Dissolved aluminum, particulate aluminum, and silicic acid in northern Gulf of Alaska coastal waters: Glacial/riverine inputs and extreme reactivity

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A B S T R A C T

The coastal northern Gulf of Alaska receives significant fluvial inputs from the numerous glaciers and rivers that border the region. The distribution of dissolved (soluble and total) and particulate aluminum (leachable and total) was examined in coastal surface water transects and vertical profile samples from shelf stations in the northern Gulf of Alaska in August and September 2007. Both dissolved and particulate aluminum concentrations were dramatically increased in low-salinity plumes, indicative of the significant riverine/glacial input to coastal waters in the region. The percent-leachable particulate Al fraction in these low-salinity plumes was quite low (∼7%), indicative of the large refractory nature of the lithogenic material being delivered to the coastal waters. A consistency in Si:Al ratios from different time periods in the freshwater endmembers that mix to form the low-salinity plumes is discussed in terms of the weathering of biotite in this region. The dissolved Al in these coastal waters appears entirely in the soluble (<0.03 µM) fraction, likely a consequence of the freshwater sources to the region being very low in dissolved organic carbon and organic colloidal complexes. An extreme decreasing gradient of dissolved Al in surface waters was observed moving offshore and into the waters of the Alaskan subarctic gyre where some of the lowest dissolved Al concentrations reported in the world ocean were observed. A high-degree of particle scavenging of dissolved Al in the coastal waters is discussed with a residence time of dissolved Al in coastal shelf waters estimated to be ∼10 days.

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1. Introduction

Aluminum (Al) is the third most abundant element in the Earth’s crust (8.2% by weight; Taylor, 1964) yet the oceanic levels of dissolved Al are found at trace concentrations, less than a few nM in surface waters of the Pacific ocean. Sources of Al to the world’s oceans include riverine inputs, atmospheric inputs, and dissolution from sediments. The concentrations of dissolved Al in riverine waters are highly variable, ranging from ∼50 nM to >1 µM (Hydes and Liss, 1977; Mackin and Aller, 1984a; Morris et al., 1986; Upadhyay and Sen Gupta, 1995; Takayanagi and Gobeil, 2000). Oceanic levels of dissolved Al are found at trace concentrations, ranging from less than 1 nM in intermediate and deep waters of the N. Pacific to ∼25 nM in surface waters of the eastern N. Atlantic where high eolian dust input from the Saharan desert is observed (Orians and Bruland, 1986; Kramer et al., 2004; Measures et al., 2008; Buck et al., 2010). While Al can exist as organic complexes in natural waters (Perdue et al., 1976), Al speciation in the oceans is thought to be dominated largely by the dissolved inorganic hydrolysis species Al(OH)2⁺, Al(OH)3³⁻, and Al(OH)4⁻ with the Al(OH)4⁻ species being dominant at the pH of surface seawater.

The fact that oceanic levels of dissolved Al are relatively low compared to that of the riverine systems implies one, if not several, removal mechanisms of Al in the delivery of riverine Al to oceanic waters. Walker et al. (1988) showed that aluminosilicate clay mineral surfaces can act as adsorption sites for aqueous Al(III) hydrolysis species, a scavenging mechanism removing dissolved Al from seawater. Bruland and Lohan (2003) note that Al has hydrolysis chemistry similar to that of thorium (Th), an extremely particle-reactive element. They show that the mean life of 234Th with respect to removal via particle scavenging is ∼6–10 days in productive surface waters of the subarctic Alaskan gyre and California Current system while estimates in the oligotrophic subtropical North Pacific were 100–300 days. Orians and Bruland (1986) argued that dissolved Al removal would be similar in pattern but at a slower rate. They attributed the low (<1 nM) surface water Al concentrations of the California Current to scavenging of Al by biogenic particles in the high-productivity surface waters with high export production. More recently, Gehlen et al. (2002) showed that Al can also be removed from the seawater as it is incorporated into diatomos during silica frustule biosynthesis. Han et al. (2008) have developed a global model for surface water Al cycling which estimates that particle scavenging of Al dominates removal processes in ∼70% of the surface ocean while biological uptake of Al in silicous frustule biosynthesis accounts for ∼30% of Al removal. They suggest that biological uptake will exceed...
particle scavenging where silica production is high and dust flux is low. Additional removal mechanisms of Al from seawater during river–ocean mixing have also been proposed: salt-induced flocculation of dissolved organic–Al complexes upon river–ocean mixing (Sholkovitz, 1976) and Al removal with respect to an authigenic aluminosilicate mineral formation equilibrium (Mackin and Aller, 1984a,b).

The Gulf of Alaska (GoA) is a semi-enclosed basin of the North Pacific Ocean, bordered to the west, north, and east by a mountainous coastline containing many glaciers and rivers and open to the subarctic Alaskan gyre waters to the south. The circulation of the GoA is dominated by two current systems. The upwelling, cyclonic, subarctic Alaskan gyre is bounded by the Alaska Current in the northeastern GoA and the Alaskan Stream in the northwestern GoA (Fig. 1). As the northward flowing Alaska Current approaches the head of the GoA, the current turns southwestward, following the isobaths and forming the Alaskan Stream (Stabeno et al., 2004). Further inshore over the continental shelf, the circulation is dominated by the Alaskan Coastal Current (ACC; Fig. 1), a coastal feature with a marked freshwater core (salinity >26–29) observed from Icy Pt. in the northeastern GoA to Unimak Pass near the end of the Aleutian island chain (Stabeno et al., 2004). The ACC drives the surface circulation over the continental shelf and controls the transport of lithogenic and biogenic material. Royer (1981) showed that the ACC is a baroclinic, coastal feature resulting predominantly from a large coastal freshwater discharge and, to a lesser degree, local downwelling winds.

Annual freshwater discharge into the GoA (∼2.4×10⁴ m³ s⁻¹) is comparable to that of the Mississippi River (∼2.0×10⁴ m³ s⁻¹) and reaches a maximum in the late summer months due to melting snowpack and summer rains (Brabets, 1997). Approximately 20% of the watershed of the GoA is covered by glaciers (Royer, 1981). These glaciers have been referred to as “buzzsaws” of the mountainous regions they cover due to the rapid erosion they cause (Spotila et al., 2004) and are thus responsible for large inputs of sediment to the freshwater discharge into the GoA. Feely et al. (1979) suggested that the Copper River basin is the major source of sediment discharge to the northern GoA with peak discharge occurring from June through September. The wind field of the GoA is dominated by strong cyclonic winds from fall through spring as the region is the end of the North Pacific storm track (Stabeno et al., 2004). These along-shore winds result in Ekman pumping in the subarctic gyre and downwelling along the coast. This downwelling helps confine the freshwater discharge mentioned above along the coast leading to the formation of the ACC with a marked freshwater core. Feely et al. (1979) measured suspended particulate loads of >6 mg L⁻¹ in the coastal surface waters of the northern GoA influenced by the Copper River. Assuming 8.2 wt.% Al measured in particulate material collected in the surface mixed layer (Feely et al., 1979), which agrees with the average wt.% Al found in continental crust (Taylor, 1964), this equates to an estimate greater than 18 µM total particulate Al assuming that the particulate material is predominantly lithogenic. Anders et al. (2003) report riverine dissolved Al concentrations of 1.8–3.0 µM at several sites at or near the mouth of the Copper River. Thus, it follows that dissolved and particulate Al concentrations in northern GoA coastal waters should be dramatically increased relative to the offshore waters of the subarctic gyre due to significant glacial/riverine inputs along the coast and relatively little atmospheric input of Al to the central Alaskan subarctic gyre (Duce and Tindale, 1991).

This paper describes the distributions of soluble, dissolved, and particulate (leachable and total) Al as well as silicic acid in northern GoA coastal waters during the relatively high runoff, late summer months of August–September 2007. This is the first-ever dissolved Al data reported in the coastal waters of the northern GoA. Such data is lacking in high-latitude regions with glacial inputs. The study aimed to characterize dissolved and particulate Al distributions in northern GoA coastal waters and relate freshwater inputs and Al removal mechanisms to observed Al concentrations. A coastal source of dissolved Al and silicic acid to the region is discussed in terms of chemical weathering and the distribution of dissolved Al between colloidal and soluble forms is investigated in low-salinity coastal waters dominated by glacial/riverine input. In addition, dissolved and particulate Al were examined in waters of the Alaskan subarctic gyre (GAK line) and in coastal upwelled waters of lower Cook Inlet to compare/contrast with observed Al distributions in regions dominated by coastal runoff.

2. Methods

2.1. Sample collection and filtration

Seawater samples were collected aboard the R/V Thomas G. Thompson (University of Washington) in the northern GoA from August 15, 2007 to September 20, 2007 in conjunction with an NSF-funded study of mesoscale eddies in the northern and central GoA. Surface (∼1 m) sampling was conducted using an underway clean
surface pump "fish" system described in detail elsewhere (Bruland et al., 2005; Aguilar-Islas and Bruland, 2006; Lohan and Bruland, 2006). Briefly, this system utilizes an all PTFE Teflon™ diaphragm pump and PFA Teflon™ tubing mounted to a PVC depressor vane 1 m above a 20-kg PVC fish, allowing for clean surface water sampling while underway at speeds of 4–10 knots. Concomitant underway surface salinity and temperature measurements were obtained using a YSI CTD Sonde attached to the PVC fish. The YSI CTD Sonde system was calibrated with the ship’s SeaBird CTD system, which, in turn, was calibrated by the University of Washington’s CTD group just before the research cruise got underway. Underway fluorescence data was obtained through the ship’s flow-through seawater system. Vertical profile samples were collected using 30-L Go-Flo bottles (General Oceanics) deployed on Kevlar line. Vertical profiles of hydrographic data (temperature, salinity, etc.) were acquired through the use of the ship’s CTD. Samples for dissolved Al collected from the “fish” system were filtered in-line through acid-cleaned 0.45 µm Teflon™ capillary filters (GE Osmonics Capsule filters) unless specified otherwise and samples for dissolved Al collected from the 30-L Go-Flo’s were filtered through acid-cleaned 0.4 µm Nuclepore polycarbonate filters.

For particulate Al samples, an unfiltered water sample was collected from the surface fish system or 30-L Go-Flo bottle directly into a 2-L acid-cleaned low-density polyethylene (LDPE) bottle. All filtered volumes were approximately 0.3 L. Filtrations were determined by mass difference and then dried and weighed and the total suspended material concentrations were calculated based on the calibration of instrument response (see Brown and Bruland, 2008 for details). Blank analysis was performed using acidified MQ water which was loaded onto the IDA column for a similar time as the samples being analyzed. Working Al standards were made by serial dilutions of a 1000 ppm Al stock standard (SPEX, Edison,NJ; Fisher Scientific). Al standards made by standard additions of the working standards to volumes of low-Al seawater were analyzed daily. This method has a detection limit of 0.1 nM Al when preconcentrating 10 mL of sample and a precision of 2.5% based on replicate analyses of a 5 nM Al sample when preconcentrating 2.5 mL of sample.

Procedures for estimating leachable particulate Al (LP Al) were performed on select 47 mm Nuclepore filters according to an optimal method outlined in Berger et al. (2008). LP Al is Al associated with easily dissolved particulate phases such as Al-oxyhydroxide coatings on particle surfaces, associated with Fe or Mn oxyhydroxides, adsorbed or in acid labile forms with biogenic particles, and Al that might possibly be associated with carbonates. In short, filters are subjected to a two-hour weak acid leach (25% acetic acid, pH ~2) with a mild reducing agent (0.02 M hydroxylamine hydrochloride) and an initial short heating step (10 min at 90–95 °C). The leachate was then transferred to a quartz beaker with the filter being rinsed with 4 1-mL aliquots of sub-boiled quartz-distilled water. The leachate solution was then acidified with 100 µL of concentrated trace metal grade (TMG) nitric acid (HNO₃) and evaporated down to dryness on a hotplate. The dry residue was then brought up in a second 100 µL of concentrated TMG HNO₃ and evaporated to dryness again. Finally, the ensuing residue was brought up in 8 mL of 1 N TMG HNO₃ containing a 10 ppb Ga/1 ppb Rh internal standard spike. Refractory particulate Al (RP Al) is relatively inert aluminum that is locked within mineral lattices. In order to estimate RP Al, all leached filters (with the remaining RP Al fraction) were bomb-digested in a microwave oven with 3 mL concentrated TMG HNO₃ and 1 mL concentrated TMG hydrofluoric acid in PFA Teflon™ bombs with pressure relief valves (Savillex, Minnetonka, MN). The resulting solution was evaporated down to dryness on a hotplate. The dry residue was then brought up in 8 mL of 1 N quartz-distilled HNO₃ containing an internal standard solution (10 ppb Ga and 1 ppb Rh) and heated briefly (~10 min) on a hot plate before being transferred to an acid-cleaned 15 mL LDPE bottle. The concentrations of LP Al and RP Al were measured at the University of California Santa Cruz using a Thermo- Electron Element I high-resolution inductively coupled mass spectrometer (ICPMS) (Berger et al., 2008; Hurst and Bruland, 2007). It should be noted that total particulate Al (TP Al) concentrations presented herein are the sum of the LP Al and the RP Al concentrations. Both acetic acid leachate and bomb-digestion solutions of 1 N TMG HNO₃ with the Rh/Ga internal standard were transferred to acid-cleaned 7 mL vials and heated briefly (10 min) on a hot plate before being transferred to an acid-cleaned 15 mL LDPE bottle.

The concentrations of LP Al and RP Al were measured at the University of California Santa Cruz using a Thermo- Electron Element I high-resolution inductively coupled mass spectrometer (ICPMS) (Berger et al., 2008; Hurst and Bruland, 2007). It should be noted that total particulate Al (TP Al) concentrations presented herein are the sum of the LP Al and the RP Al concentrations. Both acetic acid leachate and bomb-digestion solutions of 1 N TMG HNO₃ with the Rh/Ga internal standard were transferred to acid-cleaned 7 mL vials and analyzed in medium resolution on the ICPMS. Al concentrations were calculated based on the calibration of instrument response against Al standards ranging from 1 ppb to 500 ppb prepared from dilution of 1000 ppm stock Al solution (SPEX, Edison,NJ; Fisher Scientific).
3. Results

3.1. Surface transects

3.1.1. Transect 1

The locations of the northern GoA transects are shown in Fig. 2. Tables 1–5 show silicic acid, dissolved Al, and particulate Al data as well as corresponding hydrographic data for each surface transect.

Transect 1 was sampled on August 19–20, 2007 beginning at 58.8°N, 138.2°W, southeast of Yakutat, AK with the intention of sampling the plume of the Alsek River that has a maximum flow in July and August (USGS Station 15129000; Alsek River). The transect initially moved in a general northwest direction along and parallel to the inner shelf to near Dry Bay which is the entry point of the Alsek River into the ocean. After the plume of the Alsek River was encountered two pronounced “doglegs” were then undertaken that carried the sampling further offshore and then back to the inner shelf. The transect ended at 59.9°N, 143.3°W. Initial temperature and salinity of the shelf waters were ∼16 °C and 31, respectively, with silicic acid and dissolved Al concentrations of 13–14 µM and ∼30 nM. Initial LP Al was ∼35 nM and initial TP Al was ∼120 nM.

Both temperature and salinity decreased dramatically upon entering the Alsek River plume to minimum values of ∼9 °C and 6.8, respectively, indicative of a marked freshwater plume near 59.1°N, 138.8°W, herein referred to as T1 Plume A (Fig. 3). In these low-salinity plume waters silicic acid concentrations increased by a factor of 2.5 to ∼33 µM while dissolved Al concentrations increased by over a factor of 40 to a maximum value of ∼1300 nM. TSS concentrations increased from background concentrations of ∼3–8 mg l⁻¹ to concentrations of 14–19 mg l⁻¹ (data not shown). LP Al concentrations increased to ∼1750 nM (50-fold increase) while TP Al concentrations increased to a maximum value greater than 25,000 nM (>200-fold increase; Fig. 3).

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Fig. 2. Coastal transect map for the 2007 Eddy Cruise in the northern and central Gulf of Alaska. Coastal surface water transects are shown with the black lines while vertical profile stations are given by white dots. The depth contour intervals shown are 100 m, 250 m, 500 m, 1000 m, and 4000 m.
Temperature and salinity for the first third of Transect 3 were quite uniform at 13.5–13.8 °C and 28.0–28.2 °C, respectively (Fig. 4). Silicic acid concentrations were ~9–10 µM and dissolved Al concentrations were 160–180 nM over this interval. TSS concentrations were quite consistent at 3–4 mg L⁻¹ (data not shown). LP Al concentrations ranged from ~20–75 nM while TP Al concentrations ranged from ~230 to 340 nM. Silicic acid decreased significantly in a low-salinity Copper River plume from ~28 to a minimum value of ~19.2 at 60.19°N, 145.40°W (Julian Day 240.94 in Fig. 4). Dissolved Al increased to concentrations in excess of 600 nM while silicic acid concentrations increased to ~22 µM. TSS concentrations increased to ~12.5 mg L⁻¹ (data not shown). LP Al and TP Al concentrations increased to ~720 nM and 12,000 nM, respectively.

After exiting the low-salinity plume surface waters, salinity increased to ~27.5 with corresponding decreases observed in dissolved Al, LP Al, TP Al, silicic acid, and TSS concentrations. A second low-salinity plume region with minimum salinity (~19.5°) found near 60.29°N, 146.08°W (Julian Day 241.05 in Fig. 4) was observed with increases in dissolved Al and silicic acid to >600 nM and ~21 µM, respectively (Fig. 4). These values were nearly identical to those observed in the first low-salinity region sampled. Interestingly, leachable particulate Al and total particulate Al only increased to 330 nM and 5000 nM, respectively, compared to values of ~720 nM and 12,000 nM in the first low-salinity region where a very similar minimum salinity was observed. Similarly, the TSS concentrations increased to only ~7.5 mg L⁻¹ in this low-salinity plume while increasing to ~12.5 mg L⁻¹ in the first low-salinity plume. Once out of the second low-salinity plume surface water, significant decreases were observed in dissolved Al, LP Al, TP Al, and silicic acid.

Soluble Al concentrations along Transect 3 were nearly identical to the dissolved Al concentrations (Fig. 4). In the higher salinity (~28.2 °C) waters in the first third of the transect soluble Al concentrations ranged from ~130 nM to 180 nM while increasing to maximum values of 620 nM and 680 nM in the two lower salinity (~19.2–19.5°) plumes sampled. The average ratio of soluble Al to dissolved Al along 144.5°W, moved initially in a northeast direction along Kayak Island to 60.0°N, 144.5°W, and ended at 60.13°N, 145.91°W.
Transect 3 was 0.98. Thus, it appears that dissolved Al existed almost entirely in the soluble (<0.03 µm) fraction with virtually no Al in the colloidal (0.03 µm–0.45 µm) size fraction.

### 3.1.3. Transect 4

Starting at 59.8°N, 149.4°W along the inner shelf just offshore of Seward, Alaska, Transect 4 followed the GAK (Seward) line which has been sampled by the University of Alaska since 1970 (Stabeno et al., 2004). The transect ran from the inner shelf in a southeast direction across the continental shelf and shelf break and into the waters of the subarctic Alaskan gyre out to 58.2°N, 147.9°W. Initial temperature and salinity on the inner shelf were ∼13.4 °C and 25.4, respectively, with this salinity being the lowest observed along the entire transect. Transect maxima in dissolved Al (152 nM), LP Al (37 nM), and TP Al (450 nM) were observed in these relatively lower salinity inner shelf surface waters (Fig. 5). No TSS samples were taken here. Silicic acid concentrations were quite low with values less than 1 µM.

In mid-shelf surface waters salinity increased to values of ∼29–31 and temperature decreased slightly to ∼12.8 °C. A dramatic, rapid decrease in dissolved Al was observed moving offshore across the shelf with concentrations of 2–4 nM observed in the mid-shelf region (Fig. 5). LP Al and TP Al concentrations also decreased significantly to ∼3–7 nM and ∼40–90 nM, respectively, while silicic acid concentrations increased to concentrations of 10–15 µM. TSS concentrations were ∼3–5 mg L⁻¹.

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In the HNLC subarctic Alaskan gyre surface waters offshore from the shelf break, salinity became quite constant at ∼32.5 (Fig. 5). It should be noted that dissolved Fe concentrations in these waters were very low (~50–80 pM; Lohan, pers. comm.) while nitrate concentrations were ∼9 µM. Silicic acid concentrations in these waters were

### Table 5

Dissolved aluminum and leachable particulate aluminum with corresponding hydrographic data for Transect 6 starting just off the Aialik Glacier in Aialak Bay southeast of Seward, AK. The symbol “–” denotes that no data was obtained for the given sample.

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<td>3.8</td>
<td>4.6</td>
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</table>
∼10–12 µM. Dissolved Al concentrations in these waters were extremely low (<0.1 nM) and LP Al and TP Al concentrations had decreased to ∼3 nM and 10–12 nM, respectively. TSS concentrations decreased to 1.7–2.7 mg L⁻¹.

3.1.4. Transect 5
Starting at 59.4°N, 152.5°W in lower Cook Inlet north of Kodiak Island, Transect 5 ran in a southerly direction followed by a southeasterly direction through Kennedy–Stevenson entrance, which separates the waters of Cook Inlet from the open continental shelf waters, to 58.9°N, 151.7°W. The transect then ran in a northeasterly direction to an ending location of 59.2°N, 150.8°W off the Kenai Peninsula just south of Gore Point.

Initial temperatures in lower Cook Inlet and Kennedy–Stevenson entrance were relatively cool (9–11 °C) while salinities were elevated at 30.5–31.7 (Fig. 6). Silicic acid concentrations in the relatively cooler surface waters were also elevated at ∼16–20 µM. Dissolved Al concentrations in these cooler, nutrient-rich surface waters were ∼3–6 nM (Fig. 6). Both LP Al concentrations and TP Al concentrations in these higher salinity (31.4–31.8), silicic acid-rich (16–20 µM) waters were variable, ranging from 5–10 nM and 38–110 nM, respectively.

3.1.5. Transect 6
Starting at 59.9°N, 149.7°W just off the Aialik Glacier in Aialik Bay southeast of Seward, AK, Transect 6 was sampled on September 3, 2007 prior to a personnel exchange in Seward. The transect was relatively short and ended on the GAK line at 59.7°N, 149.3°W. The influence of the Aialik Glacier was evident as the initial temperatures and salinities were somewhat low at ∼10.4 °C and 23.1. Dissolved Al and LP Al in these lower salinity waters in close proximity...
to the glacier were elevated at ∼210 nM and ∼380 nM while silicic acid concentrations were ∼2.0–2.5 µM. As the ship moved away from the influence of the glacier, salinity increased significantly to maximum values of ∼30.6. Silicic acid concentrations in these surface waters decreased to <1 µM while dissolved Al values decreased to 60–80 nM (Fig. 7). As the transect approached the GAK line dissolved Al values decreased to ∼3–5 nM and LP Al decreased to ∼5 nM.

### 3.2. Water column dissolved and particulate Al in the shelf waters

While the focus of this manuscript is on the surface water dissolved and particulate Al, samples collected at select vertical profile stations over the GoA shelf are presented to support the interpretation of the surface water data. Transect 2 consisted of a series of vertical profile stations (both CTD casts and Go-Flo sampling) starting from the inner shelf near Yakutat (YAK1) and extending across the shelf and into the waters of the Alaskan subarctic gyre (Fig. 2). Vertical profiles of temperature, salinity, silicic acid, dissolved Al, LP Al, and TP Al for shelf Stations 1, 2, and 3 (YAK1, YAK2, and YAK3) along Transect 2 are shown in Fig. 8. YAK1, YAK2, and YAK3 were located at the inner shelf, mid-shelf, and outer shelf just at the shelf break, respectively.

The salinity profile at YAK1 compared to YAK 2 and YAK 3 (which look very similar) shows the influence of the lower salinity ACC along the inner shelf not just in the near-surface waters but in the deeper waters as well (Fig. 8B). For example, at a depth of 50 m salinity at YAK1 is 31.9 while it increases to ∼32.2 at YAK2 and YAK3. Silicic acid concentrations at YAK1 are somewhat higher in the water column than at YAK 2 and YAK3, particularly from ∼50 m to 100 m (Fig. 8C). Significant decreases in dissolved Al, LP Al, and TP Al are observed in moving from inner shelf YAK1 to the mid- and outer shelf stations (Fig. 8D, E, and F). At 50 m depth dissolved Al concentrations decrease from ∼13 nM at YAK 1 to ∼3 nM at YAK 3 while TP Al concentrations decrease from 700 nM to ∼50 nM. The cause of the increase in dissolved Al at 25 m at YAK1 is not clear.

Three vertical profile stations were occupied along Transect 4 (GAK line) beginning with the nearshore, innershelf Station 1 (GAK-A) and ending with offshelf Station 3 (GAK-C) which sampled HNLC deeper waters of the subarctic Alaskan gyre. Vertical profiles of temperature, salinity, silicic acid, dissolved Al, LP Al, and TP Al for Transect 4 (GAK line) stations GAK-A, GAK-B, and GAK-C are shown in Fig. 9. The temperature profiles show warmer subsurface (∼30–110 m) waters at innershelf GAK-A relative to GAK-C, likely a result of the cooler, upwelled waters of the Alaskan gyre (Fig. 9A) while the salinity profiles clearly show the influence of the lower salinity ACC from the surface to ∼50 m depth at GAK-A (Fig. 9B). Subsurface dissolved Al concentrations range from ∼2 nM to 13 nM at GAK-A and GAK-B with a maximum value found at 10 m depth at nearshore GAK-A. Dissolved Al, LP Al, and TP Al concentrations at offshelf GAK-C are significantly lower than the concentrations observed at GAK-A and GAK-B (Fig. 9D, E, and F).

Finally, two vertical profile stations designated Kodiak Source Water (KSW) stations were sampled on the continental shelf northeast of Kodiak Island (KSW1) and in the waters of the lower Cook Inlet/Shelilof Strait (KSW2; see Fig. 2).

Vertical profiles of temperature, salinity, dissolved Al, LP Al, and TP Al are shown in Fig. 10. Water column temperature was slightly lower and water column salinity was higher at KSW1 relative to KSW 2 (Fig. 10A and B). However, the influence of the lower salinity ACC was not observed at either station. With the exception of a single questionable data point at 25 m at KSW1 (dissolved Al ∼9 nM) water column dissolved Al values were quite consistent at both stations with concentrations of ∼1–3 nM. No significant variation with depth was observed (Fig. 10D). Both LP Al and TP Al were relatively low in the upper water column (0–100 m) with increases in concentration near the bottom indicative of a benthic nepheloid layer (Fig. 10E and F).

### 4. Discussion

#### 4.1. Comparison with previous data

The dissolved and particulate Al data reported here are the first reported direct measurements of Al in the northern and central GoA. Therefore, there is no Al data for direct comparison in the region. The data do show tremendous variation in moving from coastal surface waters into surface waters of the Alaskan subarctic gyre.

The background dissolved Al in coastal waters along Transect 1 and Transect 3 was ∼20–70 nM (salinity ∼30.4–31.3) and 160–180 nM (salinity ∼28.0), respectively (Figs. 3 and 4). These dissolved Al values are significantly elevated relative to the Columbia River region off the Oregon coast, another shelf region highly influenced by fluvial input. Brown and Bruland (2009) report much lower background dissolved Al values of ∼4–10 nM at salinities of ∼30 in near-field Columbia River plumes. Ren et al. (2006) reported dissolved Al concentrations of ∼30–60 nM in low-salinity (23.0–27.0) shelf waters of the East China Sea dominated by Yangtze river discharge. In the most nearshore sample of a survey of Arctic Ocean surface waters, Measures (1999) observed a dissolved Al concentration of ∼22 nM. Maxima in dissolved Al in the Arctic interior were not correlated with fluvial input which has been shown to be relatively insignificant to the region (Kenison Falkner et al., 1997) but correlated with ice-rafted sediment loads. It appears that dissolved Al concentrations in the GoA coastal waters are quite elevated compared to other coastal shelf regions. In addition, the dissolved Al maxima in the low-salinity plume waters along Transects 1 and 3 are significantly greater than those reported by Brown and Brulud (2009) in Columbia River plumes off the coast of Oregon and Washington. Maximum dissolved Al concentrations of ∼1.3 µM and ∼500 nM were observed along Transect 1 at salinities of ∼7 and 19.2, respectively. Maximum dissolved Al reported by Brown and Bruland...
In a survey of the distribution and transport of suspended material in the northern Gulf of Alaska, Feely et al. (1979) observed particle concentrations of 1.5–6.7 mg L\(^{-1}\) in plumes of turbid water extending offshore from the northern GoA coastline in the Copper River region and just west of Kayak Island. The source of the turbid water was attributed to be discharged of sedimentary material from the Copper River and from coastal streams draining various glaciers east of Kayak Island. Particle analysis indicated mostly inorganic material of terrestrial origin (Feely and Cline, 1977). Landing and Feely (1981) measured 8.2 wt.% Al in a composite of three suspended particulate material samples from northern GoA. Assuming 8.2% Al in northern GoA particulate material, 1.5–6.7 mg L\(^{-1}\) equates to 4600–20,000 nM total particulate Al. This estimate is in good agreement with the TP Al concentrations observed in the three low-salinity plumes in the ACC off Yakutat (Transect 1) and the Copper River (Transect 3) where total maximum particulate Al concentrations ranged from 4800 nM to 25,000 nM. It is clear that the coastal discharge of the northern GoA delivers tremendous amounts of particulate Al to coastal waters.

The particulate Al concentrations from the northern GoA surface waters show more similarity to the Oregon coast shelf waters than do the dissolved Al concentrations. In low-salinity, near-field Columbia River plume surface waters sampled in summer 2004, Berger et al. (2008) measured LP Al concentrations of 220–920 nM and TP Al concentrations of ∼2000–8700 nM at salinities of 21.2–26.4. Brown and Bruland (2008) measured LP Al concentrations of ∼440–720 nM and TP Al concentrations of ∼8000–12,000 nM in near-field Columbia River plume surface waters in summer 2006. In comparison, LP Al concentrations in the low-salinity plume sampled along Transect 3 (salinity ∼20.4) were 720 nM and TP Al concentrations were 12,000 nM.

A drastic decrease in water column and surface water Al was observed in moving across the shelf from the nearshore northern GoA coastal waters offshore into the Alaskan subarctic gyre. In moving from the inner shelf near Yakutat towards the shelf break along Transect 2 (Fig. 8) subsurface dissolved Al concentrations in the water column decreased from inner shelf values of 7–16 nM (YAK1) to outer shelf values of 1–2 nM (YAK3). A similar dramatic subsurface gradient in both LP Al and TP Al was observed in moving across the shelf off Yakutat. Surface water dissolved Al concentrations along Transect 4 (GAK line) decreased from values greater than 50 nM along the innershelf to concentrations less than 0.2 nM along the outer GAK line (Transect 4) in the HNLC surface waters of the GoA. These are some of

Fig. 8. Temperature (A), Salinity (B), silicic acid (C), dissolved Al (D), leachable particulate Al (LP Al; (E)), and total particulate Al (TP Al; (F)) along Transect 2 shelf stations YAK1, YAK2, and YAK3 across the continental shelf in the northern GoA. YAK1 was located along the inner shelf (bottom depth = 94 m); YAK2 was located mid-shelf (bottom depth = 135 m); and YAK3 was located at the outer shelf just at the shelf break (bottom depth = 630 m).
the lowest surface water dissolved Al concentrations reported in the world oceans. Similar minimal dissolved Al values (∼0.3 nM) were observed between 70°S and 45°S latitude along 150ºW longitude in the South Pacific during the CLIVAR P16S repeat hydrography cruise (Measures and Landing, pers. comm.) The extremely low dissolved Al values in these waters are attributed to a lack of eolian dust input to the region. Along transects between California and Hawaii, Orians and Bruland (1986) and Johnson et al. (2003) observed surface water dissolved Al and dissolvable Al of ∼0.3–0.7 nM and ∼0.5 nM, respectively, in California Current surface waters. In this case, the dissolvable Al includes the dissolved Al fraction plus a portion of the weak acid LP Al (samples were filtered only through a 20 µM pre-filter and pH adjusted in-line to 5.5 prior to analysis; Johnson et al., 2003). The low concentrations of dissolved Al within the California Current system are attributed to enhanced particle scavenging by sinking biogenic particles which provide surface adsorption sites for dissolved Al, transporting it out of the surface water (Orians and Bruland, 1986).

It is likely that the extremely low dissolved Al concentrations in the subarctic gyre waters of the northern GoA are due to a combination of intense scavenging of fluvially-derived dissolved Al in the particle-rich coastal waters and a lack of significant atmospheric dust input to the region.

4.2. Dissolved Al in the low-salinity coastal surface waters

Property-salinity plots for dissolved Al and silicic acid are shown in Fig. 11 for the low-salinity plume water encountered along Transect 1 Plume A, Transect 3, and Transect 6. For both dissolved Al and silicic acid in Transect 1 Plume A, Transect 3, and Transect 6, a very linear relationship with salinity is observed indicating conservative behavior and control largely by physical mixing of the high silicic acid, high dissolved Al freshwater endmember with a relatively low dissolved Al, low silicic acid coastal endmember (Fig. 8). Extrapolation of the mixing lines to zero-salinity for Transect 1 Plume A and Transect 3 yield average dissolved Al and silicic acid freshwater endmember concentrations of ∼1770 nM and 43 µM, respectively, for the August 2007 sampling period. The extrapolation of the dissolved Al data from the low-salinity plume near Yakutat Bay and the Alsek River to a theoretical zero-salinity endmember (1792 nM; Transect 1 Plume A) is remarkably similar to that of the Copper River (1740 nM; Transect 3) while the silicic acid extrapolated zero-salinity endmember is 39 µM and 48 µM, respectively, for Transect 1 Plume A and Transect 3. The average extrapolated dissolved Al zero-salinity endmember value of 1770 nM observed in late August 2007 is slightly higher than the 1100–1400 nM dissolved Al concentrations observed in the two grab samples from the

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**Fig. 9.** Temperature (A), salinity (B), silicic acid (C), dissolved Al (D), leachable particulate Al (LP Al; (E)), and total particulate Al (TP Al; (F)) at vertical profile stations GAK-A, GAK-B, and GAK-C along Transect 4 (GAK line) across the continental shelf in the northern GoA. GAK-A was located along the inner shelf (bottom depth = 94 m); GAK-B was located mid-shelf (bottom depth = 153 m); and GAK-C was located offshore in the HNLC waters of the Alaskan subarctic gyre (bottom depth = 1450 m).
Copper River collected September 24, 2007. Average world riverine concentrations of dissolved Al and silicic acid are 1480±740 nM Al and 150 µM H$_4$SiO$_4$ (Meybeck, 1988; Treguer et al., 1995). Thus, it appears that the freshwater sources of the two low-salinity plumes measured on Transect 1 Plume A and Transect 3 are comparable to world rivers in terms of dissolved Al yet are relatively silicic acid poor.

Fig. 10. Temperature (A), salinity (B), silicic acid (C), dissolved Al (D), leachable particulate Al (LP Al; E), and total particulate Al (TP Al; F) at Kodiak Source Water (KSW) Stations 1 (KSW1) and Station 2 (KSW2) on the continental shelf in the northern Gulf of Alaska. KSW1 was located along the inner shelf (bottom depth = 215 m) southeast of the Kenai Peninsula and KSW2 was located along the inner shelf within the Sheilokof Strait/lower Cook Inlet (bottom depth = 185 m).

Fig. 11. Dissolved Al vs. salinity (left) and silicic acid vs. salinity (right) along Transect 1 Plume A (black), Transect 3 (grey), and Transect 6 (open triangles) in the northern Gulf of Alaska.
Anders et al. (2003) measured dissolved (0.45 µm-filtered) Al and silicic acid at a number of sites within the Copper River basin of south central Alaska in July 2000. Close to the mouth of the Copper River, an average dissolved Al concentration of 2500 ± 400 nM and an average silicic acid concentration of 63 ± 2 µM was observed from nine sampling sites. Although the dissolved Al and silicic acid concentrations observed by Anders et al. (2003) in the lower Copper River are greater than either the Copper River dissolved values we observed in September 2007 or the theoretical zero-salinity endmember dissolved Al or silicic acid concentrations derived from the mixing lines in Fig. 11 from late August 2007, the Si:Al (mol:mol) ratios from the two different sampling periods for the freshwater endmember are remarkably consistent at 24.3–25.2. This consistency in the Si:Al ratios is indicative of a common source of Si and Al to the freshwaters of the region. The linear relationship of dissolved Al and silicic acid with respect to salinity and the consistency of the Si:Al ratio of the freshwater end member and the plume waters both point to the lack of dissolved Al removal during active mixing and formation of the plume. It appears that for silicic acid and dissolved Al there is simple conservative mixing between the river and coastal seawater to form the Alsek River and Copper River plumes.

Biotite, a hydrous potassium aluminosilicate [K(Mg,Fe)3(Al,Fe)Si₂O₁₀(F,OH)]₄, has been shown by many researchers to be the primary mineral associated bedrock (Blum et al., 1994; Axtmann and Stallard, 1995; Anderson et al., 2000). Nesbitt and Young (1996) suggest that silicate weathering in subglacial environments is dominated by biotite weathering because biotite is susceptible to physical weathering by glacial erosion and abrasion leaving fresh mineral surfaces to be weathered. At the Bench Glacier in south central Alaska Anderson et al. (2000) found biotite to be the dominant silicate phase to chemically weather.

In a laboratory study of biotite dissolution, Malmstrom and Banwart (1997) show a strong pH dependence on the stoichiometry of biotite dissolution. Under acidic conditions, a strong preferential release of mineral framework metal ions (Mg,Fe, and Al) was observed relative to Si. At pH 2, steady-state rates of biotite dissolution (moles m⁻² h⁻¹) of Si, Al, and Fe were 10⁻⁶.⁵, 10⁻⁶.⁵, and 10⁻⁶.⁵, respectively. However, in moving toward the near-neutral pH region, there was a transition to preferential release of Si. At a pH of 8, similar to that of the Copper River (Anders et al., 2003), steady-state rates of biotite dissolution for Si, Al, and Fe were as follows: ~10⁻⁸.⁷5 moles Si m⁻² h⁻¹, ~10⁻⁸ moles Al m⁻² h⁻¹, and ~10⁻⁸.⁷5 moles Fe m⁻² h⁻¹. Malmstrom and Banwart (1997) concluded that biotite was weathered incongruently to vermiculite during the weathering process. Based on the given biotite dissolution rates, Si:Al ratios are expected to be ~10:1. However, removal of the released ions through re-adsorption of ions into the primary mineral phase or secondary mineral formation could affect the observed Si:Al ratios and lead to the observed ratios of ~25:1 in the Copper River and Alsek River freshwater endmembers.

Malmstrom and Banwart (1997) specifically noted that Fe was normally retained in the biotite solid phase as compared to all other ions during the laboratory experiments. While significant increases in both dissolved Al and silicic acid were observed in low-salinity plumes along Transects 1 and 3, it is worth noting that dissolved Fe concentrations remained remarkably constant at 2–3 nM with no appreciable increases in concentration in the freshwater plumes (Lohan, pers. comm.; Lippiatt et al., in prep.). It is likely that the trends observed in dissolved Al, Fe, and silicic acid concentrations in the zero-salinity river endmember that mixes to form the low-salinity plumes in the coastal northern GoA are a result of biotite weathering, dissolution, and secondary mineral formation within the weathering basin.

Another point related to the dissolved Al concentrations in the low-salinity plume surface waters is that there is a distinct difference in the zero-salinity endmember for dissolved Al and silicic acid concentrations between Transect 6, which sampled the fresh glacial melt of Aialik Glacier southeast of Seward, and Transects 1 and 3 which sampled river runoff in the Copper River region and eastward, likely originating from glacial melt but traveling over vegetation, soil, and bedrock in the glacial melt/riverine delivery to the ocean. The theoretical zero-salinity endmember dissolved Al and silicic acid concentrations for the low-salinity plumes along Transects 1 and 3 are 1770 nM and ~43 µM, respectively (Si:Al = 42.3). The zero-salinity endmember values for Transect 6 were significantly lower at 900 nM dissolved Al and 15 µM silicic acid (Si:Al = 16.7; Fig. 11). These differences are reflective of the chemical weathering and precipitation reactions that takes place as fresh glacial meltwater travels across soil, vegetation, and bedrock prior to discharging into the ocean. Similarly, Anderson et al. (2000) noted an increase in silicate denudation rates with increasing distance from a glacier due to the establishment of vegetation causing an increase in silicate weathering.

4.3. A contrast in silicic acid in two low-salinity plumes

Property-salinity plots for dissolved Al and silicic acid within the two low-salinity plumes along Transect 1 (T1 Plume A and T1 Plume B) are shown in Fig. 12. Silicic acid along T1 Plume A showed a linear relationship with salinity indicative of physical control of silicic acid distributions within the plume by dilution of the relatively silicic acid-rich river endmember with a lower silicic acid coastal endmember. T1 Plume B showed drastically different distributions with silicic acid concentrations decreasing in the low-salinity plume waters. At a salinity of ~20, silicic acid concentrations in the low-salinity waters of T1 plume B were roughly ~6 µM. The mixing line along T1 Plume A predicts silicic acid concentrations of ~22 µM at a salinity of 20. Thus, there appeared to be a silicic acid drawdown of ~15 µM in the low-salinity waters of T1 Plume B. It should be noted that nitrate values in the low-salinity plume waters of T1 Plume A increased from <0.05 µM to greater than 2 µM while maximum nitrate values in T1 Plume B showed were only ~0.07 µM.

It could be argued that T1 plume B is an “aged” plume coming from the same source as T1 plume A. However, the temperatures of the low-salinity plume core on both T1 Plume A and T1 Plume B are both ~9 °C while background temperatures along Transect 1 are 15–16.5 °C. If T1 plume B were an “aged” plume coming from the same source as T1 Plume A, it could be argued that the temperature of the plume would warm after mixing with warmer background surface waters. Alternatively, the source region of T1 Plume B is fed directly by the Bering, Guyot, and Malaspina glaciers while the source of T1 Plume A is the Alsek River. It could be that these glacial sources were responsible for T1 Plume B and therefore delivered lower concentrations of silicic acid relative to dissolved Al as was observed in Transect 6. It could also be that the zero-salinity riverine endmember of T1 Plume B was initially cooler than that of T1 Plume A and the agreement of the temperatures in the two plumes is coincidental as both T1 Plume A and T1 Plume B warmed upon mixing with warmer coastal surface waters.

Underway fluorescence and biogenic silicic acid (BSi) data along Transect 1 are presented in Fig. 13. The fluorescence data showed significant increases in the region from 141°W longitude to 142.5°W longitude, which correspond well with the location of T1 Plume B. Concomitant increases in BSI from background values of ~0.2 µM to 6–10 µM were observed. These increases in BSI are somewhat lower in magnitude than the ~15 µM silicic acid removal observed in T1 Plume B. However, it is evident that a diatom bloom was occurring in the low-salinity waters of T1 Plume B. It is likely that a combination of both lower silicic acid: dissolved Al ratios due to the glacial source of T1 Plume B and then further silicic acid assimilation by biota lead to the low silicic acid concentrations in T1 Plume B.
Transect 4 (along the GAK over the Aialik glacier in Aialik Bay sampled lower salinity coastal surface waters 
into two groups based on differing hydrography. Transect 1 off the Copper River, and Transect 6 off the 
particulate Al, and dissolved Al concentrations. Transect 5 near the southern tip of the 
freshwater endmember has been diluted with a higher salinity, low-Al coastal seawater endmember. It is 
reiterated that the dissolved Al concentrations as well as LP Al concentrations in the low-salinity glacial melt waters of Transect 6 were significantly lower than those observed in plume waters of Transects 1 and 3 (discussed in Section 4.2). TSS concentrations in the coastal seawater strongly influenced by the glacial melt water were only \(-4\) mg L\(^{-1}\) at a salinity of \(\sim 11.5\).

Percent-leachable particulate Al (% LP Al; calculated as (LP Al/TP Al)\times 100%) averaged 7.4 \pm 1.1\% \((n = 4)\) in the low salinity plumes along Transects 1 and 3 (Tables 1 and 2). This average value agrees very well with a % LP Al of \(7.3 \pm 0.6\%\) reported by Brown and Bruland (2008) in a near-field low salinity Columbia River plume off the Oregon coast. The relatively low % LP Al values are indicative of the relatively refractory nature of particulate Al in the weathered continental material being delivered to the coastal waters. The refractory Al portion consists of Al bound in mineral lattices in crustal material while the leachable portion is likely Al-hydroxide coatings on particle surfaces or Al associated with biogenic material (Berger et al., 2008).

With the exception of a narrow band of relatively lower salinity \((\sim 25)\) surface water with elevated dissolved Al, LP Al, and TP Al water just offshore along Transect 4 (GAK line), the midshelf and offshore surface waters of Transect 4 were relatively higher salinity \((\sim 30.0–32.5)\) waters with drastically decreased dissolved Al and particulate Al concentrations. Transect 5 near the southern tip of the Kenai Peninsula sampled the cooler, higher salinity surface waters of lower Cook Inlet brought to the surface by intense tidal mixing at the Kennedy Entrance. Similarities and differences in dissolved and total particulate Al as well as TSS concentrations from these three different groups will be discussed.

Of all the surface waters sampled in this study, dissolved Al, LP Al, and TP Al were at maximum values in the coastal low-salinity plume waters of Transects 1 and 3 in the ACC along the northeast boundary of the Gulf of Alaska (dissolved Al \(\sim 1200\) nM, LP Al \(\sim 1700\) nM, and TP Al \(\sim 20000\) nM along Transect 1 at a salinity \(\sim 7\)). In these low-salinity waters the TSS concentrations \((14–19\) mg L\(^{-1}\)) were also at a maximum for the study, indicative of the significant input of lithogenic material from the mountainous coastline to the coastal waters. All of these parameters decrease significantly along Transects 1 and 3 at higher salinities where the freshwater endmember has been diluted with a higher salinity, low-Al coastal seawater endmember. It is reiterated that the dissolved Al concentrations as well as LP Al concentrations in the low-salinity glacial melt waters of Transect 6 were significantly lower than those observed in plume waters of Transects 1 and 3 (discussed in Section 4.2). TSS concentrations in the coastal seawater strongly influenced by the glacial melt water were only \(-4\) mg L\(^{-1}\) at a salinity of \(\sim 11.5\).

Percent-leachable particulate Al (% LP Al; calculated as (LP Al/TP Al)\times 100%) averaged 7.4 \pm 1.1\% \((n = 4)\) in the low salinity plumes along Transects 1 and 3 (Tables 1 and 2). This average value agrees very well with a % LP Al of \(7.3 \pm 0.6\%\) reported by Brown and Bruland (2008) in a near-field low salinity Columbia River plume off the Oregon coast. The relatively low % LP Al values are indicative of the relatively refractory nature of particulate Al in the weathered continental material being delivered to the coastal waters. The refractory Al portion consists of Al bound in mineral lattices in crustal material while the leachable portion is likely Al-hydroxide coatings on particle surfaces or Al associated with biogenic material (Berger et al., 2008).

With the exception of a narrow band of relatively lower salinity \((\sim 25)\) surface water with elevated dissolved Al, LP Al, and TP Al water just offshore along Transect 4 (GAK line), the midshelf and offshore surface waters of Transect 4 were relatively higher salinity \((\sim 30.0–32.5)\) waters with drastically decreased dissolved Al, LP Al, and TP Al. This same variation was observed in the water column values of dissolved Al, LP Al, and TP Al at vertical profile station GAK-A relative to GAK-C with significantly higher concentrations at GAK-A relative to GAK-C (Fig. 9).

Gehlen et al. (2002) provided evidence for the incorporation of Al during siliceous frustule biosynthesis. In laboratory diatom cultures, the authors reported maximum Al:Si ratios of \(\sim 7.00 \times 10^{-3}\) while similar ratios were observed in two natural marine diatom assemblages. Fig. 12 also shows dissolved Al–salinity relationships for T1 Plume A and T1 Plume B. At a salinity of \(\sim 20\), the mixing line for T1 Plume A where no silicic acid drawdown was observed yields a dissolved Al concentration of \(\sim 600\) nM. It is interesting to note that in the T1 Plume B plume core waters, where a significant increase in biogenic silica was observed, two samples at a salinity of \(\sim 20\) show dissolved Al concentrations of \(\sim 500\) nM, 100 nM less than what would be predicted from the mixing line of T1 Plume A. Utilizing a potential Al removal of \(\sim 100\) nM with a silicic acid removal of \(\sim 10–15\) \(\mu\)M yields Al:Si (mol:mol) uptake ratios of \(\sim 6.7 \times 10^{-3}\) to \(10 \times 10^{-3}\), very similar to the Al:Si (mol:mol) ratios observed by Gehlen et al. (2002). While it is realized that two data points do not give substantial evidence of biological Al uptake, the data is consistent with biological Al uptake occurring in these surface waters.

4.4. Surface transects and relationships between total suspended solids, particulate Al, and dissolved Al

The surface transects (Transects 1, 3, 4, 5, and 6) can be divided into three groups based on differing hydrography. Transect 1 off Yakutat Bay, Transect 3 off the Copper River, and Transect 6 off the Aialik glacier in Aialik Bay sampled lower salinity coastal surface waters dominated by fluvial/glacial input with significantly increased dissolved and particulate Al concentrations. Transect 4 (along the GAK line), once further offshore from the influence of coastal runoff, largely sampled midshelf and offshore surface waters characterized by relatively higher salinities and drastically decreased dissolved Al and particulate Al concentrations. Transect 5 near the southern tip of the Kenai Peninsula sampled the cooler, higher salinity surface waters of lower Cook Inlet brought to the surface by intense tidal mixing at the Kennedy Entrance. Similarities and differences in dissolved and total particulate Al as well as TSS concentrations from these three different groups will be discussed.
concentrations were ∼2-3 orders of magnitude lower in the high salinity surface waters of Transect 4 relative to the low-salinity plume coastal waters of Transects 1 and 3, likely a result of the extreme scavenging of the high Al signal in the coastal waters of the northern GoA. TSS concentrations were only ∼20% of that observed in the low-salinity waters along Transects 1 and 3. The decreases in TSS, LP Al, and TP Al are likely due to particle settling as the particle-rich, lower salinity coastal waters move away from their source. The drastic decrease in dissolved Al is very likely due to adsorption of Al onto particle surfaces and removal of Al as these particles sink out. As mentioned previously, in comparison to central Pacific oligotrophic gyre surface waters, the residence time of Al in waters of the subarctic Alaskan gyre is suggested to be significantly less (3–4 years vs. ∼35 days; Orians and Bruland, 1986). In particle-rich northern GoA coastal shelf waters, it is argued here that dissolved Al might be removed even more rapidly, reflected in the extreme decreasing gradient of dissolved Al between the low-salinity coastal waters and the higher salinity midshelf and outershelf waters where some of the lowest reported dissolved Al concentrations in the world ocean have been observed. It is worth noting that the % LP Al along Transect 4 (Table 3) increases to the values of ∼22%–44%, significantly greater than 5 LP Al in Transects 1 and 3 low-salinity plume waters. This increase in the % LP Al fraction is suggestive of removal of dissolved Al onto particle surfaces. Utilizing the water column Al data from the shelf vertical profile stations (YAK1, YAK2, YAK3, GAK-A, GAK-B, KSW1, and KSW2) an average water column dissolved Al concentration of ∼4 nM can be estimated. Using a freshwater input of 2.4 × 10^6 m^3 s^-1 (Brabets, 1997), a zero-salinity endmember Al concentration of 1700 nM, and a continental shelf length, width, and depth, respectively, of 1500 km, 50 km, and 100 m, an average residence time of dissolved Al in northern GoA shelf waters of ∼10 days is estimated. While this calculation contains a degree of uncertainty, it clearly shows that the removal of dissolved Al in these particle-rich coastal waters is relatively rapid compared to oligotrophic gyre surface waters.

Fig. 14 shows dissolved Al concentrations as a function of TSS concentrations for Transects 1, 3, and 4. There is a remarkable degree of variability in dissolved Al concentrations for a given TSS concentration. For example, at a TSS concentration of ∼4 mg L^-1, dissolved Al concentrations from the three surface transects range from >600 nM along Transect 3 off the Copper River to <1 nM along Transect 4 along the GAK line, a difference of over two orders of magnitude. At TSS concentrations of ∼19–20 along Transect 1, dissolved Al concentrations range from 25 nM to 1200 nM. Thus, a clear relationship between dissolved Al and TSS concentrations does not exist in northern GoA coastal waters.

The cooler, nutrient-rich waters of lower Cook Inlet and Kennedy–Stevenson Entrance sampled along the first half of Transect 5 (Fig. 6) are indicative of deep, persistent tidal mixing that occurs in the region, continually supplying nutrients to the surface waters (Stabeno et al., 2004). Vertical shear measurements at Kennedy–Stevenson entrance to lower Cook Inlet showed mixing to depths greater than 50 m. This steady supply of nutrients to the surface waters of lower Cook Inlet makes it one of the most productive high-latitude shelf regions in the world (Sambrotto and Lorenzen, 1987). It follows then that the surface water dissolved Al concentrations in lower Cook Inlet might be related to subsurface dissolved Al concentrations along the shelf. Indeed, the relatively low ∼2–6 nM dissolved Al surface water concentrations in lower Cook Inlet (Fig. 6) agree very well with subsurface dissolved Al values at shelf vertical profile stations (KSW1 and KSW2, Fig. 10) near Kodiak Island and along Transect 4 (GAK-A and GAK-B, Fig. 9). Surface water LP Al concentrations in lower Cook Inlet (∼4–15 nM) are relatively low and agree with the water column LP Al concentrations at GAK-A and GAK-B. The water column LP Al concentrations at innershelf YAK1 are significantly greater, likely due to the close proximity to the particle-rich freshwater source. The % LP Al in the upwelled surface waters of lower Cook Inlet (Table 4) was variable at 8.1 ± 2.8% (n = 5) yet resembles the same fraction as that observed in the low-salinity plume surface waters of Transect 1 off Yakutat Bay and Transect 3 off the Copper River. It is possible that the relatively low dissolved Al concentrations in the surface waters of lower Cook Inlet are due to scavenging and removal of dissolved Al onto particle surfaces as both biogenic and lithogenic particles sink from the surface waters to depth and the subsequent mixing of this low dissolved Al deeper water back to the surface. However, a corresponding increase in % LP Al indicative of Al scavenging might be expected similar to Transect 4, yet this is not observed.

4.5. Dissolved Al vs. Soluble Al

As mentioned in Section 3.2, in the low salinity, high discharge coastal region near the Copper River along Transect 3, nearly all of the dissolved Al was in the soluble (<0.03 um) fraction (Fig. 4). This finding is in contrast to previous work by Brown and Bruland (2009) that showed nearly 65% of dissolved Al in a low-salinity (∼15) plume off the Oregon coast near the Columbia River was in the colloidal form, possibly existing as humic acid or fulvic acid complexes. Interestingly, it was noted that in terms of dissolved organic carbon (DOC) content, the Columbia River (∼100 µM DOC) was relatively deplete in its concentrations of DOC compared to other rivers.

In a study of a glacial estuary in Southeast Alaska, Loder and Hood (1972) observed very low concentrations of DOC (∼12 µM) in an outflow stream from a glacier while concentrations in the glacial estuary ranged from ∼12 µM to 40 µM. In a study of a glacial river–floodplain system in Switzerland, Tockner et al. (2002) measured ∼25 µM in glacial melt water. Thus, it appears that concentrations of DOC in glacial melt are significantly lower than that of the Columbia River or other major rivers. The amount of DOC in the Copper River outflow region will be determined not only by glacial meltwater but by the vegetation over which the glacial melt flows. Anderson et al. (2000) noted an increase in silicate denudation rates with increasing distance from a glacier due to the establishment of vegetation which also could release humic acids to the glacial melt. However, if the vegetation is sparse and not a major source of DOC to the glacial riverine runoff, DOC concentrations in the Copper River outflow region would be quite low. It is argued here that very low DOC concentrations and a subsequent lack of colloidal organic complexes in the runoff waters lead to the dissolved Al in surface waters existing entirely in the soluble fraction. It is suggested that low DOC concentrations in the region might also be linked to the relatively low, invariant dissolved Fe concentrations observed in the low-salinity plumes (Lippiatt et al., in prep.).
5. Conclusions

The large glacial melt/riverine discharge from the mountainous region of central coastal Alaska provides a significant source of dissolved and particulate Al to northern GoA coastal waters. With regards to other major world rivers, freshwater sources to the northern GoA appear to be rich in dissolved Al yet low in silicic acid relative to average river concentrations. Low-salinity plumes in these coastal waters were rich in dissolved Al, both leachable and total particulate Al, and total suspended solids. The percent-leachable particulate Al fraction in these low-salinity plumes was quite low (~7%), indicative of the largely refractory nature of the lithogenic material being delivered to the coastal waters. Si:Al ratios from different time periods point to a common source for dissolved Al and silicic acid in the low-salinity plume waters originating from the Copper and Alese Rivers observed in Transects 1 and 3, respectively (Si:Al ~24–25). However, the coastal surface waters strongly influenced by fresh glacial melt along Transect 6 were unique with much lower silicic acid relative to dissolved Al (Si:Al ~16.7). It is suggested that the major source of dissolved Al and silicic acid in northern GoA coastal waters is the weathering of biotite, which has been shown to be the predominant mineral to contribute to the dissolved load in Alaskan subglacial streams. The relative distributions of silicic acid, dissolved Al, and dissolved Fe (data not reported here) seem to agree with laboratory studies on biotite weathering. Differences in dissolved Al and silicic acid in the freshwater endmember from fresh glacial melt as opposed to glacial melt/riverine runoff that has traveled over vegetation, soil, and bedrock. The dissolved Al in these coastal waters appears entirely in the soluble (~0.03 µm) fraction. This is likely a consequence of the freshwater sources to the region being very low in dissolved organic carbon and a lack of organic colloidal Al-complexes.

Concentrations of dissolved Al in outershelf, HNLC surface waters in the northern GoA are some of the lowest reported in the world’s oceans. These low dissolved Al concentrations are likely due to an extreme degree of particle scavenging of the coastal-derived dissolved Al in the nearshore waters of the northern GoA (supported by significant increases in the percent-leachable particulate Al fraction), as well as a low amounts of atmospheric Al input to the region. Residence times of dissolved Al in the northern GoA shelf waters are estimated to be on the order of ~10 days.

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References


