



Sea ice-derived dissolved iron and its potential influence on the spring algal bloom in the Bering Sea

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[1] Observational and modeling studies in the Bering Sea indicate that changes in the seasonal ice cover and time of ice retreat influence open-water productivity. In particular, the timing of the spring bloom and its phytoplankton community composition are affected. Dissolved iron (DFe) data in the water column and ice cores collected during the 2007- Bering Ecosystem Study (BEST) cruise indicate that the melting ice provided substantial DFe to the water column. The additional DFe input from melting sea ice could be biologically important along the outer shelf and shelf break where in ice-free areas insufficient DFe (<1 nM) existed for the complete assimilation of available nitrate (>20 μM). Variability in sea ice dynamics are likely to result in a varying supply of DFe to the outer shelf and shelf break in early spring, and to contribute to the observed changes in the timing and community composition of the spring phytoplankton bloom. **Citation:** Aguilar-Islas, A. M., R. D. Rember, C. W. Mordy, and J. Wu (2008), Sea ice-derived dissolved iron and its potential influence on the spring algal bloom in the Bering Sea, *Geophys. Res. Lett.*, 35, L24601, doi:10.1029/2008GL035736.

1. Introduction

[2] The highly productive Bering Sea ecosystem [Walsh *et al.*, 1989; Springer *et al.*, 1996] is influenced by seasonal ice cover. Shifts in climate patterns in recent decades have affected the extent and duration of the seasonal ice cover in the Bering Sea [Stabeno and Overland, 2001]. During “cold” years (e.g., early 1970’s) the southward extent of the ice edge can overlie the nutrient-rich waters of the shelf break in late-March [Alexander and Niebauer, 1981], whereas during “warm” years, the southward ice edge does not reach this nutrient-rich area [Alexander and Niebauer, 1981]. Such fluctuations in ice dynamics have implications for the timing of the spring phytoplankton bloom [Stabeno *et al.*, 2001; Hunt *et al.*, 2002; Saitoh *et al.*, 2002] as supported by data from the NOAA/PMEL mooring M2 [Hunt and Stabeno, 2002]. Although there is less interannual variability in ice cover north of St. Matthew Island [Hunt *et al.*, 2002], climate trends of rising air and ocean temperatures, and reduction in sea ice coverage during winter-spring have caused major ecosystem shifts in the northern Bering Sea [Grebmier *et al.*, 2006]. Because the outer shelf contains much higher concentrations of macronutrients than the middle and inner shelf, an ice edge that

reaches the outer shelf in spring has the potential to support a larger ice edge phytoplankton bloom as ice begins to melt. However, high macronutrient concentrations in the outer shelf can only be fully assimilated when enough iron is available. Here we present vertical profiles of DFe and nutrients from the outer shelf of the northern Bering Sea during spring 2007, and discuss the influence of ice melt on the distribution of DFe compared to available macronutrients in this area, as well as possible implications to the spring phytoplankton bloom.

2. Sampling and Analytical Methods

[3] Water column and sea ice samples were collected for Fe analyses from several stations (Figure 1) in April–May 2007. Sample handling and analysis were conducted using rigorous trace metal clean procedures [Wu and Boyle, 2002]. Sea water was collected using UAF Fe samplers [Wu, 2007]. Ice cores spaced 20–30 cm apart were collected at > 80 m upwind from the ship from uniform, leveled surfaces using an electric drill head attached to a Mark II ice corer (Kovacs Enterprises). The corer is comprised of a lightweight filament wound composite tube (9 cm in diameter and ~1 m in length), an aluminum cutting shoe and heat-treated steel cutting teeth. Each core was immediately transferred into a plastic bag, sealed and stored frozen at -80°C onboard the ship. Whole cores (< 40 cm in length) were processed on board the ship in a climate-controlled room (-20°C) within a class 100 laminar flow hood. Each core was held in place at each end by two titanium pins, and once secured; the outer layers were carefully removed using a titanium chisel. Tests conducted prior to the cruise determined that removing the outer 5 cm was sufficient to remove contamination from the outer layers of the core (Table 1). Processed cores were placed in fluorinated polyethylene bottles and kept frozen for shipment back to the University of Alaska Fairbanks. Water column (on board) and thawed ice samples (in the lab) were filtered through 0.4 μm polycarbonate membranes (Nuclepore) and acidified to pH 2 with the equivalent of 1 ml of 12 M hydrochloric acid (Optima grade, Fisher Scientific Inc.) per liter of sample. Acidified samples were stored at room temperature for 1 month prior to analysis. Iron was determined using $\text{Mg}(\text{OH})_2$ co-precipitation isotope dilution ICPMS [Wu and Boyle, 1998] with a detection limit of ~0.03 nM and a precision of ~3% at 0.3 nM Fe level.

[4] Macronutrient samples were collected from CTD casts carried out immediately before (or after) collection of Fe samples. Nitrate and nitrite were measured using protocols of Gordon *et al.* [1993] (accurate measurements of nitrate require a correction for nitrite) and a Perstorp auto analyzer modified with Alpchem RFA 300 mixing coils.

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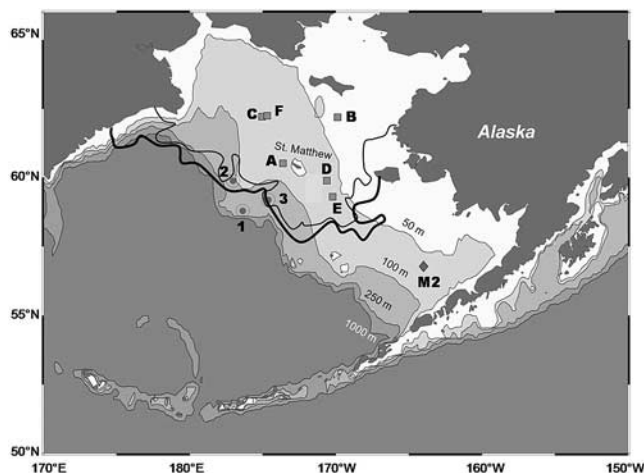


Figure 1. Map showing water column (grey circles, Stations 1–3) and ice stations (grey squares, Stations A–F), the location of NOAA’s M2 mooring (grey diamond), and approximate ice extent (20%) on 23 April 2008 (thick black line) and 3 May 2008 (thin black line). Satellite sea ice concentration data (Aqua: AMSR-E, 0.125 degrees resolution) was obtained from the OceanWatch NOAA website (<http://las.pfeg.noaa.gov/oceanWatch/>).

Samples were collected in 30 ml high-density polyethylene bottles that were rinsed first with 10% HCl, followed by rinsing at least three times with sample before filling. Due to sample backlog, some samples were kept refrigerated in the dark for 3–12 hours prior to analysis.

3. Results and Discussion

[5] The influence of melting sea ice in the Bering Sea outer shelf during spring was inferred by comparing vertical profiles of salinity, temperature, chlorophyll *a* (Chl *a*), nitrate, and DFe (Figure 2) from three outer shelf stations with different sea ice conditions, but with similar locations (Figure 1) and water column depths (128–135 m). Because the mean surface flow in the Bering Sea outer shelf follows bathymetry towards the northwest [Stabeno *et al.*, 2001], the surface water at these three stations was likely from the same source (for surface circulation see auxiliary material).¹ Station 1 (128 m deep) was sampled on 4 May 2007 in open water not influenced by the presence or the melting of sea ice, and is assumed representative of early spring conditions in the outer shelf in the absence of sea ice. The entire water column at this station (Figure 2) remained well mixed with salinity of ~ 33 , temperature of $\sim 2^\circ\text{C}$, high nitrate concentrations (~ 24 – $25 \mu\text{M}$), low Chl *a* ($\leq 0.3 \mu\text{g L}^{-1}$), and subnanomolar (0.8–0.9 nM) DFe concentrations in the upper 40 m. Values for these four parameters are comparable to those encountered offshore of the shelf break (A. M. Aguilar-Islas *et al.*, manuscript in preparation, 2008; C. W. Mordy *et al.*, manuscript in preparation, 2008) in areas where ice-free conditions persisted throughout the winter/spring. Surface DFe at Station 1 was considerably higher than surface summer values in the outer shelf ($\sim 0.1 \text{ nM}$

DFe [Aguilar-Islas *et al.*, 2007]). The higher DFe concentration measured at Station 1 in the spring reflects deep winter mixing and much diminished biological uptake. The observed low Chl *a* values throughout the water column likely resulted from light limitations due to the deep, well-mixed water column.

[6] Station 2 (135 m deep) was sampled on 23 April 2007 in an area with $\sim 80\%$ ice cover, and is representative of early ice melting conditions. Station 3 (124 m deep) was sampled ten days later (on 3 May 2007) in an area of $\sim 50\%$ ice cover, and is representative of later ice melting stages. At both stations, the influence of melting sea ice was apparent as a surface layer of lower salinity and colder water. Step changes of these parameters with depth, are consistent with different mixing (storm) events. The higher degree of ice melting at Station 3 was reflected in its lower surface salinity (~ 31.3 – 31.5) and temperature ($\sim -1.5^\circ\text{C}$) compared to Station 2 (~ 32.2 salinity and $\sim -1^\circ\text{C}$). Also, compared to the subsurface, the surface layer at both stations exhibited decreases in nitrate (of $\sim 12 \mu\text{M}$ at Station 2, and $\sim 24 \mu\text{M}$ at Station 3), and increases in Chl *a* (of $\sim 2.5 \mu\text{g L}^{-1}$ at Station 2, and ~ 4 – $6 \mu\text{g L}^{-1}$ at Station 3). The concentration of DFe at these two stations (3.14 nM at Station 2, and 1.21–1.31 nM at Station 3) was higher than at Station 1. Although not a time series, the differences in nitrate, Chl *a*, and DFe concentrations in the surface layer at Stations 2 and 3 could be interpreted as resulting from the evolution of an ice edge algal bloom. Melting sea ice can influence the physical structure, chemistry and biology of the of the water column [Lannuzel *et al.*, 2008, Schandelmeier and Alexander, 1981], producing ideal conditions for the beginning of an ice-edge phytoplankton bloom such as the one observed at these stations. Because water density is mainly a function of salinity at low temperatures, the low salinity surface layer is more effective at increasing water column stability than the warming of surface waters by insolation alone. In addition, the presence of ice dampens wind stirring and mixing, increasing water column stability. The light regime is changed by the breaking of sea ice and the formation of a surface layer; ice algae can be released seeding the surface layer [Alexander and Niebauer, 1981; Schandelmeier and Alexander, 1981], and potential sea-ice-Fe inputs can increase the concentration of DFe in the surface layer, as has been observed in Antarctica [Lannuzel *et al.*, 2008], and is suggested when comparing the DFe data at Station 1 to that of Stations 2 and 3.

[7] Prior to biological uptake, the outer shelf contained elevated macronutrient concentrations ($\sim 25 \mu\text{M}$ nitrate, $\sim 50 \mu\text{M}$ silicic acid, and $\sim 2 \mu\text{M}$ phosphate (C. W. Mordy

Table 1. Concentrations of Dissolved Fe (nM) in Layers (1 cm) Removed From Sea Ice Cores

	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5
Frozen seawater ^a	1.04	0.40	0.32	0.32	0.33
Arctic 1 ^b	5.18	2.65	1.81	1.79	–
Arctic 2 ^b	84.6	5.61	3.82	0.92	0.89
Bering Sea ^c	110	87.8	19.6	18.2	18.0

^aCore taken from frozen seawater with an original concentration of 0.32 nM Fe.

^bCores collected in the Arctic Ocean.

^cCore F1.

¹Auxiliary materials are available in the HTML. doi:10.1029/2008GL035736.

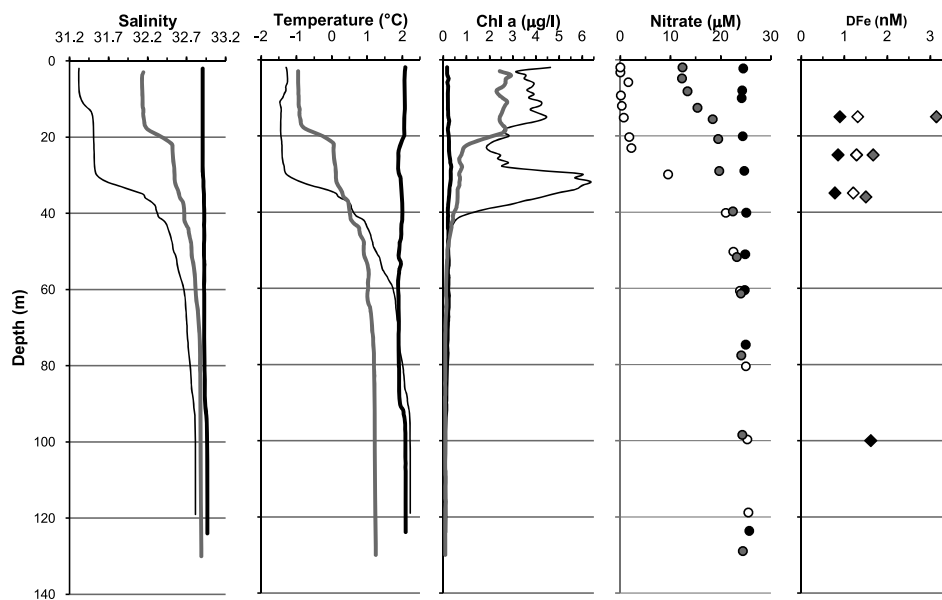


Figure 2. Water column vertical profiles of salinity, temperature, Chl *a*, nitrate, and DFe for Station 1 (thick black line and black symbols), Station 2 (thick grey line and grey symbols), and Station 3 (thin line and white symbols).

et al., manuscript in preparation, 2008)), thereby providing a nutrient-rich environment capable of supporting extensive spring phytoplankton blooms. However, these elevated macronutrient concentrations can only be fully utilized when sufficient Fe concentrations are also available. The amount of Fe needed for the uptake of a given amount of nitrate will vary according to community structure, among other factors. The high biomass sampled in the surface layer at Stations 2–3 was dominated by large chain forming diatoms with many of the species also found in the overlying sea ice associated algae (R. Sambrotto, personal communication, 2007). In laboratory experiments the neritic diatom *Thalassiosira weissflogii* has been shown to widely vary its cellular Fe:C ratio as a function of available Fe concentrations in the media [Sunda and Huntsman, 1995; Ho et al., 2003]. The cellular Fe:C ratio can vary from $< 20 \mu\text{mol mol}^{-1}$ when bioavailable Fe concentrations are $< 0.1 \text{ nM}$, to $\sim 50 \mu\text{mol mol}^{-1}$ at bioavailable Fe concentrations of $\sim 1 \text{ nM}$, to $> 100 \mu\text{mol mol}^{-1}$ in media containing $> 3 \text{ nM}$ bioavailable Fe [Sunda and Huntsman, 1995]. Laboratory and field data for cellular Fe:C ratios appear to be consistent for diatoms growing under nutrient replete conditions [Ho et al., 2003]. Following the argument of Bruland et al. [2001], we assume here that DFe at the surface was available to the phytoplankton community on time scales of days. Thus, Fe:C ratios ranging from ~ 20 – $100 \mu\text{mol mol}^{-1}$ are appropriate for the range of observed DFe concentrations at Stations 1–3.

[8] Station 1 is representative of the outer shelf in the absence of ice. Here nitrate concentrations were $\sim 24 \mu\text{M}$ throughout the water column, and low Chl *a* values (Figure 2) indicated that a spring bloom had not yet developed at this station. Assuming Redfield ratios for carbon and nitrogen, a bloom of large diatoms would require ~ 3 – 16 nM available Fe (using Fe:C ratios of 20 – $100 \mu\text{mol mol}^{-1}$) in order to fully utilize the $24 \mu\text{M}$ available nitrate. However, in the upper 40 m at Station 1 the concentration of DFe was only 0.8 – 0.9 nM . While this

DFe concentration is sufficiently high to favor the growth of large diatoms, the system would likely run out of DFe before nitrate could be fully assimilated. In contrast, Station 3 exhibited depleted nitrate, high biomass (4 – $6 \mu\text{g L}^{-1}$ Chl *a*), and residual DFe (1.21 – 1.31 nM) in its ice-melt-influenced surface layer (salinity ~ 31.3 – 31.5 and temperature $\sim -1.5^\circ\text{C}$). These data from Station 3 suggest that melting sea ice could have provided additional DFe to augment concentrations in the outer shelf, thus allowing increases in biomass and full utilization of available nitrate in the low salinity surface layer. This interpretation is consistent with previous observations that inputs of Fe from melting sea ice can influence water column productivity in seasonal sea ice regions. For example, Lannuzel et al. [2008] showed drastic decreases in the Fe stock in sea ice, together with increases of Fe in the under-ice water column in the western Weddell Sea, concluding that the melting of pack ice was a source of Fe to surface waters, and that this Fe contributed to increases in Chl *a* in the under-ice water column.

[9] Melting sea ice in the outer Bering Sea shelf can potentially affect the concentration of DFe in different ways. Initially, DFe concentrations in the surface layer can be increased (or decreased) if melt water DFe is higher (or lower) than originally present in the water column. As the newly stabilized surface layer allows the development of a phytoplankton bloom, the concomitant biological uptake of DFe to accompany the uptake of nitrate will result in subsequent decreases of DFe. Assuming that due to their proximity and similar water column depths, prior to ice melt Stations 2 and 3 exhibited a well-mixed water column with nitrate and DFe concentrations similar to those at Station 1, then Stations 2 and 3 had experienced decreases in nitrate of $\sim 12 \mu\text{M}$ and $\sim 24 \mu\text{M}$, respectively in their upper low salinity layer at the time of sampling. Using an Fe:C ratio of 20 – $100 \mu\text{mol mol}^{-1}$, this surface uptake in nitrate translates to an uptake of 1.6 – 8.0 nM DFe at Station 2, and 3.2 – 15.9 nM DFe at Station 3. Adding these concentrations to the measured surface DFe at these stations yields a concen-

Table 2. Concentration of Dissolved Fe and Total Dissolvable Fe in Ice Cores

Ice Station Core #	Collection Date	Station Depth (m)	DFe ^a (nM)	TDFe ^a (nM)
A-1	4/16/07	70	36.52	112
A-2	4/16/07	70	108.3	283
A-3	4/16/07	70	15.99	153
A-4	4/16/07	70	26.14	205
B-1	4/19/07	42	40.45	75100
C-1	4/20/07	79	5.65	365
C-2	4/20/07	79	2.92	267
C-3	4/20/07	79	15.13	475
C-4	4/20/07	79	39.82	285
D-1 top	4/24/07	62	16.9	11600
D-1 bottom	4/24/07	62	44.3	3370
D-2	4/24/07	62	185	7100
D-3	4/24/07	62	376	1365
E-1	4/29/07	60	7.86	2070
E-2	4/29/07	60	8.43	390
E-3	4/29/07	60	103	807
E-4 top	4/29/07	60	6.20	1500
E-4 bottom	4/29/07	60	4.99	5650
F-1	5/06/07	75	18.0	111
F-2	5/06/07	75	23.36	242
F-3 top	5/06/07	75	23.08	-
F-3 bottom	5/06/07	75	12.04	-
Laptev Sea ^b	10/95	10	10585 ^c	-
Laptev Sea ^b	10/95	10–40	281 ^d	-
Terra Nova Bay ^e	11/5/00–1/11/01	430	1.07–3.69	26 ^f –627 ^f
East Antarctic Sea ^g	10/01/03–10/07/03	> 3000	3.3–26.0	2.6–51.8

^aDFe, dissolved Fe; TDFe, total dissolvable Fe.

^bData from Hölemann *et al.* [1999].

^cNear Lena River Delta.

^dNot near Lena River Delta.

^eData from Grotti *et al.* [2005].

^fParticulate Fe from HNO₃ digestions.

^gData from Lannuzel *et al.* [2007].

tration of ~ 4.7 – 11.1 nM and ~ 4.5 – 17.2 nM DFe prior to biological uptake at Stations 2 and 3, respectively. These surface concentrations are much greater than those observed at Station 1, suggesting that melting sea ice provided a significant source of Fe to the water column in the seasonally ice-covered waters.

[10] An estimate of DFe in the melt water at Stations 2 and 3 was made using salinity and a simplified model of the sea ice melting process as the mixing of two end members; namely, sea ice and surface outer shelf water. Calculations using the subsurface salinity at Stations 2 and 3 and an average sea ice salinity of 6.4 (from nine ice cores collected in the Bering Sea (R. Gradinger, K. B. Iken, and B. A. Bluhm, personal communication, 2008)) suggests a mixture of 3% and 6% melt water, respectively, at these stations. The concentration of DFe for the surface outer shelf water end member was assumed to be 1 nM, and the DFe concentration for the original mixture (prior to biological uptake) was estimated from the above calculations as 4.7–11.1 nM for Station 2 and 4.5–17.2 nM for Station 3. Thus, based on the estimated melt water contribution to the surface layer at stations 2 and 3, DFe in the melt water was ~ 125 – 338 nM for Station 2 and ~ 59 – 271 nM at Station 3. The heterogeneous nature of sea ice, or C:Fe uptake ratio of phytoplankton, and/or the difference in degree of ice melt could explain the higher melt water DFe estimated for Station 2. Station 2 reflects an earlier

stage of ice melting compared to Station 3, thus the melt water added at Station 2 might have contained a higher concentration of dissolved iron relative to Station 3, based on previous observations from Lannuzel *et al.* [2008], who in a time series study observed that 70% of the total supplied Fe was delivered into the water column during the initial sea ice melting process.

[11] Values of DFe in the ice cores from Stations A–F varied from 2.92 to 376 nM (Table 2) (geometric mean of 22.9 nM), and total dissolvable iron (TDFe) (unfiltered subsamples acidified to pH 2 to allow dissolution of reactive particulate Fe) was also highly variable (111 nM to 75.1 μ M) with a geometric mean of 865 nM. These ice Fe values indicate that sea ice in the Bering Sea during the spring of 2007 contained high enough Fe concentrations to increase DFe in the water column to levels similar to our estimates provided above. The concentration of TDFe was high in our cores, indicating that particulate material with high concentrations of acid-reactive Fe was found within the ice. This reactive Fe could potentially contribute to the DFe pool within the ice in the time between formation and sampling. The particulate material in the ice cores is likely suspended sediment incorporated as ice was formed over the broad, shallow Bering Sea shelf. Sediment-laden ice (“dirty ice”) was visibly apparent at Station B where ice contained the highest measured TDFe (Table 2). Dirty ice is commonly found over the shallow, wide Siberian Arctic shelf [Hölemann *et al.*, 1999; Eicken *et al.*, 2005] and can contain exceedingly high concentrations of DFe [Hölemann *et al.*, 1999] (Table 2). In contrast, seasonal ice in areas with narrow shelves, such as Antarctica, appears to contain much lower concentrations of particulate Fe (whether dissolvable or digested) [Grotti *et al.*, 2005; Lannuzel *et al.*, 2007] (Table 2).

4. Conclusions

[12] Areas of the Bering Sea outer shelf not influenced by ice (e.g., Station 1) contained insufficient DFe for the complete assimilation of available nitrate by large diatoms. In contrast, outer shelf areas influenced by melting sea ice (e.g., Stations 2 and 3) contained sufficient DFe concentrations to support biological depletion of nitrate. In addition to providing water column stability, melting sea ice appears to provide a source of DFe to the outer shelf that is likely important in maintaining ice-edge blooms. In the absence of this input, diatoms in the outer shelf and shelf break may become limited by iron during spring, a hypothesis that could be investigated by further field observations.

[13] Variability in sea ice extent is likely to translate into a varying supply of DFe to the Bering Sea outer shelf and shelf break in early spring, and thereby contribute to the observed changes in the timing and community composition of the spring phytoplankton bloom. Variable inputs of Fe from sea ice are likely to influence spring blooms dynamics in other seasonal ice zones characterized by high macronutrients and low iron concentrations, such as Antarctic pack ice zones. Further research is needed to understand the influence of ice-derived Fe on the spring bloom in seasonal sea ice regions, and the impacts of anticipated climatic changes on this process.

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