Submarine groundwater discharge as a source of nutrients to the North Pacific and Arctic coastal ocean

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Abstract

Primary productivity in both the Arctic Ocean and the Gulf of Alaska (GOA) is nitrogen limited in the summer when light limitation is relieved, and stratification in the GOA inhibits nutrient fluxes from deep water sources. Concentrations of nutrients and trace metals in these regions are higher closer to shore, and thus rivers have been attributed as the primary coastal source of nutrients and trace metals. Here we evaluate the role of Submarine Groundwater Discharge (SGD), a previously unquantified source of nutrients and trace metals to the coastal Arctic Ocean and GOA. SGD is an especially enriched in nitrate relative to other nutrients, contributing $1.2 \pm 0.4 \text{ mol NO}_3 \text{ day}^{-1} \text{ m}^{-1}$ of shoreline of the Arctic Ocean. In the GOA, both SGD-associated nitrate flux ($4.3 \pm 2.1 \text{ NO}_3 \text{ day}^{-1} \text{ m}^{-1}$ of shoreline) and silicate flux ($13 \pm 6 \text{ SiO}_4 \text{ day}^{-1} \text{ m}^{-1}$ of shoreline), are substantial when compared to other external nutrient sources. Conservative extrapolations indicate overall SGD supplies more nitrate (1.5-17.5 times) to the GOA than rivers.

Introduction

Submarine groundwater discharge (SGD) is an important component of the hydrological cycle, and it is a conduit for solute transport from land to the coastal ocean (Moore, 2010). The importance of SGD in coastal processes has been documented throughout the world (Hwang et al., 2005; Knee and Paytan, 2011; Taniguchi et al., 2002). It has recently been shown that in high latitude environments SGD transports methane to the coastal ocean and to lakes (Lecher et al., 2015a; Paytan et al., 2015). Previous studies along the Californian coast have also shown that nutrients provided by SGD can spur growth of diatoms by providing not only an abundance of nutrients, but also nutrients in the ratios required by the diatoms (Lecher et al., 2015b).

Radium isotopes have been shown to be reliable naturally occurring tracers of SGD in coastal marine environments (Hwang et al., 2005; Knee and Paytan, 2011; Moore, 1996) and radium isotopes can be used to quantify SGD and fluxes of dissolved constituents transported via SGD to the coastal ocean (Kroeger and Charette, 2008; Null et al., 2012; Shellenbarger et al., 2006). We define SGD in this study, as in many other studies, as the mixture of seawater and freshwater that discharges at the coast as a result of hydraulic gradient and wave and tide action. We further define the coastal aquifer as the beach interface where mixing of these water types occurs, often referred to as the subterranean estuary (Moore, 1999).

Phytoplankton blooms have been documented all along the North Pacific Alaskan coast, which consist of harmful and non-harmful species (Brickley and Thomas, 2004; Horner et al., 1997; Lewitus et al., 2012; Waite and Mueter, Franz, 2013). The overall high primary productivity of the region and blooms of non-harmful species are of great importance in forming the base of the fisheries (Waite and Mueter, Franz, 2013), blooms of harmful toxic producing algae on the other hand have negative impacts on fisheries (Lewitus et al., 2012). Accordingly it

is of interest to quantify and sources and understand the processes that control nutrient and trace metal inputs in this region.

Nutrients are supplied to the surface ocean in the coastal region of Alaska primarily from deeper waters by vertical mixing and upwelling events, increasing phytoplankton biomass (Childers et al., 2005). Terrestrially-sourced freshwater discharge is also be a source if high nutrient (N, P, and Si) to coastal areas supporting plankton growth (Childers et al., 2005; Stabeno et al., 2004; Strom et al., 2007). The nutrient-rich freshwater lens, which contributes to the initial growth of phytoplankton in coastal Alaska, has been attributed to runoff which reaches the ocean via small rivers and streams (Royer, 1982; Stabeno et al., 2004). Although runoff may be especially poor in inorganic N in glaciated watersheds, and runoff is at a minimum during this time of the year, it is still large enough to cause an observable freshening of the surface ocean and could indeed be an important source of nutrients (Hood and Berner, 2009; Royer, 2005).

Iron (Fe) and Zinc (Zn) have also been identified as potential limiting trace metals in the Gulf of Alaska (GOA), although phytoplankton experiments have shown that Fe additions have the most potential to induce growth while Zn was less important (Fujishima et al., 2001; Takeda, 1998). Like in the case of major nutrients deep water (upwelling and wind-driven vertical mixing) and coastal sources have been identified as major sources of Fe and Zn to the GOA (Fujishima et al., 2001; Lippiatt et al., 2010; Waite and Mueter, Franz, 2013).

In the surface Arctic Ocean nutrient concentrations and phytoplankton abundance follow an annual pattern. During the winter when ice cover and lack of sunlight limit primary productivity, nutrient concentrations peak (Tremblay et al., 2008). As winter turns to spring, the sea ice begins to melt, receding from the coastline. The accumulated nutrients, renewed sunlight, and water column stabilization from meltwater induce increases in phytoplankton in areas of ice-

free ocean (Wang et al., 2005). Wind-induced upwelling along the ice edge brings nutrient rich
104 water to the surface where phytoplankton bloom in response (Palmer et al., 2011). The increased
primary productivity of the spring draws down nutrient concentrations in the ice-free ocean,
which then becomes N limited (Tremblay et al., 2008). Rivers at this time replenish nutrients to
the Arctic Ocean, and phytoplankton blooms often propagate at their mouths (Retamal et al.,
108 2008). While trace metal distribution and sources have not been well documented in the Arctic
Ocean, rivers have been suggested as sources of trace metals to the coastal ocean, with riverine
trace metal concentrations increasing during snowmelt (Rember and Trefry, 2004). Primary
productivity in the coastal Arctic Ocean accounts for 80% of primary productivity in the Arctic
112 Ocean (Retamal et al., 2008).

The goals of this study are to (1) determine the concentration and SGD associated fluxes
of nutrients and biologically important trace metals to the North Pacific and Arctic Alaskan
coastlines, and (2) to compare these fluxes to other nutrient sources, when data is available. This
116 is the first study to quantify nutrient and trace metal fluxes to the Alaskan North Pacific and the
Arctic Ocean through SGD, an especially important study in the Arctic Ocean, given the dearth
of nutrient and trace metal flux data in that region. With this study we also build upon previous
work, which showed the high topographic relief, high precipitation, and large tides of southern
120 Alaska are conducive to large volumes of SGD, and transport of constituents through SGD to the
North Pacific coastal ocean, and that SGD is present in the summer transporting solutes to the
Arctic Ocean, at time when it becomes N deplete (Dimova et al., 2015; Lecher et al., 2015a).

Methods

General Sampling and Site Description

Kasitsna Bay is a spit-enclosed bay located in Katchemak Bay, an off-shoot of the Cook Inlet on the Southern Coast of Alaska (Figure 1), within the area plagued by phytoplankton blooms (Brickley and Thomas, 2004). Kasitsna Bay is approximately 1 km in diameter with a maximum depth of 58 m, but most of the bay having a depth in the range of 3-30 m. The bay is subject to a large tidal range (> 8 m), and the Kenai Peninsula, on which the bay is located, is subject to high mean annual precipitation (> 870 mm) and is characterized by high topographic relief, typical of southern Alaska. Discrete seawater, groundwater, and river water samples were collected from Kasitsna Bay in August 2011 and July 2012. 68 samples were collected from the ocean surface (at approx. 0.5 m depth), and 5 samples were collected from a depth of 18 m or 10 m in concert with ocean surface samples in 2012. Groundwater samples were collected from freshly dug pits or temporary PVC well points (< 2 m) depth. A salinity time series of the coastal aquifer (subterranean estuary) was collected over 44 hours from a single well, which was sampled periodically for salinity. Surficial river water samples were collected from creeks flowing into Kasitsna Bay (see Lecher et al. (2015a) for more details).

The other study sites are located on the Arctic Ocean coast of Alaska near Point Barrow (Figure 1). Elson Lagoon is approximately 10 km across, is relatively shallow (< 3 m), and is enclosed by a spit (Point Barrow). On the other side of Point Barrow is the Beaufort Sea. These sites are subject to a small tidal range (< 0.5 m), low annual mean precipitation (< 12 cm), and low topographic relief. Continuous permafrost underlays the tundra on land while subsea permafrost extends offshore below the seafloor (Overduin et al., 2012). Discrete seawater and groundwater samples were collected from both the Beaufort Sea side and Elson Lagoon in July 2012. In the Beaufort Sea, surface samples were collected along two transects (~ 6 and 10 km) extending perpendicular from shore. Groundwater samples were also collected from the active

148 layer of the tundra in the Barrow Environmental Observatory (BEO) (see Lecher et al. (2015a)
for more details). The BEO samples are from groundwater in close contact with permafrost
under freshwater conditions. As sampling of the coastal aquifer in both of these locations is
limited to the unconfined aquifer, indeed due to the presence of continuous permafrost at Point
152 Barrow the unconfined aquifer is the only aquifer, the space of this study occupies the near
shore scale as described in Bratton, (2010).

Constituent Sampling and Statistics

Salinity and temperature were measured for all samples with a handheld YSI 85
156 multiprobe. Samples for ^{224}Ra in water were collected from each of the afore-mentioned
locations as described in Lecher et al., (2015a), and analyzed on a Radium Delayed Coincidence
Counter (RaDeCC) at the University of California at Santa Cruz within 5 days using the Mn-
fiber method (Moore and Arnold, 1996; Moore, 2008). Water samples for nutrients
160 concentrations were collected in concert with all ^{224}Ra samples, and also from additional wells
that did not yield enough water for ^{224}Ra analysis. Nutrients samples were collected in 500 mL
HPDE acid-cleaned sample rinsed bottles and stored on ice in a cooler until filtering. 40 mL
aliquots were filtered (0.45 μm) into acid-cleaned centrifuge tubes, and frozen until analysis.
164 Nitrate (NO_3), silica (SiO_4), and soluble reactive phosphate (PO_4) were measured by colorimetric
methods on a Flow Injection Auto Analyzer (FIA, Lachat Instruments Model QuickChem 8000).
Ammonium (NH_4) was also analyzed in 2012. The analytical error of the method was less than
or equal to 3%, while the detection limit was 0.01 μM . A subset of samples, consisting of all
168 groundwater, river water, and ~5 seawater samples from each site, were collected and analyzed
for trace metals using previously established methods (Chien et al., 2016).

Significant differences between river water, groundwater, and sea water for nutrient and trace metal concentrations was first determined using ANOVA ($p < 0.01$) to determine if at least one water type was significantly different from the others. If significance was found, this test was followed by the post-hoc Tukey-Kramer test ($p < 0.01$), to determine which of the water types was significantly different from the other.

Results

Error due to natural variability was much greater than analytical error, hence this larger and more environmentally meaningful variability is reported here. At Kasitsna Bay, NO_3 average concentrations are highest in the river water, $50.9 \pm 6.5 \mu\text{mol L}^{-1}$ in 2011 and $67.5 \pm 5.9 \mu\text{mol L}^{-1}$ in 2012, lowest in sea water 5.7 ± 1.9 and $3.6 \pm 0.8 \mu\text{mol L}^{-1}$ in 2011 and 2012 respectively, with groundwater falling between, 23.4 ± 5.5 and $34.4 \pm 3.3 \mu\text{mol L}^{-1}$. Differences in average concentrations between groundwater, sea water, and river water are statistically significant, while differences within each water type (groundwater, sea water, river water) are not significant. Similar to NO_3 , SiO_4 average concentrations in 2011 and 2012 are highest in river water, 143.1 ± 18.0 and $145.4 \pm 12.8 \mu\text{mol L}^{-1}$, lowest in sea water, 15.0 ± 1.2 and $18.2 \pm 1.7 \mu\text{mol L}^{-1}$, with average groundwater concentrations falling between, 26.5 ± 3.1 and $107.0 \pm 9.6 \mu\text{mol L}^{-1}$. River water SiO_4 concentrations are significantly different from groundwater and seawater. Seawater SiO_4 concentrations are statistically different than 2012 groundwater concentrations, but not 2011 groundwater concentrations. Average SiO_4 groundwater concentrations were higher in 2012 than 2011, and the difference is significant. Groundwater samples collected in 2011 all had salinity >15 , while in 2012 groundwater samples encompassed a much broader range of salinities from 1.8 to 31.3, suggesting that in 2011 the samples collected included a larger fraction of re-circulated seawater, and explaining why SiO_4 groundwater

concentrations were lower in 2011 than in 2012. PO_4 concentrations are similar in groundwater, 0.7 ± 0.1 and $1.2 \pm 0.1 \mu\text{mol L}^{-1}$ and sea water, 0.6 ± 0.1 and $0.8 \pm 0.2 \mu\text{mol L}^{-1}$, and slightly lower in river water, 0.2 ± 0.1 and $0.4 \pm 0.1 \mu\text{mol L}^{-1}$ in 2011 and 2012, respectively. Only the 2011 groundwater samples were significantly different from other end-members. Groundwater and sea water averages of NH_4 , 1.6 ± 0.4 and $1.5 \pm 0.3 \mu\text{mol L}^{-1}$, are slightly higher than river water, $0.5 \pm 0.2 \mu\text{mol L}^{-1}$. However, none are statistically different.

Average NO_3 concentrations for Beaufort Sea and Elson Lagoon are highest in coastal groundwater, 93 ± 26 and $45 \pm 10 \mu\text{mol L}^{-1}$ respectively, and lowest in sea and lagoon water, 1.3 ± 0.3 and $0.7 \pm 0.2 \mu\text{mol L}^{-1}$. Barrow environmental observatory (BEO) groundwater falls between the coastal groundwater of the two sites and the ocean and lagoon water at $16 \pm 9 \mu\text{mol L}^{-1}$. Differences in average concentrations between Beaufort Sea coastal groundwater and Beaufort Sea water, and Elson Lagoon coastal groundwater and Elson lagoon water are statistically significant. Beaufort Sea coastal groundwater is statistically different from BEO groundwater, while Elson Lagoon coastal groundwater is not different from BEO groundwater.

Average SiO_4 concentrations are higher in all groundwater than ocean and lagoon water. SiO_4 is highest in the Beaufort Sea coastal groundwater, $40 \pm 6 \mu\text{mol L}^{-1}$, lower in Elson Lagoon coastal groundwater and BEO groundwater, 25 ± 14 and $25 \pm 5 \mu\text{mol L}^{-1}$ respectively. SiO_4 is lowest in Beaufort Sea and Elson Lagoon water 8.3 ± 0.3 and $3.3 \pm 1.7 \mu\text{mol L}^{-1}$ respectively. Beaufort Sea average coastal groundwater and seawater SiO_4 concentrations are statistically different, and Elson Lagoon average coastal groundwater and seawater SiO_4 concentrations are statistically different. Beaufort Sea coastal groundwater is statistically different from BEO groundwater, while Elson Lagoon coastal groundwater is not.

PO₄ concentrations are highest in Beaufort Sea groundwater, $2.9 \pm 0.5 \mu\text{mol L}^{-1}$, while

216 Elson Lagoon groundwater, BEO groundwater, Beaufort Sea water and Elson Lagoon water are lower and similar to each other, $0.9 \pm 0.3 \mu\text{mol L}^{-1}$, $1.0 \pm 0.5 \mu\text{mol L}^{-1}$, $0.7 \pm 0.1 \mu\text{mol L}^{-1}$, $0.3 \pm 0.1 \mu\text{mol L}^{-1}$ respectively. Beaufort Sea coastal groundwater is statistically different from all other sample types, while all other sample types are not statistically different from each other.

220 NH₄ concentrations are highest in BEO tundra groundwater, $117 \pm 49 \mu\text{mol L}^{-1}$, while Beaufort Sea groundwater and ocean water and Elson Lagoon groundwater and lagoon water are lower, $13 \pm 8 \mu\text{mol L}^{-1}$, $13 \pm 3 \mu\text{mol L}^{-1}$, $25 \pm 14 \mu\text{mol L}^{-1}$, and $8.6 \pm 4.4 \mu\text{mol L}^{-1}$ respectively. BEO groundwater is statistically different from all other sample types, while they are not different
224 from each other.

Nutrient concentrations of groundwater plotted against salinity for Kasitsna Bay are shown in Figure 2. Trends for all nutrients are consistent year to year (except for NH₄ for which there is only one year of data). PO₄ displays almost no change with salinity both years, with low
228 correlation ($R^2 = 0.02-0.11$), and concentrations mostly below $2 \mu\text{mol L}^{-1}$. NH₄ displayed no trend with salinity. NO₃ and SiO₄ display inverse correlations with respect to salinity ($R^2 = 0.45-0.79$) indicating that river water and fresh groundwater are sources of these nutrients. This trend is indicative of conservative mixing in the costal aquifer between lower salinity high
232 concentration meteoric water and high salinity low concentration seawater.

Nutrient concentrations plotted against salinity for Beaufort Sea and Elson Lagoon are shown in Figure 3. BEO groundwater is removed from the regression as is it not well connected to the coastal groundwater or ocean (Lecher et al., 2015a). Trends are similar for NO₃, SiO₄, and
236 PO₄. These nutrients show a conservative mixing relationship ($R^2 = 0.25-0.49$) between high concentration coastal groundwater and low concentration sea/lagoon water.

Ratios of $\text{NO}_3:\text{SiO}_4$ and $\text{NO}_3:\text{PO}_4$ for each sample collected at Kasitsna Bay are shown in Figure 4. Best fit lines of the sample $\text{NO}_3:\text{SiO}_4$ ratios for 2012 (1:2.4) and 2011 (1:1.7) both fall slightly above the Redfield ratio (1:1, dashed line) required for diatom growth, indicating a slight surplus of SiO_4 compared to NO_3 . The best fit line of $\text{NO}_3:\text{PO}_4$ for each year deviates from the Redfield ratio line (16:1), indicating a high enrichment of NO_3 compared to PO_4 in groundwater. However, the ocean is depleted in NO_3 compared to PO_4 .

Ratios of $\text{NO}_3:\text{SiO}_4$ and $\text{NO}_3:\text{PO}_4$ for each sample from Beaufort Sea, Elson Lagoon, and the BEO are shown in Figure 5. A best fit line of the sample $\text{NO}_3:\text{SiO}_4$ ratio (3.2:1) show a ratio higher than the Redfield ratio (1:1, dashed line) required for diatom growth, suggesting a slight surplus of NO_3 compared to SiO_4 . The best fit line of $\text{NO}_3:\text{PO}_4$ ratio (50.5:1) is much higher than the Redfield ratio (16:1), indicating an enrichment of NO_3 compared to PO_4 .

Biologically important trace metals concentrations at Kasitsna Bay show different trends than nutrient concentrations. Excluding fresh samples (salinity < 2) only Co, Ni, and Cu were statistically higher in coastal groundwater (0.7 ± 0.2 , 10 ± 8 , and $17 \pm 3 \text{ nmol L}^{-1}$ respectively) than coastal ocean water (0.3 ± 0.1 , 4.2 ± 0.5 , and $10 \pm 2 \text{ nmol L}^{-1}$ respectively). Cd was statistically higher in coastal ocean water ($0.38 \pm 0.04 \text{ nmol L}^{-1}$) than coastal groundwater ($0.22 \pm 0.04 \text{ nmol L}^{-1}$). Mn, Fe, and Zn showed similar (overlapping error bars and lack of significant differences) concentrations in the coastal aquifer (16 ± 4 , 22 ± 3 , $32 \pm 5 \text{ nmol L}^{-1}$) and costal ocean water (21 ± 2 , 17 ± 9 , and $46 \pm 17 \text{ nmol L}^{-1}$). At Barrow only Ni and Fe are significantly higher in coastal groundwater (32 ± 7 and $18 \pm 5 \text{ nmol L}^{-1}$) than in ocean water (7 ± 1 and $3.0 \pm 0.5 \text{ nmol L}^{-1}$). Cd, Mn, and Co also display higher concentrations in coastal groundwater (0.7 ± 0.2 , 800 ± 700 , and $12 \pm 7 \text{ nmol L}^{-1}$) than in ocean water (0.28 ± 0.01 , 60 ± 20 , and $0.8 \pm 0.2 \text{ nmol L}^{-1}$), although the differences are not significant. Cu and Zn have higher concentrations in

coastal seawater (70 ± 30 and 100 ± 30 nmol L⁻¹) than in coastal groundwater (45 ± 8 and 60 ± 12 nmol L⁻¹), but the differences are not significant.

Trace metals Cd, Cu, Fe, Zn, Mn, Co, and Ni in groundwater and seawater are plotted against salinity for Kasitsna Bay (Figure 6) and Barrow (Figure 7). At Kasitsna Bay Cd and Zn increase with salinity although the linear regression is not strong ($R^2 = 0.56$ and 0.24 , respectively). Mn and Fe show the highest concentrations (286 and 640 nmol L⁻¹ for Mn, 125 and 232 nmol L⁻¹ for Fe) in fresh groundwater (salinity <2) and are lower and similar (3 - 41 nmol L⁻¹ for Mn and 4 - 53 nmol L⁻¹ for Fe) in brackish groundwater and seawater. Cu and Co concentrations generally decrease with salinity with the largest decrease where salinity is < 10 (10 - 142 nmol L⁻¹ for Cu and 3.0 - 0.1 nmol L⁻¹ for Co). Ni concentrations are generally similar in fresher groundwater and seawater (2 - 10 nmol L⁻¹) with some high values (up to 37 nmol L⁻¹) near the middle of the salinity range. At Barrow Cu, Fe, Zn, Mn, Co, and Ni are generally highest in concentration in the BEO and low and similar for all other samples, with no distinguishable trends even when BEO samples are removed ($R^2 < 0.25$). Excluding the BEO samples Cd shows the highest concentration in Elson Lagoon (4 nmol L⁻¹) with all other samples <1.5 nmol L⁻¹. Like the other metals, no distinguishable trend is noted, even when the sample with the highest concentration is removed ($R^2 < 0.12$).

Results of the groundwater well salinity time series at Kasitsna Bay are shown in Figure 8. Salinity shows a strong oscillation with the tide, with a salinity of up to 31 at high tide and as low as 4 at low tide. This is consistent with tidal pumping being the dominant driving force of SGD in this area and the primary control of nutrient concentration in the coastal aquifer being dilution of fresher groundwater by seawater, as seen in Figure 2 (Dimova et al., 2015; Lecher et al., 2015a).

Temperature, salinity, ^{224}Ra activity and nutrient concentrations for the five shallow/deep coupled samples collected from Kasitsna Bay are shown in Figure 9. Samples were collected about 0.5 m above seafloor, four at 18 m depth and one at 10 m depth due to it being shallow in that location. Salinity consistently increases with depth while temperature decreases with depth. ^{224}Ra activities were similar at both depths for the samples collected further from shore, while the samples closer to shore display higher activities in the shallow, lower salinity samples than in the deep samples. Nutrient concentrations all increase with depth.

Nutrient concentrations along the transects in the Beaufort Sea are shown in Figure 10. PO_4 and NO_3 have higher concentrations close to shore, $0.8\text{--}1\ \mu\text{mol L}^{-1}$ and $2\text{--}3.5\ \mu\text{mol L}^{-1}$ respectively, than in the rest of the transect for which concentrations are generally below 0.7 and $1\ \mu\text{mol L}^{-1}$. SiO_4 generally shows similar values across the length of each transect, $5\text{--}10\ \mu\text{mol L}^{-1}$, except for the point furthest from shore, $>15\ \mu\text{mol L}^{-1}$. NH_4 shows increases in concentration above background both near shore, $10\text{--}30\ \mu\text{mol L}^{-1}$, and at 5 km, $35\text{--}40\ \mu\text{mol L}^{-1}$.

Raw data for nutrient, salinity, and trace metal data for Kasitsna Bay 2012 (SI Table 1), Barrow 2012 (SI Table 2), and nutrient and salinity data for Kasitsna Bay 2011 (SI Table 3) are available in the supplementary material.

Discussion

Kasitsna Bay

In Kasitsna Bay, increasing salinity with depth indicates the presence of the freshwater lens, while decreasing temperature with depth indicates that the water column is stratified (Figure 9). This is consistent with previous studies that suggest pooling of nutrient rich freshwater in the lit surface layer, potentially fueling phytoplankton blooms common at this time of year. The freshening and source of nutrients have been attributed to river discharge (Strom et

al., 2007). However, ^{224}Ra activity in the shallow samples indicates the presence of SGD (and
308 nutrients transported by SGD) at the coastline. The lack of excess ^{224}Ra in the deep samples
indicates deep discharge of SGD is not present, and any SGD (and therein SGD-associated
solutes) in this area are entrained in the surface layer (i.e. not mixing downwards). The low NO_3
and SiO_4 in the near shore surface water samples where elevated ^{224}Ra is observed must be due
312 to biological uptake of these nutrients (e.g. non conservative behavior), despite SGD actively
transporting nutrients to this area, as shown by elevated ^{224}Ra (e.g. uptake of nutrients is faster
than the rate of replenishment by SGD).

Within the coastal aquifer SiO_4 and NO_3 concentrations are controlled by conservative
316 mixing (Figure 2), as indicated by the highest concentrations coinciding with fresh groundwater,
lowest concentrations coinciding with sea water, and a linear correlation between the two end-
members ($R^2 = 0.45\text{-}0.79$). With such large tides ($> 8\text{ m}$) and aquifer substrate with a high
hydraulic conductivity (granitic gravel), short residence times within the coastal aquifer are
320 assured. Short residence times ensure the coastal aquifer remains oxic, impeding transformations
of NO_3 caused by reducing conditions (Slomp and Van Cappellen, 2004).

Of the nutrients we tested, groundwater is an especially important source of SiO_4 with
this being the most abundant nutrient in the coastal aquifer relative to expected demand (Figure
324 4). However, the potential of SGD as a source of NO_3 , which is the limiting nutrient in the GOA
should not be overlooked as concentrations in the coastal aquifer are still much higher than in
coastal waters of the GOA. PO_4 is depleted relative to other nutrients in the coastal aquifer (e.g.
high N:P ratios) indicating that compared to other nutrients SGD is not as important as a source
328 of this nutrient to the GOA, specifically since it is present in surplus in coastal waters.

A rough estimate of nutrient fluxes can be calculated by multiplying the average nutrient concentration in groundwater by the volume flux of SGD. A SGD volume flux of $125 \pm 50 \text{ m}^3 \text{ day}^{-1}$ per meter of shoreline ($1.25 \times 10^5 \text{ L day}^{-1} \text{ m of shoreline}^{-1}$) was calculated for Kasitsna Bay using ^{224}Ra , ^{223}Ra , and ^{228}Ra at the time period that the 2012 samples were collected (Lecher et al., 2015a). Since the dominate driving force of SGD in this area is the large tidal oscillation of 8 m, as seen in the groundwater salinity time series (Figure 5), the SGD volume flux is probably similar throughout the year, as tides do not change much in magnitude throughout the year. Due to the high NO_3 and SiO_4 concentrations in groundwater compared to ocean values NO_3 and SiO_4 appear to be the only nutrients out of the four measured that SGD could be an important source for sustaining productivity in the coastal ocean. The limiting nature of NO_3 with respect to phytoplankton growth, and co-limitation of SiO_4 with NO_3 in diatom communities render these nutrients of particular interest (Strom et al., 2006, Lecher et al., 2013). Therefore we calculate only the NO_3 and SiO_4 fluxes here, and to be consistent with the SGD volume flux that was calculated based on Ra data collected in 2012 we use the 2012 NO_3 and SiO_4 concentration data.

Multiplying the average NO_3 ($34.4 \pm 3.3 \text{ } \mu\text{mol L}^{-1}$) and SiO_4 ($107.0 \pm 9.6 \text{ } \mu\text{mol L}^{-1}$) groundwater concentrations by the 2012 SGD volume flux ($1.25 \times 10^5 \text{ L day}^{-1} \text{ m of shoreline}^{-1}$) yields nutrient fluxes of $4.3 \pm 2.1 \text{ mol NO}_3 \text{ day}^{-1} \text{ m of shoreline}^{-1}$ and $13 \pm 6 \text{ mol SiO}_4 \text{ day}^{-1} \text{ m of shoreline}^{-1}$. To place the SGD-associated nutrient fluxes into context we propose a scaling analysis. The length of the GOA coastline is $8.98 \times 10^6 \text{ m}$ (Wright, 2007). Multiplying the NO_3 and SiO_4 fluxes (4.3 mol NO_3 and $13 \text{ mol SiO}_4 \text{ day}^{-1} \text{ m of shoreline}^{-1}$) by the length of coastline gives the total SGD nutrient contribution to the GOA, $3.86 \times 10^7 \text{ mol day}^{-1} \text{ NO}_3$ and $1.20 \times 10^8 \text{ mol day}^{-1} \text{ SiO}_4$. SiO_4 river concentrations in this area average $100 \text{ } \mu\text{mol L}^{-1}$, while NO_3 river

352 concentrations average 10 - 15 $\mu\text{mol L}^{-1}$ (Glass, 1999; Goering et al., 1973; Stabeno et al., 2004).
Multiplying these concentrations by the volume of river runoff into the GOA ($4 \times 10^4 \text{ m}^3 \text{ s}^{-1}$,
 $1.44 \times 10^{11} \text{ L day}^{-1}$) yields NO_3 (using the upper bound of 15 $\mu\text{mol L}^{-1}$) and SiO_4 river
contributions of $2.16 \times 10^6 \text{ mol day}^{-1} \text{ NO}_3$ and $1.44 \times 10^7 \text{ mol day}^{-1} \text{ SiO}_4$, to the GOA (Royer,
356 1982). By this calculation SGD supplies roughly 17.5 times the amount of NO_3 supplied by
rivers and 8.4 times the amount of SiO_4 supplied by rivers. For a more conservative
extrapolation, we look at just the Cook Inlet in which Kasitsna Bay is located. All of Cook Inlet
has a similar tidal range and the composition of its beaches is mainly sand-gravel, similar to
360 Kasitsna Bay. The inlet is approximately 290 km long, which yields a very conservative
estimate of its shoreline as 580 km (e.g. not accounting for bays and complexity and actual
length of the shoreline). This yields an NO_3 flux of $2.50 \times 10^6 \text{ mol day}^{-1}$, and a SiO_4 flux of 7.77
 $\times 10^6 \text{ mol day}^{-1}$. At this level of scaling, the SiO_4 associated SGD flux to Cook Inlet alone is
364 about one order of magnitude less than the total river flux to the whole GOA, but the NO_3 SGD
flux (of just the Cook Inlet) still rivals the river flux of the entire GOA. While more study is
needed to better constrain the heterogeneity of SGD in the GOA, this scaling analysis highlights
the need for SGD to be included in nutrient flux estimates to the GOA. A summary of these
368 fluxes is available in Table 2.

Metals within the coastal aquifer (Figure 6) appear to be controlled primarily by redox
conditions within the aquifer. In the fresh groundwater (salinity < 2) Fe and Mn are orders of
magnitude higher than all other groundwater or ocean samples. It is likely that anoxic conditions
372 in the fresh groundwater transfer Fe and Mn bound to minerals to their dissolved states. In areas
of the aquifer that are affected by mixing with ocean water (salinity > 2) constant tidal pumping
ensures oxygenated ocean water cycles through the coastal aquifer, preventing anoxia. This is

supported by the drastic drop in dissolved Fe and Mn in these samples, with the Fe and Mn

376 having precipitated likely as Fe and Mn-oxides. This pattern of Fe and Mn precipitating in the
oxidized and brackish portion of a coastal aquifer has been observed elsewhere (Charette et al.,
2005). Excluding the high freshwater samples, dissolved Fe and Mn concentrations in the
coastal aquifer (22 ± 3 and 16 ± 4 nmol L⁻¹ m⁻¹ respectively) and ocean water (17 ± 9 and 21 ± 2
380 nmol L⁻¹ m⁻¹ respectively) are similar and the difference is not statistically significant, hence
SGD is not an important source of these metals to the coast. Co displays a similar, but more
gradual drop at the oxic/anoxic transitions, with Co concentrations highest in fresh anoxic
aquifer water and decreasing as salinity and oxygen content increase. High Co concentrations in
384 the fresh/anoxic aquifer water are due to the release of Co adsorbed to Mn (hydr)oxides when the
Mn (hydr)oxides are dissolved under the anoxic aquifer conditions, a trend typical of other
systems (Ozturk, 1995). Unlike Fe and Mn, however Co concentrations (again excluding the
fresh samples) are statistically higher in the coastal aquifer (0.6 ± 0.2 nmol L⁻¹) than the coastal
388 ocean (0.3 ± 0.1 nmol L⁻¹) hence SGD could be a source of Co to the coast supporting the needs
of phytoplankton.

Zn and Cd concentrations in the coastal aquifer are indicative of conservative mixing,
with their concentrations increasing with salinity. Concentrations of both elements are higher in
392 coastal ocean water (Zn = 46 ± 17 nmol L⁻¹ and Cd = 0.38 ± 0.04 nmol L⁻¹) than coastal
groundwater (Zn = 32 ± 5 nmol L⁻¹ and Cd = 0.22 ± 0.04 nmol L⁻¹), although only Cd is
statistically higher in seawater. Coastal groundwater is therefore not a source of these metals to
the coastal ocean at this site.

396 Dissolved Ni concentrations are statistically higher in the coastal aquifer (10 ± 8 nmol L⁻¹
than the coastal ocean (4.2 ± 0.5 nmol L⁻¹) although there is no distinct trend with salinity.

Higher Ni concentrations in the coastal aquifer are likely due to more rock-water interaction in the aquifer than in the ocean.

400 Dissolved Cu concentrations in water are largely governed by the presence of organic ligands, which Cu has a strong affinity for (Davis and Leckie, 1978). In the coastal aquifer at Kastisna Bay, the freshest samples are orders of magnitude higher in Cu concentration than other groundwater and ocean samples. This drastic decrease in Cu with increasing salinity is probably
404 due to the presence of organic ligands larger than 0.2 μm (filter size used) in brackish and saline water and lack of such organic ligands in the fresh groundwater. Coale and Bruland (1988) estimated over 99.7% of dissolved Cu in the surface ocean of the Pacific Northeast to be associated with strong organic complexes up to 0.4 μm in size, supporting that organic ligands
408 delivered to the coastal aquifer from seawater is responsible for the drop in Cu concentrations in the coastal aquifer.

 Given the importance of Fe and significantly higher concentrations of Ni in the coastal aquifer than the coastal ocean, we calculate the SGD-associated fluxes of these trace metals in
412 the same manner as the nutrients. The general estimates of Fe and Ni fluxes were calculated to be $3 \pm 1 \text{ mmol day}^{-1} \text{ m of shoreline}^{-1}$ and $1.3 \pm 0.8 \text{ mmol day}^{-1} \text{ m of shoreline}^{-1}$, respectively. Comparing the Fe flux to the NO_3 flux (0.003 Fe: 4 N), the Fe flux is within the range for Fe needed to prevent Fe limitation based on the N demand (0.1-0.001 Fe: 16 N) (Ho et al., 2003).
416 Therefore it is likely that Fe loading through SGD is sufficient to match N loading through the same source in the ratios needed by phytoplankton.

 Eddies have been shown to transport Fe-rich coastal water to Fe-limited water beyond the shelf break in the GOA, suggesting Fe delivered to the GOA coastal waters from SGD is an
420 eventual source to the offshore Fe-limited GOA water (Johnson et al., 2005). However, dust

storms have been suggested as a greater source of Fe to the GOA than eddy transport of Fe, which would include SGD-sourced Fe (Crusius et al., 2011). It is against one such dust storm in November of 2006 that we compare our Fe fluxes. Using the same scaling technique of the
424 nutrients we calculate the Fe flux to the entire GOA and Cook Inlet to be 176 and 11 kmol yr⁻¹, while a single 18-day dust storm in November 2006 deposited a comparable 9.7-64 kmol (Crusius et al., 2011). It is not unreasonable to assume that a few such dust storms in one year would easily outweigh Fe supplied to the GOA from SGD. However, these dust storms are
428 episodic in nature usually occurring between late October and mid November when primary productivity is decreasing due to reduced sunlight. SGD occurs continuously throughout the year, and may therefore be a more important source of Fe to the GOA in the spring and early summer when primary productivity is at its highest and dust storms are less common. Indeed a
432 previous study of western North America found rivers to be an important source of Fe to phytoplankton during the summer, despite low river discharge during that time, as Fe from river discharge accumulates on the shelf throughout the lower productivity winter, which is then utilized by phytoplankton in the high productivity summer (Chase et al., 2007). Likewise,
436 continuous fluxing of Fe through SGD in the GOA, which has similar seasonal patterns with respect to productivity, river discharge, deep mixing, and upwelling, will contribute to the accumulation of Fe on the shelf that is then utilized by phytoplankton in the summer. Unfortunately, still not enough data exists to compare SGD and river fluxes of Fe in the GOA.

440 While SGD Ni fluxes are the most statistically significant of the trace metals fluxes in the GOA, a comparison of this flux to other sources is impossible due to lack of data about other Ni sources. We can simply note its presence and the need for more study of this biologically

reactive trace metal in the GOA. It is important to note that these are the first reported SGD-
444 associated trace metal fluxes of the region.

Beaufort Sea and Elson Lagoon

Within the transects of the Beaufort Sea NO_3 and PO_4 concentrations are highest near the shore, indicating a coastal source of these nutrients, such as SGD (Figure 10). NH_4
448 concentrations are also higher at the shore than most of the transect. However, both transects exhibit a maximum NH_4 concentration 3-4 km from shore, likely due to either advection of high NH_4 concentration water from the predominant southwesterly currents of the area or biological activity (Weingartner et al., 1998). SiO_4 concentrations are slightly higher at the shore than most
452 of the transect, but the highest concentration is at the furthest data point from shore (~10 km) indicating a potential offshore source of this nutrient, such as upwelling beyond the wide continental shelf. PO_4 at this offshore data point is also high and similar in concentration to the near shore, indicating the offshore source of SiO_4 may also be supplying PO_4 to that location. Of
456 these nutrients, NO_3 and NH_4 are the most in demand by the N-limited Arctic Ocean ecosystem and coastal aquifer water is especially rich in NO_3 .

While thawing permafrost has been shown to be a source of NO_3 to the active layer, under the anoxic conditions typical to the water saturated soils of the tundra it is often quickly
460 denitrified to N_2O and/or N_2 which degasses to the atmosphere, resulting in low concentrations of NO_3 in the active layer (Repo et al., 2009). This is consistent with the low NO_3 concentrations we observe in the BEO active layer, and high NH_4 concentrations of the same samples (Figure 3, Figure 11). The reducing conditions in the active layer are not present in the
464 coastal aquifers of the Beaufort Sea and Elson Lagoon where NO_3 concentrations are high, and NH_4 is low. In the coastal aquifer, permafrost degradation contributes NO_3 to the coastal aquifer

while the lack of reducing conditions prevents denitrification, and ensures concentrations stay high. NO_3 in the coastal aquifer decreases as salinity increases, indicating conservative mixing with seawater. Without the large tides of Kasitsna Bay, it is the shallowness of the coastal aquifer that ensures it remains oxic and that NO_3 is not reduced, maintaining mixing as the dominant regulator of NO_3 concentrations in the coastal aquifer (Slomp and Van Cappellen, 2004).

SiO_4 concentrations follow a similar trend to NO_3 at these sites (Figure 3), low in oceanic and BEO active layer water, while concentrations in the coastal aquifer are higher and decrease as salinity increases. However, the trend is due to different processes than those NO_3 is subject to. The source of SiO_4 to aquifer systems is the dissolution of aquifer substrate, and different types of substrate (Si poor and organic matter rich soil in the BEO versus Si rich mineral gravel in the coastal aquifer, from our observations) may account for the difference in concentrations. PO_4 follows a similar trend to the other two nutrients, being higher in the coastal groundwater than the BEO, likely due to dissolution of aquifer substrate. However, groundwater in the coastal aquifer is more enriched in NO_3 compared to PO_4 and SiO_4 (Figure 5), a relationship which may make SGD of particular importance to the Arctic Ocean that becomes N deplete in the summer (Tremblay et al., 2008).

Again general nutrient fluxes can be calculated by multiplying the average nutrient concentration in groundwater by the volume flux of SGD. SGD volume fluxes of $13.0 \pm 0.2 \text{ m}^3 \text{ day}^{-1}$ per meter of shoreline ($1.3 \times 10^4 \text{ L day}^{-1} \text{ m of shoreline}^{-1}$) and $12 \pm 4 \text{ m}^3 \text{ day}^{-1}$ per meter of shoreline ($1.2 \times 10^4 \text{ L day}^{-1} \text{ m of shoreline}^{-1}$) were calculated for the Beaufort Sea and Elson Lagoon, respectively using ^{224}Ra , ^{223}Ra , and ^{228}Ra at the time period that the samples were collected (Lecher et al., 2015a). Nutrient fluxes can be calculated by multiplying the SGD

volume flux by the concentration of each nutrient in the coastal groundwater. SGD could be an important source of NO_3 , SiO_4 and PO_4 to the coastal ocean, due to the high concentrations in the coastal groundwater. Therefore, we calculate only the NO_3 , SiO_4 , and PO_4 fluxes here.

492 Multiplying the average NO_3 (93 ± 26 and $45 \pm 10 \mu\text{mol L}^{-1}$), SiO_4 (40 ± 6 and $25 \pm 14 \mu\text{mol L}^{-1}$), and PO_4 (2.9 ± 0.5 and $0.9 \pm 0.3 \mu\text{mol L}^{-1}$) groundwater concentrations for the Beaufort Sea and Elson Lagoon by the corresponding SGD volume fluxes ($1.3 \times 10^4 \text{ L day}^{-1} \text{ m of shoreline}^{-1}$ and $1.2 \times 10^4 \text{ L day}^{-1} \text{ m of shoreline}^{-1}$) yields nutrient fluxes of 1.2 ± 0.4 and 0.5 ± 0.3 mol $\text{NO}_3 \text{ day}^{-1} \text{ m of shoreline}^{-1}$, 0.52 ± 0.09 and 0.3 ± 0.3 mol $\text{SiO}_4 \text{ day}^{-1} \text{ m of shoreline}^{-1}$, and 0.04 ± 0.01 and 0.01 ± 0.01 mol $\text{PO}_4 \text{ day}^{-1} \text{ m of shoreline}^{-1}$, for Beaufort Sea and Elson Lagoon, respectively. Indeed the elevated NO_3 and PO_4 concentrations close to shore with higher concentrations in coastal groundwater than in open ocean water are consistent with SGD being a source of these nutrients to the Beaufort Sea. Elevated NO_3 closer to shore is consistent with previous observations in this area (Hill and Cota, 2005). Lower concentrations further from shore are a result of mixing with low nutrient open ocean water and biological uptake (drawdown in the water) of these nutrients. SiO_4 is similarly higher in coastal groundwater than ocean water. However, no clear decrease with distance from shore is observed. This may indicate that SiO_4 is utilized to a lesser degree when compared to NO_3 and PO_4 , which show decreases in concentration due to uptake.

504 NH_4 is similar in coastal groundwater of the Beaufort Sea and Beaufort Sea water, yet a slight increase in NH_4 near the shore is observed. This increase may be indicative of flow from the tundra (BEO), which has much higher NH_4 ($117 \pm 49 \mu\text{mol L}^{-1}$) than the coastal groundwater ($13 \pm 8 - 25 \pm 14 \mu\text{mol L}^{-1}$). It is possible preferential flow paths exist between the tundra and the Beaufort Sea that allow for transport of high NH_4 groundwater from the tundra to the ocean,

or that there are coastal locations where groundwater is more similar to BEO groundwater in composition (as discussed in (Lecher et al. (2015a)). Because NH_4 is likely transported to the coastal ocean via freshwater preferential flow paths, which we did not systematically sample, we cannot calculate that flux we can only note its presence.

The importance of SGD as a conduit of nutrients to the coastal Arctic Ocean will likely vary with the seasons. During the winter, when nutrient concentrations peak and primary productivity is at a minimum, nutrients from other sources (such as SGD) are not needed to fuel primary productivity. Moreover, SGD is probably limited during this time due to sea ice infringing upon the coast and extensive permafrost. As temperatures increase, sea ice retreats from the coast and the permafrost thaws allowing more SGD flow, and SGD becomes a more important source of nutrients to the very near coast, especially in areas where rivers are not present. Sea ice extent has been decreasing over the past decades, and as a result primary productivity in the Arctic Ocean is increasing, which may cause a shift to longer N limited periods (Pabi et al., 2008). Should this continue, SGD will become a more important source of nutrients to the Arctic Ocean as it offsets some of the nutrient limitation. In addition as temperatures increase, the flux of SGD will increase due to longer or more extensive permafrost melt increasing the relative importance of this nutrient source.

Trace metals in the coastal aquifers of the Beaufort Sea and Elson Lagoon (Figure 7) are lacking clear trends with no strong correlations to salinity (all $R^2 < 0.2$). Fe, Mn, Ni, Co and Cd concentrations are slightly elevated in the gravel coastal aquifer than in ocean water due to high rock-water interactions in the coastal aquifer and dilution and uptake in the ocean. However, only Fe and Ni are statistically different in groundwater than in coastal waters. The range of Zn concentrations generally increase with salinity, with the highest Zn concentrations occurring in

Arctic Ocean water. The range of Cu concentrations is the same in the coastal aquifer and ocean
536 water. These data indicate that SGD is not an important source of Cu or Zn to the Arctic Ocean.

With only Fe and Ni being statistically higher in coastal groundwater than coastal ocean
water we calculated the SGD-associated fluxes of these metals for the Beaufort Sea to be $0.23 \pm$
 $0.07 \text{ mmol day}^{-1} \text{ m}^{-1}$ and $0.4 \pm 0.1 \text{ mmol day}^{-1} \text{ m}^{-1}$. Comparing the Fe flux to the NO_3 flux

(0.00023 Fe: 1.2 N) Fe is enriched in SGD compared to N when considering the average demand
540 by phytoplankton, making it a potentially important source of this trace metal to the Arctic
Ocean. Trace metal flux data to the Arctic Ocean is extremely limited, and without other fluxes
to compare to, we simply note the presence of SGD-associated Fe and Ni fluxes to the coastal
544 Arctic Ocean.

Conclusions

SGD should be taken into account as a source of NO_3 , SiO_4 , Fe, and Ni to Cook Inlet and
the greater GOA. SGD-associated NO_3 and SiO_4 fluxes in this area not only rival but may be
548 much greater than river contributions. The high SGD associated NO_3 and SiO_4 fluxes are mostly
due to large tides forcing tidal pumping of the coastal aquifer, large tides being a characteristic
unique to these latitudes. Fe discharged through SGD in the GOA is present in a ratio to N that
that meets the needs of phytoplankton. It may be a more important source of Fe to the GOA in
552 the spring and summer though, when the largest source of Fe to the GOA, dust storms, are less
likely. This is the first study to assess the importance of SGD-associated nutrient and trace metal
fluxes in the Gulf of Alaska.

In the Arctic Ocean, SGD fills a niche of supplying nutrients to the N limited coastal
556 ocean during summer. As ice extent will decrease with a changing climate, the Arctic Ocean
will experience longer periods of nutrient limitation, and the relative importance of SGD to the

coastal ocean nutrient budget will increase. Currently SGD is an important source of Fe to the Arctic Ocean, although more study is needed to compare SGD to other sources of Fe and N in

560 the Arctic Ocean. As in Kasitsna Bay this is the first study to assess the importance of SGD as a source of nutrients to the coastal Arctic Ocean.

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Table 1: SGD-associated nutrient fluxes at the study sites. Units for NO_3 , SiO_4 , and PO_4 are in $\text{mol day}^{-1} \text{ m of shoreline}^{-1}$. Units for Fe and Ni are in $\text{mmol day}^{-1} \text{ m of shoreline}$.

Location	NO_3 flux	SiO_4 flux	PO_4 flux	Fe flux	Ni flux
Kasitsna Bay	4.3 ± 2.1	13 ± 6	-	3 ± 1	1.3 ± 0.8
Beaufort Sea	1.2 ± 0.4	0.52 ± 0.09	0.04 ± 0.01	0.23 ± 0.07	0.4 ± 0.1
Elson Lagoon	0.5 ± 0.3	0.3 ± 0.3	0.01 ± 0.01	-	-

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800 Table 2: Extrapolations of the SGD fluxes to the entire Gulf of Alaska (GOA), just the Cook Inlet, and River Contribution for NO₃ and SiO₄

	SGD GOA Extrapolation (mol day ⁻¹)	SGD Cook Inlet Extrapolation (mol day ⁻¹)	GOA River Contribution (mol day ⁻¹)
NO ₃	3.86×10^7	2.50×10^6	2.16×10^6
SiO ₄	1.20×10^8	7.77×10^6	1.44×10^7

Figure 1: A map of the study sites in Alaska. Kasitsna Bay and Elson Lagoon are well defined by the spits that enclose them, while the Beaufort Sea is more exposed to ocean interactions. Symbols in Kasitsna Bay represent shallow/deep coupled samples.

Figure 2: PO_4 (top row), NO_3 (second row), SiO_4 (third row), and NH_4 (bottom row) plotted versus salinity for 2012 (left column) and 2011 (right column) for groundwater, sea water, and river water at Kasitsna Bay. Regressions are based on groundwater only. Units are in $\mu\text{mol L}^{-1}$.

Figure 3: NO_3 (first row), SiO_4 (second row), PO_4 (third row), and NH_4 (bottom row) plotted versus salinity for groundwater (Beaufort Sea, BEO, and Elson Lagoon) and sea water (Beaufort Sea and Elson Lagoon). Regressions are based on coastal groundwater only. Units are in $\mu\text{mol L}^{-1}$.

Figure 4: Ratios of $\text{NO}_3:\text{SiO}_4$ (top row) and $\text{NO}_3:\text{PO}_4$ (bottom row) for 2012 (left column) and 2011 (right column) at Kasitsna Bay. Solid line is the best fit line, and the dashed line is the Redfield ratio for diatoms. Units are in $\mu\text{mol L}^{-1}$.

Figure 5: Ratios of $\text{NO}_3:\text{SiO}_4$ (top row) and $\text{NO}_3:\text{PO}_4$ (bottom row) for the Beaufort Sea, BEO, and Elson Lagoon. Solid line is the best fit line, and the dashed line is the Redfield ratio for diatoms. Units are in $\mu\text{mol L}^{-1}$.

Figure 6: Biologically important trace metals in groundwater and ocean water in 2012 at Kasitsna Bay plotted against salinity. Regressions $R^2 < 0.2$ not shown. Units are in nmol L^{-1} .

Figure 7: Biologically important trace metals in groundwater and ocean water in 2012 at Barrow plotted against salinity. Regressions $R^2 < 0.2$ not shown. Units are in nmol L^{-1} .

Figure 8: Salinity (dashed lines) and tide stage (solid line) plotted against time for the

time series of the coastal aquifer of Kasitsna Bay. Tide stage is in m-mean sea level.

Time is in hours since the first high tide of the time series.

Figure 9: Five shallow/deep-coupled samples of Kasitsna Bay. Symbols of each sample set correspond to locations on Figure 1. Units for temperature are in degrees Celsius, ^{224}Ra are in dpm 100 L^{-1} and nutrients are in $\mu\text{mol L}^{-1}$.

Figure 10: PO_4 (top row), NO_3 (second row), SiO_4 (third row), and NH_4 (bottom row) plotted against distance from shore for two transects in the Beaufort Sea. Transects locations are shown on Figure 1. Units are in $\mu\text{mol L}^{-1}$.

Figure 11: NO_3 versus NH_4 for groundwater in northern sites. Units are in $\mu\text{mol L}^{-1}$.

Figure 1: Map(s)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11