COASTAL MARINE INSTITUTE

Distribution and Abundance of Select Trace Metals in Chukchi and Beaufort Sea Ice

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Given the ongoing changes in sea ice extent and volume in the Arctic Ocean, there has been unprecedented interest in better understanding the Arctic marine environment. This project builds on many previous monitoring studies that were charged with providing an understanding of the background trace metal concentrations in rivers, snow, seawater, and sediments in the Alaskan North Slope development area. To add to these previous studies, we built, tested, and employed a unique sea ice corer to collect some of the first trace-metal-clean sea ice samples in the nearshore Beaufort Sea. In this project, we assessed the trace metal concentrations and distributions in seawater, snow, and sea ice in the nearshore Beaufort Sea prior to the 2015 spring freshet. Overall, the concentrations found in seawater below the ice during the early spring of 2015 align well with concentrations of dissolved metals reported during past studies. Some evidence was found to suggest remineralization of biogenic metals such as Cd and perhaps Zn during the winter months. For other metals like Ba, lower, more uniform concentrations were found during our spring 2015 sampling when compared to open-water concentrations where freshwater from rivers had a much greater influence. Concentrations of Pb also decreased between the two seasons, likely due to scavenging of dissolved Pb during the winter months under the ice. Concentrations of dissolved metals in the sea ice were lower when compared to the water column, which was surprising given the high concentrations of suspended particles found in some of the cores. However, as the ice aged during the warmer spring months, dissolved metals could have begun to drain from the sea ice through brine channels before we were able to collect the samples.

In addition to the Beaufort sampling effort, results from seawater samples collected during a fall 2013 cruise in the Chukchi Sea are reported. These provide a broader sampling of trace metal concentrations on the American Arctic shelves where development is already established or exploration may be considered for the future. The Chukchi Sea dataset also includes a two-week occupation of a single station, which demonstrated how variable conditions can be over a short period of time. For some metals, such as Fe and Zn, there was a distinct decrease in concentrations along a transect from the Bering Strait to the northern boundary of the Chukchi Shelf. The decrease may be related to a drawdown of these biologically active metals in the productive Chukchi Sea over the summer months. Other metals, such as Cu and Ni, did not change substantially on the Chukchi Shelf along the south to north transect, reflecting minimal input and removal. A first-order look at the variability of dissolved metals and other parameters at the time-lapse station suggests that salinity, concentrations of dissolved metals, dissolved oxygen, and particle concentrations are highly susceptible to oceanic fronts that can produce considerable changes over very short periods of time.

INTRODUCTION

Overview

The Alaskan Arctic shelves are rich in mineral resources and support an ecosystem heavily impacted by sea ice dynamics. Offshore exploration and extraction of mineral resources are occurring under a changing sea ice environment, emphasizing the need to better understand the role of natural environmental processes in the retention, transport, and subsequent release of trace metals in sea ice. Concentrations of trace elements in the seawater and sediments of the nearshore Beaufort Sea development area have been well constrained by numerous studies during the last 20 years (e.g., Crecelius et al., 1991; Trefry et al., 2003; 2009). In contrast, there are no data for dissolved trace metals in Alaskan Arctic sea ice and a very limited number of unpublished data points for sea ice particulate metals. The need to understand the natural environment in order to detect potential future perturbations to that environment is a reoccurring theme in the Arctic Nearshore Impact Monitoring in the Development Area (ANIMIDA, cANIMIDA) studies sponsored by Bureau of Ocean Energy Management (BOEM). This Beaufort Sea monitoring theme was continued during the ANIMIDA III project, which began during the fiscal year 2013. Sea ice samples were collected during the cANIMIDA project, but contamination issues stemming from the type of corer used precluded the measurement of dissolved trace elements. This project complements the ANIMIDA III: Contaminants, Sources and Bioaccumulation project by adding a dissolved and particulate sea ice component and investigating the range of concentrations and processes influencing the cycling of trace metals in sea ice, an important but under-studied aspect of Arctic biogeochemistry.

Studies addressing dissolved trace metals in sea ice, primarily with Antarctic and subarctic pack ice, indicate that the concentrations of some metals (cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn)) are substantially elevated in sea ice when compared to the underlying seawater (Aguilar-Islas et al., 2008; Grotti et al., 2005; Holemann et al., 1999; Kanna and Nishioka, 2016; Lannuzel et al., 2007; 2011). From these observations, it is expected that natural sea ice dynamics in the Arctic also have the potential to alter the concentration of dissolved trace metals in surface Arctic waters during the melting season. Anthropogenic contaminants from local, regional, or global sources can contribute to the abundance and distribution of trace metals in sea ice and, therefore, could greatly affect the distribution of dissolved trace metals in surface waters. Offshore exploration and development products (e.g., drilling muds, produced water, or oil) are potential local and regional sources, while atmospheric emissions from industrialized regions captured in winter snow are potential regional and global sources. This type of information could play a role in future management decisions with respect to the discharge of produced water or other by-products of oil and gas exploration in the Arctic.

Dissolved trace elements are of interest as some are essential nutrients for microbial communities in sea ice and the water column, and some can become toxic at elevated concentrations. Low dissolved Fe concentrations have been shown to limit primary productivity, while other metals such as Cd, Cu, and Zn are essential nutrients that become toxic at higher concentrations. Cadmium and other potential contaminants (e.g., Pb and mercury (Hg)) can bioaccumulate and become toxic to organisms in higher trophic levels. In addition to these biological interactions, trace elements can be used as tracers. For example, Aluminum (Al) is used to trace continental inputs, vanadium (V) and lead (Pb) to trace anthropogenic emissions, and barium (Ba) has been used in the Arctic to differentiate freshwater inputs from North American and Eurasian rivers and is commonly found in barite, a mineral used in drilling muds.

Processes controlling natural dissolved metal concentrations in sea ice are poorly understood. Possible mechanisms include: 1) trace metals mobilized into the dissolved phase from suspended sediments that were trapped during sea ice formation, 2) trace metals mobilized from aerosols deposited onto the sea ice as snow begins to melt, 3) trace metals that vary only as a function of salinity and have limited particle reactivity (i.e., Ba and Al), or 4) trace metals concentrated within brine channels during ice formation, and as the base of the sea ice interacts with the upper water column during the growing season. Understanding the relative importance of these mechanisms will provide the basis for understanding how trace metals (naturally occurring and anthropogenic) are retained, transported, and released by sea ice.

Sediment inclusions within Arctic sea ice are highly variable and are mainly dependent on the suspended sediment load of the seawater from which the sea ice formed (Darby et al., 2011). Researchers have previously shown that sediment inclusions primarily form in brine channels within the sea ice matrix (Stierle and Eicken, 2002). These inclusions potentially provide a centralized location for solubilization of trace metals allowing for some elements to concentrate in sea ice. This suggests that processes capable of altering sea ice sediment inclusions play an important role in the concentration of dissolved trace metals within Arctic sea ice and therefore are likely important in the retention and transport of dissolved trace metals by sea ice.

Atmospheric transport and deposition of continental aerosols (natural and anthropogenic) have been shown to magnify the concentration of trace metals in snow over the sea ice within estuaries of the Chukchi and Beaufort Seas (Garbarino et al., 2002). Enhanced deposition of aerosol trace metals over marine areas compared to terrestrial areas is expected due to the nucleating effects of sea salt, and the increased rates of fog-related deposition within marine ice fog. These concentrating mechanisms make Arctic snowfall a potentially important external source of trace metals to the underlying sea ice and water column during the melting season (Douglas et al., 2008).

The dearth of trace element data combined with our limited understanding of the processes affecting trace metal cycling in sea ice prevent us from predicting how alterations to the sea ice environment will affect the biogeochemistry in the Alaskan Arctic. This project combined field and laboratory observations focusing on the dissolved and particulate concentrations of nine trace elements of interest (Al, Ba, Cd, Cu, Mn, molydenum (Mo), Pb, V, and Zn). Results complement previous trace metal projects in the region.

Similar to the ANIMIDA, cANIMIDA, and ANIMIDA III projects, this study provides “natural background environmental” data. Here the emphasis is on dissolved and particulate metal concentrations for fast sea ice, the underlying water column, and the overlying snow in Oliktok Point in Harrison Bay. Field data obtained from the Chukchi Sea shelf and slope regions targets the water column dissolved and suspended particulate data. These samples provide information on potential sources of metals to the coastal Beaufort Sea and on the effects of ice melt on surface waters downstream in the Beaufort Gyre and lease regions of the Chukchi Sea. In addition to field data, laboratory experiments targeted mechanisms involved in the cycling of trace metals within the sea ice matrix. Understanding the baseline oceanographic parameters of resource-rich Arctic shelves, including chemical and physical parameters, allows government agencies such as BOEM to better understand the potential ramifications of resource extraction accidents, such as an oil spill, in sea ice impacted regions. The objectives of this study are listed next.

Objectives

1. Manufacture and test the trace metal clean ice corer.
2. Conduct laboratory-based experiments on sea ice retention and release of trace metals.
3. Determine dissolved and particulate trace metals in laboratory-grown sea ice and the resulting brine/seawater mixture.
4. Collect seawater samples from the *R/V Mirai* in the Chukchi Sea and near ice floes.
5. Determine dissolved and particulate trace element concentrations in offshore surface seawater samples collected from the *R/V Mirai*.
6. Collect surface seawater, snow, and first-year sea ice cores near Oliktok Point.
7. Determine dissolved and particulate trace metal concentrations and ratios in ice cores collected near Oliktok Point.
8. Determine dissolved and particulate trace metal concentrations and ratios in snow samples collected near Oliktok Point.

Study Area

The study region comprises the broad shelf of the Chukchi Sea, Chukchi Sea slope waters (Canada Basin), and Oliktok Point, a near-coastal region on the narrow Beaufort shelf (Figures 1 and 2). Water column trace metal data for the Chukchi Sea are limited, however, collaboration with Japanese colleagues on a 2013 Arctic cruise allowed us to expand upon data we collected in the western Arctic during 2010 (Aguilar-Islas et al., 2013). This region is dominated by the influx of relatively fresh and nutrient-rich Pacific Water (PW) that enters through the Bering Strait and then follows bathymetric features northward before entering the Makarov or Canada Basins (Figure 2) (Weingartner et al., 2005a). The fresher Alaska Coastal Current (ACC) enters the Chukchi Sea through the easternmost section of the Bering Strait, in close proximity to the Alaskan Peninsula (Figure 2, bottom), and provides another important source of fresher water to the study region (Weingartner et al., 2005b). In addition to fresh water and nutrients, the influx of water from the Bering Strait likely contributes to the trace metal budget of Arctic waters. The influx of nutrients from the Pacific fuels production and the resulting organic matter from the shallow, productive Chukchi shelf settles to the seafloor. This organic matter supports benthic communities and promotes high rates of sedimentary remineralization and oxygen utilization, which lead to sedimentary denitrification (Brown et al., 2015; Chang and Devol, 2009). The reducing conditions within the sediment promote the mobilization of nutrients and trace metals into subsurface shelf waters (Aguilar-Islas et al., in prep.). As sea ice forms in fall and winter, the cold, rejected brine is laterally advected into the basin. This modified Chukchi shelf water maintains the halocline of the Canada Basin and transports high concentrations of nutrients and trace metals, such as Fe at mid-depths (Aguilar-Islas et al., 2013).

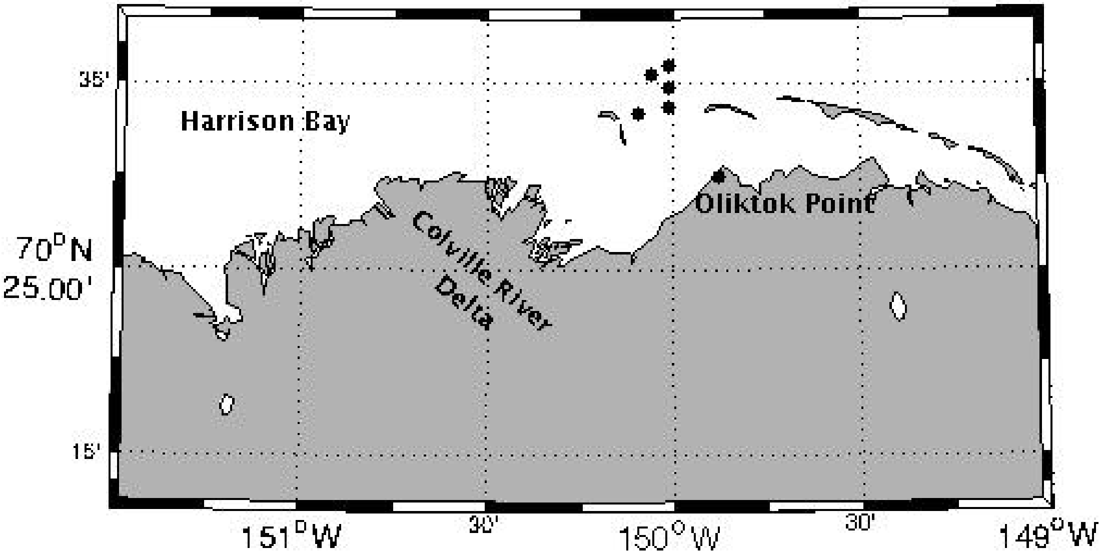

Figure 1. Map detailing the trace metal stations off Oliktok Point, and location of Colville River delta.

The narrow Beaufort shelf is also impacted by sea ice cycles and freshwater input from the Mackenzie and smaller Arctic Alaska rivers. In particular the largest Arctic Alaska River, the Colville, influences trace metal input in our Beaufort shelf study region (Rember and Trefry, 2004). Collaboration with the BOEM funded ANIMIDA III project allowed us to overlap our sampling in space and time with the ANAMIDA III spring freshet sampling program in Harrison Bay (Figure 1). The focus of the ANIMIDA III project is the buoyant plume of the Colville River that results from the spring freshet and spreads above and beneath the sea ice covering Harrison Bay.

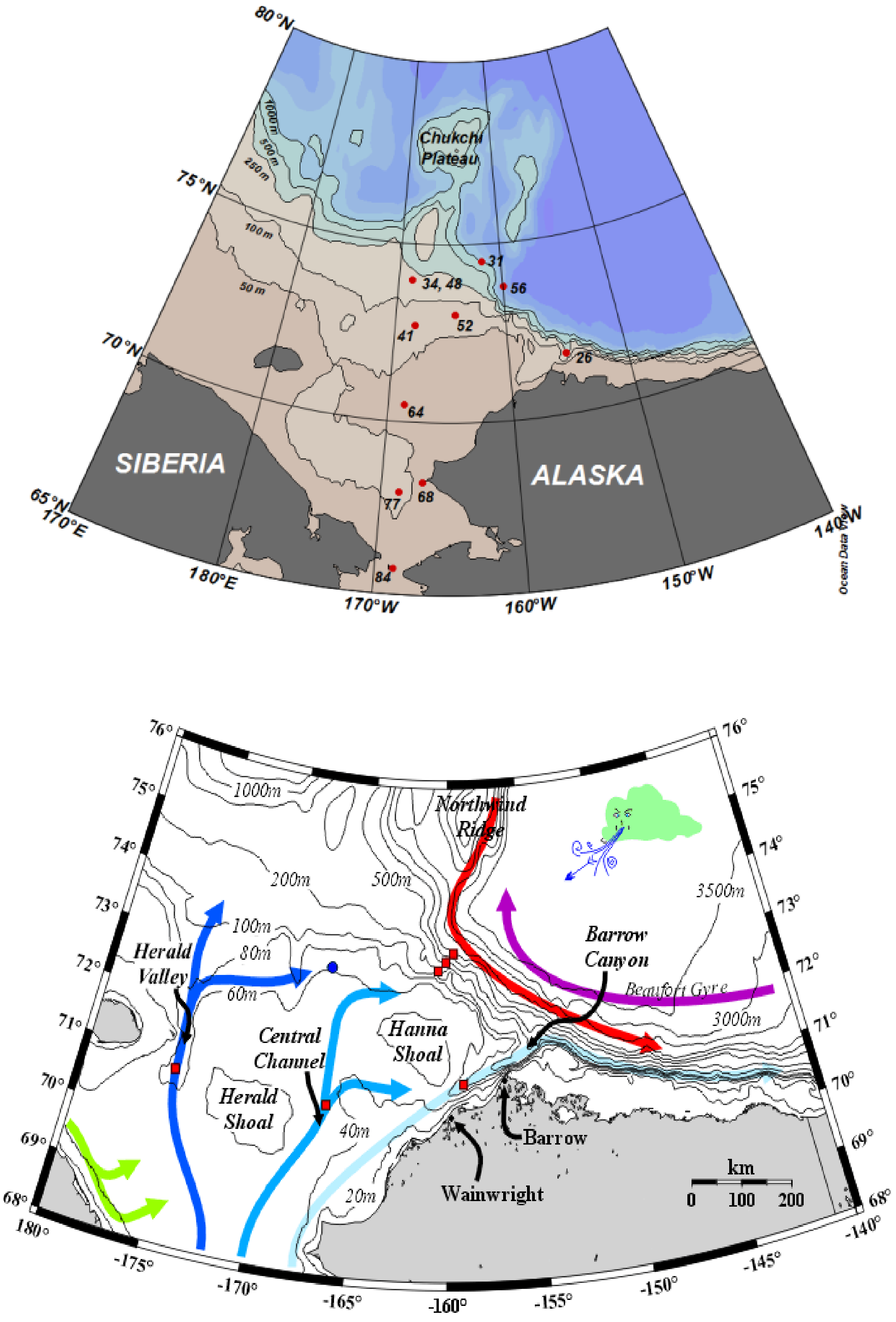

Figure 2. Map detailing the trace metal stations (top) and circulation in the Chukchi and southern Beaufort Seas (bottom). Image courtesy of T. Weingartner.

METHODS

Field Sampling

Water column sampling in the western Chukchi Sea was carried out September–October 2013 onboard the *R/V Mirai.* Although most of the sampling was done opportunistically, samples were obtained from stations across the shelf and slope and at a time-series station (Station 41) on the northern Chukchi shelf (Figure 2, top). Seawater samples were collected using a "clean" 12-position rosette water sampling system. The system consists of a powder-coated aluminum frame, titanium exposed metal surfaces, a Sea-Bird Electronics, Inc. 19plus unit, a Wet Labs EcoView fluorometer, a Wet Labs C-Star transmissometer, and a Sea-Bird Electronics Inc. auto fire module (AFM) programmed to fire bottles at pre-determined depths. Teflon-coated 5-L Niskin-X bottles with Teflon-coated external-springs were used during collection. These were washed with phosphate-free detergent and treated with 0.5 M trace-metal-grade hydrochloric acid (HCl). Bottles were stored with ultra-pure water (Milli-Q) prior to use. Weight restrictions on the Kevlar wire used for deployment limited casts to a maximum of nine bottles per rosette. To avoid potential contamination from the ship's hull, the shallowest sample was collected at 15 m. Samples were filtered through 0.4 μm polycarbonate filter discs (Nuclepore, track etched), and filtered seawater was collected in acid cleaned 500 ml low-density polyethylene (LDPE) bottles. Filter discs were frozen until analysis.

Coastal Beaufort Sea sampling sites were accessed via snow machine from the Atmospheric Radiation Measurement (ARM) Climate Research Facility at Oliktok Point. Sampling time on the ice was cut short due to inclement weather, lodging availability, and the early and rapid breakup of the Colville River in 2015. Despite these difficulties, we occupied five sites in Harrison Bay near the Colville River Delta (Figure 1) and collected 50 ice cores, 5 snow samples, and 8 water samples over two sampling days (16–17 May).

An auger was used to drill eight-inch holes through the ice for under-ice water sampling. Prior to sampling, the holes were covered by an ice tent and left to flush for more than an hour to minimize potential contamination from the drilling process. Under-ice seawater was collected using a Teflon-coated (ETFE) magnetic drive centrifugal pump (3.2 GPM, Cole-Parmer EW-72011-00) equipped with acid-washed Teflon-lined Tygon tubing attached to a Teflon weight that was lowered to the desired sampling depth. In all cases, prior to sample collection, a minimum of five gallons was pumped into a 5-gallon bucket to flush the pump head and Tygon tubing and then discarded. Seawater samples were collected in acid cleaned 2-L bottles, placed in plastic bags, labeled, and stored in a cooler prior to filtration. At select stations, bottom water was also collected to assess metal concentrations of throughout the water column. These samples represent the first seawater samples collected for trace metal analysis from bottom waters under the ice in the nearshore Beaufort Sea during any ANIMIDA spring sampling effort. In addition to seawater collection, conductivity, temperature, and depth (CTD) profiles were taken at each location using a Seabird 19plus CTD.

Snow samples were collected using a trace-metal-clean scoop to remove the surface layer of snow, normally hardened by the wind, and then packing the underlying snow into acid cleaned 1-L bottles, placed in plastic bags, and stored in a cooler until further processing.

Sample Processing

Seawater and melted snow samples were filtered within 12–24 hours of collection under a positive pressure environment in a laminar flow hood constructed in the warehouse of the ARM Climate Research Facility at Oliktok Point. Samples were vacuum filtered through 0.4 μm polycarbonate membranes (Nuclepore) mounted on acid-washed Teflon filter holders (Savillex). The filtrate was collected into acid-washed LDPE bottles, and particle bearing membranes were sealed in acid-washed Petri dishes. These and unfiltered seawater samples were placed in plastic bags and transported back to the International Arctic Research Center (IARC) at the University of Alaska Fairbanks (UAF) for further processing and analysis. The ANIMIDA III project collected samples for a suite of geochemical measurements including dissolved oxygen, pH, total suspended solids, dissolved and particulate metals N, P, C, and $\delta^{18}O$ from the same region in Harrison Bay. Our samples were collected just prior to the breakup of the Colville River, and sea ice data were shared with the ANIMIDA III project to better constrain inputs to the region during the spring freshet period.

Our sea ice sampling scheme for these stations was designed to investigate the variability between five cores collected within a defined 1 m^2 area compared to five cores collected randomly within a defined 10 m^2 surrounding area (Figure 3). Sea ice is heterogeneous by nature, and this design allowed us to constrain the spatial variability in particulate and dissolved trace metals within a small area of sea ice, as compared to randomly sampled cores nearby. In addition, we directly compared defined areas from the five stations in an attempt to characterize the ice in the region.

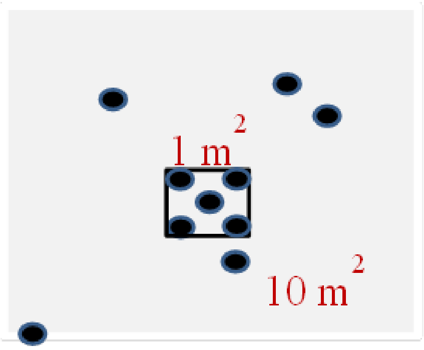

Figure 3. Diagram describing the sampling scheme for sea ice at stations off Oliktok Point.

Sea ice samples were collected to the maximum depth of the corer (1 m) after snow was removed from the sampling area. The corer was removed from the hole and the inner sleeve containing the ice core sample was quickly separated from the corer, capped, taped closed, and then placed in a plastic-lined aluminum case (Zarges) for transport. Due to the lack of freezer space at the ARM Climate Research Facility, the shipping cases were buried in snow until the ice cores could be transported to Prudhoe Bay for shipment (maximum two days).

Sea ice samples were shipped frozen (overnight) to IARC for further processing. Samples were kept frozen inside their collection sleeves prior to processing, which began immediately after the cores arrived. Core processing took approximately one week. Individual cores were allowed to melt in custom-designed high-density polyethylene melting chambers (Figure 4), which had been previously acid washed. Once melted, the chambers were pressurized with ultra-pure nitrogen gas (UPN) and the melted core was filtered through a 90 mm 0.2 μm Supor filter (Pall Corporation). The solution passing through the filter was collected in acid-washed LDPE bottles. Due to the large sediment load incorporated into the ice, large diameter filters were required for the filtration of each core (~5 L of water). Prior to processing, each filter was divided into four sections and set to air dry inside a laminar flow hood to create replicate filter pieces from each core.

Liquid samples (filtered and unfiltered seawater, snow, and filtered sea ice) were acidified with Optima grade HCl to $pH < 2$ at least one week prior to analysis. Particulate samples (suspended particles and sea ice particle inclusions) were first leached using a solution of 25% acetic acid with a reducing agent (Berger et al., 2008). Leached filters then underwent complete digestion using a sequential scheme with a combination of HCl, nitric acid (HNO_{3})), and hydrofluoric acid (HF). For select ice cores, multiple filter subsections were leached and digested to ensure that a representative value was obtained.

Figure 4. Custom-made chambers for melting sea ice cores. Chambers can be outfitted with individual filter discs to capture particles released by the melted ice or linked with tubing to collect a single homogenized sample.

Laboratory Analysis

Analysis of all samples was done at IARC using a ThermoFinnigan Element2 inductively coupled plasma mass spectrometer (ICP-MS).

Trace metals in suspended sediments

Concentrations of leached and refractory (digested) particulate metals were determined by calibration curve and direct injection into the ICP-MS. The sensitivity was monitored with an indium spike (1 ppb). Total particulate metals were obtained from the sum of the acetic-acid-leached and refractory fractions.

Dissolved trace metals in seawater, snow, and sea ice

Acidified seawater, snow, and sea ice samples were analyzed for trace metals using a seaFAST S2 system (Elemental Scientific) specifically designed for low-level trace element work. The seaFAST S2 draws a 7 ml sample into a series of valves where the pH is adjusted to ~6.2 prior to passing across a resin that retains the trace metals but not major salts present in seawater. The trace metal sample retained on the resin is then eluted with HNO_3 directly into the ICP-MS and quantified by either isotope dilution (Fe, Ni, Cu, Zn, Cd, Ba and Pb) or calibration curve (Mn) (Rember et al., in prep). The major advantage of this system is that minimal sample handling/processing is required after acidification (i.e., adding enriched isotopic spike or indium to monitor sensitivity prior to analysis).

Quality Assurance and Quality Control

All seawater, snow, and sea ice samples were collected, transported, and stored by personnel from the University of Alaska, Fairbanks. Upon return to or arrival at the laboratory, each sample was inspected to ensure that it was intact and that the sample label was legible.

Instrument calibration

All pipets (both electric and manual) were calibrated prior to use. The ICP-MS was initially checked for stability and sensitivity prior to instrument calibration. Prior to metal analysis, the instrument was standardized with a calibration curve consisting of four to six points, and a linear correlation of r^2 greater than or equal to 0.999. Analysis of the standard curves or standard check was repeated routinely every 20 samples until the analysis were complete. The relative standard deviation (RSD) between calibration and standard check was required to be <5% or recalibration and reanalysis of the affected samples were performed.

Quality control measurements for analysis

Quality controls included duplicate sample analysis, certified reference material (CRM) analysis, reagent blank analysis, isotopic spike calibration, and standard checks. With each batch of sediment samples, at least two reagent blanks, two CRMs, and two duplicate samples were analyzed. With each batch of dissolved samples, several system blanks, sample duplicates, and reference seawater with consensus values were analyzed for a suite of trace elements.

At least two procedural blanks were processed during each batch of leached and digested samples to monitor for contamination of labware or reagents. The blanks were processed and analyzed using the same handling techniques and procedures as the field samples.

For seawater, melted snow, and sea ice samples, procedural blanks for the SeaFAST S2 system were determined from the analysis of acidified ultra-pure Milli-Q water treated in the same manner as acidified field samples. Specifically, the multi-element isotope spike was added to the acidified Milli-Q water to determine the procedural blank for metals quantified by isotope dilution, and an indium spike was added to acidified Milli-Q water to determine the procedural blank for metals quantified against calibration curves.

The CRM MESS-3, Beaufort Sea marine sediment from the National Resource Council of Canada (NRC), was used to evaluate the accuracy of our suspended sediment analytical procedures. Metal concentrations are required to be within 20% of accepted values for the certified metals. Results for the dissolved metals were monitored using a seawater CRM from NRC, NASS-6, as well as other seawater samples with consensus values determined by the oceanographic community for the US GEOTRACES program. Results for all the CRMs are in the Appendix.

RESULTS

2013 Chukchi Sea Water Column

We participated in the Japanese Marine-Earth Science and Technology (JAMSTEC) *R/V Mirai* cruise in the Chukchi Sea during September/October 2013. Data from this cruise are highly relevant to BOEM as the study area overlapped with a number of oil-related activities on the Chukchi Shelf at the time of the expedition. A total of 21 vertical profiles were collected from 11 stations (Figure 2, top). Eleven of the profiles originated from a single site (Station 41) that was reoccupied multiple times over a 16-day period.

Here we will highlight three sets of results from our Chukchi Sea fieldwork including results from a northward transect over the shelf, results from the time series at Station 41 located towards the north of the shelf (72.5^o N), and results from offshore stations (including 2010 data).

Three stations collected along 168 W (Stations 64, 77 and 84) show variability in water column structure and trace metal partitioning across the shelf. The Bering Strait station (Station 84) had a three-layer system (Figure 5A) with a thin layer of low-density, fresh water above ~3 m, a layer of mid-density occupying the upper 5–15 m, and below this depth, a well-mixed, subsurface, denser layer with relatively higher suspended particles as seen in the transmissometer data (Figure 5B). At Station 77, where PW entering the Chukchi Sea bifurcates into the Central Channel and Herald Valley branches, the water column was mostly completely mixed (Figure 5A). Data show particles from a bottom nepheloid layer mixed up almost into the surface layer (Figure 5B). The northernmost station exhibited a two-layer system with fresher, less dense surface waters mixed down to depths of almost 30 m overlaying a thin, denser, and turbid bottom layer (Figure 5).

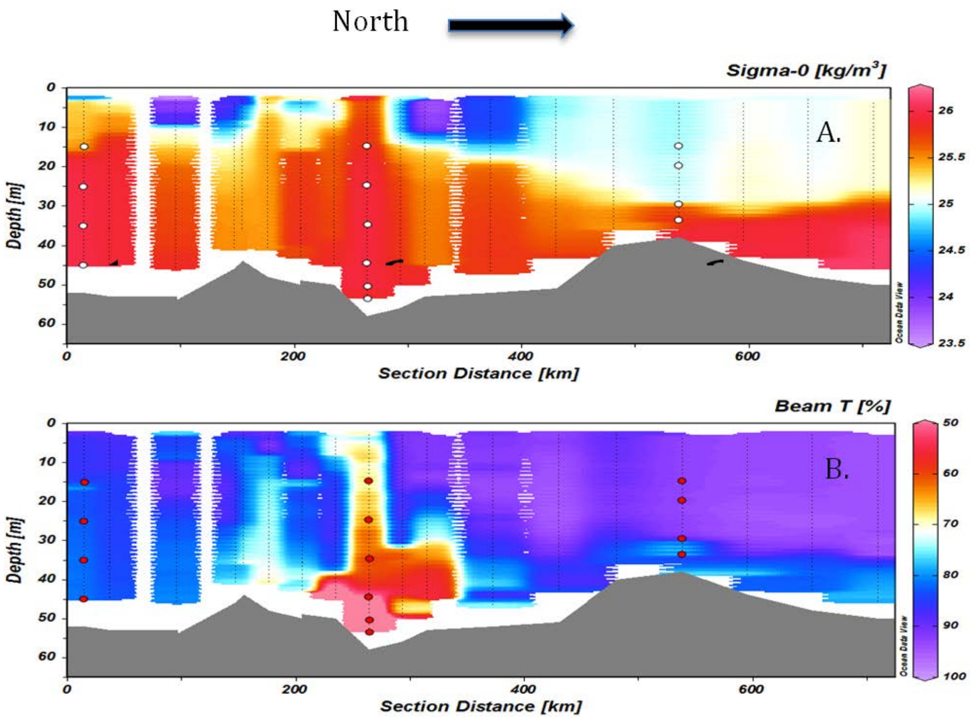

Figure 5. Density (A) and transmission data (B) on the transect from Bering Strait to the northern Chukchi Sea along 168 W. Red/white dots indicate the location of samples taken for trace metal analysis at stations (from left to right) 84, 77, and 64.

Dissolved and particulate trace elements data along the 168 W transect are presented in Figure 6. Concentrations of Mn, Fe, and Cu (also Al and Pb, not shown) in the leachable and refractory particulate phases show very different trends along the transect, as do the concentrations of dissolved Fe, Mn and Cu. In general, the refractory fraction of suspended particles (darkest color circles in Figure 6) was substantially greater than the leachable fraction at all depths and across the shelf for Fe (note the logarithmic scale) and Al (not shown), while for Mn, Cu, and Pb these particulate fractions had relatively similar magnitudes. Although similar in magnitude, the partitioning of suspended particles for Mn, Cu and Pb differ in that the Mn refractory fraction decreased across the shelf, Cu consistently exhibited a slightly higher refractory fraction, while Pb was consistently higher in the leachable fraction. For all metals, sedimentary resuspension was apparent, particularly at the middle station where transmissometer data shows enhanced concentrations of suspended particles (Figure 5B). Surface dissolved Mn and Cu were higher across the shelf, while surface dissolved Fe decreased from the Bering Strait northward. Subsurface input of dissolved Fe is also apparent at these three shelf stations (Figure 6).

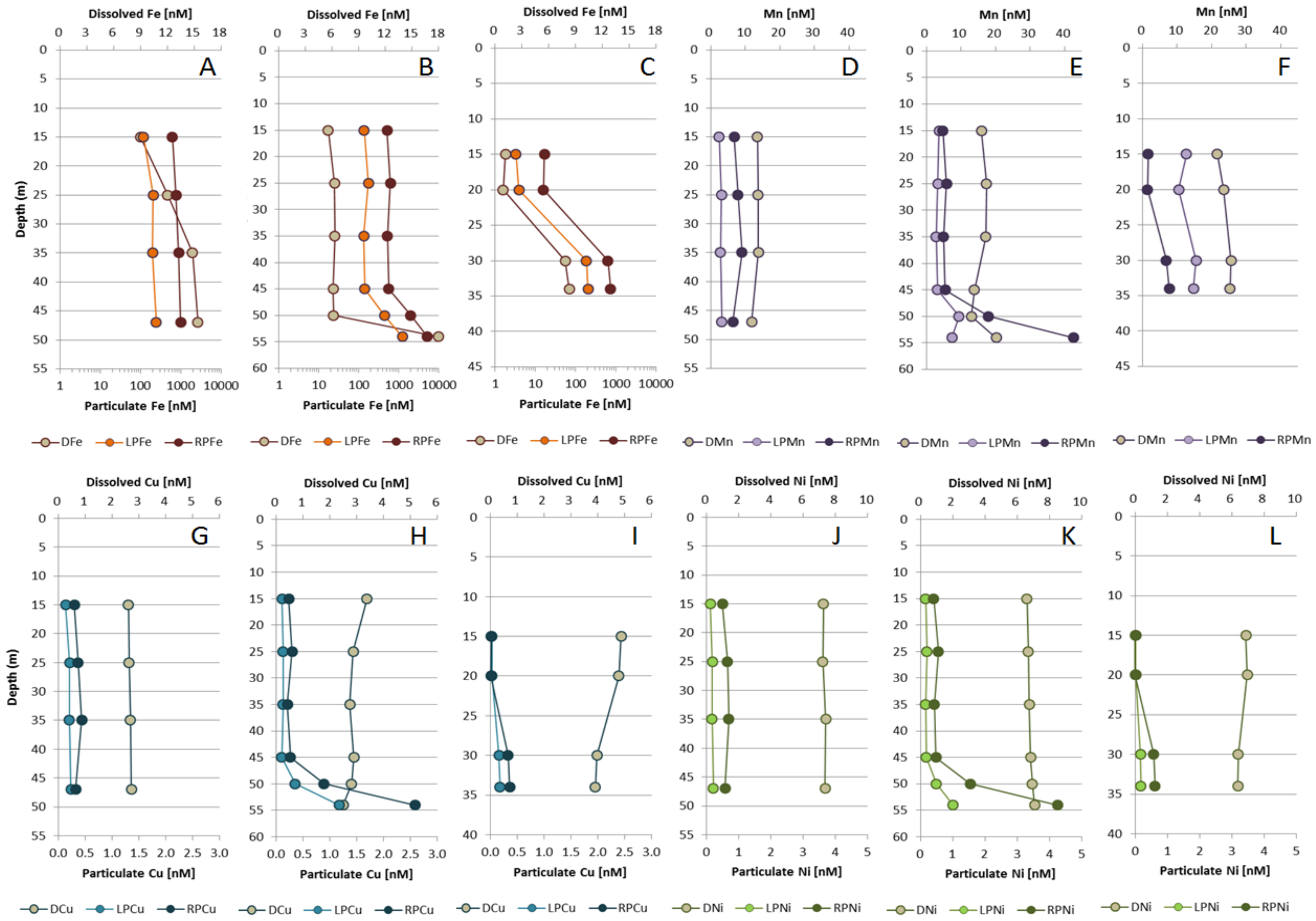

Figure 6. Concentrations of dissolved (D), leachable particulate (LP) and refractory particulate (RP) Fe, Mn, Cu, and Ni for Stations 84 (A, D,G,J), 77 (B, E,H,K) and 64 (C, F,I,L) along the Chukchi Shelf (168° W). Note the log scale for particulate Fe.

This field effort allowed for the reoccupation of a single station (Station 41) over a two-week period. During that period, CTD profiles and water samples were collected every six hours to investigate the temporal variability in physical and chemical parameters. A summary of select CTD data is presented in Figure 7. Samples for trace metals at this station were taken on alternating days during the first week and daily during the second week. The structure of the water column at this station exhibited a fresh, low-density layer in the upper 20 m with low suspended particle load and intermediate dissolved oxygen values. Density and oxygen concentrations increased below this layer, while the suspended particle load was diminished. Within the densest layer, adjacent to the sediment, suspended particles exhibited maxima (nepheloid layer), and dissolved oxygen concentrations exhibited minima throughout the sampling period. Temporal variability in dissolved oxygen, beam transmission and density showed that approximately half way through the occupation, denser surface water relatively enriched in oxygen and suspended particles moved into the sampling region.

This feature was also evident towards the end of the second week of sampling in the bottom 10 m, and resulted in a reduction in beam transmission (enhanced suspended particles), increased dissolved oxygen, and lower density (Figure 7). These observations suggest advection of subsurface waters promoting sediment resuspension.

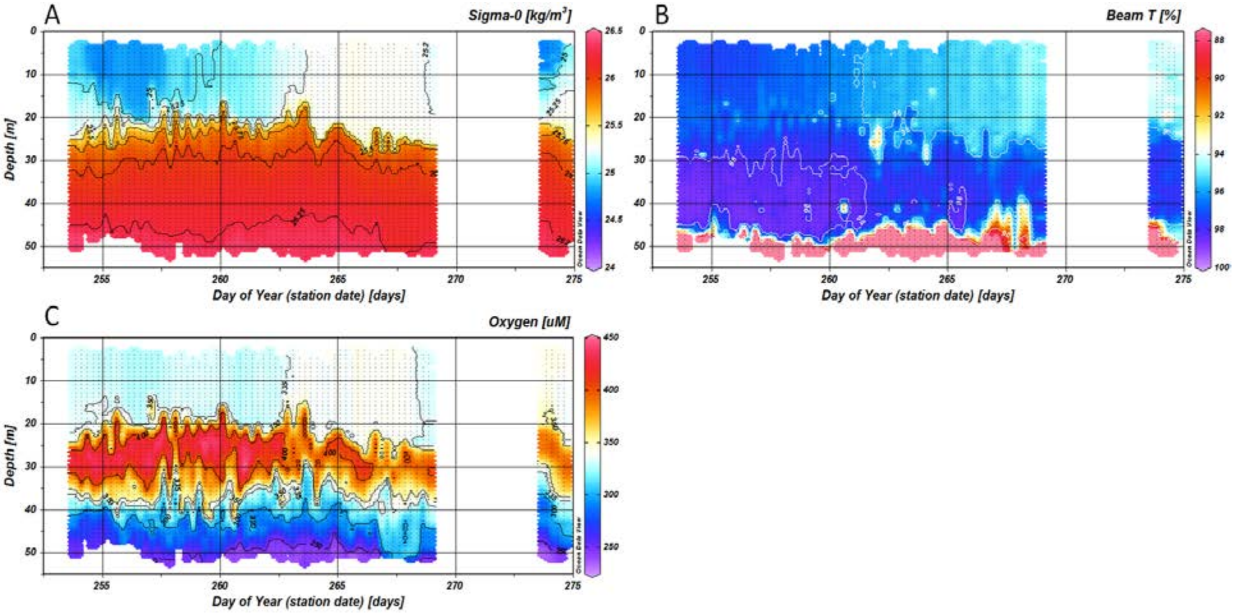

Figure 7. Density data (A), beam transmission (B), and dissolved oxygen (C) collected from CTD profiles collected four times daily during a two-week occupation of Station 41 in the Chukchi Sea.

Short-term variability in shelf trace metal concentrations can be exemplified by Fe and Mn profiles at Station 41. Concentrations of dissolved Fe and Mn followed hydrographic trends. In general, concentrations increased with depth, and were highest below 40 m in the region where dissolved oxygen showed a decreased gradient towards its minimum. Surface dissolved Fe and

Mn were impacted by the higher density surface water moving through the region on the second week of the occupation (Figure 8). Particle resuspension in the denser subsurface layer was evident in the leachable and refractory fraction of both metals, with highest concentrations in the bottommost samples.

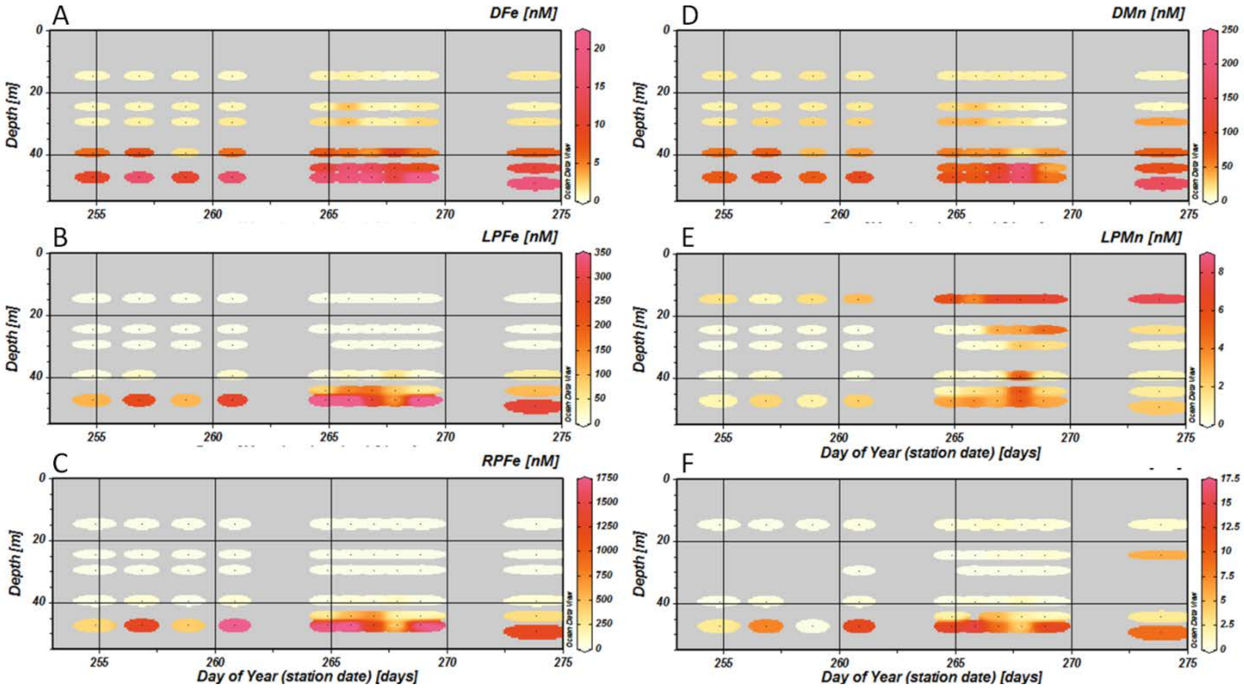

Figure 8. Dissolved (A, D), leachable (B, E), and refractory (C, F) Fe and Mn data (11 profiles) collected during an extended occupation of a single station (Station 41) in the northern Chukchi Sea.

Dissolved trace element profiles collected from the southern Canada Basin (Figure 9) during 2010 and 2013 represent some of the very limited dissolved trace element measurements available from the region. The depths sampled during these summer occupations allowed us to quantify trace metal concentrations in surface waters, water masses of Pacific and Atlantic origin, waters impacted by fresh water inputs (melted sea ice and/or riverine input), and waters modified along the Chukchi Shelf and advected in subsurface layers into the Canada Basin.

Within the upper 1000 m, the concentration range for dissolved metals (Fe ~ 0.5–1.5 nM, Mn ~ 0.2–11.5 nM, Cu ~ 1.5–6 nM, Ni ~ 3.0–8.5 nM, and Pb ~ 2–10 pM) tended to be the lowest in Atlantic waters (depth > 300 m) (Figure 9). Concentrations of dissolved metals in Atlantic Water showed little variability with depth and were consistent in the two years we sampled in this region. Relative to the deeper Atlantic Water, concentrations of dissolved metals were elevated and much more variable within depths < 300 m in Pacific Water (Figure 9). Distinct profiles for each metal observed in these offshore waters. Dissolved Mn and Pb had surface maxima while dissolved Fe, Cu and Ni had maxima in the subsurface between 100 and 200 m.

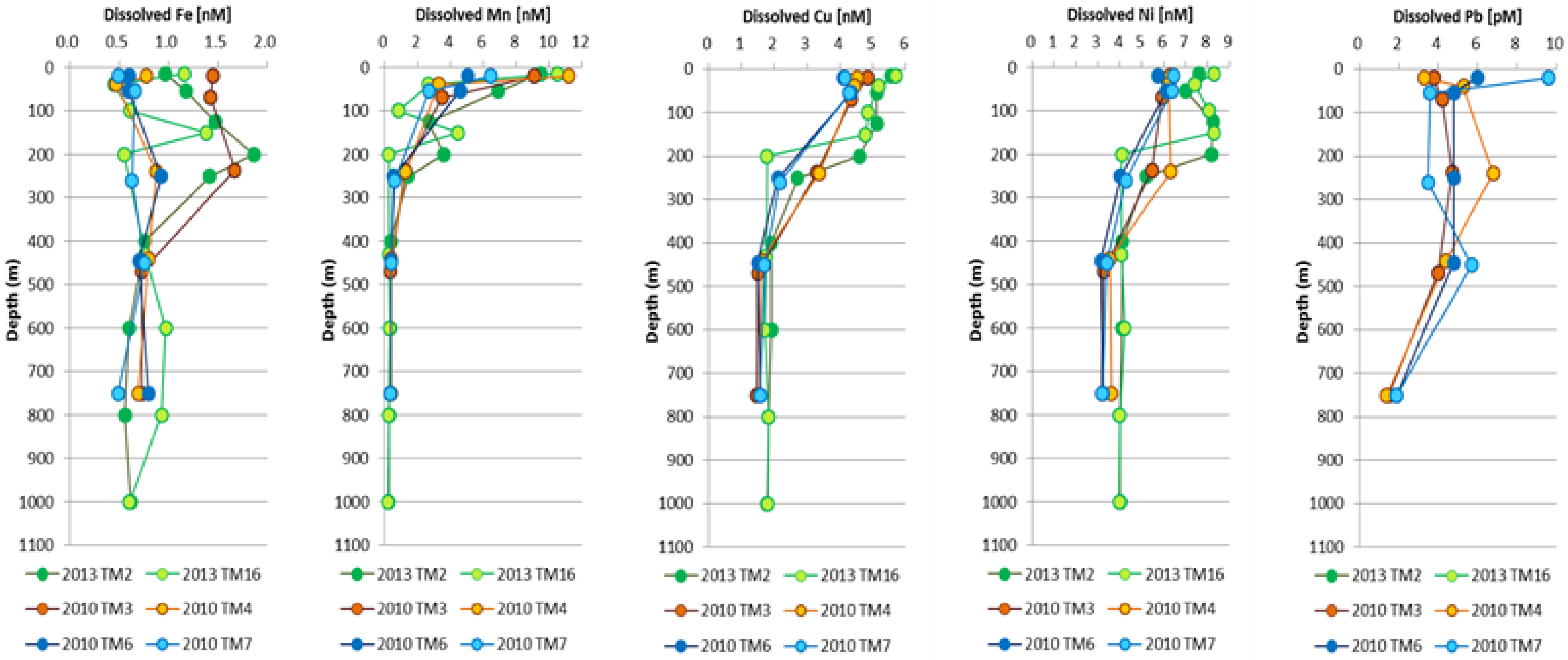

Figure 9. Profiles of dissolved metals for the southern Canada Basin collected in 2010 and 2013.

Sea Ice Tank Experiments

We successfully tested the prototype of our ice corer in early 2014 in our outdoor clean van. Initial testing of the prototype showed that the corer design was satisfactory for drilling and collecting sea ice cores, trace-metal-clean with respect to concentrations of metals commonly known to contaminate during sampling, and durable enough to withstand collecting a large number of sea ice cores before servicing cutting blades. After this initial testing, warm weather prevented us from continuing outdoor work.

Tank experiments began in late October 2014. A clean enclosure was constructed to keep positive pressure over a tank and working area in the cold room of the Geophysical Institute at UAF. There was a steep learning curve to understand how to control the tank temperature so it would freeze slowly over a period of days to weeks for the ice growing experiments.

In the first experiment, we froze approximately 180 liters of filtered Gulf of Alaska seawater slowly over a two-week period (Figure 10). Filtered seawater was used to initiate the experiment in the absence of particles. Samples were then collected weekly over a four-week period. Each sampling interval included extracting a pair of ice columns (sea ice grown inside acid-clean polycarbonate tubes placed inside the tank) (Figure 10) and a sample of the unfrozen water from the bottom of the tank (through a spigot).

Figure 10. Filtered seawater from the Gulf of Alaska was frozen in a large polyethylene tank in the cold room of the UAF Geophysical Institute (left photo). Polycarbonate tubes were suspended in the seawater during ice formation (middle photo). The tubes were extracted from the tank and transported to a class 100 laminar flow hood where subsamples were collected (right photo).

Results from the tank experiment suggest that metals partition between the sea ice and the seawater water from which it forms. Two examples of partitioning of the metals are shown in Figure 11. Although sediment was not included during the first experiment, concentrations of Fe in unfiltered samples (tank and sea ice) (Figure 11A) showed substantial additional Fe than filtered samples. This was the case throughout the experiment. These data suggest that as seawater freezes, the resulting concentration of salts in brines can act as a mechanism to promote precipitation and transfer Fe from the dissolved phase to the particulate phase. This appears to happen early in the ice formation process (by week 1 dissolved Fe had already partitioned into the particulate phase) and is likely an abiotic mechanism of colloidal aggregation. This partitioning was more pronounced in the melted sea ice than in the seawater under the ice, suggesting that Fe in sea ice is preferentially retained in the particulate phase. In contrast to the results for Fe, precipitation of Cu during ice formation was much less evident (filtered and unfiltered samples were more similar in concentration) (Figure 11B). Concentrations of filtered and unfiltered Cu increased in the tank during the experiment, while Cu in the ice decreased over the same time period. These results suggest that during the formation of sea ice, Cu is not retained as dissolved nor as newly precipitated particles, but instead is rejected along with the brine.

In the second tank experiment, two grams of Beaufort Sea sediment from the CRM MESS-3 (NRC) was added to the tank and mixed and suspended throughout the experiment with a magnetic stirrer and Teflon-coated bar. Results show a clear rise in dissolved concentrations for all metals in the tank due to desorption of metals from the added particles (notice change in y-axis ranges in Figure 11). Overall, a similar trend as in the first experiment was observed for both Fe (Figure 11C) and Cu (Figure 11D). Partitioning between dissolved and particulate phases was greater for Fe than for Cu. Concentrations of Cu in the seawater under the ice increased with time as Cu concentrations decreased in the sea ice. Interestingly, the removal of Fe from sea ice over time is much more pronounced when sediment is present.

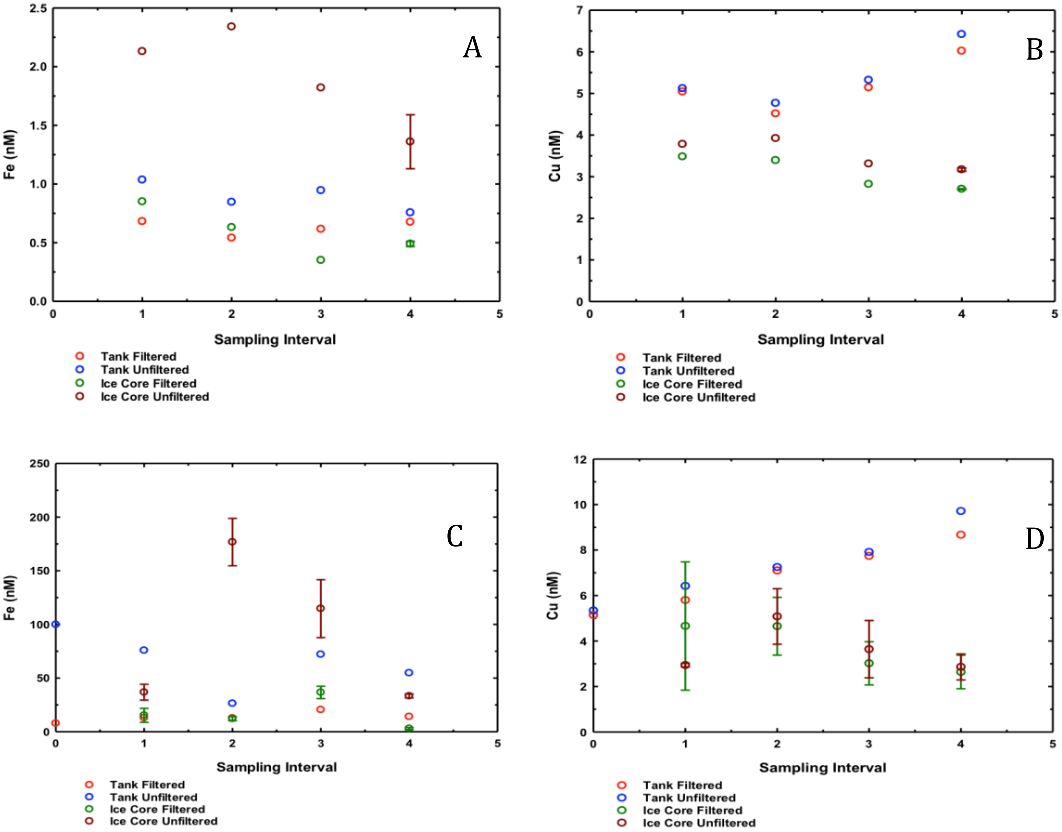

Figure 11. Select results from the ice tank experiments conducted in 2014. The first experiment (A and B) was conducted in the absence of particles; suspended sediment was added in the second experiment (C and D).

Sea Ice Field Sampling

Delays in the manufacture of the ice corer caused a one-year delay in the ice sampling from the coastal Beaufort Sea. Due to a very tight sampling window surrounding the spring freshet, we targeted our field time to coordinate with the ANIMIDA III project trace metal sampling effort in mid-May 2015, before the rivers began to flow, and were able to sample in in conjunction with the ANIMIDA III investigators. Although we were ready to sample on May 15, we lost one day of sampling due to bad weather. On May 16 and 17, we were able to complete five stations (Table 1) and collect a total of 50 ice cores from fast ice north of Oliktok Point (Figure 1). Our sea ice data compliment dissolved and particulate data collected by Dr. Trefry (water column and river chemistry) and by Dr. Kasper (physical parameters), and add another aspect to examining the physical and chemical changes that occur in the winter to spring transition on the Beaufort Sea shelf.

Table 1. Station Locations for stations occupied during May 2015 off Oliktok Point. Station names are consistent with ANIMIDA III stations.

Station	Latitude	Longitude	Sample Date	Water Depth (m)
E10	70° 34.823	150° 0.603	May 16	9.2
E11	70° 35.949	150° 0.623	May 16	9.5
NM5	70° 35.505	150° 3.468	May 16	9.5
W07	70° 36.080	150° 14.211	May 17	10.9
S01	70° 33.345	150° 5.502	May 17	5.9

Data from CTD profiles (Figure 12) suggest that ~80% of the water column under the ice was well mixed. Considering the relatively small area (13 km^2) encompassed by our study, we encountered considerable variability within the CTD profiles (Figure 12). Salinities varied from less than 33 to almost 36. The temperature scale is exaggerated to show small deviations throughout the water column. Temperature across the entire study area ranged between -1.86°C and -1.79°C. Overall, the water column was fairly well mixed at most sites with slight decreases in temperature and increases in salinity in the bottom waters.

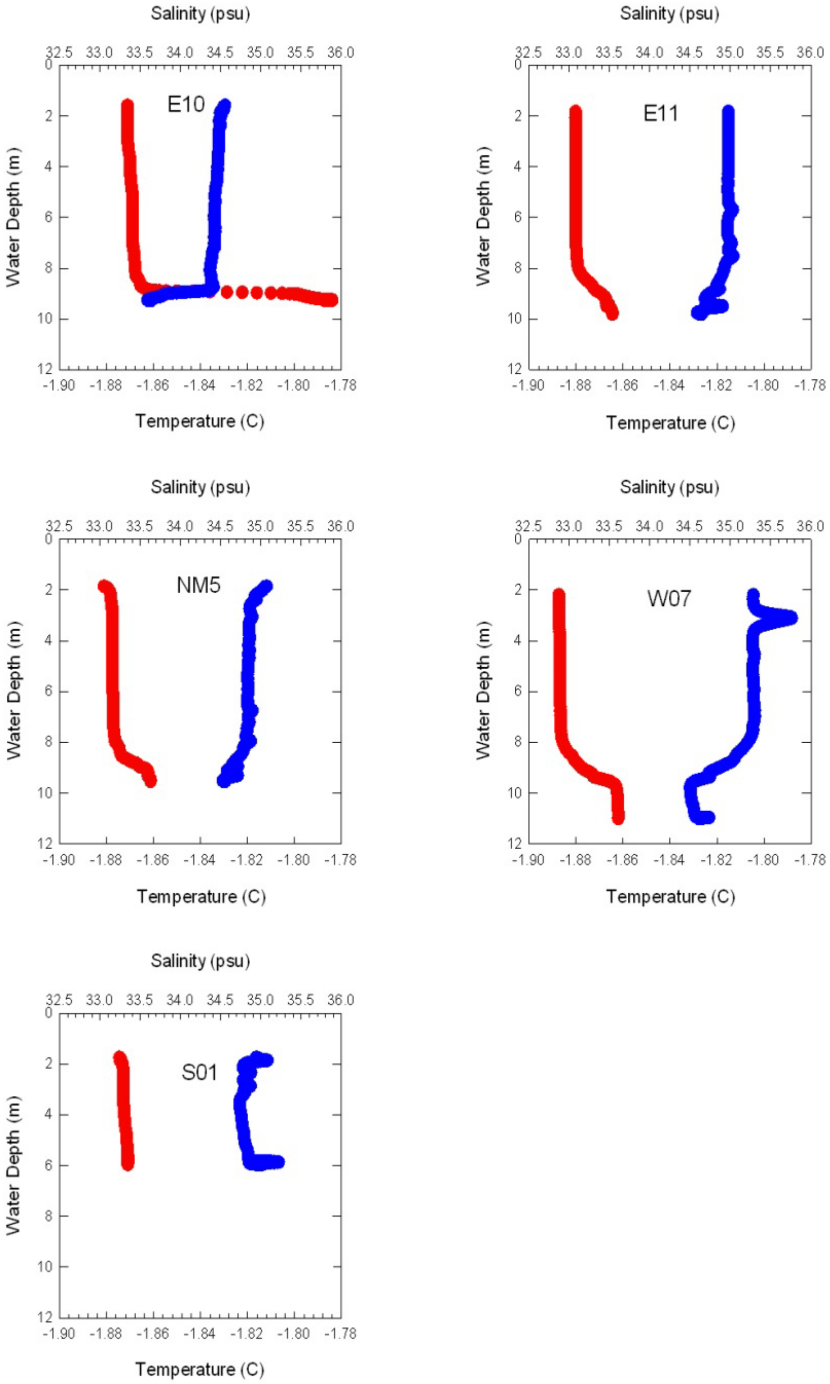

Figure 12. Salinity (red) and temperature (blue) profiles collected at the five stations occupied during May 2015 off Oliktok Point.

Concentrations of dissolved metals in seawater under the ice were within normal coastal concentrations (Figure 13, Table 2) for the Beaufort Sea, and the Chukchi Sea (MIRAI 2013 cruise data, Trefry et al., 2009). The concentrations compared well with data collected during the open-water season from previous BOEM funded projects in the region with a few exceptions. Metals such as Cu, Ni, Cd, and Ba show less than 6% variability in the water column suggesting that any processes occurring in the bottom waters do not considerably alter concentrations of those elements.

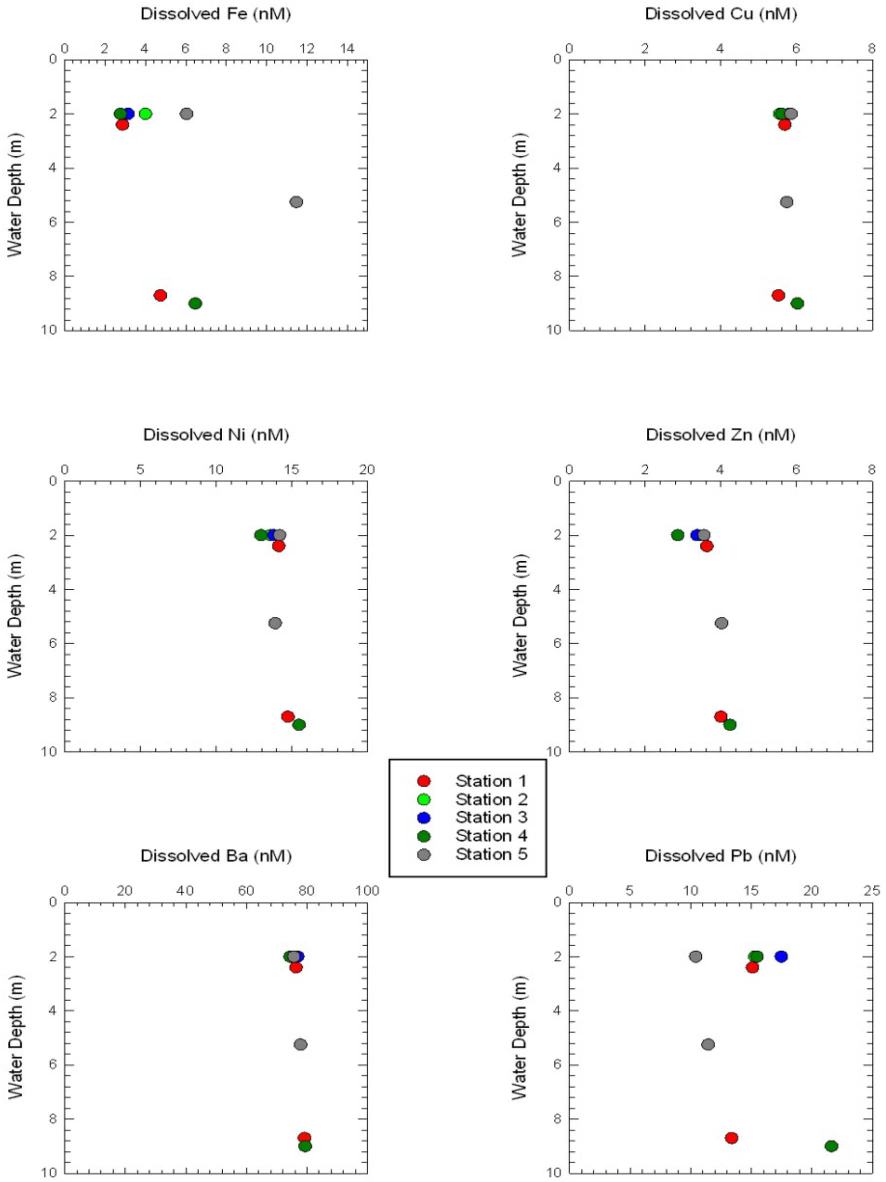

Figure 13. Concentrations of select dissolved metals at the five stations occupied during May 2015. Stations 1–5 are E11, NM5, E10, W07, and S01, respectively.

Table 2. Concentrations of dissolved trace metals in the seawater collected below the ice at stations occupied during spring 2015 near the mouth of the Colville River. Concentrations in brackets are standard deviations for each associated concentration.

Station	Depth (m)	Fe (nM)	Ni (nM)	Cu (nM)	Zn (nM)	Cd (pM)	Ba (nM)	Pb (pM)
E10	2	3.14	13.8	5.80	3.37	796.8	76.9	17.5
E11	2.4	2.86	14.1	5.69	3.63	825.1	76.3	15.11
	8.7	4.74	14.7	5.52	4.00	856.3	79.2	13.4
NM5	2	4.00	13.6	5.56	3.39	798.4	76.3	15.3
W07	2	2.76	13.0	5.61	2.86	766.9	74.4	15.5
	9	6.47	15.5	6.02	4.24	848.2	79.4	21.6
S01	2	6.03	14.2	5.85	3.55	819.9	75.6	10.4
	5.25	11.5	13.9	5.74	4.02	833.1	77.8	11.5
Average Under Ice 2015		5.19	14.08	5.72	3.63	817.9	76.8	15.1
		(2.91)	(0.75)	(0.17)	(0.44)	(29.5)	(1.7)	(3.7)
Coastal Beaufort Sea*	Surface Water	-	-	6.34	2.95	303	119	44.5
				(1.90)	(1.03)	(89)	(55)	(14)

*Coastal Beaufort surface water comprises water taken during the open-water season from 2000 to 2006 during ANIMIDA and cANIMIDA (Trefry et al., 2009).

These results are somewhat surprising given that the amount of sediment varied substantially among the 50 ice cores (Figure 14). The range of total suspended solid (TSS) concentrations ranged from 1.47 to 174 mg/L among the 50 cores. Each station consisted of ten cores, cores 1–5 were collected within the 1-m^2 area, and cores 5–10 were collected randomly near the defined area. These data clearly demonstrate the heterogeneity of sea ice with TSS varying by as much as ~120 fold in cores collected within a relatively small area.

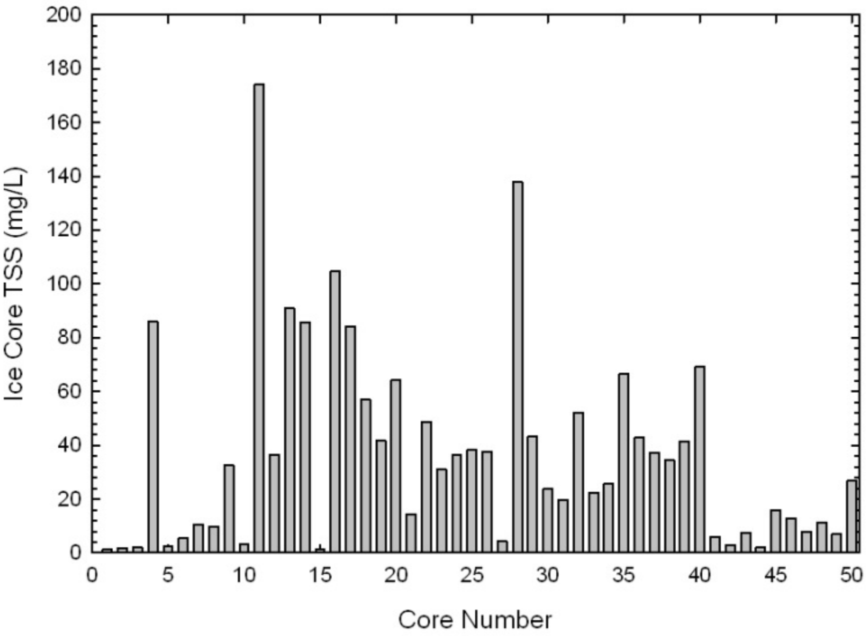

Figure 14. Concentration of total suspended solids (TSS) in sea ice cores collected during spring 2015.

At stations where surface and subsurface water were sampled (E11, W07, and S01), dissolved Fe, Zn, and Cd consistently showed higher concentrations at the subsurface. Concentrations of dissolved Fe were approximately double in subsurface waters when compared to the surface, while the increases in dissolved Zn and dissolved Cd were less pronounced (Table 2). Concentrations of dissolved Pb were relatively low and were lower at the surface for Stations W07 and S01, but higher at Station E11.

Sea ice cores obtained during the spring of 2015 were collected as two spatially distinct groups as detailed previously (Figure 3). In Table 3, concentrations of dissolved metals from each of the five cores collected either inside of the 1-m^2 box or randomly outside the box are averaged to give a representative concentration for each population, at each station. Our results suggest that significant differences did not exist between the concentrations of dissolved metals in the two ice core populations for most metals ($p > 0.05$). At site W07, the coefficient of variance for samples collected within the defined area to those collected randomly ranged from a low of 5% for Fe to a high of 15% for Pb. Moreover, we found that the concentrations of dissolved metals did not vary greatly among stations. On average, dissolved Fe was 1.66 ± 0.44 nM in cores taken from within the 1-m^2 box at all stations, and 1.85 ± 0.57 nM in cores taken randomly outside the box. Similarly, the average concentrations of dissolved Ni, Cu, Zn and Ba in cores taken inside the 1-m^2 box were similar to those taken randomly (2.39 ± 0.94 nM, 1.14 ± 0.29 nM, 1.99 ± 1.54 nM, and 10.7 ± 2.2 nM, respectively inside, vs. 2.09 ± 0.56 nM, 1.16 ± 0.32 nM, 1.44 ± 0.67 nM, and 10.8 ± 2.2 nM, respectively for randomly collected cores). The same was true for Cd and Pb, however, these were three orders of magnitude lower, with the average of all cores inside the 1-m^2 box containing 38.6 ± 13.1 pM Cd, and 2.9 ± 2.1 pM Pb, and the randomly collected cores containing an average of 34.3 ± 5.6 pM Cd, and 1.9 ± 0.8 pM Pb.

These results are somewhat surprising given that the amount of sediment varied substantially among the 50 ice cores (Figure 14). The range of total suspended solid (TSS) concentrations ranged from 1.47 to 174 mg/L among the 50 cores. Each station consisted of ten cores, cores 1-5 were collected within the 1-m^2 area, and cores 5-10 were collected randomly near the defined area. These data clearly demonstrate the heterogeneity of sea ice with TSS varying by as much as ~120 fold in cores collected within a relatively small area.

Table 3. Concentrations of dissolved trace metals in the sea ice collected at stations occupied during spring 2015 near the mouth of the Colville River. Concentrations in brackets are standard deviations for each associated concentration.

Station	Core	Fe (nM)	Ni (nM)	Cu (nM)	Zn (nM)	Cd (pM)	Ba (nM)	Pb (pM)	TSS (mg/L)
E11	In	1.26 (0.66)	3.97 (0.93)	1.29 (0.47)	4.69 (2.10)	60.2 (39.5)	11.2 (3.9)	6.4 (5.5)	18.7 (37.6)
	Out	0.96 (0.90)	2.92 (0.86)	0.68 (0.2)	2.57 (1.19)	40.6 (16.4)	7.8 (2.3)	2.04 (1.4)	12.3 (11.7)
NM5	In	2.16 (0.53)	1.98 (0.21)	1.38 (0.25)	1.45 (0.36)	30.5 (12.9)	11.7 (4.2)	1.1 (0.9)	77.8 (65.4)
	Out	2.09 (0.69)	2.13 (0.55)	1.53 (0.44)	1.35 (0.35)	38.3 (14.8)	11.6 (2.4)	1.0 (0.2)	70.4 (24.5)
E10	In	2.04 (0.28)	1.79 (0.27)	1.37 (0.16)	1.12 (0.20)	35.7 (9.0)	13.8 (1.2)	2.7 (0.6)	33.8 (12.6)
	Out	2.51 (0.67)	1.49 (0.54)	1.33 (0.37)	0.96 (0.38)	28.7 (12.8)	13.8 (2.9)	2.8 (1.2)	49.4 (51.8)
W07	In	1.65 (0.22)	2.54 (0.34)	0.90 (0.18)	1.72 (0.49)	40.2 (9.3)	8.06 (1.35)	1.6 (0.5)	37.2 (20.8)
	Out	1.77 (0.23)	2.25 (0.15)	1.03 (0.21)	1.42 (0.22)	36.5 (5.6)	8.88 (1.11)	1.3 (0.2)	45.0 (13.9)
S01	In	1.21 (0.42)	1.69 (0.35)	0.76 (0.34)	0.98 (0.25)	26.5 (6.1)	9.2 (2.3)	2.7 (0.3)	6.9 (5.5)
	Out	1.94 (0.54)	1.67 (0.51)	1.25 (0.39)	0.89 (0.30)	27.7 (13.1)	11.4 (2.9)	2.5 (0.5)	13.2 (7.9)
In Average		1.66 (0.44)	2.39 (0.94)	1.14 (0.29)	1.99 (1.54)	38.6 (13.1)	10.7 (2.2)	2.9 (2.1)	34.9 (40.7)
Out Average		1.85 (0.57)	2.09 (0.56)	1.16 (0.32)	1.44 (0.67)	34.3 (5.8)	10.8 (2.2)	1.9 (0.8)	38.0 (33.7)
All Average		1.76 (0.49)	2.24 (0.75)	1.15 (0.29)	1.72 (1.16)	36.5 (18)	10.7 (2.4)	1.9 (2.3)	36.5 (37.0)

Total particulate metals in sea ice show a striking similarity to the bottom sediments when comparing the metal/Al ratios (Table 4). Select elements displayed some deviation between the ice core particulate materials and the bottom sediments. For example, while the Fe/Al ratio in the ice cores was higher than that found in bottom sediments it does match suspended matter ratios previously published in BOEM Reports from the first ANIMIDA project (Boehm, 2001). In all cases the metal/Al ratio determined for suspended particles in the ice cores displayed a correlation coefficient of 0.8 or greater, suggesting that sediment grain size is the primary variable controlling concentrations as has been previously shown by Trefry et al. (2003) (Figure 15).

Table 4. Metal to Al ratios for particulate trace metals in the sea ice cores collected at stations occupied during spring 2015 near the mouth of the Colville River.

Station	Mn/Al	V/Al	Fe/Al	Ni/Al	Cu/Al	Zn/Al	Cd/Al	Ba/Al	Pb/Al
Ice Cores	48	21.9	0.55	5.0	4.0	18.7	0.07	74.7	2.2
Beaufort Sea Sediment	50	22.7	0.49	6.4	5.8	20.5	0.06	72.9	2.4

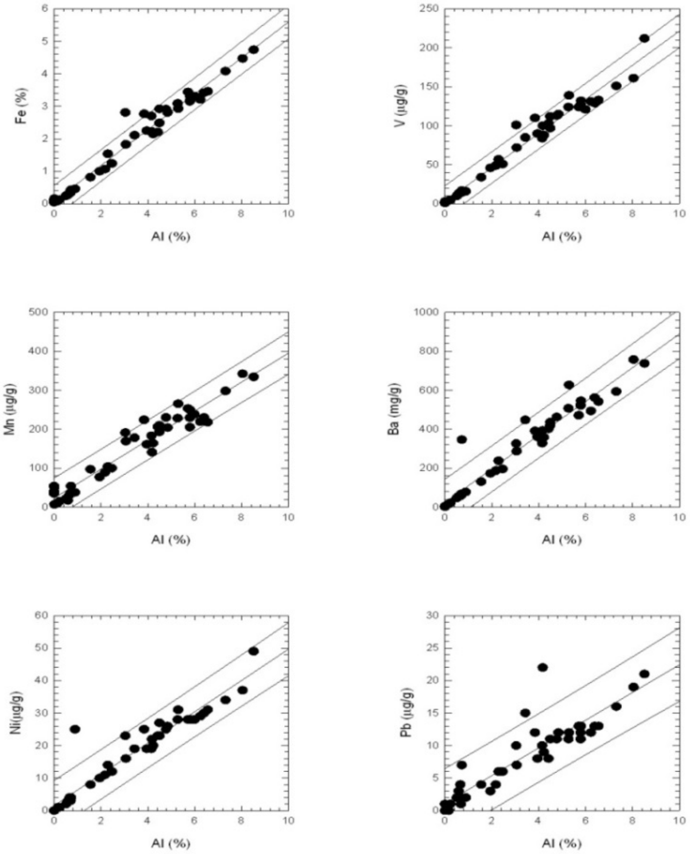

Figure 15. Metal to Al ratios in sea ice cores collected during May 2015 from the Colville River Delta. Regression lines and 99% prediction intervals are shown.

Trace metal concentrations in snow are presented in Table 5. For Ni, Cu, Zn, and Ba, concentrations in the snow were lower than those found in the sea ice and underlying water. Cadmium concentrations at stations E10, E11, and NM5 were elevated when compared to the remaining two samples but not when compared to the underlying seawater. Concentrations of dissolved Fe were higher in snow samples when compared to the sea ice and seawater. This is to be expected, as Fe has a lower solubility in saline solutions and particles in the snow are likely to leach metals and contribute to the dissolved fraction during the melting process. Concentrations of Pb, one of the most anthropogenically disturbed and labile metals on earth, were highly elevated in snow when compared published Arctic snow concentrations (Rember and Trefry, 2004), and to the underlying seawater. The close proximity of the snow samples to industrial activities suggests infrastructure present on the North Slope is a potential source of the observed snow Pb.

Table 5. Concentrations of dissolved trace metals in the snow collected at stations occupied during spring 2015 near the mouth of the Colville River. North Slope samples were taken during the ANIMIDA project in 2001 south of Prudhoe Bay.

Station	Fe (nM)	Ni (nM)	Cu (nM)	Zn (nM)	Cd (pM)	Ba (nM)	Pb (pM)
E11	77.2	0.30	0.23	1.09	309	2.29	132
NM5	108.7	0.51	0.53	3.36	342	3.45	232
E10	26.6	0.34	0.46	1.86	71.2	3.15	313
W07	63.6	0.19	0.18	0.94	6.03	2.15	105
S01	26.8	0.18	1.97	0.92	7.43	2.60	147
North Slope*	17.8(7.1)	-	0.91(0.47)	-	-	5.0(0.8)	30(7)

*Rember and Trefry, 2004.

DISCUSSION

Chukchi Sea Trace Metal Distributions

Ocean circulation plays an important role in the concentrations of dissolved and particulate metals throughout the world’s ocean. The convergence of water masses in the Chukchi Sea and Canada Basin is perhaps unparalleled. Sources of water to the Chukchi Sea include the Alaska Coastal Current, the Bering Sea (Pacific Water), the Anadyr Current, the East Siberian Current, melting sea ice and snow, and occasional Mackenzie River water. Water moving north from Bering Strait through the Chukchi Sea follows along three potential paths prior to entering the Canada Basin (Figure 2, bottom). These three pathways, while having different characteristics and variable residence times on the shelf (Weingartner et al., 2005a), eventually help shape the chemical composition of the upper 100–200 m of much of the Arctic Ocean. For example, Pacific Water, characterized by higher concentrations of dissolved phosphate relative to Atlantic Water, can be traced to the North Pole, into the Eurasian Basin, and eventually into the North Atlantic (Yamamoto-Kawai et al., 2006). Therefore, changes in the chemical composition of water masses due to varying residence times and freshwater sources in the Chukchi Sea can influence not only the regional chemical and biological inventories but, to some extent, the global inventories as well. 2

The data gathered on the 2013 *R/V Mirai* expedition were able to provide a basic understanding of the processes influencing metal concentrations on the shelf. We were able to conduct a cross-shelf transect from the Bering Strait (~66 °N) to the northern Chukchi at ~72 °N, a distance of over 500 km. In addition, we participated in a Japanese experiment to study the variability at one site on the northern end of the Chukchi Shelf (Station 41) over a two-week period.

Dissolved Fe and Zn data along the transect showed a decrease (from south to north) in these elements within the productive surface waters of the Chukchi Sea shelf. Differences between surface and subsurface waters were also evident. Figures 6A–C show these trends for dissolved Fe. Dissolved Zn data are not shown. Concentrations of surface (15 m) dissolved Fe decreased from ~ 9 nM at the Bering Strait station, to ~ 6 nM at the next northward station (Station 77), to ~ 1 nM at the northernmost station (Station 64). This change in dissolved Fe across the shelf is about an order of magnitude and may result from the biological uptake of this micronutrient in surface waters, the advection of a different water mass from the East Siberian Sea at the northern station, or a combination of these. In subsurface waters, concentrations of Fe over the shelf appear to vary in response to suspended particulate matter (Figure 5B), with higher concentrations of dissolved and particulate Fe in areas of lower beam transmission. This sedimentary input of dissolved and particulate Fe is constrained within the bottom layers (Figure 6A-C).

Similar to the Chukchi shelf observations, Aguilar-Islas et al. (2007) observed substantial decreases in cross-shelf dissolved Fe, and much higher concentrations of this micronutrient in subsurface waters, in the summer-stratified surface waters of the productive broad shelf of the Bering Sea. In combination, these data sets suggest that dissolved Fe has a sedimentary source in these productive shelves, but vertical input into surface waters is inhibited by stratification. The trends in the dissolved Zn data are analogous to the dissolved Fe data, with the highest concentrations found in the Bering Strait and at depth at the stations further north (data not shown). Low surface concentrations of micronutrients such as Fe and Zn are expected in productive regions due to their biological removal. In bottom waters over shallow shelves, elevated concentrations of dissolved micronutrients are consistent with sedimentary remineralization of organic matter and the subsequent flux into the water column.

The concentrations of dissolved Mn along this transect were in contrast to those of dissolved Fe and Zn. Manganese is also an essential micronutrient; however, its concentration in the water column can be substantially increased in surface waters by photo-reduction of suspended particles. Similar to Fe, sedimentary input can enhance dissolved and particulate Mn. In the shallow waters of the Chukchi Sea, dissolved Mn concentrations throughout the water column increased northward along the transect (~11 nM at Bering Strait (Station 84) to ~15 nM at Station 77, and > 20 nM at Station 64) while concentrations of particulate Mn decreased in the upper 25 m. (Figure 6D–F). These results suggest that, in combination with water circulation, the accumulation of dissolved trace metals over the Chukchi shelf (whether on the subsurface or throughout the water column) provides a mechanism for the input of these elements into Arctic basins. Inputs from Arctic shelves likely influence the inventory of trace metals in Arctic basins and the associated sea ice that incorporates dissolved constituents into brine pockets. A trace metal signal from shelf inputs was observed in water profiles collected offshore in 2010 and 2013 (Aguilar-Islas et al., 2013) and will be described in the following discussion.

Similarly to dissolved Mn, the concentration of dissolved Cu increased from south to north, although not to the same extent (data not shown). Like Mn, dissolved Cu concentrations had only slight variations with depth for a given station. Dissolved Cu was on average 2.7, 2.8 and 4.4 nM at Stations 84, 77, and 64, respectively. Unlike Mn, particulate Cu is not susceptible to photo-reduction in surface waters, and the higher concentrations observed in the northern Chukchi Sea could have resulted from water advected from Siberian Shelves into the region. If water from Siberian Shelves is higher in dissolved Cu, this element might serve as a tracer of this water mass. Concentrations of dissolved Ni were high in the study area (data not shown) and consistent with concentrations found in the North Pacific. Concentrations varied by only ~5% for all samples among the three shelf stations, suggesting that there is neither an important removal process nor a varying source of dissolved Ni to the Chukchi Sea shelf during summer.

The reoccupation of a single station over the time of the field effort was extremely valuable as it provided an opportunity to determine short term variability used to inform interpretation of representative profiles from sites occupied once during the expedition. In summer 2013, we were able to reoccupy Station 41 on the northern Chukchi shelf multiple times. The CTD data collected at Station 41 clearly show how dynamic the water column can be over a short period of time. The first week that the site was occupied shows a narrow (~10 m) but somewhat variable benthic boundary layer characterized by denser water with lower oxygen concentrations, generally < 275 μM, and lower % beam transmission (higher suspended particles) (Figure 7). A front of higher density surface water moved through the site toward the end of the first week and coincided with an enhanced mixing of the benthic boundary layer (Figure 7). The front caused changes in the dissolved oxygen concentration and the suspended particle content. As a result, the benthic boundary layer was ventilated and oxygen concentrations increased to > 300 μM. Particle resuspension was enhanced with suspended particles penetrating further up into the water column over the same period of time. When the site was reoccupied a week later, less dense water had returned at the surface, oxygen concentrations in the bottom waters were again <250 μM, and % beam transmission had also decreased.

Trace element profiles collected during the occupation of Station 41 suggest that in these shallow waters, concentrations can vary greatly depending on external variables such as fronts and associated events. Trace metal profiles were initially collected every other day, but collection was changed to daily after observing the variability in CTD profiles over the first week of the occupation. Initially, concentrations of dissolved metals did not vary substantially in the upper 30 m. Concentrations were more dynamic in the bottom boundary layer where the interaction between the water column and the sediments alters concentrations of some metals at rates that can be observed on daily cycles (Figure 8). As the above-mentioned front progressed into the study area, concentrations of dissolved Ni (data not shown) and labile particulate Mn increased in surface waters, marking the potential advection of a different water mass. Deeper in the water column, the enhanced mixing that coincided with the front caused increased concentrations of dissolved and leachable Fe, Mn (Figure 8), and Ni (data not shown). In some cases, during the strongest mixing, the higher concentrations permeated through the entire water column as it became less stratified.

The extended occupation of Station 41 showed that the oceanographic conditions in the Chukchi Sea can change substantially over very short periods of time, especially bottom water and the suspended particulate metal fractions. The chemical and physical properties measured throughout the entire water column were altered in some way during the time the station was sampled. This can lead to several conclusions. Single profiles are truly only a snapshot of the oceanographic environment in the Chukchi Sea and extrapolation of these data to explain weekly, monthly, or annual trends has the potential to lead to large uncertainties in data interpretation or modeling. Connecting the dots along transects in a complex oceanographic regime such as the Chukchi Sea, where currents and sources of water are in constant flux, can lead to difficulties in fully understanding how the northern and southern regions of the Chukchi Sea interact. While there are well-defined current flows, there also seem to be events that can dramatically shift water column properties such that the concentrations of particles, dissolved metals, density, and oxygen can change from day to day.

Few profiles of dissolved metals were available in the literature for the Canada Basin, particularly prior to the 2013 *R/V Mirai* cruise. We now have several profiles from 2010 and 2013 for waters deeper than 1000 m and profiles from others (e.g., Nakayama et al., 2011) that can be used to infer how shelf processes impact the deep basin. The Canada Basin is unique in that Pacific Water, modified by its transect through the Bering and Chukchi Seas, overlays Atlantic Water entering through Fram Strait or the Barents Sea. By the time the Atlantic Water reaches the Canada Basin, dissolved metal concentrations in the core of this water mass do not appear to vary substantially. These waters have traveled several thousand kilometers along the margin and seem generally unaffected by local exchange with the margin or local particle export (Figure 9). At offshore stations, dissolved metals showed variability in the upper 300 m, reflecting surface influences from melting sea ice and either enhancement or scavenging at mid-depths from shelf waters advected offshore and mixing with basin waters. Below 300 m, the approximate top range of the Atlantic Water layer, dissolved metal concentrations became much more uniform among the various profiles. The most uniform concentrations were observed within the core of the Atlantic Water layer, underscoring the minimal spatial and interannual variability.

In surface waters down to approximately 250 m, where Pacific Water and shelf influences determine offshore profiles, metal concentrations showed considerable spatial variability among stations. These surface waters also tended to be more concentrated in dissolved metals. For example, concentrations of dissolved Cu and Ni were 2–3 times higher in layers influenced by Pacific Water than they are in the depths below (Figure 9). A similar trend exists in the Fe and

Mn data where in some cases concentrations are elevated in the layer between 150 and 250 m, particularly at stations closer to the shelf (Figure 9). This denser ‘cold layer’ is Pacific Winter Water and is likely indicative of the export of dissolved Fe and Mn found in the bottom waters on the shelf. Fe and Mn may accumulate over the winter months when organic matter produced over the summer months is consumed in the sediment and diagenetic processes result in a flux of these metals from the sediment to bottom waters. Overall, dissolved Fe and Mn concentrations are greatly reduced in the basin when compared to shelf water likely due to dilution, uptake, and scavenging, but the peaks do coincide with water masses of known shelf origin (e.g., Aguilar-Islas et al., 2013; Nakayama et al., 2011), which suggests a shelf source.

These noted peaks and higher concentrations suggest that water masses on the shelf are directly exported to the deep basins and that shelf processes can influence the chemical composition of the deep basin. This would include the export of nutrients, heat, salt, and, in this case, elevated levels of trace metals, which can be biologically important micronutrients.

Sea Ice Tank Experiments

Over the past several decades our understanding of trace metal concentrations in the nearshore Beaufort Sea environment has gradually increased with the continuation of numerous projects funded by BOEM and other funding agencies. Until recently, due to the inability to collect clean samples, very little was known about the concentrations of dissolved and particulate metals in sea ice. The primary goal of this project was to build and test an ice corer capable of collecting trace-metal-clean samples. Initially, we intended to build a titanium corer similar to designs used by sea ice researchers in other countries. This proved to be exceedingly difficult given costs, and problems sourcing materials and finding welders capable of working with titanium. Therefore, we shifted our focus to a corer built primarily out of plastic but strengthened with sections of titanium and cutting parts made from titanium. Initial tests with a prototype showed that the design worked very well but construction materials needed to be altered due to the inability to acid wash some of the plastics used in the original design. Given the time constraints of the project and the delays in manufacturing, we decided to move forward with a scaled-back version of the tank experiments. These experiments were performed by growing sea ice from filtered seawater in a 200-L tank in a cold room (-5^{o}C) under trace-metal-clean conditions. The ice from the tank experiments was not collected with a corer; instead, we were able to grow cores inside individual polycarbonate sleeves and harvest them weekly over a month-long period. By growing the cores rather than trying to core from a tank, the operation was cleaner (with respect to trace metals) and the conditions were likely a good representation of initial ice growth stages like those taking place in the nearshore Beaufort Sea during the transition from an open-water state to an ice-covered ocean.

Concentrations of dissolved metals in the filtered seawater used in the experiment are within the range we would expect to find in the Beaufort Sea. Due to time limitations, we decided to concentrate on three metals, Fe, Cu, and Zn. The metals selected are biologically important as they are essential micronutrients and key to biological production, but have different chemistries in seawater. In addition, Fe and Zn are easy to contaminate, and elevated values in sea ice would signify that a sample was comprised during the growth or the sampling process. The filtered seawater did not contain phytoplankton, this removed biological processes that are present during natural sea ice formation, but allowed us to concentrate on the chemical processes that influence the cycling of trace metals in sea ice.

In the first experiment, concentrations of dissolved Fe in the tank (filtered after collection) did not vary substantially, concentrations ranged from 0.55 to 0.7 nM throughout the entire experiment (Figure 11A). Dissolved concentrations of Fe in the ice tended to decrease over the duration of the experiment from ~0.8 nM to less than 0.5 nM. During the experiment, concentrations of dissolved Fe started out as being elevated in the sea ice relative to the seawater in the tank. Over the one-month period, this relationship reversed and, in the last two samples, concentrations were higher in the seawater than in the sea ice. Although preliminary, these results suggest that, as sea ice is forming and brine is rejected, dissolved Fe may also be rejected, decreasing the concentration over time in the ice matrix. The complication with the Fe dataset is that an unacidified solution containing Fe will tend to decrease (slightly) in concentration as Fe is adsorbed onto the walls of the container, in this case, the tank. Therefore, tank concentrations could reflect container artifacts, as well as natural processes. The Fe data suggest that no observable contamination from the tank or sample handling was encountered during the experiment.

Copper is not subject to the same adsorption problems as Fe and a more conclusive trend is illustrated in Figure 11B. During the first two weeks of the experiments, there was no substantial change in dissolved or unfiltered Cu in the tank or the ice. However, in the final two weeks, concentrations of dissolved and unfiltered Cu increased gradually in the tank, while concentrations in the sea ice decreased. These trends indicate that Cu in the tank, both in dissolved and unfiltered samples increased (concentrated) as ice was formed and suggests that, along with brines, Cu was being excluded from the ice during sea ice formation.

To conduct the second experiment, the ice from the first tank experiment was thawed and mixed thoroughly using a large Teflon stirring bar on a large stirring plate. Canadian CRM (MESS) sediment (originally sourced from the Canadian Beaufort Sea) was added to the tank with continued stirring. The initial results from the experiment showed an immediate increase in the concentration of dissolved Fe in the tank as labile Fe, likely from the particles transitioning into the colloidal phase (Figure 11C). The exchange of Fe between colloidal and particulate phases is well known for marine waters. Concentrations of dissolved Fe in the ice cores ranged from 2.3 to 41 nM with concentrations remaining relatively constant during the first two weeks and then doubling to an average of 36 nM before decreasing to ~2.5 nM during week four. A similar trend was noted in the unfiltered sea ice fraction. Although this trend is difficult to explain based on this limited dataset, one potential explanation is that this particle experiment demonstrates the heterogeneity of sea ice and highlights that two cores collected side by side can have very different properties. This may be magnified in a closed system where some cores could potentially contain more sediment than others depending on the amount of sediment incorporated as sea ice formed. However, another potential explanation is that sediment is continually entrained into the sea ice as it grows (first two weeks), and Fe is continually leached from the particles within the sea ice, increasing the concentration in the unfiltered fraction in the ice. As the ice grows, Fe is gradually released during brine rejection and the concentration decreases over time. In this case, the concentration of Fe in the ice cores in the unfiltered fraction decreased from ~175 nM in week two to 33 nM in week four. An important distinction between this experiment with particles and the previous tank experiment with filtered seawater is that concentrations in this experiment were at least an order of magnitude higher due to the addition of the sediment, which allowed for exchange between dissolved and particulate phases.

Similarities between the first and second tank experiments for Cu were striking. Overall, tank concentrations were slightly higher in the second experiment and generally increased over time, but these observations highlight the limited source of Cu from sediments. Concentrations of Cu in the ice cores decreased over time from a high of 6.7 nM in the first set of cores to a low of 2.1 nM in the final core collected.

Although this dataset is somewhat limited due to the difficulty in setting up a large-scale clean experiment, the results suggest that concentrations of metals (in this case Fe and Cu) decrease over time whether the original seawater contains suspended sediment or not. This trend was also observed for Zn in filtered and unfiltered samples (data not shown). The results seem to be counterintuitive as metals should be more soluble in ‘fresher’ sea ice than in the higher salinity seawater below. Possible conclusions are that metals are excluded during sea ice formation by a physical process such as brine rejection, or that they precipitate in high salinity brine pockets. A more detailed study that included biological parameters would be required to fully investigate the impact of sea ice formation and brine rejection on the evolution of trace metals concentrations during the ice growing season.

Partitioning of metals between the ice and the water in the tank suggests that, in the absence of particles, there were distinct differences in abundance between the three metals studied; however, the trend for different elements can be similar. In the first experiment, which used filtered seawater, the data indicate that on average 20–30% of the Fe in the sea ice was dissolved with the remainder classified as acid labile particulate (>0.4 μm) Fe, as unfiltered samples were acidified. Therefore, the data suggest that some of the dissolved Fe aggregates or precipitates as sea ice is forming from clean filtered seawater. Similar results were found for Zn and Cu but with larger fractions in the dissolved phase, approximately 52% and 40%, respectively. When particles were added (Figure 11D), a decrease in dissolved Fe, Cu, and Zn was observed in the sea ice between week two and week three. Yet, in the two subsequent sampling periods, concentrations of dissolved metals in the sea ice increased relative to acid labile particulate metals. These results suggest two scenarios: 1) particles formed during the freezing process, or from included sediment, are rejected during the process of ice formation/brine rejection, or 2) particles in the acid labile particulate fraction are leaching into the ice cores and increasing the dissolved concentrations. However, this is not substantiated by the ice core data.

Field Samples

Dissolved trace metals in seawater

In May 2015, five stations near the mouth of the Colville River were occupied at a time coincident with the ANIMIDA III sampling effort. As these are some of the first measurements of dissolved metals in seawater and sea ice in the coastal Beaufort Sea during the spring, our primary focus was on sample handling and cleanliness to be sure we collected a representative uncontaminated sample. With respect to ice cores, we designed the study to address heterogeneity among ice cores collected at each site. Due to the effort required to collect samples at each site, and given the limited amount of time we had after losing a day to weather, we decided to limit the size of the study area in lieu of more samples, and thus we collected 50 cores in total from five stations.

To avoid contamination of the seawater, the salinity and temperature profiles collected during field sampling were taken from separate ice holes (within 20 m of the holes used to pump seawater for the trace metal samples). Overall, the profiles resemble a well-mixed water column at the shallowest station (~6 m, S01), with other stations showing a slight increase in salinity (<0.5 psu) in the bottom water (E11, NM5, and W07). These more saline and colder bottom waters are likely the results of brine drainage from sea ice formation over the 2014–2015 winter months.

Few data sets exist that include dissolved trace metals for under-ice seawater collected during the spring on Arctic shelves. We are aware of a few samples collected during cANIMIDA 2006 at the time of the spring freshet. We collected a total of eight seawater samples ranging from depths of 2–9 m (Table 2) from the five stations. When compared to concentrations of several samples collected during the open-water period between 2000 and 2006, during the ANIMIDA and cANIMIDA projects, there were a few important differences. For example, concentrations of dissolved Cd were 63% higher under the ice than they were during the summer. The higher concentrations in the winter ice-covered months were likely related to biological respiration of organic materials produced during the summer. Relative to concentrations of dissolved Pb observed in the summer months (44.5±14 pM) during the ANIMIDA and cANIMIDA projects (Trefry et al., 2004; 2009), our observed spring Pb concentrations were approximately 66% lower (15.1 ± 3.7 pM) and compare well with some of the lower concentrations observed in 2006 (>10 pM, Trefry et al., 2009). Dissolved Pb is highly particle reactive and when isolated from inputs such as the atmosphere and rivers during the winter months, concentrations are expected to decrease as Pb is stripped from the water column over time. Higher Pb concentrations are commonly found during the summer months from riverine and atmospheric inputs directly into seawater. The concentration of dissolved Ba exhibited little variability among the eight samples collected, with concentrations averaging 76.8 ± 1.7 nM. These concentrations were not influenced by river water concentrations as the rivers had yet to begin discharging into the coast. During the cANIMIDA project in 2006, samples collected at depths greater than 2 m during the freshet were on average 84 nM in dissolved Ba, while much higher concentrations of 152 nM were observed in surface waters (Trefry et al., 2009), reflecting the riverine input of this element. Concentrations below 2 m from 2006, compared well with our observed spring concentrations, and the slightly lower values of dissolved Ba we observed in spring may reflect interannual variability of this inner shelf water. For example, the surface mixed layer of the Canada Basin averages approximately 75 nM (Guay and Faulkner, 1997) and summer Pacific Water averages between 65 and 80 nM (Guay et al., 2009). There has also been evidence in the Arctic for drawdown of Ba on the shelves as organisms can substitute Ba for Ca when building shells (Abrahamsen et al., 2009).

Concentrations of dissolved Cu averaged ~5.5 nM in water deeper than 2 m in 2006 (Trefry et al., 2009). Data in this study for dissolved Cu were very similar, averaging 5.7 ± 0.17 nM for the eight samples. Surface water during the spring freshet can increase to over 8 nM dissolved Cu, but once mixed with deep waters during the summer months, it was found to average approximately 6.3 ± 1.9 nM (Trefry et al., 2009). Concentrations of dissolved Zn from samples collected in 2015 are slightly lower and less variable (3.63 ± 0.44 nM) than those collected from waters below 2 m depth by the cANIMIDA project in 2006 (4.89 ± 1.22 nM). This difference may be related to variability in the biological drawdown of Zn between the two years, or possibly sampling locale and depth, as Zn (and Fe, Mn) exhibited greater stratification with depth than other elements.

Trace metals measured as a part of this study that were not a part of prior under-ice investigations included Fe, Mn, and Ni. Concentrations of dissolved Ni were high even when compared to deep open ocean concentrations, 14.1 ± 0.75 nM (Boehm, 2001). Nickel normally has a nutrient type distribution in the ocean similar to Cd, increasing with depth as organic matter is regenerated by bacterial respiration. Therefore, we suggest that, like Cd, the higher concentrations observed in the winter under the ice were the result of the respiration of organic matter. There are no historical data for dissolved Fe and Mn in the coastal Beaufort Sea during the ice-covered periods. Along with Zn, these two elements displayed the highest variability in concentrations between surface waters (under the ice) and water from the benthic boundary layer. The concentration gradient from surface waters to depth likely reflects sedimentary inputs from diagenetic processes occurring at the sediment-water interface where concentrations can be more than double concentrations in the upper water column. Overall concentrations of dissolved Mn were high (27.8 ± 6.2 nM) when compared to the highest values found in the Chukchi Sea (~20 nM) during the fall of 2013; however, the higher concentrations likely reflect convective mixing of bottom waters (influenced by diagenetic processes) up into the water column over the winter months and a lack of wind or important advective currents to move the water during that time period. The range of concentrations for dissolved Fe was greater than any other element, from 2.86–11.5 nM. The range of concentrations was similar to those found on the Chukchi Sea shelf in 2013, as is the trend of higher concentrations near the sediment water interface relative to waters directly below the ice.

Trace metals in sea ice

The continual decline of sea ice extent (and volume) has received a large research focus in recent years. Many of these studies were able to be conducted using traditional instrumentation while others required substantial changes to established methods of sample collection. Sometimes these changes were due to the harsh conditions found in the Arctic, other times tools commonly used by Arctic scientists needed modifications to study variables sensitive to contamination brought on by sampling. Thirty to forty years ago, trace metals chemists interested in oceanographic processes had to learn to sample the ocean cleanly using variations of existing technology. The story is the same today as we begin to investigate the concentrations of trace metals in sea ice to better understand how melting ice will change the chemical and biological properties/processes occurring in the euphotic zone in the Arctic Ocean.

A major goal of this project was to ascertain a protocol that would allow us to assign representative trace metal concentrations to sea ice. Sea ice is well known for being highly heterogeneous with respect to some physical and biological parameters. If the same were true for trace metals, then gaining any considerable understanding of sources and sinks would be difficult if not impossible without representative values.

Sea ice formation is complex and highly difficult to predict, as ice does not grow at a constant rate and as a single slab. Instead, smaller pieces of ice (grease, pancakes, etc.) grow, often overlapping and eventually forming a skin on the surface of the ocean. If that initial skin is not broken apart by other ice floes or a storm then the ice will grow from below until it reaches its full thickness in spring. At this point, it is easy to understand how sea ice could be heterogeneous, as ice often breaks apart only to be replaced by other ice later. In addition, some ice floes travel long distances while forming so they are continually adding layers from seawater of different sources. Ice that forms in the nearshore environment is likely to contain trace metals at much higher concentrations than ice formed over the deep basins because periodic fall storms are more likely to create near complete mixing of the water column and high turbidity.

The ice we sampled in the spring of 2015 was land-fast ice that likely experienced various water column conditions during its winter growth. Concentrations of total suspended solids in the 50 sea ice cores ranged from ~1.5 to almost 180 mg/L. While there was a large variability between the highest and lowest concentrations, the average concentration of TSS in the ten ice cores collected at each station was relatively small. For example, at station E11, the average for the two groupings of cores, at adjacent and random collection locations, were 18.7 mg/L and 12.3 mg/L respectively. At station NM5, the cores within the square meter contained 77.8 mg/L relative to 70.4 mg/L for cores collected randomly outside the one square meter. Similar results were found for the other stations, where the average of ten cores at each station seems to provide a reasonable estimation of the variability in total suspended solids. Our data suggest that, while there is variability among and within stations, the within station variability can be minimized by collecting a few samples randomly throughout a station. To fully understand the impact of TSS on the concentrations of dissolved metals, a more detailed study would be needed where ice cores were sectioned into 10–20 cm segments rather than melted in bulk. Yet, our bulk results add an important component to the understanding of trace metal cycles in the coastal Beaufort Sea. Much of the previous work done in and around Prudhoe Bay has been predicated on providing an understanding of the natural environment in order to monitor the impacts of onshore and offshore development and, to some extent, climate change in this region. These data add one more component to conceptual and applied models.

The ice sampled during the 2015 field effort was approximately 7–8 months old. When the trends in the much shorter tank experiments are extrapolated over a longer period of time, we would predict that concentrations of metals in the sea ice should decrease if these closed-system experiments are representative of sea ice growing naturally. When comparing the average trace metal concentrations from the 50 sea ice cores measured to historical fall seawater and spring under-ice seawater concentrations, the trend was similar to what would be predicted. Sea ice concentrations are, in some cases, more than an order of magnitude lower that the seawater from which the ice formed. For example, concentrations of dissolved Cd in sea ice averaged 36.5 ± 18.0 pM when all the cores were averaged. Typical fall concentrations are approximately eight fold higher, whereas seawater under the ice is 22 times greater than the sea ice concentration. Other metals, such as Ba and Pb also exhibit at least an order of magnitude shift between the average seawater concentrations found in the fall relative to those determined for sea ice. Average concentrations of Fe, Ni, Cu, and Zn are all lower in the sea ice than either fall or spring seawater concentrations but not as depleted as Cd, Ba, or Pb. (Trefry et al., 2004; Trefry et al., 2009; Boehm, 2001). The partitioning of each of these metals between seawater and ice over winter and spring suggests that there is a process or multiple processes that are excluding, diminishing, or reducing the concentrations of dissolved metals in sea ice prior to summer melting.

Mn was the one exception to the extreme partitioning between seawater and sea ice. The average concentration of dissolved Mn in sea ice samples was 22.5 nM, which is only 7% lower than the average surface seawater under the ice (< 2.5 m) and within 20% when the whole water column is averaged. While our data do not provide enough information to explain the different behavior of dissolved Mn, we suggest either the removal mechanism is considerably different for Mn or there is a source of (labile) Mn in the sea ice that counteracts the removal processes.

This study was primarily designed to gather preliminary data to understand broadly the interaction between surface seawater and sea ice and the potential for sea ice to influence the concentrations of metals in surface waters. The first hurdle was to create a field tool capable of collecting a clean sea ice sample and eliminating the need to manipulate the cores postcollection. We also attempted to find field sites with proximity to previous stations occupied by the ANIMIDA III study and that had ice suitably flat and large enough to allow trace metal sample collection and CTD casts to occur simultaneously. Given the relatively low concentration of trace metals in the ice samples collected, and the small variability in dissolved trace metal concentrations in cores collected within a site and among all the sites, it appears that the newly designed corer works very well.

A secondary goal of the project was to understand, given the heterogeneity of sea ice, how many cores need to be collected to fully characterize a sampling site. The variability in concentrations between the cores collected within a specified area, and those selected randomly, suggest that five cores per site are adequate to capture a representative number for a chosen area. Finally, the collection of representative samples of sea ice provides data that can be used by managers (and others) interested in background concentrations of trace metals in the nearshore Beaufort Sea prior to substantial environmental changes, be they natural or man-made.

PROJECT OUTREACH

Graduate student Vincent Domena traveled to St. Paul Island for Bering Sea Days. This program was developed by the Aleut Community of St. Paul Island (Tribal Government). The five day program focused on giving K–12 students the opportunity to learn about marine science and marine science careers by bringing in scientists to present hands-on activities. Mr. Domena presented a module on sea ice, where among other activities, students took a field trip to a cold chamber and grew ice. They then looked at the crystalline stucture of the ice including brine channels, took salinities of the ice and the remaining unfrozen water. Students learned about our Beaufort Sea ice project along with processes that occur during ice formation, such as brine rejection and incorporation of impurities. They also learned about processes that take place in the spring as ice warms and the melting begins. The activities presented were well received and provided a outlet for Mr. Domena to interact with students and pass on what he has learned during the time spent working on this project (Figure 16).

Figure 16. Graduate student Vincent Domena lectures to students during Bering Sea Days on St. Paul Island in October 2016.

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STUDY PRODUCTS

Rember, R.D., Aguilar-Islas, A.M. Distribution and behavior of select trace metals in Beaufort Sea ice. In: University of Alaska Coastal Marine Institute Annual Report 20, Calendar Year 2013. Fairbanks, AK. OCS Study BOEM 2014-0052.

Aguilar-Islas, A.M., Rember, R.D. Distribution and behavior of select trace metals in Beaufort Sea ice: preliminary findings. CMI Annual Review oral presentation, Anchorage, AK, January 15, 2014.

Aguilar-Islas, A.M., Seguret, M., Rember, R.D., Nishino, S. Sedimentary input of trace metals from the Chukchi Shelf. 2014 Fall Meeting AGU, San Francisco, CA, December 15–19, 2014.

Aguilar-Islas, A.M., Rember, R.D. Distribution and behavior of select trace metals in Beaufort Sea ice: preliminary findings. CMI Annual Review oral presentation, Anchorage, AK, January 23, 2015.

Rember, R.D., Aguilar-Islas, A.M. Distribution and behavior of select trace metals in Beaufort Sea ice. In: University of Alaska Coastal Marine Institute Annual Report 21, Calendar Year 2014. Fairbanks, AK. OCS Study BOEM 2015-015.

Domena, V., Aguilar-Islas, A.M., Rember, R.D. Dissolved and particulate trace metal concentrations in sea ice at Oliktok Point, Alaska. Alaska Marine Science Symposium, Anchorage, AK, January 26, 2016.

Aguilar-Islas, A.M., Rember, R.D. Distribution and behavior of select trace metals in Beaufort Sea ice: preliminary findings. CMI Annual Review oral presentation, Anchorage, AK, January 29, 2016.

Rember, R.D., Aguilar-Islas, A.M. Distribution and behavior of select trace metals in Beaufort Sea ice. In: University of Alaska Coastal Marine Institute Annual Report 22, Calendar Year 2015. Fairbanks, AK. OCS Study BOEM 2016-013.

REFERENCES

Abrahamsen, E.P., M. Meredith, K. Faulkner, S. Torres-Valdes, M. Leng, M. Alkire, S. Bacon, S. Laxon, I. Polyakov, and V. Ivanov (2009). Tracer derived freshwater composition of the Siberian shelf and slope following the extreme Arctic summer of 2007. Geophysical Research Letters, 36(7).

Aguilar-Islas, A.M., R.D. Rember, S. Nishino, and M. Itoh (2013). Partitioning and lateral transport of iron to the Canada Basin. Polar Science, 7(2), 82–99.

Aguilar-Islas, A.M., R.D. Rember, C.W. Mordy, and J. Wu (2008). Sea ice-derived dissolved iron and its potential influence on the spring algal bloom in the Bering Sea. Geophysical Research Letters, 35(24).

Aguilar-Islas, A.M., M.P. Hurst, K.N. Buck, B. Sohst, G.J. Smith, M.C. Lohan, and K.W. Bruland (2007). Micro- and macronutrients in the southeastern Bering Sea: Insight into iron-replete and iron-depleted regimes. Progress in Oceanography, 73, 99–126.

Chang, B.X., and A.H. Devol (2009). Seasonal and spatial patterns of sedimentary denitrification rates in the Chukchi Sea. Deep Sea Research Part II: Topical Studies in Oceanography, 56(17), 1339–1350.

Boehm, P (2001). ANIMIDA Phase I: Arctic nearshore characterization and monitoring of the physical environment in the Northstar and Liberty development areas. Final Report OCS Study MMS 2001-104. Prepared by Arthur D. Little, Inc. for USDOI, MMS Alaska OCS Region, Anchorage, AK.

Brown, Z.W., K.L. Casciotti, R.S. Pickart, J.H. Swift, and K.R. Arrigo (2015). Aspects of the marine nitrogen cycle of the Chukchi Sea shelf and Canada Basin. Deep Sea Research Part II: Topical Studies in Oceanography, 118, 73–87.

Berger, C.J.M., S.M. Lippiatt, M.G. Lawrence, and K.W. Bruland (2008). Application of a chemical leach technique for estimating labile particulate aluminum, iron, and manganese in the Columbia River plume and coastal waters off Oregon and Washington, Journal of Geophysical Research, 113, C00B01. doi:10.1029/2007JC004703.

Crecelius, E.A., J.H. Trefry, M.S. Steinhauer, and P.D. Boehm (1991). Trace metals in sediments from the inner continental shelf of the western Beaufort Sea. Environmental Geology and Water Sciences, 18(1) 71–79.

Darby, D.A., W.B. Myers, M. Jakobsson, and I. Rigor (2011). Modern dirty sea ice characteristics and sources: The role of anchor ice. Journal of Geophysical Research, 116, C09008.

Douglas, T.A., M. Sturm, W.R. Simpson, J.D. Blum, L. Alvarez-Aviles, G.J. Keeler, D.K. Perovich, A. Biswas, and K. Johnson (2008). Influence of snow and ice crystal formation and accumulation on mercury deposition to the Arctic. Environmental Science and Technology 42(5), 1542–1551.

Garbarino, J.R., E. Snyder-Conn, T.J. Leiker, and G.L. Hoffman (2002). Contaminants in arctic snow collected over northwest Alaskan sea ice. Water, Air, and Soil Pollution, 139:183. doi:10.1023/A:1015808008298.

Grotti, M., F. Soggia, C. Ianni, and R. Frache (2005). Trace metals distributions in coastal sea ice of Terra Nova Bay, Ross Sea, Antarctica. Antarctic Science, 17(2), 289–300.

Guay C.K., and K.K. Falkner (1997). Barium as a tracer of Arctic halocline and river waters. Deep Sea Research Part II: Topical Studies in Oceanography, 44(8), 1543–1569.

Guay, C.K., F.A. McLaughlin, and M. Yamamoto-Kawai (2009). Differentiating fluvial components of upper Canada Basin waters on the basis of measurements of dissolved barium combined with other physical and chemical tracers. Journal of Geophysical Research, 114, C00A09.

Kanna, N., and J. Nishioka (2016). Bio-availability of iron derived from subarctic first-year ice. Marine Chemistry, 186, 189–197. doi:10.1016/j.marchem.2016.09.009.

Lannuzel, D., V. Schoemann, J. de Jong, J.-L. Tison, and L. Chou (2007). Distribution and biogeochemical behaviour of iron in the East Antarctic sea ice. Marine Chemistry, 106(1–2), 18–32.

Lannuzel, D., A.R. Bowie, P.C. van der Merwe, A.T. Townsend, and V. Schoemann (2011). Distribution of dissolved and particulate metals in Antarctic sea ice. Marine Chemistry, 124(1–4), 134–146.

Holemann, J. A., M. Schirmacher, and A. Prange (1999). Dissolved and particulate trace elements in newly formed ice from the Laptev Sea (Transdrift III, October 1995). In: Land–Ocean Systems in the Siberian Arctic: Dynamics and History, Eds: H. Kassens, H.A. Bauch, I.A. Dmitrenko, H. Eicken, H.-W. Hubberten, M. Melles, J. Thiede, and L.A. Timokhov, Springer Verlag, Berlin. pp. 101–112.

Nakayama, Y., S. Fujita, K. Kuma, and K. Shimada (2011). Iron and humic-type fluorescent dissolved matter in the Chukchi Sea and Canada Basin of the western Arctic Ocean. Geophysical Research Letters, 116.

Rember, R.D., and J.H. Trefry (2004). Increased concentrations of dissolved trace metals and organic carbon during snowmelt in rivers of the Alaskan Arctic. Geochimica et Cosmochimica Acta, 68(3), 477–489.

Stierle, A.P., and H. Eicken (2002). Sediment inclusions in Alaskan coastal sea ice: Spatial distribution, interannual variability, and entrainment requirements. Arctic, Antarctic, and Alpine Research, 34(4), 465–476.

Trefry, J., R. Rember, R. Trocine, and J. Brown (2003). Trace metals in sediments near offshore oil exploration and production sites in the Alaskan Arctic. Environmental Geology, 45(2), 149–160.

Trefry, J.H., R.D. Rember, R.P. Trocine, and J.S. Brown (2004). Partitioning of potential contaminants between dissolved and particulate phases in waters of the coastal Beaufort Sea. ANIMIDA Task Order 7 Final Report. OCS Study MMS 2004-031, U.S. Department of Interior, Anchorage, AK.

Trefry, J.H., R.P. Trocine, M.B. Alkire, C.M. Semmler, M. Savioe, and R.D. Rember (2009). Sources, concentrations, composition, partitioning and dispersion pathways for suspended sediments and potential metal contaminants in the coastal Beaufort Sea. Final Report to USDOI MMS, OCS Study MMS 2009-014.

Weingartner, T., K. Aagaard, R. Woodgate, S. Danielson, Y. Sasaki, and D. Cavalieri (2005a). Circulation on the north central Chukchi Sea shelf. Deep-Sea Research Part II: Topical Studies in Oceanography, 52, 3150–3174.

Weingartner, T.M., S.L. Danielson, and T.C. Royer (2005b). Freshwater variability and predictability in the Alaskan Coastal Current. Deep-Sea Research Part II, 52(2-Jan), 169–191. doi: 10.1016/J.Dsr2.2004.09.030.

Yamamoto-Kawai, M., E. Carmack, and F. Mclaughlin (2006). Nitrogen balance and Arctic throughflow. Nature, 443(7107), 44. doi: 10.1038/443043a.

APPENDIX

Table A1. Certified CRM concentrations and values obtained during this study.

Element	HISS-1 (mg/kg)	This Study (mg/kg)	MESS-3 (mg/kg)	This Study (mg/kg)	NASS-6 (μg/L)	This Study (μg/L)
V	6.8±0.78	6.1±0.37	243±10	201±6	-	-
Al	0.73±0.05	0.60±0.01	8.59±0.23	6.51 ±	-	-
Fe	0.25±0.01	0.22±0.01	4.34±0.11	4.22±0.13	0.495±0.046	0.490±0.003
Mn	66.1±4.2	56.4±0.10	324±12	246±10	0.516±0.047	0.522±0.003
Cu	2.29±0.37	2.00±0.18	33.9±1.6	24.8±1.3	0.248±0.025	0.249±0.002
Ni	2.16±0.29	1.94±0.10	46.9±2.2	36.0±1.9	0.301±0.025	0.300±0.001
Zn	4.94±0.79	2.66±0.41	159±8	89±3.2	0.257±0.02	0.256±0.004
Pb					0.006±0.002	0.006±0.000
Cd					0.031±0.002	0.030±0.000

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the sound use of our land and water resources, protecting our fish, wildlife and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation.The Department assesses our energy and mineral resources andworks to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island communities.

The Bureau of Ocean Energy Management

The Bureau of Ocean Energy Management (BOEM) works to manage the exploration and development of the nation's offshore resources in a way that appropriately balances economic development, energy independence, and environmental protection through oil and gas leases, renewable energy development and environmental reviews and studies.