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Title: Iron size classes in the Gulf of Alaska: Effects on productivity and community structure Period: from September 2011 to January 2015
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Research Priority: The role of iron in GOA productivity and ecosystem structure
Summary of Proposed Work: The Gulf of Alaska (GOA) is a region with contrasting ecosystems. The central GOA exhibits what is known as high-nutrient-low-chlorophyll (HNLC) conditions, in which primary productivity is lower than expected due to the insufficient supply of the essential micronutrient iron (Fe). Consequently, other nutrients, such as nitrate, are not fully utilized and remain high throughout the year. In contrast, the coastal GOA is highly productive; glacial freshwater inputs provide an ample supply of Fe, but are poor in nitrate. This can lead to coastal waters where primary productivity is limited by nitrate. Areas over the GOA shelf where Fe-rich coastal waters and nutrient-rich offshore waters mix have the potential to support high primary productivity. Our knowledge of the transport and cycling of Fe in the GOA is limited despite its importance to the ecosystem. The overarching goal of the proposed work is to better understand how the distribution of different forms of Fe is affected by oceanographic processes in the Gulf of Alaska. This will contribute towards an improved understanding of the factors that affect the primary productivity of this important region. We propose to join the funded Gulf of Alaska Integrated Ecosystem Research Program (GOA-IERP) field season and examine Fe in various size classes within the water column. Collaboration with the GOA-IERP lower trophic level (LTL) component will serve to place the proposed Fe work into an ecosystem context, while results from this work will contribute significantly to the scientific goals of the GOA-IERP-LTL and modeling projects.
Community Involvement: Community involvement does not apply to this proposal.

1 **A. Iron size classes in the Gulf of Alaska: Effects on productivity and community structure**

2 Short Title: **Iron in the GOA**

3
4 **B. PROPOSAL SUMMARY**

5 The Gulf of Alaska (GOA) is a region with contrasting ecosystems. The central GOA exhibits what is
6 known as high-nutrient-low-chlorophyll (HNLC) conditions, in which primary productivity is lower than
7 expected due to the insufficient supply of the essential micronutrient iron (Fe). Consequently, other
8 nutrients, such as nitrate, are not fully utilized and remain high throughout the year. In contrast, the
9 coastal GOA is highly productive; glacial freshwater inputs provide an ample supply of Fe, but are poor
10 in nitrate. This can lead to coastal waters where primary productivity is limited by nitrate. Areas over the
11 GOA shelf where Fe-rich coastal waters and nutrient-rich offshore waters mix have the potential to
12 support high primary productivity. Our knowledge of the transport and cycling of Fe in the GOA is
13 limited despite its importance to the ecosystem.

14 The overarching goal of the proposed work is to better understand how the distribution of different
15 forms of Fe is affected by oceanographic processes in the Gulf of Alaska. This will contribute towards an
16 improved understanding of the factors that affect the primary productivity of this important region. We
17 propose to join the funded Gulf of Alaska Integrated Ecosystem Research Program (GOA-IERP) field
18 season and examine Fe in various size classes within the water column. Collaboration with the GOA-
19 IERP lower trophic level (LTL) component will serve to place the proposed Fe work into an ecosystem
20 context, while results from this work will contribute significantly to the scientific goals of the GOA-
21 IERP-LTL and modeling projects.

22
23 **C. PROJECT RESPONSIVENESS TO NPRB RESEARCH PRIORITIES OR IDENTIFIED PROJECT NEEDS**

24 This proposal is in response to the 2011 RFP, specifically to the “General Research Priorities on
25 Ecosystem Components” which as part of “Oceanography and Lower Tropic Level Productivity” seeks to
26 address “The role of iron in GOA productivity and ecosystem structure” (Limit \$500K).

27 The RFP states that “The NPRB is seeking proposals that will provide proper in situ iron
28 measurements in the GOA and will quantify physical, biological and chemical processes controlling iron
29 distribution and transformation and its linkages to ecosystem processes”. A critical first step in obtaining
30 “proper” Fe measurements in order to successfully investigate its role in a given marine ecosystem is to
31 ensure the collection of uncontaminated samples. Collecting trace-metal-clean (TMC) seawater and
32 making accurate measurements of Fe in seawater is particularly difficult due to the extremely high
33 concentrations at which Fe is found in ships and terrestrial environments, when compared to the low
34 concentrations found in seawater. Specialized equipment, expertise, and extreme caution are needed
35 during all aspects of sampling, processing and analysis. Also, to detect changes in the exceedingly low
36 concentrations at which Fe is found in seawater, it is necessary to utilize analytical methods with
37 extremely low detection limits. Our group has considerable expertise in collecting and analyzing seawater
38 samples for Fe and other trace metals (see PIs Curricula Vitae). We propose to join GOA-IERP cruises
39 that will take place on vessels capable of accommodating the specialized equipment we will use for the
40 collection of TMC samples. Our approach will be to investigate Fe in various size classes within the water
41 column across and along the GOA shelf. This will provide information about the different Fe pools that
42 are potentially available to phytoplankton in the eastern (EGOA) and western (WGOA) coastal GOA. In
43 conjunction with the Fe measurements we will examine the Fe nutritional status of ambient
44 phytoplankton communities. We also propose to collaborate with PIs from the lower-trophic-level
45 component of the GOA-IERP to explore the importance of different physical processes in controlling the
46 distribution and transport of Fe in the GOA, and to place our results in an ecosystem context. These new
47 observations will be related to published GOA Fe data and will be useful for evaluating NPZ models of
48 the GOA that include Fe. This work will also contribute to the goals of the GOA-IERP-LTL by providing
49 a better understanding of Fe biogeochemical cycling in the GOA. The outreach activities will teach high
50 school students and the general public about the GOA ecosystem and the role of nutrients in the seasonal
51 cycles of this region.

52 D. PROJECT OBJECTIVES

53 The objectives for the proposed research will be used to address our hypotheses, as well as to relate this
54 project to the goals of the GOA-IERP-LTL.

55 **Objective 1: *Determine the distribution of iron in the eastern and western GOA during early spring***
56 ***and fall.***

57 In seawater, Fe exists as several species which vary in size as well as reactivity and biological
58 availability. We will measure 1) total particulate Fe (TPFe) (> 0.4 μm), 2) total dissolved Fe (TDFe) (<
59 0.4 μm), and 3) truly soluble Fe (SFe) (< 0.02 μm). The difference between TDFe and SFe will provide 4)
60 colloidal Fe (CFe). We will also determine the fraction of TPFe that is 5) labile. These fractions are
61 operationally defined. This ambitious study will provide a detailed look into the different Fe pools that are
62 potentially available to phytoplankton and their transformation across the GOA shelf. With this objective,
63 the proposed work will begin to address the role of Fe in the GOA and will contribute meaningfully to the
64 GOA-IERP-LTL. In particular, the LTL Objective 2 requires integrating physics, chemistry and biology
65 to determine their influence on “the distribution, timing and magnitude of phytoplankton productivity in
66 the two regions” (eastern and western GOA). This objective will also generate detailed observational data
67 that could be used for model evaluation.

68 **Objective 2: *Determine which processes best explain the observed distribution of iron size classes***
69 ***across and along the shelf.***

70 The distribution of the various Fe size classes is controlled by a combination of inputs and the
71 oceanographic processes that transform and transport them. This objective requires concurrent
72 information on physical, biological, and other chemical processes that might influence the speciation and
73 distribution of iron in the study region. This objective will be achieved by working in close collaboration
74 with GOA-IERP-LTL PIs, as they will investigate many of the same oceanographic processes of interest
75 (e.g. water transport across the shelf, primary production). This objective will allow for more accurate
76 predictions regarding the distribution of Fe within the GOA.

77 **Objective 3: *Determine the Fe nutritional status of ambient phytoplankton communities in the eastern***
78 ***and western GOA during early spring and fall***

79 Iron limitation affects the ability of cells to photosynthesize. The photosynthetic efficiency of cells is thus
80 a useful diagnostic of their Fe nutritional status. We will use Fast Repetition Rate Fluorescence (FRRF)
81 to provide measurements of the photosynthetic characteristics of ambient phytoplankton communities.
82 This, together with Objective 1, will allow us to examine the response by phytoplankton to the natural Fe
83 supply, and in conjunction with biological data from the GOA-IERP-LTL, will provide information to
84 investigate the effect of Fe size classes on primary productivity and community structure.

85
86 E. SOUNDNESS OF PROJECT DESIGN AND CONCEPTUAL APPROACH

87 The GOA is a region with contrasting ecosystems. The central GOA is a classic HNLC regime, where
88 primary productivity is lower than expected due to the insufficient supply of Fe (e.g. Martin et al., 1989;
89 Boyd et al., 2004). In contrast, the coastal GOA can exhibit high phytoplankton production and it
90 supports diverse and abundant higher trophic level species such as invertebrates, fishes, seabirds and
91 marine mammals. Yet, given that the glacial freshwater discharging into the GOA is rich in Fe, but poor
92 in nitrate, primary productivity in the GOA inner shelf can become limited seasonally by the availability
93 of nitrate (Strom et al., 2006). Patterns of phytoplankton biomass in the coastal GOA are complex (Figure
94 1) and likely result from a combination of environmental factors. The availability of iron, in addition to
95 controlling the HNLC conditions of the central GOA (e.g. Martin et al., 1989; Boyd et al., 2004), is
96 thought to be a key parameter for understanding productivity patterns in the coastal GOA (Sambrotto and
97 Lorenzen, 1986; Stabeno et al., 2004; Strom et al., 2006). The sources, transport and cycling of Fe in the
98 GOA remain poorly understood.

99 Iron size classes vary in reactivity, and those that are more kinetically labile are thought to be more
100 biologically available. Thus, the highly labile soluble (< 0.02 μm) Fe species are regarded as the most

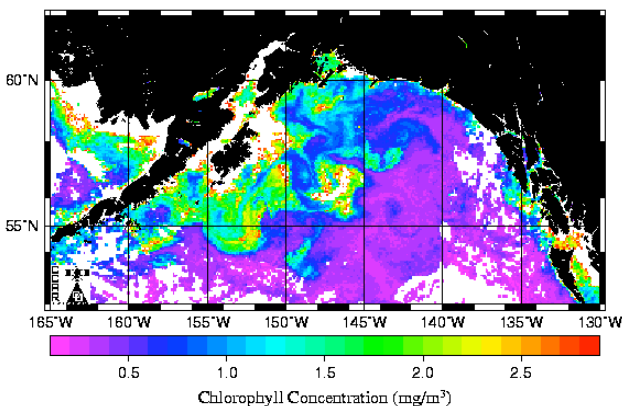


Figure 1: Complex patterns of sea surface Chlorophyll concentrations in the GOA from June/July 2004. The image was generated from Aqua-MODIS level 3 data using the CCAR Global Near-Real-Time SSH Anomaly/Ocean Color Data Viewer
<http://argo.colorado.edu/~realtime/modis/>

101 biologically available end member; whereas the refractory crystalline Fe oxide suspended particles are
 102 considered unavailable to phytoplankton, with all other species somewhere in between. Exchange among
 103 the different Fe pools affects the time scales at which water column Fe can be available to phytoplankton.
 104 The distribution of Fe size classes across and along the GOA shelf can provide insight into the potential
 105 availability of Fe in a given region. We propose to examine different iron pools in the GOA to test the
 106 following null hypotheses:

107
 108 **Hypothesis 1:** *The relative distribution of Fe size classes across the shelf does not vary between the*
 109 *WGOA and the EGOA.*

110 **Alternative:** *The relative distribution of different Fe size fractions vary between the two regions as a*
 111 *result of differences in physical setting (e.g. shelf width).*

112
 113 **Hypothesis 2:** *The distribution of Fe is affected to the same degree by identical oceanographic processes*
 114 *in the WGOA and the EGOA.*

115 **Alternative:** *The hierarchy of processes affecting the distribution of Fe is distinctive in each region.*
 116 *Processes that affect the distribution of Fe, such as primary productivity or sedimentary Fe input, are*
 117 *likely to be different in the two regions.*

118
 119 **Hypothesis 3:** *The cross-shelf Fe nutritional status of phytoplankton in the GOA does not vary between*
 120 *the WGOA and the EGOA*

121 **Alternative:** *Phytoplankton Fe nutritional status across the shelf varies between the two regions as a*
 122 *result of differences in community composition and the availability of Fe.*

123 124 **Background**

125 **Physical Setting**

126 The Alaska Gyre dominates the circulation in the Gulf of Alaska. The eastward North Pacific Current
 127 provides its southern boundary. This current bifurcates at the continental margin into the California
 128 Current which flows south, and the northward flowing Alaska current. The Alaska Current meanders
 129 northwestward forming the western boundary of the gyre, then, flowing around the coast of Alaska and
 130 accelerating near Kodiak Island, becomes the Alaskan Stream, which is the intense western boundary
 131 current of the gyre (Figure 2 insert). Inshore of the Alaska Current-Alaskan Stream is the Alaska Coastal
 132 Current (ACC) (Figure 2 insert), which originates off British Columbia and flows along the GOA coast to
 133 Unimak Pass. This narrow, swift current is driven largely by freshwater runoff and downwelling-
 134 favorable winds. The ACC is modified by the broad-scale Ekman transport, episodic entrainment events
 135 and topographic steering along the tortuous coastline. Numerous glaciers and rivers are responsible for
 136 the large freshwater discharge into the ACC, which reaches its maximum in late summer/early fall due
 137 melting and summer rains. Downwelling-favorable winds dominate in winter, and are relaxed during
 138 April to September.

170 et al., 2006). The timing of the spring bloom appears to affect its intensity, with blooms that begin earlier
171 in the season being more intense (Henson 2007). Other factors contribute to the high productivity of the
172 coastal GOA. Higher productivity observed over banks and channels (Stabeno et al., 2004) is likely the
173 result of enhanced mixing due to topography and tides. Filaments of high chlorophyll concentrations
174 associated with eddies are also common features observed remotely (Figure 1) over the GOA.

175 Several studies have evoked iron as a key parameter for understanding productivity patterns in the
176 GOA. Okkonen et al. (2003) suggested that eddies may play an important role in relieving the Fe
177 deficiency of offshore phytoplankton communities by advecting continental Fe into the basin. Stabeno et
178 al. (2004) suggested that the high productivity of the coastal GOA may result from the convergence of
179 nitrate-rich offshore waters, and Fe-rich coastal waters. Based on GLOBEC studies in the WGOA during
180 which strong cross-shelf gradients in nutrient utilization, growth rates, and phytoplankton community
181 composition were observed, Strom et al. (2006) suggested that a gradient in Fe availability across the
182 shelf resulted in some degree of iron limitation being experienced by phytoplankton communities of the
183 outer shelf throughout the growing season. Neither of these studies had iron data to support their
184 hypotheses.

185 186 **Iron**

187 Iron is crucial to the metabolic processes of phytoplankton. It is an essential element in electron transport
188 for both photosynthesis and respiration. Iron is also critical in nitrogen assimilation via nitrate reductase,
189 nitrite reductase, and nitrogenase, as well as in chlorophyll synthesis (Raven et al., 1999; Sunda, 2001).
190 Since Fe is essential for these important cellular metabolic processes, Fe cell quotas are the highest
191 relative to other micronutrients (Ho et al., 2003). Yet, Fe concentrations in seawater are extremely low.

192 Although truly soluble ($< 0.02 \mu\text{m}$) inorganic Fe (SFe), appears to be easily accessible to
193 phytoplankton (e.g. Maldonado and Price, 2000), it is found at exceedingly low concentrations due to the
194 extreme low solubility of inorganic Fe in oxygenated seawater. Organic complexation increases the
195 solubility of Fe in seawater (e.g. Liu and Millero, 2002), and $>99\%$ of the total dissolved ($< 0.4 \mu\text{m}$) Fe
196 (TDFe) is organically complexed, but the bioavailability of these complexes have been shown to be
197 variable (e.g. Rijkenberg et al., 2006). The labile (leachable in 25% acetic acid, or at $\text{pH} = 2$) particulate
198 ($>0.4\mu\text{m}$) Fe pool is potentially biologically available, and in high particle regimes it can be at least an
199 order of magnitude higher than TDFe. The leachable particulate Fe pool may provide a ready source of
200 reactive Fe that can be mobilized into the dissolved or soluble pools. Knowledge of the different iron
201 pools in a given system is of interest as Fe availability significantly regulates the growth activities of
202 phytoplankton. Similar to N, P, and Si, Fe is released during microbial decomposition of organic matter
203 or during the dissolution of sinking biogenic material. Unlike macronutrients, Fe tends to adsorb onto the
204 surface of sinking particles and is removed from the water column becoming progressively depleted
205 relative to macronutrients along the thermohaline circulation pathway (Wu and Boyle, 2002). As Fe-
206 deficient deep water upwells to the euphotic zone in the subarctic Pacific, Fe is depleted prior to
207 macronutrients by phytoplankton, resulting in surface waters that are high in nutrients, but support lower
208 than expected chlorophyll (HNLC conditions). If external sources of Fe are not available, the surface
209 waters remain in a state of Fe limitation. The availability of Fe influences not only the overall primary
210 productivity, but also the algal community composition. In general, open ocean phytoplankton require
211 less Fe than do coastal species. Decreasing their Fe requirements can be accomplished by reducing cell
212 size and the number of Fe-containing enzymes. Small cells, such as flagellates and *Synechococcus*,
213 depend on these strategies to succeed in Fe-limiting waters. Large cells, such as diatoms, are capable of
214 luxury Fe uptake (the uptake of more Fe per unit carbon) which allows them to take advantage of episodic
215 Fe inputs. Thus, diatoms tend to become the dominant species when Fe limitation is relieved by either
216 natural or artificial iron enrichment. Diatoms growing under insufficient iron concentrations preferentially
217 assimilate silicic acid relative to nitrate (e.g. Hutchins and Bruland 1998), and when relieved of Fe stress
218 diatom silicic acid requirement are once again reduced.

219 For the WGOA, Strom et al. (2006) found that large phytoplankton cells (mainly chain-forming
220 diatoms) were associated with high phytoplankton biomass in the inner and mid shelf in spring. By

221 summer, the inner shelf was still dominated by
 222 large cells, while the community of the mid shelf
 223 was dominated by small cells and exhibited low
 224 biomass. The outer shelf community had low
 225 biomass and was dominated by small cells in both
 226 spring and summer. The availability of Fe is
 227 likely a factor in determining the observed
 228 gradients, and recent Fe measurements from the
 229 WGOA (Wu et al., 2009; Lippiatt et al., 2010)
 230 lend support to this idea. These studies observed
 231 decreased surface Fe concentrations as a function
 232 of distance from shore. Although Fe limitation in
 233 the central GOA has been established (e.g. Martin
 234 et al., 1989; Boyd et al., 2004), it is unknown
 235 whether the shelf experiences any Fe limitation.

236 A main source of iron to the shelf is
 237 freshwater runoff. The various glaciers along the
 238 mountainous coastline cause rapid erosion and contribute to the high sediment load carried into the GOA
 239 by rivers and episodic wind storm events (Figure 3). Although terrestrial particles are high in Fe, this
 240 rapid physical weathering produces particles with a low labile Fe component. Lippiatt et al. (2010) found
 241 that on average ~11% of the Fe in suspended particles from the Alsek and Copper River plumes was
 242 labile. Fresh water runoff is at its peak between June and September, and higher concentrations of Fe
 243 have been observed in July as compared to May in the inner shelf of the WGOA (Wu et al., 2009) (Figure
 244 4A). It is worth noting that although observed labile particulate Fe and TDFe in the ACC were high (10^2 -
 245 10^3 nM and 2-8 nM respectively) (Wu et al., 2009; Lippiatt et al., 2010), values decreased rapidly across
 246 the shelf indicating most fluvial input of Fe into the shelf is confined within the ACC (Figure 4). The
 247 ACC has the potential to act as an Fe reservoir, and alongshore vehicle for its transport (Wu et al., 2009).
 248 The concentration of dissolved organic Fe-binding ligands likely caps the amount of TDFe (Figure 4C),
 249 but inorganic colloidal Fe is potentially an important component of the dissolved Fe pool in the high
 250 particle regime of the inner shelf (Figure 4B).

251 The ubiquitous eddies of the GOA have been suggested as a mechanism for transporting Fe-rich

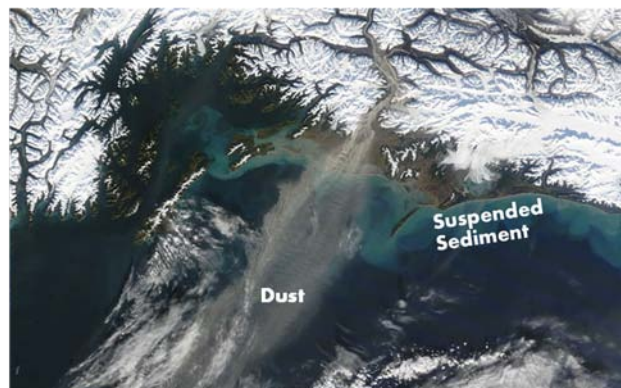


Figure 3: Satellite images of a dust storm and suspended particulate matter from river plumes entering the GOA. SeaWiFs true color image from October 30, 2009.

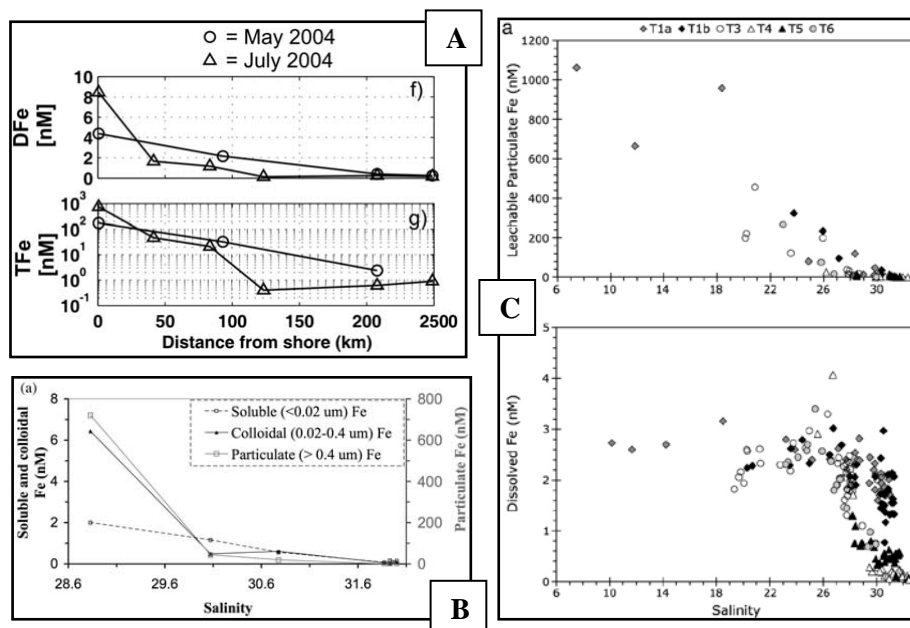


Figure 4: A) total dissolved Fe (DfE in figure) and labile particulate Fe (TfE in figure) along the Seward line (Wu et al., 2009). B) Iron size fractions (SfE, CfE and labile particulate Fe) as a function of salinity along the Seward line (Wu et al., 2009). C) Labile particulate Fe and TDFe as a function of salinity in the coastal GOA (Lippiatt et al., 2010)

252 inshore waters across the shelf (e.g. Okkonen et al., 2003; Stabeno et al., 2004). Ladd et al. (2009)
 253 sampled mesoscale eddies (formed off Sitka and Yakutat) in the EGOA. They observed Fe concentrations
 254 characteristic of coastal waters at the center of eddies and much lower concentrations in the surrounding
 255 waters. An interesting feature of the vertical distribution of Fe in these eddies was a subsurface maximum
 256 in the eddy core which was twice as high in the Yakutat eddy than in the Sitka eddy. There is a wider
 257 shelf off Yakutat than off Sitka. Ladd et al. (2009) suggest that the Yakutat eddy formed over the shelf in
 258 shallower waters where sedimentary inputs provided higher subsurface Fe concentrations to the eddy
 259 core. This argument suggests that the width of the shelf in eddy formation regions plays a role in the
 260 amount of Fe that the eddy can transport in its westward trajectory.

261

262 **Approach**

263 Our proposed approach is a collaborative, multi-disciplinary study that makes effective use of resources
 264 already operating in the area of interest. We will examine the distribution of different iron size classes
 265 across the narrow shelf of the EGOA and the broad shelf of the WGOA in conjunction with making
 266 observations of phytoplankton quantum yields. We will collaborate with LTL PIs to develop a more
 267 complete view of bottom-up controls in the Gulf of Alaska. In particular, we will address the objectives
 268 and hypotheses stated above through a combination of oceanographic research cruises, chemical and
 269 biological analyses, and collaborative data analysis.

270

271 **Observational approach**

272 Our proposed field campaign consists of participation in four GOA-IERP-LTL oceanographic research
 273 cruises with the main purpose of collecting uncontaminated samples for the analysis of Fe, and of
 274 determining in the photosynthetic efficiency of cells. During these cruises we will also be responsible for
 275 providing uncontaminated seawater to conduct collaborative on-deck incubation experiments with LTL PI
 276 Strom. The four cruises we propose to join are: 1) A spring cruise during 2011 on board the *R/V Thomas*
 277 *G. Thompson*, and possible transfer onto the *M/V Tiglax*. 2) A fall cruise during 2011 on board the *M/V*
 278 *Tiglax*. 3) A 2013 spring cruise on a UNOLS vessel (e.g. *R/V Thomas G. Thompson*) and possible transfer
 279 to the *M/V Tiglax*, and 4) A 2013 fall cruise on board the NOAA ship *Oscar Dyson*. We will sample the
 280 surface layer with our towed fish (see below) and the water column with our UAF Fe samplers (see
 281 below). The spring cruises will originate in Seattle and move towards Kodiak. We will sample vertical
 282 profiles at twelve stations during the spring cruises and the fall cruise in 2013. The fall cruise in 2011 will
 283 be restricted to the WGOA where the *M/V Tiglax* will operate, because the fishing vessel charter by the
 284 UTL component cannot accommodate TMC activities. We will measure the photosynthetic efficiency of
 285 the ambient community during the fall cruise of 2011 and during both 2013 cruises.



Figure 5:
 Left. UAF Fe sampler being attached to a hydrowire in the Bering Sea.
 Right. Surface towed fish sampling system. Photo courtesy of Ken Bruland (UCSC)

286

287 *Surface Sampling.* The surface towed fish sampling system will be modeled after the system designed
 288 and utilized by the Bruland Lab (University of California Santa Cruz) (Figure 5, right). This type of
 289 system has been proven to collect uncontaminated surface samples (e.g. Lippiatt et al., 2010), and is being
 290 currently used by the US GEOTRACES program. A goal of the international GEOTRACES program is to
 291 determine distributions of selected trace elements (including Fe) and isotopes in high resolution across the

292 ocean basins. PI Aguilar-Islas has experience deploying this type of towed fish sampling system from
293 various platforms and under widely different condition (*R/V Point Sur* off the California Coast; *R/V*
294 *Wecoma* in the Columbia River plume; and *R/V Nathaniel B. Palmer* in the Ross Sea polynya,
295 Antarctica). The system consists of an all PTFE Teflon™ diaphragm pump (Bruiser™, Osmonics) and
296 PFA Teflon™ tubing mounted to a PVC depressor vane 1 m above a 20-kg PVC fish. The PVC depressor
297 vane and fish are attached by a Yacht-Braid™ dacron line (New England rope), and deployed off the side
298 of the ship using the ship's crane to suspend the fish outside of the wake with the intake at a depth of
299 approximately 2 m (Figure 5). The PFA tubing is directed to a clean enclosure on the ship where
300 sampling takes place (see below). A CTD (YSI 600 OSM CTD) and a turbidity sensor (YSI 6136) will be
301 mounted on the PVC fish to collect-real time surface data.

302
303 **Water Column Sampling.** Vertical profiles will be sampled using UAF Fe samplers (Wu, 2007)
304 (Figure 5, left). These samplers have been shown to collect uncontaminated samples during international
305 inter-calibration exercises (e.g. Johnson et al., 2007). Briefly, these samplers attach to a hydrowire, and
306 are able to collect uncontaminated samples by the use of a plastic vane that keeps the sample bottle
307 upstream of the hydrowire. A plastic encapsulated motor opens and closes the caps of the sample bottles
308 in-situ at pre-determined times, which are programmed via radio frequency prior to deployment. Bottles
309 are filled with DI when deployed; the DI is replaced by the denser seawater. After retrieval, the closed
310 sample bottles are brought into a clean enclosure (see below) for processing. PI Rember has extensive
311 experience using UAF Fe samplers (Atlantic Ocean: *R/V Knorr*, *R/V Endeavor*; Pacific Ocean: *R/V*
312 *Wecoma*, *R/V Kilomoana*; Bering Sea: *USCGC Healy*).

313
314 **Sample Processing.** Surface samples will be filtered in-line using Pall Acropak Supor capsule filters
315 (0.2 µm). Vertical profile samples will be vacuum-filtered through polycarbonate membranes (Nuclepore
316 0.4 µm) and through 0.02 µm Anodisc (Whatman) mounted on Teflon filter holders (Savillex) (Aguilar-
317 Islas et al., 2009). Incubation experiments will also be sampled and filtered through polycarbonate (PC)
318 membranes (Nuclepore 0.4 µm) mounted on Teflon filter holders (Savillex). Filtrates will be collected in
319 low density polyethylene bottles and acidified with quartz distilled hydrochloric acid (Q-HCl) to pH 1.7.
320 Suspended particles for the determination of leachable and total particulate Fe will be collected on PC
321 membranes (Nuclepore 10 µm and 0.4 µm) from unfiltered 2-liter subsamples. All samples will be
322 processed inside a clean enclosure. The clean area is maintained dust-free and protected from possible
323 contamination from the ship by being enclosed in plastic, and maintained under positive pressure using a
324 Class 100 HEPA filter unit.

325
326 **Biological Sampling.** To measure the photosynthetic efficiency of cells, a FRRF (SatAtlantic) will be
327 installed to operate in continuous and discrete modes. This system will not be included in the spring 2011
328 cruise.

329 **Incubation Experiments**

330 As time permits, iron-amended incubations will be performed on deck under simulated *in situ* conditions
331 (JGOFS protocols) to estimate effects on growth and community composition. The added Fe source will
332 come from natural sources: ACC surface waters and bottom shelf waters. Surface outer shelf water will
333 be collected in a TMC fashion and mixed with natural Fe sources. Controls will contain only Surface
334 outer shelf water. The experiment design will follow (Hurst and Bruland, 2007). These experiments will
335 be carried out in collaboration with LTL PI Strom. We will provide TMC seawater to Strom for additional
336 photosynthesis – irradiance experiments that will deliver estimates of phytoplankton photosynthetic rates
337 and parameters under the range of Fe environments encountered.

338 **Analytical approach**

339
340 **Chemical Measurements.** Analysis of Fe will be made upon return to the lab. PIs Rember and Aguilar-
341 Islas have access to an analytical lab with TMC facilities and a high resolution inductively coupled
342

343 plasma mass spectrometer (ICP-MS) at UAF. The concentration of Fe in all the samples will be
344 determined using ^{57}Fe isotope dilution with ICP-MS detection in medium resolution mode. Isotope
345 dilution ensures accuracy, and ICP-MS detection provides the needed low detection limit. Iron in samples
346 for the analysis of TDFe, SFe will be concentrated in the lab using $\text{Mg}(\text{OH})_2$ co-precipitation after Wu
347 and Boyle (1998). This method requires small sample volumes (1.6 ml per replicate). Colloidal Fe will be
348 calculated from the difference between TDFe and SFe. Labile particulate Fe, and TPFe will be leached
349 and digested following the methods of Berger et al. (2008) and Lippiatt et al. (2010), respectively. The
350 leaching method takes 2 hours and utilizes a 25% acetic acid leach in combination with a reducing agent
351 (0.02 M hydroxamine hydrochloride) and a short heating step (10 min. at 90 to 95 °C). The digestion of
352 refractory particles is accomplished with a microwave bomb digestion method that utilizes hydrochloric
353 acid, nitric acid, and small quantities of hydrofluoric acid.
354 The organic speciation of Fe and the characterization of natural Fe-binding organic ligands for selected
355 surface samples will be obtain in collaboration with Dr. Kristen Buck (BIOS) (see letter of support). Dr.
356 Buck has extensive experience making these kinds of measurements

357
358 *Biological Measurements.* The fast repetition rate fluorometer, based on variable fluorescence of
359 chlorophyll *a* (Chl *a*), is capable of real-time high frequency determination of phytoplankton quantum
360 yield, with respect to the ambient irradiance, which in turn can be substituted to estimate instantaneous
361 gross primary production (e.g. Kolber and Falkowski, 1993;). Measurements of photosynthetic
362 competence of Photosystem II (Fv/Fm) have been successfully used to identify Fe limitation in natural
363 communities (e.g. Kolber and Falkowski, 1993; Boyd and Abraham, 2001). In addition, it has been well
364 established that Fv/Fm is positively correlated with Fe availability and negatively correlated with nutrient
365 stress (e.g. Kolber and Falkowski, 1993), and responds rapidly to nutrient inputs and changed light
366 conditions (Brunet et al., 2008). The FRRF will provide a non-invasive *in situ* evaluation of Fe nutritional
367 status in phytoplankton, and will serve as a complementary data set to the labor-intensive measurements
368 of particulate and dissolved Fe. A SatAtlantic FRRF (FIRE) will be used with a dark adaptation time of
369 >30 min for discrete samples. In collaboration with LTL PIs, data on macro-nutrient fields (i.e., nitrate,
370 phosphate, and silicate) and changing phytoplankton assemblages will also be obtained.

371 372 F. EDUCATION AND OUTREACH

373 In addition to outreach activities planned by NPRB for the GOA-IERP, we will produce two professional
374 quality short videos that can be used in classrooms or downloaded to portable media devices. The first
375 video will be descriptive and the second will be instructional. (1) Three to 5 minute movie - GOA
376 Ecosystem Description. The goal of this descriptive movie is to provide a context for where research is
377 taking place, and introduce the viewer to the structure of the GOA ecosystem. Visuals will establish the
378 study location using satellite maps and labels. Text labels and graphics will define the GOA ecosystem
379 and underscore the patterns of productivity and the abundance of higher trophic levels. Scientist voice-
380 over will provide descriptive information tying visual information together. (2) Three minute movie -
381 Instructional. The goal of the instructional movie is to provide basic understanding of the reasons
382 underlying the proposed study. The movie will describe seawater in terms of particulate and dissolved
383 constituents with graphics showing a continuum of these size classes using a whale, jellyfish, krill, sand
384 and as typical particles, and a colloidal humic substance, a protein and a simple chemical compound as
385 dissolved examples. The “particle” diatom will be highlighted as an example and further explained in
386 context of its interaction with dissolved chemicals. The movie will show how the diatom uptakes
387 dissolved nutrients to multiply and how the phytoplankton community structure changes depending on the
388 availability of nutrients. The key points for this video are to show the viewer that there is a size class
389 continuum, and that the ecosystems function differently when large cells dominate versus when small
390 cells dominate. These movies will be targeted to high school and general public audiences and will be
391 made available through the PIs websites, the NPRB website, and YouTube. In addition, SFOS public
392 relations office can assist in posting news-worthy activities through the SFOS website.

393

394 G. TIMELINE AND MILESTONES

395 Our field season schedule will be dependent on the timing of the cruises organized by the LTL. Cruises
 396 will take place in 2011 and 2013, beginning on April 14, 2011. This initial cruise will be on-board the *R/V*
 397 *Thomas Thompson*, a ship capable of accommodating our specialized equipment. We propose to join this
 398 cruise which will sample most of the study area during spring, a critical time for this region. We
 399 appreciate that the outcome of this proposal will not have been decided prior to this cruise. However,
 400 funds can come from the LTL budget and will be returned at a later date (see letter of support), provided
 401 this proposal is funded. Our participation in other cruises has been mentioned above. Analysis will
 402 commence upon return from the field, and data will be deposited in the repository of choice as soon as
 403 they are available. The design the outreach videos will begin in 2012 to ensure timely completion. A
 404 project website will also be set up at the beginning of 2012.
 405

TASK	2011		2012		2013		2014	
	Jan-Jun	Jul-Dec	Jan-Jun	Jul-Dec	Jan-Jun	Jul-Dec	Jan-Jun	Jul-Dec
Planning and Preparation	■	■						
Field Work								
LTL Cruise, (<i>Tiglax</i>)		■						
LTL Cruise, (UNOLS)	■							
LTL Cruise, (NOAA)						■		
Sample Analysis								
Process Spring Cruise Samples						■	■	
Process Fall Cruise Samples					■	■	■	■
Coordination with GOA-IERP								
Program and Cruise Planning		■	■	■	■	■	■	■
Sharing data with LTL								■
Obtaining field data from LTL					■	■	■	■
Measureable Milestones								
Attend PI Meetings			■		■		■	
Attend National Meeting								■
Submit manuscript(s)								■
Outreach Activities			■	■	■	■	■	■
Metadata Submission			■	■	■	■	■	■
Data Submission			■	■	■	■	■	■
Final Report Submission								■

406 **Products**

407 The major products anticipated from this project are: (1) An increased understanding in the
 408 biogeochemical cycle of Fe in the GOA; (2) presentation of results at the Alaska Marine Science and
 409 other national/international meetings; (3) publication of results in the peer-reviewed literature; (4)
 410 education of a Ph.D. student; (5) production of instructional videos for high school and general audiences.
 411

412 H. PROJECT MANAGEMENT

413 **Aguilar-Islas:** Ana M. Aguilar-Islas will oversee the project, participate in PI meetings, and be
 414 responsible for synthesis and preparation of the final report to NPRB. During cruises, Aguilar-Islas will

415 collect and process samples, and will collaborate with LTL PIs in setting up and sampling incubation
 416 experiments. She will oversee and participate in sample processing and analysis in the lab. Aguilar-Islas
 417 has recently join SFOS at UAF, and has more than 3 years experience in marine trace metal research in
 418 Alaskan waters. She has participated in several interdisciplinary projects globally, including the recent
 419 BEST program in the Bering Sea. She has experience managing projects, and has worked closely with the
 420 other PIs in this project. This work proposes to collaborate with the lower trophic level component of the
 421 GOA-IERP. Significant scientific interaction is expected with this component, as well as sharing of
 422 resources and infrastructure available for GOA-IERP.

423 **Rember:** Robert Rember will be responsible for field logistics and sample analysis. During cruises,
 424 Rember will be responsible for setting up equipment, collecting and processing samples. He will
 425 participate in PI meetings. Rember has more than 10 years experience in marine trace metal research,
 426 including at-sea experience, and has worked extensively in Alaskan waters. He has participated in several
 427 interdisciplinary projects, including the recent BEST program in the Bering Sea and the GLOBEC
 428 project. He has experience organizing field operations including currently coordinating all mooring and
 429 chemistry work on the NABOS program.

430 **Stockwell:** Dean Stockwell will be responsible for the collection and processing of fluorometric
 431 assessment of phytoplankton fields. He will interact with LTL PIs interested in macronutrient
 432 distribution, trace metal distribution, and primary productivity. Stockwell has participated in several
 433 multidisciplinary research projects in the past twenty-five years in the capacity of cruise leader, chief
 434 scientist, project director or investigator in interdisciplinary cruises. Stockwell has thirty-five years
 435 experience studying phytoplankton/nutrient cycles in rivers, estuaries, and coastal areas of the world, and
 436 has studied phytoplankton ecology world-wide. During the past decade, Stockwell has participated in the
 437 GOA GLOBEC and Seward Line programs looking at primary productivity and phytoplankton standing
 438 crop in the GOA as related to nutrient distributions and to pink salmon production. As a participant of the
 439 Bering Sea Ecosystem Program (BEST), he provided fluorometric data to project investigators.

440 *Graduate Students*

441 One Ph.D. student will participate in the project from 2012 to 2014. He/she will receive full support
 442 during this time.s The student will participate in the field season in 2013, and will be responsible for the
 443 processing and analysis of particulate samples.
 444

445 I. FIGURES AND TABLES. Inserted in the text.
 446

447 J. REFERENCES

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PROFESSIONAL PREPARATION:

University of California Santa Cruz	Ph.D. in Ocean Sciences	2007
University of California Santa Cruz	B.S. in Chemistry	2002

APPOINTMENTS:

June 2010 – present Assistant Professor, School of Fisheries and Ocean Sciences, UAF
 Apr. 2007 – June 2010 Postdoctoral research fellow, IARC, UAF
 Jan. 2007 – Mar. 2007 Associate in Ocean Sciences, UCSC. Taught graduate level *Chemical Oceanography* (OCEA 220)
 Jan. 2003 – Mar. 2003 Teaching assistant, UCSC, *The Oceans* (OCEA 01)

CURRENT ACTIVITIES:

- Development of Chemical Coastal Processes course at UAF
- Participant in the first US GEOTRACES cruise. North Atlantic. October/November 2010. This cruise was dedicated to sampling seawater for the determination of trace metals and their isotopes.
- GEOTRACES contributor to the intercalibration of aerosol-derived trace metals (2009-present)
- GEOTRACES contributor to the intercalibration of dissolved trace metals in seawater(2008-present)
- Sampling and Analysis of Fe (SAFe) cruise participant and contributor: International collaboration of standardizing sampling and analysis of dissolved Fe (2005-present).
- Journal reviewer: *Limnology and Oceanography Method, Environmental Chemistry, Marine Chemistry, Geochimica et Cosmochimica Acta.*
- Grant reviewer: National Science Foundation

RECENT/RELEVANT PUBLICATIONS: (5 selected)

- Wu, J., **A. Aguilar-Islas**, R. Rember, T. Weingartner, S. Danielson, and T. Whitley. 2009. Size-fractionated iron distribution on the northern Gulf of Alaska. *Geophysical Research Letters*, 36, doi:10.1029/2009GL038304.
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Mount Allison University	B.Sc. in Chemistry	1995

APPOINTMENTS:

Mar. 2004 – present	Research Professional IV, IARC, UAF
Jan. 2002 – Feb. 2004	Research Scientist, DMES, FIT
Sept. 1998 – Dec. 2002	Research Associate, DMES, FIT.
Sept. 1995 – August. 1998	Teaching assistant, Marine and Environmental Chemistry, DMES, FIT

CURRENT ACTIVITIES:

- Participant in the IARC Nansen and Amundsen Basins Observational System. Lead Investigator for new chemistry program. Also responsible for all mooring deployments/recoveries and logistics.
- Participant in the first US GEOTRACES cruise. North Atlantic. October/November 2010. This cruise was dedicated to sampling seawater for the determination of trace metals and their isotopes. GEOTRACES contributor to the intercalibration of dissolved trace metals in seawater (2008-present)
- Sampling and Analysis of Fe (SAFe) contributor: International collaboration of standardizing sampling and analysis of dissolved Fe (2005-present).
- Journal reviewer: *Marine Chemistry*, *Geochimica et Cosmochimica Acta*, *Geophysical Research Letters*
- Grant reviewer: National Science Foundation

RECENT/RELEVANT PUBLICATIONS: (5 selected)

- Wu, J., A. Aguilar-Islas, **R. Rember**, T. Weingartner, S. Danielson, and T. Whitley. 2009. Size-fractionated iron distribution on the northern Gulf of Alaska. *Geophysical Research Letters*, 36, doi:10.1029/2009GL038304.
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Professional Experience:

2008-present Associate Research Professor, University of Alaska Fairbanks, Institute Marine Science
 2000-2008 Assistant Research Professor, University of Alaska Fairbanks, Institute Marine Science
 2000-2001 Associate Program Director, NSF, Antarctic Biology & Medicine, 1 year rotator.
 1998-2000 Assistant Research Professor, University of Alaska Fairbanks, Institute Marine Science,
 pigment distributions Gulf of Alaska and Bering Sea
 1990-1998 Research Associate, The University of Texas, Phytoplankton Primary Productivity,
 HPLC and Pigment analyses, and Brown Tide studies.
 1991 Instructor for class entitled "Marine Phytoplankton", Oregon Institute of Marine Biology,
 University of Oregon, Summer Program.
 1987-1990 Post-doctoral fellow, The University of Texas, Marine Science Institute, Port Aransas,
 TX.
 1982-1987 Teaching and research assistant in oceanography, Marine Education and Public Relations
 Assistant, University of Rhode Island.

Five Most Relevant Publications:

Sukhanova, I.N., M.V. Flint, L.A. Pautova, **D.A. Stockwell**, J.M. Grebmeier, and V.M. Sergeeva. 2009.
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Related activities:

Participated in Shelf Basin Interactions (SBI) program as part of the service group, providing all working groups with water column chlorophyll data (Chukchi and Beaufort Seas).

Participated in NOAA Ocean Exploration cruise, summer 2005, assessing water column and ice related primary productivity and pigment distribution in Canadian Basin.

Participated in NOAA/NSF GLOBEC cruises, 1997-2004, assessing water column primary productivity in Gulf of Alaska and providing pigment data.

Participated in NSF Inner Fronts program, (Bering Sea) assessing water column primary productivity and phytoplankton distributions. Published results on anomalous phytoplankton blooms in the Bering Sea.

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08 December 2010

Dear Ana,

I am writing this letter to enthusiastically support your planned proposal submission to the North Pacific Research Board to investigate the role of iron in the Gulf of Alaska. Per our discussion, I can offer to analyze dissolved iron (Fe) organic speciation in filtered seawater from stations you will sample on the proposed 2011 and 2013 spring and fall cruises (a total of 36 surface samples from across and along the shelf). From this work, I will provide dissolved Fe-binding ligand concentrations and conditional stabilities of these ligands in the samples using competitive ligand exchange- adsorptive cathodic stripping voltammetry. Put into the context of your planned size-fractionated (soluble, colloidal, dissolved, and particulate) Fe measurements, I believe this work can greatly bolster our understanding of Fe biogeochemistry in the Gulf of Alaska.

Cheers,

Kristen N Buck



UNIVERSITY OF ALASKA FAIRBANKS

School of Fisheries and Ocean Sciences

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Dec 9, 2010

Dear Ana,

The lower trophic level component of the GOA-IERP wishes to offer its full endorsement to your NPRB proposal “Iron size classes in the Gulf of Alaska: Effects on productivity and community structure”. Iron has been a crucial missing piece of the GOA puzzle for more than a decade when the GLOBEC program suggested its key role in controlling productivity in the region. As we discussed, the goals of your proposed research complement ours, and I believe this collaboration is essential in furthering our understanding of the Gulf of Alaska ecosystem.

Determination of iron concurrently with the collection of our data will finally allow us (both observationalists and modelers) to answer long-standing questions on the factors controlling the productivity of the GOA shelf and offshore waters. Additionally, your ability to provide uncontaminated seawater for our group makes it possible for us to conduct on-deck photosynthesis-irradiance experiments that will deliver accurate estimates of phytoplankton photosynthetic rates under the range of Fe concentrations that exist in the Gulf of Alaska.

In terms of logistics, we will be able to provide space for two people during spring and fall cruises in 2011 and 2013. Given the tight timing of the spring 2011 cruise to funding decisions, I am prepared to help you secure the resources you will need to participate in that cruise. Furthermore, given the inability of the fishing vessel chartered for fall 2011 by the UTL component to conduct trace metal clean sampling, I will work with you to mobilize the *Tiglax* in September 2011 to conduct sampling along the Seward Line, and several other stations in the western GOA.

We wish you the greatest success with this proposal, and are eager to commence an exciting and successful collaboration.

Sincerely,

Dr. Russell R. Hopcroft
Professor
hopcroft@ims.uaf.edu