining coastal sources of iron to the North Pacific. This represents a unique opportunity, both because the importance of iron inputs to the ocean demands that we develop our understanding of iron sources and because there are several upcoming international oceanographic initiatives from which this effort can benefit (GEOTRACES, IMBER, OCCC (discussed later)). In each case, a research emphasis on coastal processes would allow the USGS to carve out a niche within much larger oceanographic programs.

In the following pages we expand on this introduction to: 1) provide some background on iron limitation in the ocean; 2) discuss some linkages between iron supply, ecosystem structure and the carbon cycle; 3) discuss possible sources of iron to the ocean; and 4) discuss the possible components of a proposed multi-year interdisciplinary USGS program examining the fluxes of trace elements from coastal areas of the NE Pacific Ocean. This is written as a broad, long-term vision, inclusive of many possible foci such a project could have, and their interconnections. At the end of this document we also outline a modest plan for the first two years of such a project, assuming limited available resources.

Because of the economic importance of Alaskan fisheries (Beamish and Bouillon, 1993; Rogers 2001) and the opportunity for participation by scientists from numerous USGS programs, we hope to be able to generate enough funding to see significant parts of this vision come to fruition. It is also our expectation that there are enough interested parties among international (Canadian, Russian, and Japanese), U.S. academic, and other

government researchers (NOAA and AK state employees), that components beyond our budget could be addressed by others. It is worth noting that the focus of this document is on Alaska, but similar issues are relevant in coastal CA, OR and WA, and field work in those locations could also be incorporated with additional funding.

While an important goal of this project will be to better understand the processes and the rates of iron delivery to surface waters of the northern NE Pacific Ocean from coastal sources, the science will be driven as well by the following broad questions: 1) How important are diagenetic remobilization, sediment resuspension, riverine inputs and groundwater fluxes to the overall iron inputs to the northern North Pacific Ocean? 2) What controls the rate of removal of iron and other trace elements from surface waters in coastal waters? 3) If extreme storm events become more frequent in the future, as most climate models suggest, how will iron delivery from rivers and from sediment resuspension be impacted? 4) How might climate-change-induced sea level rise affect iron delivery due to sediment resuspension and coastal erosion? 5) How will melting of permafrost in arctic regions affect iron delivery? 6) How do anoxic regions in eutrophic nearshore waters impact iron delivery offshore? 7) How does carbon export from surface waters, and surface-water pCO_2, vary as a function of iron delivery? 8) Assuming sustained increases in iron delivery to surface waters leads to sustained increases in algal productivity and carbon export, how will upper trophic levels (e.g. salmon, marine mammals, sea birds, etc.) be impacted? These are among the compelling questions driving this research, which can only be answered with an interdisciplinary research program.

2. Iron limitation in the ocean-background

Dissolved iron is a major constituent of the earth's crust, yet its concentration is extremely low in the ocean, due to its low solubility in seawater. For years, oceanographers and fisheries scientists paid little attention to the behavior of iron in the ocean, partly due to the difficulty of making accurate measurements, which contributed to our poor understanding of its importance. During that period, oceanographers became aware of extensive regions of the ocean where concentrations of key nutrients (such as nitrate and silicate), normally thought to limit phytoplankton growth, remained at elevated concentrations throughout the year, while levels of chlorophyl, a pigment indicative of algal biomass, remained low. These regions were termed High-Nutrient, Low-Chlorophyl (HNLC) regions. Over the last ten years, iron enrichment experiments in several HNLC regions have demonstrated convincingly that increases in algal biomass can be triggered merely by the addition of dissolved iron to surface waters (Martin et al., 1994; Kolber et al., 1994; Coale et al., 1996; Tsuda et al., 2003; Boyd et al., 2004; Coale et al., 2004; Saito et al., 2005b; Suzuki et al., 2005). We now realize that iron is one of several key limiting nutrients in the ocean, and that iron limitation affects 30-40% of the ocean surface, including the northern North Pacific (Figure 1) and coastal waters off western North America (Bruland et al., 2001; Fitzwater et al., 2003).

The best known impact of iron limitation is on nitrogen fixation. Lab data suggest that *Trichodesmium*, a nitrogen fixer, requires five times more Fe when grown on N_2 than on

NH_4 (Hoffman et al. 1997; Mino et al., 2002). Hence, iron limitation exacerbates N limitation in the subarctic Pacific Ocean and impacts ecosystem structure in the phytoplankton and zooplankton communities and throughout the marine food web to upper trophic levels (Lui et al. 2004; Saito et al 2005a). Interactions between biochemical processes and marine food webs will be expected to vary in different habitats such as continental shelf margins with coastal upwelling, near shore habitats at the mouths of large rivers, and surface waters over deep ocean environments (Bakun 1996; Butler 1998; Bruland et al. 2001). The emphasis of this document is on iron, but other trace elements, such as Co, Ni, Cu and Zn are used in various biochemical functions (Morel and Price, 2003). Many of these elements are present at extremely low concentrations in surface-waters of the North Pacific Ocean (http://www.agu.org/eos_elec/97025e.html), and may limit critical biological processes.

3. Linkages between iron supply and ecosystem structure

Conflicting data have been published as to whether the abundance of higher trophic level species, such as fish, is directly related to the local supply of essential nutrients and the exchange of energy through the food web (Scheffer et al., 2000; Wang, 2002; Quinn et al., 2003). Modern food web studies search the dynamic association of combined top-down and bottom up forces regulating food web function and structure (Vander Zanden et al., 2005. In the marine food web there are several steps in the food chain between phytoplankton and fish, and processes such as grazing by zooplankton, climate, habitat loss, low reproductive potential, changes in species associations and overfishing can exert significant influences on the upper trophic levels, which could obscure any direct linkages between the fish and phytoplankton populations (Pauly et al. 1998; Myers and Worm, 2003; Bundy 2005). However, recent research within the highly productive waters of the northern NE Pacific (Figure 3) supports the hypothesis that fish in the NE Pacific are controlled from the "bottom up", in that the abundance and growth of fish residing in near shore regional areas of the ocean are tightly coupled to the biomass of the phytoplankton (Figure 4; Ware and Thomson 2005). In these locations, therefore, the availability of essential nutrients such as iron may exert fairly direct influence on the ecosystem structure and on the distribution and abundance of fish.. The fisheries of the Bering Sea, the Gulf of Alaska, and other coastal Northeast Pacific locations are among the most productive in the world. Given the ever-increasing human population and demand for fish, there is an urgent need to understand controls on commercially important fish yields so that fisheries can be managed sustainably. Furthering our understanding of the linkages between the supply of iron (and other nutrients) and fish distribution and abundance is therefore important. We must point out, however, that other research on fish production has focused on the role of top-down processes, i.e. predator activity including humans "fishing down the food web" (Pauly et al., 1998; 2005). Thus, more research is required to better understand the linkages among supply of iron and other nutrients, phytoplankton biomass and fish yield.

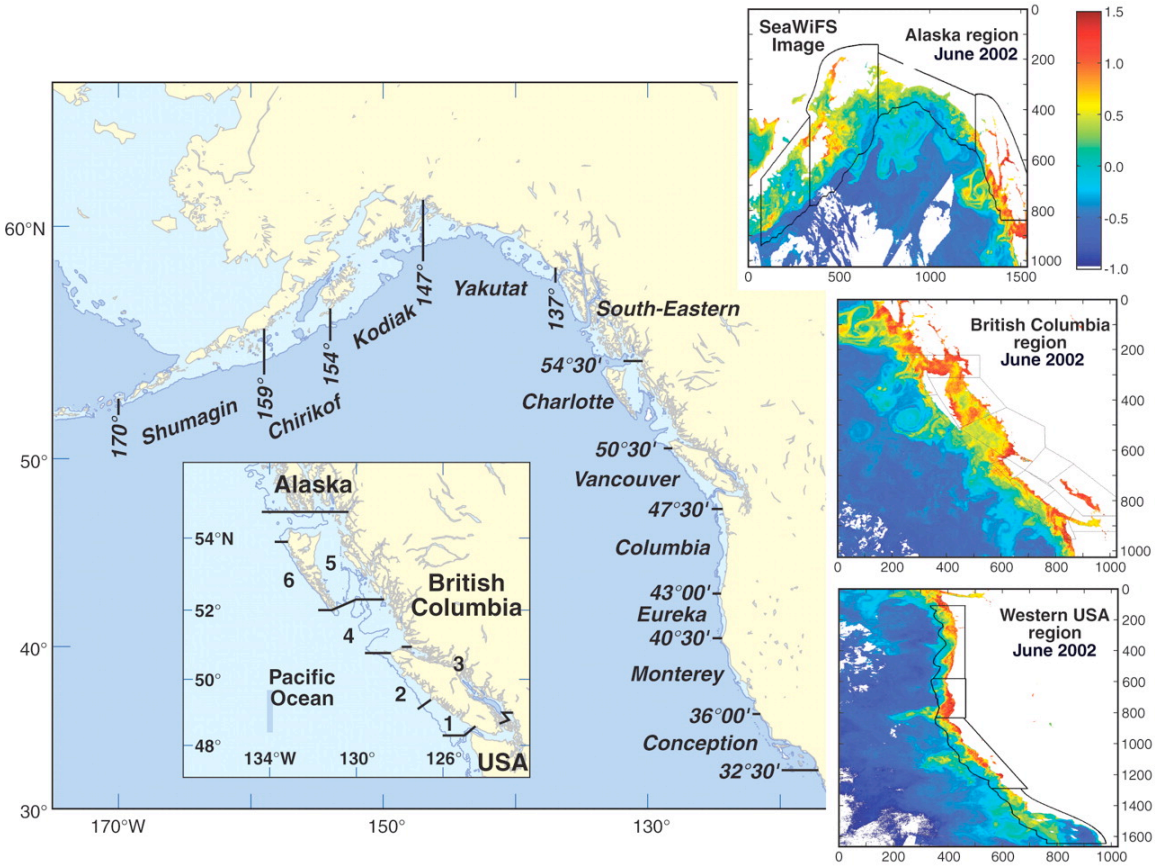

Figure 3: Map of the 11 North Pacific Anadromous Fish Commission (NPAFC regions), extending from Conception off California to Shumagin off western Alaska. (Left inset). The areas covered by the six British Columbia subregions. (Right insets). Examples of monthly mean SeaWiFS chl-a maps for the Alaska, British Columbia, and western U.S. regions; grids are in pixels, at 1.1 km/pixel; the color bar denotes concentration in log(chl-a in mg m^{-3}). Graphics are from Ware and Thomson, 2005.

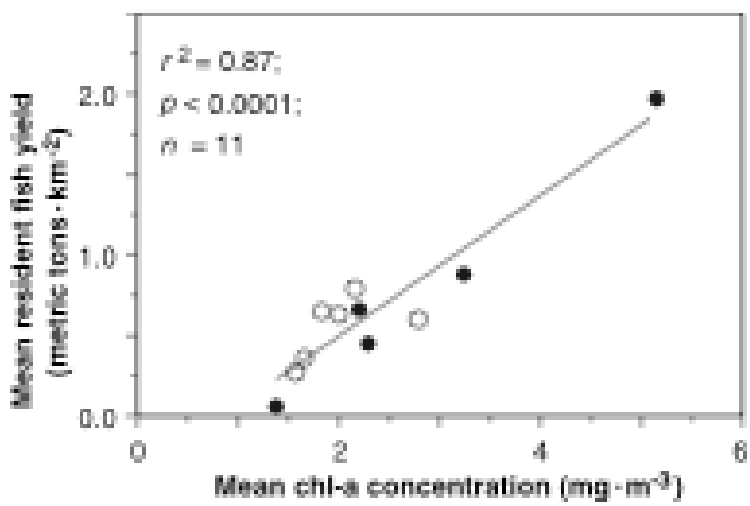

Figure 4: Correlation between the annual mean chl a concentration and the long-term annual yield of resident fish for each of 11 North Pacific Anadromous Fish Commission (NPAFC) regions. Solid circles represent upwelling regions; open circles downwelling regions (from Ware and Thomson, 2005).

4. Linkages between iron and carbon cycles

It is generally accepted that enhanced utilization of nutrients in HNLC regions of the ocean, such as the North Pacific, would result in greater carbon export from surface waters and hence a reduction in atmospheric CO_2 levels (e.g. Martin, 1990). Indeed, reductions in surface-water pCO_2 have been observed in some iron addition experiments (Figure 5). However, it is not clear just how much atmospheric CO_2 levels would be reduced by such iron additions. The gap in our understanding lies in our inability to predict how efficiently iron is recycled in the surface ocean following addition. Thus far, the iron addition experiments carried out in HNLC regions have not resulted in sustained carbon export (Nodder et al., 2001; Buesseler and Boyd, 2003; Boyd et al., 2004), perhaps because of rapid iron removal from surface waters. Thus, it is possible that sustained addition of iron is necessary to achieve a significant CO_2 decrease. Additional research is needed to clarify these issues.

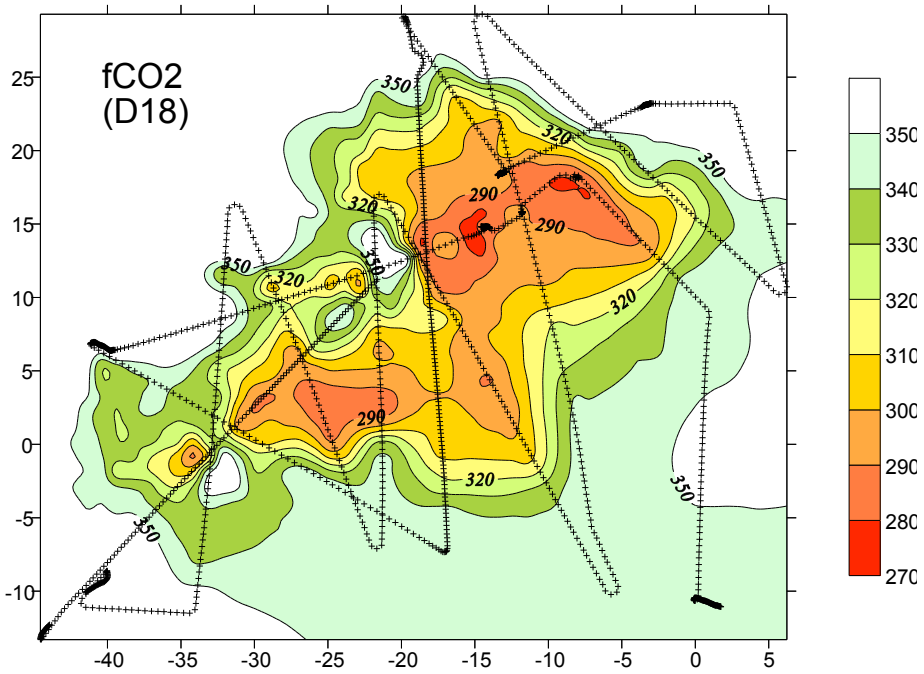

Figure 5: Data from the NE Pacific iron addition (Boyd et al., 2004), showing CO_2 levels (µatm) in the iron-enriched patch on day 18 following the onset of iron additions (black crosses denote data coverage, patch scale is in km). Note how CO_2 levels have decreased from typical atmospheric levels of ~370 µatm, due to algal uptake of CO_2.

Within the framework of this proposed work for examining coastal iron sources, there will be excellent opportunities for collaboration and/or sharing of resources with the

ocean carbon cycle community. A recent Ocean Carbon and Climate Change report (OCCC; Doney et al. 2004) outlined future research plans envisioned by this community. It is worth noting that this report states that two of twelve possible coastal sites for ocean CO_2 measurements include the Bering Sea and the Gulf of Alaska. Hence, it should be possible to determine the magnitude of a possible CO_2 sink that might be linked to iron sources in a particular location, via collaboration with this carbon cycle community. Furthermore, a number of stated goals of this OCCC report address issues that are also relevant to and/or compatible with the study of the coastal iron cycle, including:

- improving our understanding of carbon cycling on continental margins to better constrain whether they are a source or sink of CO_2 to the atmosphere.
- quantification of the influence of river and groundwater inputs on margin biogeochemical processes.
- incorporation of sediment transport and resuspension studies into coastal observing networks to help facilitate quantification of cross-shelf carbon transport; this infrastructure and dataset can help to quantify the cross-shelf iron transport, as well.
- monthly ship-based cross-shelf surveys to assess onshore/offshore variability in CO_2. The datasets will help quantify the CO_2 source or sink, while the cruises may afford ships of opportunity that could benefit iron studies.

Opportunities for collaboration with this OCCC community are certain to emerge, as the OCCC report also emphasizes the need to leverage coastal projects that exist or are being planned, such as our coastal iron sources process study. Finally, it is worth noting that in this OCCC report, iron addition is being discussed as a possible carbon sequestration strategy to mitigate rising CO_2 levels. We clearly need to better understand how iron inputs affect carbon sequestration and the marine ecosystem before we contemplate this sort of large-scale ocean engineering.

5. Present-day iron sources

We are now well aware of the stimulus provided by iron to North Pacific phytoplankton, and the above discussion alludes to possible impacts of iron additions on the marine ecosystem and carbon cycle. However, we know very little about the processes, and the rates, of iron delivery to surface waters of the ocean, which limits our ability to predict the linkages. Aeolian transport has long been thought to be the main mode of transport delivering iron to the surface waters of the ocean; therefore it is the best-studied mechanism. The primary source of dust to the atmosphere is the Sahara (Jickells et al., 2005; Figure 6). Of course various types of particles from Asian continental sources, sometimes called “Asian dust”, have been measured as far away as the North Sea, suggesting this dust could also be a source of iron to the North Pacific Ocean (Okada et al. 1990; Chul-Un et al. 2001; de Hoog et al., 2005). However, recent work suggests that coastal sources of iron are also important, including rivers (Chase et al., 2002), diagenetic remobilization from sediments (Elrod et al., 2004), sediment resuspension (Johnson et al., 1999; Chase et al., 2002; Nakano et al., 2004; Measures, personal communication 2005), and groundwater (Charette and Sholkovitz, 2002; Windom, Moore and Jahnke unpublished data, 2005). The USGS can play an important role quantifying the

importance of these coastal processes on iron delivery to surface waters by initiating studies aimed at examining all possible fluxes in perhaps two key locations. Evaluation of some of these processes will require collaboration with academic partners. The rationale for a focus on each of these sources is laid out below.

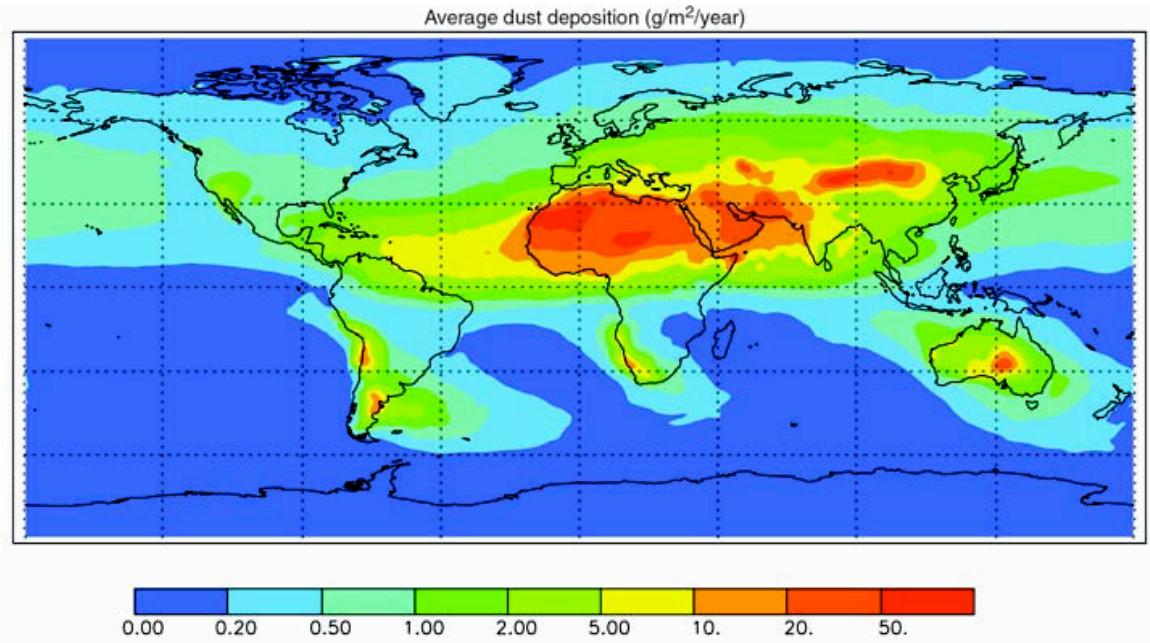

Figure 6: Map of global dust deposition, highlighting the high dust fluxes from the Sahara desert. Note there is little dust deposition in the Northeast Pacific (waters offshore of AK, WA and OR), because prevailing westerly winds, together with large distances from Asia (the upwind land mass), lead to limited atmospheric transport from dust. (Figure from Jickells et al., 2005).

5.1 Rivers

Rivers have the potential to deliver significant quantities of iron to the coastal ocean in both dissolved and particulate forms. Indeed, inputs from the Columbia River have been suggested to be an important iron source to the NE Pacific (Chase et al., 2002; Whitney et al., 2005). The Columbia River is by far the largest single river discharging into the NE Pacific, and ocean currents carry much of this freshwater influence northward towards the Gulf of Alaska (in the California Undercurrent (see Whitney et al., 2005)). A basic question that needs addressing is how far this riverine iron is transported into the ocean. We need to evaluate how much of this iron is removed by biological processes and by scavenging during transit, and how much is recycled and later remobilized along this trajectory towards the Gulf of Alaska. This significant flux from the Columbia River was documented within the coastal ocean, despite the fact that removal of the vast majority of riverine dissolved iron has been observed in a series of estuaries (e.g. Boyle et al., 1977). This removal was caused by coagulation of colloids, in which iron is complexed with dissolved organic matter, during mixing of river water and seawater. Particulate iron removal would also be expected within the estuaries, especially when estuaries widen

towards the river mouth, resulting in greatly reduced surface-water velocities. Basic questions remain regarding how ubiquitous and seasonally variable these iron removal processes are in estuaries, and as a consequence, how seasonally variable riverine iron inputs are to the NE Pacific.

While individual Alaskan rivers discharging into the Gulf of Alaska do not transport nearly as much water as the Columbia River, the cumulative freshwater discharge of these smaller rivers is comparable to that of the Mississippi river (Stabeno et al., 2004), so the cumulative iron discharge is no doubt important. For this reason, research is also needed to evaluate how important iron discharge is from Alaskan rivers. Efforts to examine iron load and removal from Alaskan estuaries would benefit a great deal from ongoing USGS WRD work examining river flows and particulate load in both the Copper and Yukon Rivers (T. Brabets, personal communication, 2005). It might also be interesting to examine the differences in the riverine particulate and dissolved loads for glacierized and unglacierized watersheds, since iron fluxes from melting glacial ice contributing to river runoff is likely to vary with climatic conditions. It has been documented that the particulate load is higher from glacierized watersheds, due to the erosive effects of the glacier (Edwards et al., 2000). Is the corresponding dissolved Fe load also higher for the glacierized watershed? How would increased modern-day melting of glaciers, due to global warming, impact the Fe load? How would the disappearance of these glaciers impact the Fe load?

5.2 Sediment resuspension

Another process recently suggested to contribute to iron delivery to surface waters is sediment resuspension. Evidence for the importance of this process include data from offshore of the Columbia River (e.g. Chase et al., 2002) and from a unique recent dataset from the Southern Ocean, where elevated concentrations of Fe, Mn and Al near depths of 100 m suggest transport towards the open ocean from the continental shelf (Figure 7). If only Fe and Mn revealed elevated concentrations this might be interpreted to be driven by redox processes, which can release Fe and Mn to the water column (as discussed below). However, resuspension seems a more likely cause, due to the fact that Al, a major component of aluminosilicate materials that is not influenced by redox processes, is also enriched. Similar resuspension processes are no doubt occurring in the North Pacific, and they may lead to significant transport of iron to surface waters in regions of localized upwelling (e.g. Whitney et al., 2005). It is worth noting that there is a fairly extensive area of shallow continental shelf in the Gulf of Alaska and especially the Bering Sea (Figure 2), which may promote iron fluxes due to sediment resuspension.

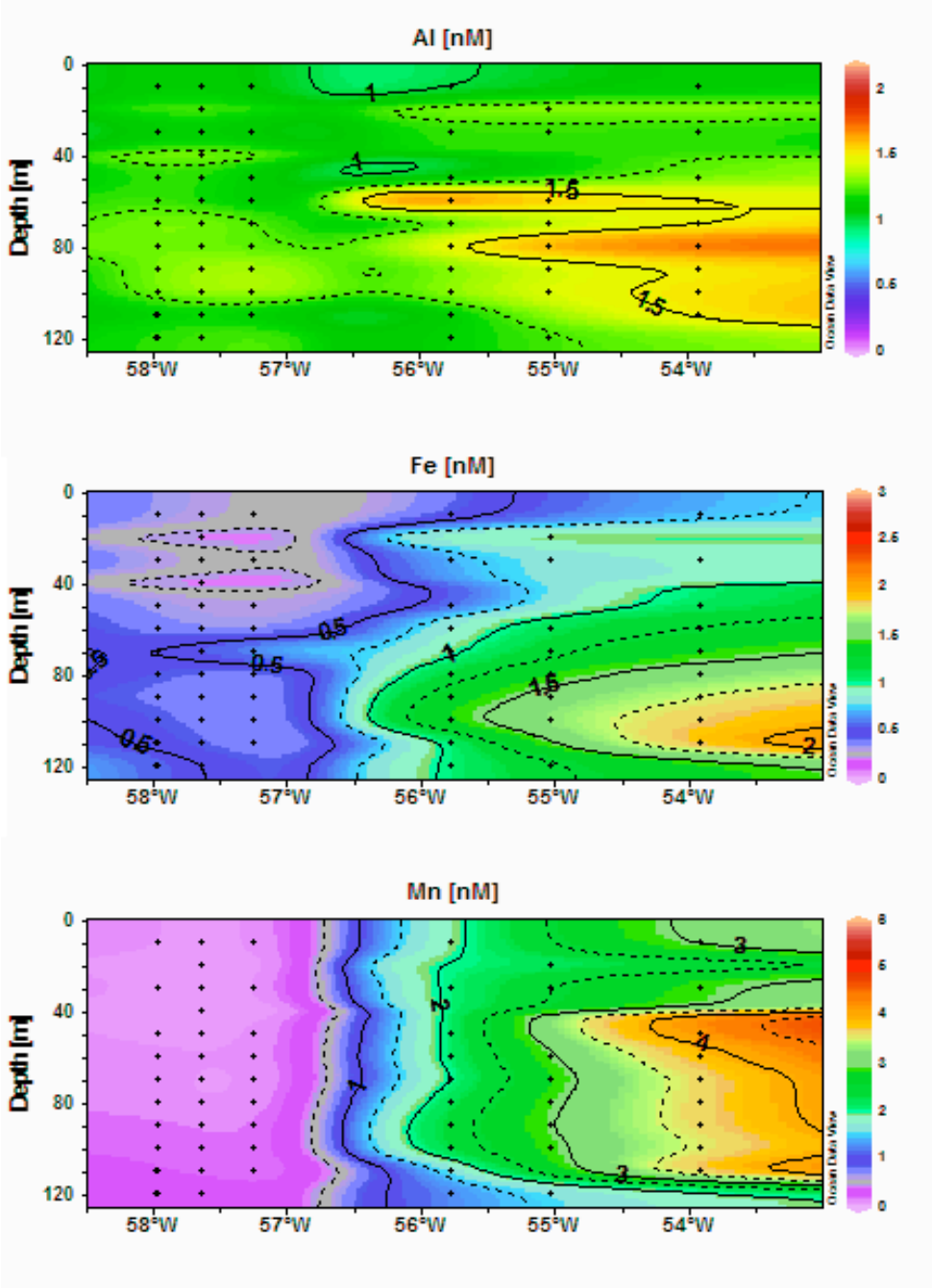

Figure 7: Shallow-water dissolved Al, Fe and Mn data, highlighting advection of shelf-derived metals towards the open ocean from the coast of Antarctica (orange and red indicate high concentrations). Land is to right in the image. The horizontal distance spanned by the figure is just under 200 miles. The same processes are certain to be occurring in other coastal areas. These data are shown because they were collected at unprecedented spatial resolution, and highlight the process as never before (from Chris Measures, U. Hawaii, personal communication, 2005).

Understanding dissolved iron fluxes to surface waters due to resuspension requires an understanding both of the resuspension process and of how much iron is released into

solution during resuspension. Scientists from the Coastal and Marine Geology Program (CMGP) have extensive experience studying sediment transport and the instrumentation required to quantify this. This work could therefore benefit a great deal from this infrastructure. Arguably, one could evaluate a good location for a detailed process study evaluating iron transport by sediment resuspension by deploying some of the continuously recording instrumentation available to this group of researchers. Once a location was so identified, a more detailed study including measurements of iron in the water column and benthic boundary layer could be included as well, in collaboration with academic colleagues (see discussion of synergy below).

The fact that shelf-borne metals may be important to iron delivery to surface waters suggests that human-induced coastal erosion could have an important impact on the delivery of iron and other metals to the ocean. There are no data available on this subject (to our knowledge), but we clearly need to improve our understanding of how coastal erosion might impact iron supply and hence ecosystem structure of the northern North Pacific Ocean. It is important to point out in this context that recent work suggests that humans have simultaneously increased the sediment transport to global rivers, due to soil erosion, and reduced the sediment load reaching the coast, due to retention in reservoirs (Syvitski et al., 2005). It is not known how dams have affected delivery of dissolved and particulate iron from rivers (e.g. the Columbia River).

5.3 Diagenetic remobilization

Diagenetic remobilization from sediments is another potential source of iron to surface waters of the ocean. Indeed, recent work from coastal sediments off California has suggested that Fe fluxes delivered via this process are at least as large as atmospheric inputs (Elrod et al. 2004). The mechanism invoked by these researchers was iron release during organic matter oxidation. These authors described an important role for bioirrigation enhancement of iron fluxes via porewater irrigation, based on their observation that iron fluxes inferred from benthic chambers were much higher than fluxes inferred from porewater profiles. The impacts of these fluxes were claimed to be observed hundreds of kilometers offshore, as inferred from satellite images (Elrod et al., 2004). It is worth noting that low bottom-water oxygen concentrations below depths of 150-200 m throughout much of the Gulf of Alaska (Figure 8) may enhance iron fluxes by diagenetic remobilization, because dissolved iron is released into solution from solid iron oxyhydroxides under chemically reducing conditions. Of course, careful work will be required to distinguish the offshore impacts of diagenetic remobilization from those of sediment resuspension. Because the driving force behind each of these mechanisms is quite different, there is a need to distinguish between these two processes, in order to improve our ability to predict iron fluxes.

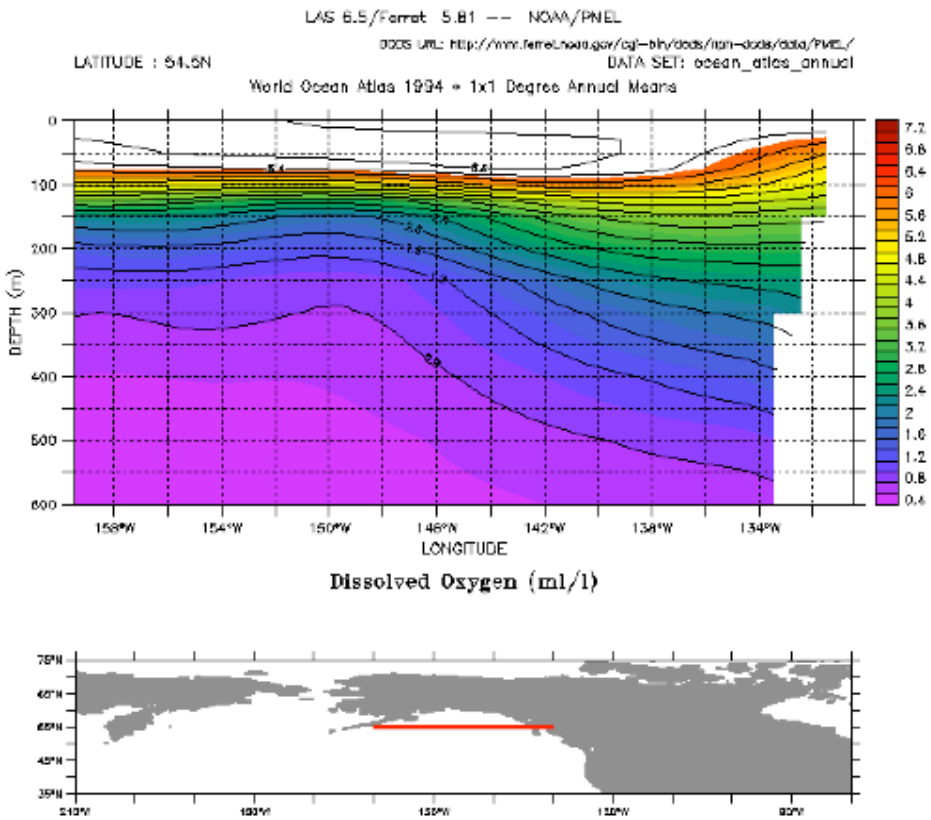

Figure 8: (top) Vertical section from 0-600 m depth showing dissolved oxygen concentrations along 54.5 °N, in the northern North Pacific Ocean. Note low oxygen levels below 150-200 m depth throughout the entire section. Low oxygen levels would help to promote diagenetic remobilization of iron. At these shallow depths released iron could be readily mixed up to surface waters. Lower figure shows location of vertical section (red line) in North Pacific Ocean. Figure created using ferret. Ferret is a product of NOAA's Pacific Marine Environmental Laboratory. (Information is available at www.ferret.noaa.gov).

5.4 Inputs from submarine groundwater discharge

It has recently been observed that chemically-reducing coastal groundwater can deliver significant concentrations of iron to the coast, leading to substantial iron enrichment of coastal sediments (Charette and Sholkovitz, 2002). If submarine groundwater (SGD) were to discharge to the ocean as discrete springs, dissolved iron could conceivably be delivered directly to surface waters. Indeed, this has been suggested in recent work (Windom, Moore and Jahnke, unpublished data, 2005). However, in the work of Charette and Sholkovitz (2002), groundwater-derived iron was oxidized and adsorbed to the solid phase near the sediment-water interface, and wasn't directly discharged to the ocean. Nevertheless, tidal pumping of seawater through sediments is well documented and has the potential to deliver iron to the oxic sediment surface. Even if this pool of reduced iron never advances above the sediment-water interface, it adds to the pool of Fe-rich surface sediments that are available from which diagenetic remobilization and

resuspension can release iron to the water column (see above). This phenomenon of iron transport via groundwater towards the coast is virtually unstudied. It remains to be seen if this process is important in the North Pacific regions discussed. Certainly, permafrost melting in response to global climate change has the potential to enhance the flow of groundwater which, together with enhanced oxidation of organic matter, could substantially increase the delivery of reducing groundwater and hence iron towards the Alaskan coast. Hence, this process merits close study.

These same processes of SGD may also be a significant source of nutrients other than iron to coastal waters of Alaska, such as dissolved nitrogen (nitrate and ammonium ion) and dissolved silica. Again, this has not been studied to our knowledge. The balance between all fluxes of nutrients will determine whether SGD induces or alleviates iron limitation in various coastal locations.

5.5 Quantifying transport towards open ocean

The transport of coastally-derived iron towards the open ocean is driven by physical oceanographic processes. The northern NE Pacific Ocean experiences strong downwelling-favorable winds in the winter and essentially no upwelling-favorable winds in the summer (Whitney et al., 2005), which leads to limited offshore transport of coastal waters. However, transport of high-iron water from intermediate waters to surface waters probably occurs via localized upwelling, which does occur, caused by enhanced alongshore winds in the nearshore area compared to those offshore (Figure 9; Stabeno et al., 2004). Eddies are also known to lead to considerable offshore transport. This mechanism has been suggested to be important for transport of iron to the central Gulf of Alaska from northern British Columbia (Johnson et al., 2005) and southern Alaska (near Yakutat; Stabeno et al., 2004)). This transport mechanism, and its impact on the regional iron budget, warrants considerable attention. It is worth keeping in mind that the high productivity of these waters (e.g. Ware and Thomson, 2005) implies mechanisms exist to transport nutrients to surface waters despite the limited upwelling that occurs.

Evaluating the transport of coastally-derived materials towards the open ocean is difficult, due to these complex physical oceanographic processes in the coastal zone. However, it has recently been demonstrated that long-lived Ra isotopes have the potential to allow quantification of lateral mixing rates (Moore, 2000; Nozaki and Yamamoto, 2001). Using this approach, perhaps together with sediment transport and hydrodynamic modeling, scientists from CMGP could estimate the integrated offshore transport of nearshore waters which, together with water-column measurements of dissolved iron and other metals, could quantify the flux of dissolved iron in these regions towards the open ocean.

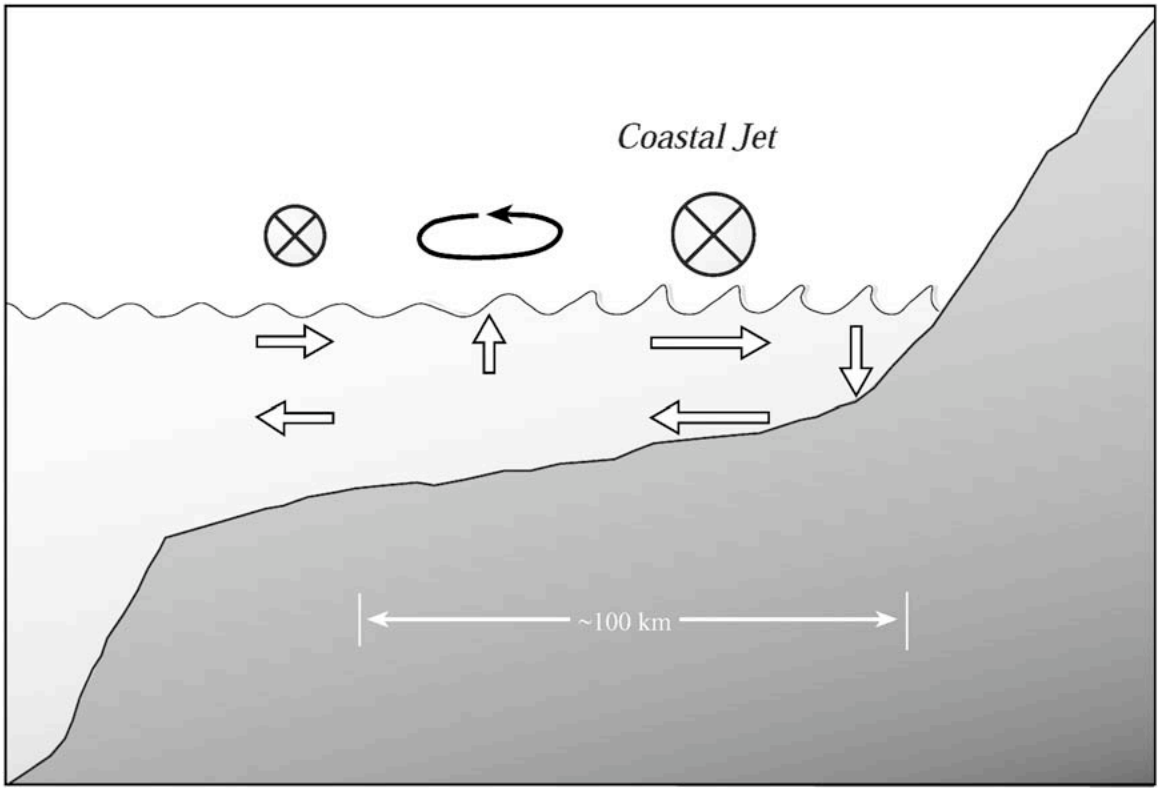

Figure 9: Schematic showing how stronger alongshore winds (into the page) in the nearshore area (indicated by the size of the circle), could lead to greater onshore transport in the nearshore area (compared to offshore sites) and hence cause offshore upwelling (from Stabeno et al., 2004).

5.6 Atmospheric inputs

Dust inputs have long been thought to be the dominant source of iron, although recent work (discussed above) challenges that notion on many fronts, in many different regions of the ocean. Still, the atmospheric input is an important flux, especially in the open ocean. Evaluating the impact of this atmospheric flux requires addressing numerous issues, including the magnitude of the dust flux, the origin of the dust, and the fraction of iron in the dust that is bio-available. This topic is likely to be addressed by academic colleagues who have both open-ocean experience and buoys for collecting marine aerosol samples (e.g. Sholkovitz et al., 2001). However, the USGS currently has researchers actively studying far-traveled dust and modeling dust transport (Muhs et al., 2004). Possible USGS roles in this work could include examining rates of present-day and past dust accumulation (from loess deposits) and identifying isotopic and/or geochemical signatures of aerosol provenance to distinguish among possible sources within Alaska and to distinguish Alaskan from Asian dust.

5.7 Bioavailability of iron sources

For all of the above possible sources of iron, the question arises as to what portion of the total iron flux is bio-available to phytoplankton. This is a challenging frontier where additional work is needed to clarify the availability of most of the above-mentioned iron sources.

6. Influence of climate change and anthropogenic impacts

6.1 Impacts on iron delivery

Changes in future climate have enormous potential to alter both the delivery of iron to the North Pacific Ocean and the structure of the marine ecosystem therein. Iron delivery could be altered by changes in wind strength or direction or in continental aridity, either in Asia or in Alaska. Melting glaciers may impact iron delivery to coastal waters, as well. On balance, most of the glaciers in the Wrangell and Chugach mountain ranges in Southern Alaska are thought to be receding due to global climate change (Molnia et al., in press). Spanning the next few decades this may well lead to enhanced iron delivery from the Copper River. If these glaciers continue to disappear at the current rate of wasting, however, they are projected to disappear within the next few centuries (Molnia et al., in press). Once the glaciers have disappeared, the iron delivery from these sources would diminish drastically. Permafrost melting could have yet another influence on iron delivery, either by releasing large amounts of water, contributing to weathering, or by exposing long-frozen soils to oxidation processes, leading to discharge of iron-rich reducing groundwater. This process could be important in much of coastal Alaska, but is probably unimportant in the vicinity of the Gulf of Alaska (southern Alaska), where there is currently no permafrost. Finally, if the projected global climate change results in either sea-level rise or increased frequency of extreme storm events, the delivery of dissolved iron from coastal erosion and from rivers is likely to increase. In short, there are many possible influences of climate variability on iron delivery to the ocean. Evaluation of the magnitude of future flux changes is complex and requires a better understanding of the present-day controls on iron delivery.

Other processes unrelated to climate also have the potential to alter the rate of iron delivery to the ocean over time. These influences include changes in the areal extent of anoxic regions of the ocean and coastal erosion caused by increased development. Natural processes such as volcanic activity could also impact iron delivery to the ocean.

6.2 Climate feedbacks

In addition to the direct effects of a changing climate on iron delivery to the ocean, there are important feedbacks, as well. For example, up to an eight-fold increase in dimethyl sulfide (DMS) concentrations are seen in iron addition experiments (Turner et al., 2004 in Jickels et al., 2005). DMS is oxidized in the atmosphere to form sulfate aerosol, an effective scatterer of solar radiation (Jickels et al., 2005). Some models have suggested a two-fold rise in DMS concentrations produces a global temperature decrease of 1 °C,

providing a feedback linking iron supply, DMS production and climate (Zhuang et al., 1992). In summary, the connections between iron, the carbon cycle and climate are complex (Jickels et al., 2005). While it has been suggested that we might be able to reduce CO_2 levels in the atmosphere via iron additions, we clearly need a far better understanding of both the present-day sources of iron and the interconnections between iron supply and climate before we can begin to consider such a high-risk undertaking.

6.3 Paleoceanographic components

Our ability to predict possible future trends in iron fluxes, and their impacts, will benefit greatly from understanding past changes in these processes as recorded in ice cores, sediments, and possibly other archives. Some of the best-known and often-cited information regarding iron inputs from the past stems from research on the Vostok ice cores, which implies much higher dust fluxes occurred during the last glacial maximum than during interglacial periods (Barnola et al., 1987). This information was part of what led John Martin to hypothesize that the well-documented 90 ppmv reduction in atmospheric CO_2 levels that occurred during the glacial period was a response to iron fertilization of HNLC regions of the ocean (Martin, 1990). This would have led to increased biological productivity, a drawdown of surface-water pCO_2, and a consequent decrease in atmospheric CO_2 concentrations. At present, oceanographic records do not suggest the ocean responded in this way during the last glacial maximum (Kienast et al., 2004). However, at other times during the past tens of thousands of years, there is evidence from the sedimentary record that there have been periods of greatly enhanced biological productivity spanning significant portions of the North Pacific Ocean (Crusius et al., 2004; McDonald et al., 1999). The mechanism causing these productivity events is not well established, but it seems likely that they resulted from increased iron delivery to surface waters, since they occurred in waters that are currently iron-limited. Given the potential for significant impacts caused by future possible changes in iron delivery to the North Pacific, study of present-day iron and carbon cycling must be aware of the range of possible natural conditions as informed by paleoceanographic records.

7. Synergy with other organizations

This research program would fit in very well with several upcoming international research initiatives, including GEOTRACES, IMBER, BEST and OCCC. GEOTRACES is an upcoming ten-year international biogeochemistry program whose mission is "to identify and quantify processes that control the distribution of key trace elements and isotopes in the ocean, and their sensitivity to changing environmental conditions, in order to elucidate sources of micronutrients, contaminant dispersal and tracers of present and past ocean conditions." (GEOTRACES science plan draft, Feb, 2005; http://www.ldeo.columbia.edu/res/pi/geotraces/). If the past is any guide, coastal processes, while important, may receive insufficient attention in this global oceanographic study. Hence, the USGS has a unique opportunity to carve out a niche within GEOTRACES examining these coastal processes. Members of the academic communities from both the U.S. and Canadian GEOTRACES communities envision a North Pacific component. Indeed, Bob Anderson, GEOTRACES co-chair, and Roger

Francois, the Canadian group leader, have expressed strong support for our proposed work (see attached letters of support). Possibilities also exist to forge ties and interact with the Japanese academic community, who also have strong interest in iron sources to North Pacific and who have recently established a program looking at iron deposition in the western Pacific Ocean (Dr. Yasunori Sakurai, Hokkaido University, Japan, pers. comm.)

IMBER (the Integrated Marine Biogeochemistry and Ecosystem Research) is another integrated research program (www.imber.info/). The goal of IMBER is quite broad, "to understand how interactions between marine biogeochemical cycles and ecosystems respond to and force global change". Clearly, our proposed study of the many interconnections between iron supply, marine biogeochemical processes, and climate and anthropogenic impacts fits in well with IMBER's objective to "understand the mechanisms by which marine biochemical cycles control marine life and, in turn, how marine life controls biochemical cycles". One theme IMBER promotes is the study of interactions between biogeochemical pathways and marine food webs in an effort to understand fundamental interactions and complex forcings within ecosystems in relation to global change on time scales ranging from years to decades. Their research focus is on large-scale climatic variation, changing physical dynamics, carbon cycle chemistry, nutrient fluxes and the impacts of marine harvesting.

Another important NSF-funded research program recently initiated in the Bering Sea also overlaps with the objectives of this proposal and provides opportunities for collaborations outside of USGS. The goal of the Bering Sea Ecosystem Study (BEST) Program (http://www.arcus.org/Bering/index.html) is "to develop a fundamental understanding of how climate change will affect the marine ecosystem of the Eastern Bering Sea, the continued use of its resources, and the economic, social and cultural sustainability of the people who depend on it." One of their major objectives is to understand the physical and biological mechanisms that control links between global and regional climate processes and physical and biological ocean conditions in the eastern Bering Sea. Dr. George Hunt, University of Washington School of Aquatic & Fishery Sciences, directs this program and suggested that our research goals investigating nutrient dynamics and the impacts of climate, food web interactions and physical-biological coupling are parallel to parts of their own research agenda (see Hunt et al. 2002); a collaborative approach to research on the eastern Bering Sea shelf is encouraged.

Finally, the OCCC (Ocean Carbon and Climate Change) program will focus research on the marine carbon cycle. As discussed earlier, many of the goals of this carbon cycle community involve quantifying the importance of coastal biogeochemical processes on the global carbon cycle. As a result, considerable infrastructure will be available to support efforts to assess coastal iron sources, their impacts and its cross-shelf transport.

All of this research will benefit from (indeed require) collaboration with a wide variety of researchers. It seems quite likely that the U.S. and Canadian academic communities will lead the ocean section studies that will emphasize measurements of metals in the marine water column. These sections will span the oceans, but also extend onto the continental

shelves, ending at a site (or sites) of a coastal ocean process study. Other likely emphases of the academic community will include quantification of iron removal rates by scavenging and of the rates of aerosol delivery to the open ocean. Finally, we anticipate that the academic community will provide the physical oceanographic constraints on coastal upwelling/downwelling which will help to constrain the rate of metal delivery to surface waters. It is likely that there will be opportunities to interact with Alaskan academics through the Alaskan Sea Grant program, or other state or federally funded research programs. Clearly there is some overlap on possible research topics of interest to the USGS and the academic community. This overview should be viewed merely as an initial guideline subject to change as plans evolve. We will examine what NOAA ships of opportunity will be available in the region, in addition to other vessels.

Prior to holding a planning meeting it is difficult to predict how much of this vision will be carried out by USGS researchers and how much will require input from academic colleagues. At this preliminary state, however, we can predict which components will involve a substantial USGS role. These include:

- evaluations of the impacts of iron fluxes on ecosystem function and structure and how such fluxes affect the balance of top-down versus bottom-up forcings through the zooplankton community to upper trophic levels
- quantification of iron fluxes from groundwater, from coastal sediments and from rivers
- quantification of cross-shelf transport of iron towards the open ocean

8. Possible Process Study locations

At this early stage of planning it is premature to designate specific sites for process studies focused on sources of iron and other trace metals. These decisions need to be made by the collective research group that will be working on the project. However, certain process study sites can be reasonably well predicted. We envision developing a program of coastal trace metal studies that will build on existing and planned studies by USGS and other scientists. For example, the Gulf of Alaska is iron-limited, and extends into Canadian waters, where Canadian scientists are planning complementary research (see attached letter from R. Francois). Hence, it seems likely that some focus on the Gulf of Alaska, and perhaps local rivers such as the Copper River, will be warranted. Similarly, the Bering Sea is iron-limited in some locations and times seaward of the shelf break (Neil Price, personal communication, 2005). Yet the Bering Sea is underlain by a broad area of shelf (Figure 10) which may supply significant iron offshore at certain times of year. Hence the Bering Sea is another possible location. Decisions about process study locations will also be driven by the availability of supporting infrastructure to facilitate the work (e.g. ships, moorings, existing field programs) and realistic granting opportunities. For this reason, work on both the Copper and Yukon rivers seems likely, as USGS scientists are already carrying out research there. Other possible process study sites that could be targeted by USGS scientists and by Canadian or US academic researchers, and the motivation behind their candidacy, are outlined in Table 2.

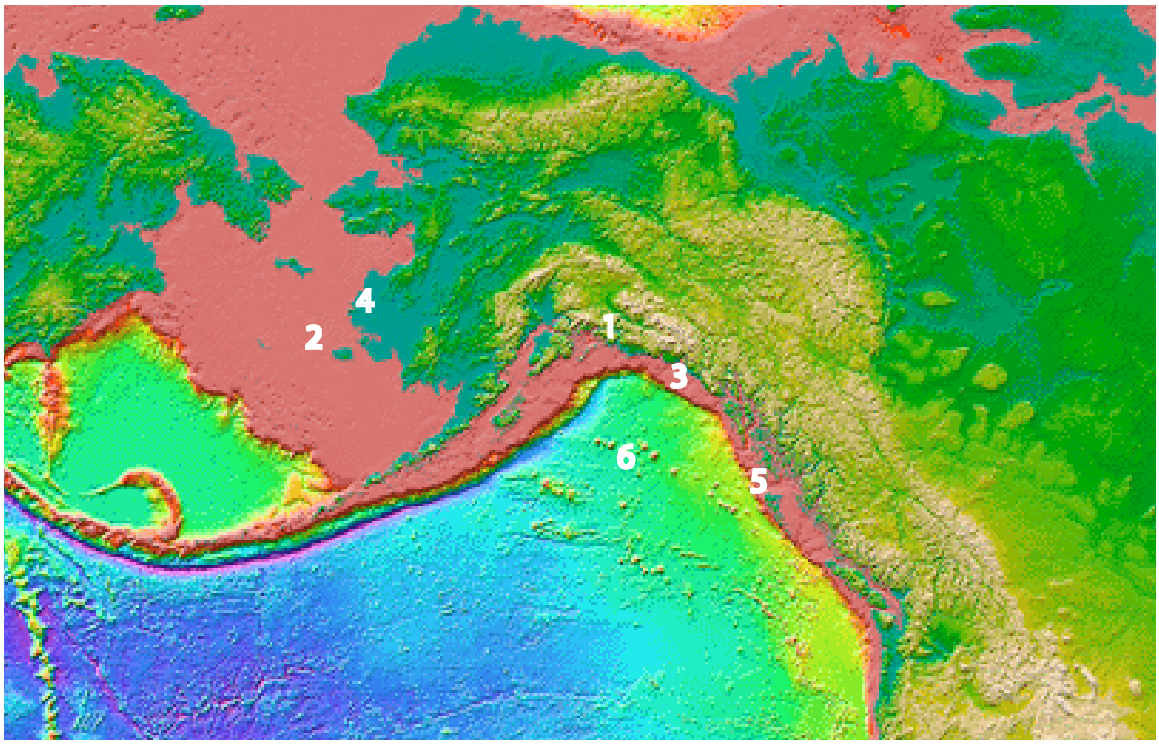

Figure 10: Bathymetry of the region near the Gulf of Alaska. The orange-colored regions represent continental shelf (from Smith and Sandwell, 1997). The numbers correspond to possible sites of process studies discussed in Table 2.

Table 2: Possible sites for process studies examining iron fluxes from the coastal North Pacific Ocean. For locations, see Figure 10).

number	possible site	motivation
1	Copper River	Largest source of fresh water to Gulf of Alaska, glacierized and non-glacierized tributaries, ongoing work by WRD and BRD fisheries in collaboration with US Forest Service
2	Bering Sea	BEST program, extensive shelf can provide iron, ongoing USGS involvement in Bering Sea Ecosystem program funded by NSF.
3	Yakutat eddy formation site	Formation site of eddies documented to transport materials to western Gulf of Alaska
4	Yukon River	One of N. America's largest rivers, ongoing work by WRD and BRD, drains into Bering Sea
5	Haida Eddy formation site	Formation site of eddies documented to transport materials to western Gulf of Alaska (in Canadian waters)
6	Gulf of Alaska	Modest shelf, site of Canadian process study (strong collaboration possibility).

Initial Plans: This section outlines preliminary plans for the first two years of such a program. Given that we envision a planning year, all of the plans and schedules below should be considered very preliminary.

Year "zero"

This paper outlines a broad vision of a possible multi-disciplinary study examining iron cycling in the coastal NE Pacific Ocean. In order to organize these concepts into a focused research program, there is an urgent need to bring together interested scientists to forge our plans for collaboration. We propose to hold an initial planning meeting in the spring of 2006 to initiate this process. We intend to hold this meeting in a location where we can minimize travel costs. Anchorage is a possibility, as this is the logical organizational center for such an effort, as this work focuses on Alaskan coastal waters and several scientists from the Alaskan Science Center are likely to participate. However, other west-coast locations, such as Seattle, may offer reduced travel and meeting costs.

Year one

Plans for the first full year of this program will be driven by discussions held in the initial planning meeting. Hence, we cannot be certain of the full focus of this initial research. However, it is quite possible that we will initiate iron measurements in the Yukon River, and possibly its tributaries. We will also seek ships of opportunity to allow us to initiate cruises within the Bering Sea to examine offshore transport of this riverine iron, in addition to other shelf sources of iron. If these initial measurements demonstrated a significant iron flux, we can envision this work evolving into an instrumented field program in the vicinity of the Yukon River. This would include measurements of suspended matter and dissolved iron in the estuary and on the adjacent continental shelf, and possibly benthic chamber deployments on the continental shelf and slope.

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LAMONT-DOHERTY
EARTH OBSERVATORY
THE EARTH INSTITUTE AT COLUMBIA UNIVERSITY

20 April, 2005

Dear Sir or Madam:

I am writing in support of John Crusius' efforts to initiate a USGS-funded project examining coastal sources and fluxes of trace elements to the North Pacific ocean. It is well known that certain trace elements (e.g. iron) limit biological productivity and influence ecosystem structure in the subarctic North Pacific. However, we have an extremely poor understanding of the origin of these trace elements. The project Crusius is proposing would fit in very well with both Canadian and U.S. plans envisioned for GEOTRACES, an international study of marine biogeochemical cycles of trace elements and isotopes (http://www.ldeo.columbia.edu/res/pi/geotraces/). The academic community is poised and committed to conducting large ocean section studies examining trace element profiles in many locations, including the North Pacific. What is sorely needed to complement this work is coastal process studies that can help pinpoint sources and fluxes of trace elements in as many places as possible. It's a big ocean… in order to be successful, GEOTRACES needs as much support as possible from U.S. national and international agencies. Hence, we enthusiastically support the work Crusius proposes.

Sincerely,

Robert F. Anderson
Co-chair GEOTRACES Planning Committee

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20 April, 2005

Dear Sir:

I am the lead scientist on a developing Canadian initiative to study the marine biogeochemical cycles of trace elements and isotopes. We view our effort as the Canadian component of GEOTRACES, an international project with the same focus. Although our work is still in the planning phases, we expect to have a North Pacific component, motivated by the fact that iron limits biological productivity, and influences marine ecosystems, in much of the North Pacific ocean. I am writing this letter in support of John Crusius' efforts to initiate a USGS project aimed at determining coastal sources and fluxes of trace elements to the North Pacific. Crusius' proposed study would very nicely complement Canadian efforts to study these elements in the North Pacific. Our Canadian infrastructure for this sort of ambitious program is modest. Hence, having U.S. partners, focused particularly U.S. territorial waters adjacent to Canadian waters, would provide an extremely nice complement to our own initiative. We could envision planning joint research cruises spanning both sides of the border, carrying out complementary process studies, etc. In summary, I'm fully behind Crusius' efforts.

Sincerely,

Roger Francois
Chair, Canadian GEOTRACES planning group