Offshore Oil/Gas Wastewater Study: 2014 Assessment of Simpson Lagoon

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June 2016

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Table of Contents

Executive Summary 4
Chapter 1: Final Report Simpson Lagoon & Gwydyr Bay 2014 Alaska Monitoring and Assessment Program Survey 5
Introduction 5
Field Study Redesign 5
Station Sampling Sequence 5
Stations and Sampling Activities 6
Field/Laboratory Methods and QA/QC 6
Database 6
Results and Discussion 10
Descriptive Statistics 10
Water Column 10
Sediments 11
Macroinvertebrates 15
Baseline Comparison with 1977 Data Set 15
References 15
Chapter 2: Effects of a 2014 Storm Surge on Sediment Trace Metal Concentrations in a Shallow Arctic Lagoon: Observed in Comparisons of 1977 and 2014 Data *16*
Introduction 16
Environmental Setting 17
August 2014 Storm surge 18
Selection of Sample Sites & Trace Metals for Analysis 20
1977 20
2014 20
Field Methods 20
1977 20
2014 20
Analytical Methods 21
1977 21
2014 21
Dataset Comparability 1977 and 2014 22
Statistical Analysis 22
Results & Discussion 22
Water Column Characteristics 22
Sediment Characteristics 22
Descriptive Trace Metal Concentrations 23
Baseline Comparison of 1977 to 2014 Results 26
Correlation Analysis 28
1977 Baseline Linear Regression Model 28
Conclusions 33
References 34

Figures

Figure 1 – 2014 Sample Stations 7
Figure 2 – Oil and Gas Development 7
Figure 3 – Practical Salinity Unit Observations at Stations 13
Figure 4 – As Concentrations at Stations 13
Figure 5 – TPAH Concentrations at Stations 14
Figure 6 – Naphthalene Concentrations at Stations 15
Figure 7 - Oil and Gas Development 17
Figure 8 - 1977 and 2014 Simpson Lagoon Stations 18
Figure 9 – 2014 Storm Surge Sea Level Observations 19
Figure 10 – 2014 Storm Surge Wind Speed and Direction 19
Figure 11 - 1977 and 2014 Cr, Cu, Ni, and Zn 25
Figure 12 – 1977 and 2014 Iron 25
Figure 13 - 1977 and 2014 Manganese 26
Figure 14 – Mud versus Cr (a), Cu (b), Ni (c), Zn (d), Mn (e), and Fe (f). 31

Tables

Table 1: Station Activities 8
Table 2: Station Locations 10
Table 3: Water Column CTD Results 11
Table 4: Water Column Total and Dissolved Nutrients 11
Table 5: Sediment Grain Size 12
Table 6: Sediment Trace Metals 12
Table 7: Sediment Polycyclic Hydrocarbons 14
Table 8 – 1977 and 2014 Sediment Characteristics 24
Table 9 - 1977 and 2014 Sediment Trace Metals 24
Table 10 - 1977 Simpson Lagoon Sediment Trace Metal Correlations 27
Table 11 - 2014 Simpson Lagoon Sediment Trace Metal Correlations 27
Table 12 – Transformations and results of regressions that were applied to the 1977 Simpson Lagoon Mud versus trace metal data.. 28

This project is primarily funded with qualified outer continental shelf oil and gas revenues by the Coastal Impact Assistance Program, U.S. Fish and Wildlife Service, and U.S. Department of the Interior. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the opinions or policies of the U.S. Government. Mention of trade names or commercial products does not constitute their endorsement by the U.S. Government. Additional support was provided by North Slope Borough/Shell Baseline Studies Program.

Executive Summary

In 2014 the Alaska Department of Environmental Conservation and University of Alaska Fairbanks Institute of Marine Science partnered through the Alaska Monitoring and Assessment Program (AKMAP) to conduct a study of sediment and water quality in Simpson Lagoon and Gwydyr Bay. The survey objective was to obtain current information on trace metals and hydrocarbons in amphipods, mysids and sediment, and to assess several water quality parameters. This report provides study results and a comparison with a 1977 study of sediment trace metals. Complete data from the project is available from AKMAP.

Sediment and water samples were collected from 20 stations, biological sample collection was attempted at 14 of the 20 stations. Sediment quality indicators included trace metals, total carbon, total organic and inorganic carbon, hydrocarbons, sediment grain size, carbon and nitrogen isotopes, and macroinvertebrates. Water quality indicators included temperature, pH, salinity, total and dissolved nutrients, dissolved oxygen, and chlorophyll a. Amphipod and mysid traps were deployed at 14 sites but were unsuccessful, possibly due to stormy weather conditions.

With the exception of As, mean sediment trace metal levels all fell below Effects Range Low (ERL) values. As exceeded ERL at all but two sites, which is not uncommon in Alaska sediments resulting from arsenopyrite presence in many Alaska geological formations. 2014 concentrations of Cr, Cu and Ni trace metal in sediment were depleted in comparison with the 1977 study, this project concludes depletion was caused by the storm surge. For those sediment polycyclic aromatic hydrocarbons with ERL and Effects Range Median (ERM) guidelines, none of the guidelines were exceeded.

Chapter 1: Final Report Simpson Lagoon & Gwydyr Bay 2014 Alaska Monitoring and Assessment Program Survey

Introduction

In August of 2014 the Alaska Department of Environmental Conservation (DEC) and University of Alaska Fairbanks Institute of Marine Science (IMS) worked collaboratively through the Alaska Monitoring and Assessment Program (AKMAP) to conduct a Beaufort Sea Oil/Gas Wastewater Study in Simpson Lagoon and Gwydyr Bay (hereafter referred to as Simpson Lagoon). The study planned originally for western Harrison Bay was shifted to Simpson Lagoon because high winds created unsafe sea conditions for operations in Harrison Bay. The AKMAP survey objective was to provide current information on trace metals and hydrocarbons in amphipods, mysids, and sediments. Additional water quality information, such as nutrients and dissolved oxygen were also part of the assessment.

Chapter two provides a detailed technical discussion of sediment trace metal findings and effects of the storm surge on sediment chemistry. This chapter is formatted for submittal to a peer reviewed journal.

All data is available to download or view through an interactive map, Alaska's Water Quality Map, at http://dec.alaska.gov/water/wqsar/map.html. More information on this survey can be found at http://dec.alaska.gov/water/wqsar/monitoring/2014Offshore.html.

Field Study Redesign

Gale force winds and high seas along the Beaufort Sea coast made sampling in Harrison Bay dangerous. With safety concerns the R/V Ukpik and our team remained docked at Prudhoe Bay West Dock hoping for weather improvement for the first five days of our charter. The weather pattern continued to deteriorate and it became unlikely that we would be able to sample western Harrison Bay within the charter schedule.

A decision was made to relocate the survey to the closest region that could be safely sampled. Simpson Lagoon was selected due to proximity, historic and current oil and gas activities, and protection provided by barrier islands. A target sampling frame was bounded by water depths of 1.5 to 2 meters, the minimum depth for R/V Ukpik operations. Figure 1 illustrates oil and gas unit boundaries in the study area and the Simpson Lagoon sample frame. This alternate plan supported the original survey design goals and 20 stations were sampled in Simpson Lagoon (Figure 2).

Station Sampling Sequence

At each station the following sampling events occurred:

1. Confirm site location within ± 0.02 nm (37m) against vessel GPS readings.
2. Anchor the boat to stay within the site radius.
3. Water and sediment sampling activities were carried out in the listed order:
    a. Collect water sample for chlorophyll a, nutrients, salinity, pH and DO analysis from a 0.5-meter depth using a niskin sampler.

b. Water column profiled with a Seabird 19plus SeaCAT CTD profiler for conductivity, dissolved oxygen, pH and pressure (depth).
c. Collect sediment samples with a Ponar 0.05 m^2 grab sampler for benthic infaunal abundance, and sediment grain size and chemical analysis.

4. Deploy amphipod and mysid traps overnight to be recovered in the morning.

Stations and Sampling Activities

Sampling occurred August 10th -13th and is detailed in Table 1, station coordinates are provided in Table 2. The tables include the 20 sampled stations, including duplicates, and one attempted station (AKSL-09). The attempted station was too shallow for sampling and was replaced with AKSL-21.

From August 10th – 12th, twelve amphipod and mysid traps were set. The first set of traps set on the 10th may not have stayed on the bottom, which was corrected for subsequent sampling. Amphipods and mysids proved scarce and none were collected in the 12 sampling attempts. At test of the amphipod trap, earlier while at West Dock did show the trap could collect amphipods.

It was not possible to positively establish why the traps did not collect amphipods and mysids, though previous scientific studies in the region have encountered periods of scarcity. The minnow trap mesh was small enough to collect the size amphipods of interest, but would have allowed escape of smaller amphipods. The weather and sea conditions stirred up marine sediments and could have caused altered currents, both of which may have interfered with the collection of amphipods and mysids. Similar efforts to collect biological samples such as amphipods in Beaufort coastal waters have had similar difficulties (Brown et al., 2005).

Field/Laboratory Methods and QA/QC

The project planning, data quality objectives, measurement quality objectives, field activities, data handling and processing, and other critical elements (with the exception of amphipod and mysid collections) study are covered in four EPA documents:

- National Coastal Condition Assessment: Quality Assurance Project Plan (EPA 841-R-09-004)
- National Coastal Condition Assessment: Field Operations Manual (EPA 2010A)
- National Coastal Condition Assessment: Laboratory Methods Manual (EPA, 2010B)
- National Coastal Condition Assessment: Site Evaluation Guidelines (EPA, 2010C)

These documents and additional support information are available at: http://water.epa.gov/type/oceb/assessmonitor/ncca.cfm. A Beaufort Sea Oil/Gas Wastewater Study addendum QAPP approved by DEC described methods and quality assurance aspects for amphipod and mysid collection methods, specific parameters being measured, and measurement quality objectives.

The specific Texas A&M Geochemical and Environmental Research Group (GERG) laboratory analysis of sediments for trace metals, total organic carbon and hydrocarbons follow GERG standard operating procedures (SOP). Sediment carbon and nitrogen isotope analysis follow protocols established at the UAF Alaska Stable Isotope Laboratory (http://ine.uaf.edu/werc/asif/).

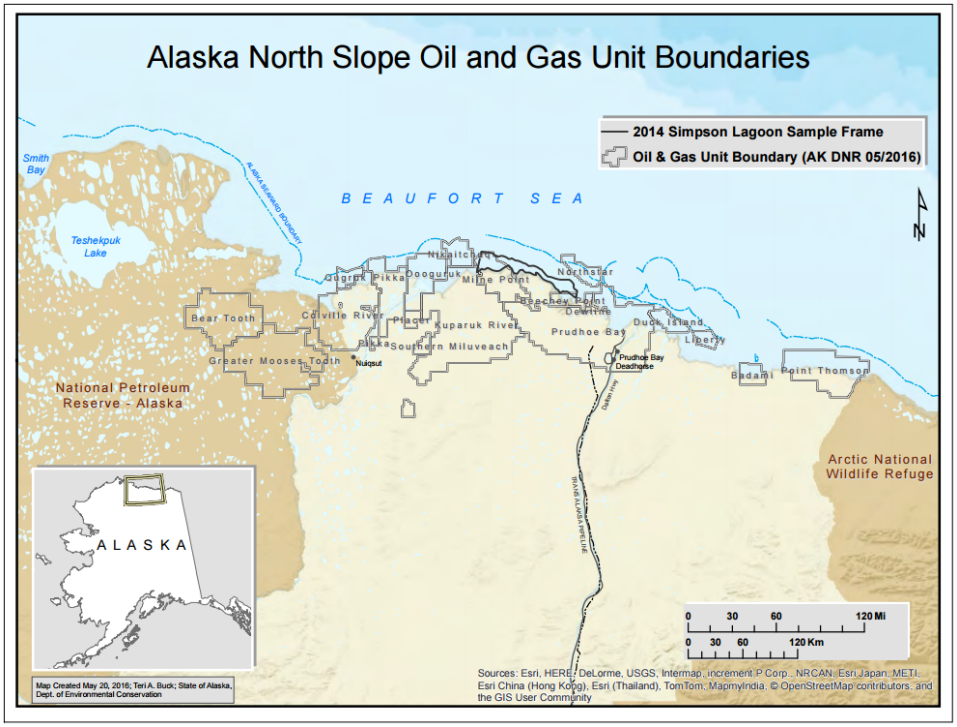

Figure 1 – Oil and gas unit boundaries and the Simpson Lagoon sample frame.

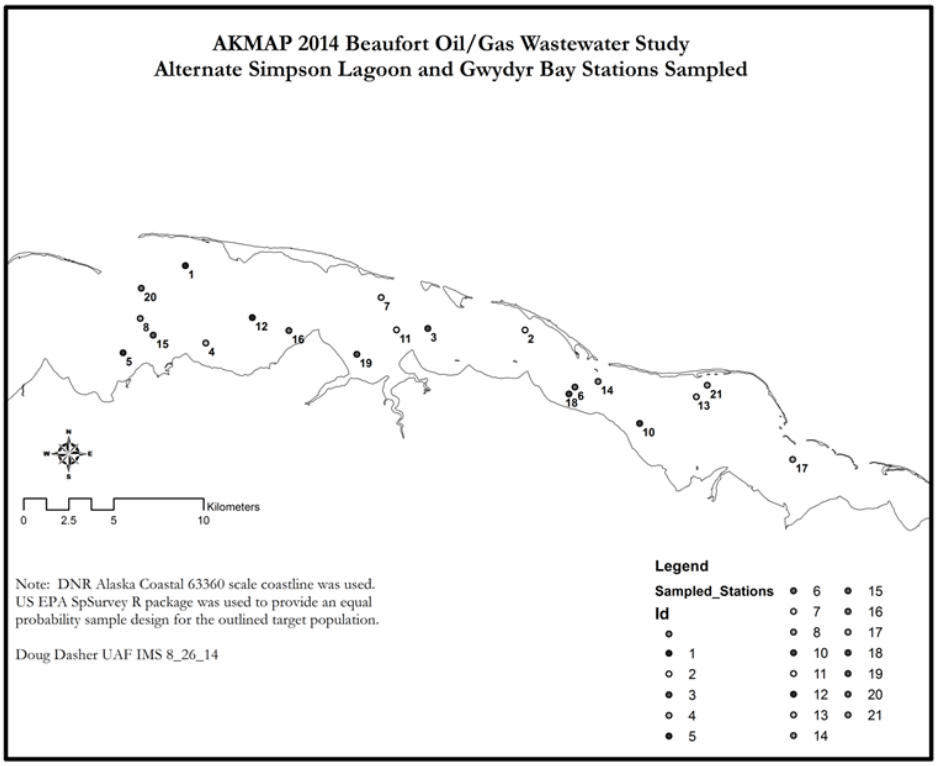

Figure 2 – 2014 Sample Stations

Table 1: Station Activities

Table 1. List of activities accomplished at stations on the 2014 AKMAP Beaufort Sea Simpson Lagoon Survey												
Date	10-Aug	10-Aug	10-Aug	10-Aug	10-Aug	10-Aug	11-Aug	11-Aug	11-Aug	11-Aug	11-Aug	11-Aug
Station ID (abbreviated)	**13**	**14**	**06**	**18**	**02**	**03**	**07**	**19**	**11**	**16**	**16D**	**12**
Depth, ft	6.6	8.5	7	6.3	6.8	7	4.7	6.8	6.6	5.4	5.4	7.1
Depth, m	2	2.6	2.1	1.9	2.1	2.1	1.4	2.1	2	1.7	1.7	2.2
ACTIVITY												
Water samples												
Total Nutrients	X	X	X	X	X	X	X	X	X	X	X	X
Dissolved Nutrients	X	X	X	X	X	X	X	X	X	X	X	X
Chlorophyll a	X	X	X	X	X	X	X	X	X	X	X	X
Microbial Degradation*	X	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
CTD Profile	X	X	X	X	X	X	X	X	X	X	X	X
Sediment Samples												
Organic	X	X	X	X	X	X	X	X	X	X	X	X
Inorganic	X	X	X	X	X	X	X	X	X	X	X	X
TOC	X	X	X	X	X	X	X	X	X	X	X	X
Carbonate	X	X	X	X	X	X	X	X	X	X	X	X
Grain Size	X	X	X	X	X	X	X	X	X	X	X	X
Macro-invertebrates	X	X	X	X	X	X	X	X	X	X	X	X
Carbon & Nitrogen Isotopes	X	X	X	X	X	X	X	X	X	X	X	X
Microbial Degradation*	X	X	X	NS	NS	NS	X	X	X	NS	NS	NS
Amphipod & Mysid Traps	X	X	X	X	NS	NS	X	X	X	X	NS	NS

Table 1: Station Activities - Continued

Table 1. List of activities accomplished at stations on the 2014 AKMAP Beaufort Sea Simpson Lagoon Survey											
Date	12-Aug	12-Aug	12-Aug	12-Aug	12-Aug	12-Aug	13-Aug	13-Aug	13-Aug	13-Aug	13-Aug
Station ID (abbreviated)	**04**	**01**	**20**	**08**	**15**	**05**	**10**	**09**[3]	**21**	**17**	**17D**
Depth, ft	7.1	6.5	7.6	7.4	6.8	7.3	4.5	>4	5.6	4.2	4.2
Depth, m	2.2	2	2.3	2.3	2.1	2.2	1.4	>1.2	1.7	1.3	1.3
ACTIVITY											
Water samples											
Total Nutrients	X	X	X	X	X	X	X	NS	X	X	X
Dissolved Nutrients	X	X	X	X	X	X	X	NS	X	X	X
Chlorophyll a	X	X	X	X	X	X	X	NS	X	X	X
Microbial Degradation*	NS	NS	NS	NS	X	NS	NS	NS	NS	NS	NS
CTD Profile	X	X	X	X	X	X	X	NS	X	X	X
Sediment Samples											
Organic	X	X	X	X	X	X	X	NS	X	X	X
Inorganic	X	X	X	X	X	X	X	NS	X	X	X
TOC	X	X	X	X	X	X	X	NS	X	X	X
Carbonate	X	X	X	X	X	X	X	NS	X	X	X
Grain Size	X	X	X	X	X	X	X	NS	X	X	X
Macro - invertebrates	X	X	X	X	X	X	X	NS	X	X	X
Carbon & Nitrogen Isotopes	X	X	X	X	X	X	X	NS	X	X	X
Microbial Degradation*	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Amphipod & Mysid Traps	X	X	X	X	X	X	NS	NS	NS	NS	NS
*Samples collected for partner organization.											

[3] This station was attempted, but not sampled due to depth <4 feet. Oversample station AKSL-21 was sampled instead.

Table 2: Station Locations

Station ID	Latitude	Longitude
AKSL14-01	70.55331	-149.650
AKSL14-02	70.50888	-149.161
AKSL14-03	70.51319	-149.302
AKSL14-04	70.51356	-149.628
AKSL14-05	70.51131	-149.75
AKSL14-06	70.47816	-149.094
AKSL14-07	70.53055	-149.367
AKSL14-08	70.52817	-149.721
AKSL14-10	70.45734	-149.004
AKSL14-11	70.51359	-149.348
AKSL14-12	70.52484	-149.557
AKSL14-13	70.46866	-148.918
AKSL14-14	70.48016	-149.06
AKSL14-15	70.51927	-149.704
AKSL14-16	70.51702	-149.505
AKSL14-17	70.43317	-148.785
AKSL14-18	70.47498	-149.103
AKSL14-19	70.50265	-149.409
AKSL14-20	70.54342	-149.717
AKSL14-21	70.47403	-148.901

Datum - NAD83 Alaska Albers Equal Area

Results and Discussion

Descriptive Statistics

Water Column

Tables 3 and 4 provide descriptive statistics of the water column for temperature, dissolved oxygen and practical salinity units, collected from the CTD profile at each station.
Samples were collected in a Niskin bottle at ~ 0.5 meters and analyzed for total and dissolved nutrients, chlorophyll a, dissolved oxygen (DO), and salinity. Results do not indicate high nutrient or chlorophyll *a* concentration. Proximity to freshwater inputs can have an effect on sample results, Figure 3 shows this effect on Practical Salinity Units (PSU). Effects of the storm surge on mixing of off-shore and near-shore waters and a possible increase in suspended sediments on water quality could not be assessed within the scope of this study.

Table 3: Water Column CTD Results

Water Column[4]	N	Min	Max	Mean	SD	CV
Temp˚ C	20	0.966	5.231	4.127	1.13	0.27
pH	20	6.929	8.295	7.632	0.40	0.05
DO mg/L	20	8.039	10.19	9.265	0.60	0.06
DO % Saturation	20	72.08	87.98	80.89	4.63	0.06
Practical Salinity Units (PSU)	20	12.09	28.41	19.64	4.58	0.23

Table 4: Water Column Total and Dissolved Nutrients

Water Column Nutrients	N	Min	Max	Mean	SD	CV
NO_3 and NO_2 µmol/L (filtered)	19	0.75	2.43	1.62	0.49	0.30
NO_3 and NO_2 µmol/L (unfiltered)	20	1.05	2.46	1.79	0.45	0.25
NO_2 µmol/L (filtered)	19	0.03	0.34	0.07	0.07	0.98
NO_2 µmol/L (unfiltered)	20	0.04	2.18	1.01	0.52	0.51
NH_4 µmol/L (filtered)	19	ND	ND	ND	NA	NA
NH_4 µmol/L (unfiltered)	20	0.00	3.12	1.04	1.02	0.98
PO_4 µmol/L (filtered)	19	0.47	0.87	0.65	0.13	0.19
PO_4 µmol/L (unfiltered)	20	0.42	4.36	2.45	0.97	0.40
SiO_2 µmol/L (filtered)	19	9.89	22.34	16.37	3.87	0.24
SiO_2 µmol/L (unfiltered)	20	14.31	29.57	20.39	4.75	0.23
NO_3 µmol/L (filtered)	19	0.70	2.37	1.55	0.49	0.32
NO_3 µmol/L (unfiltered)	20	0.01	1.71	0.78	0.55	0.71

Sediments

Sediment descriptive statistics for trace metals, grain size, total and organic carbon, and hydrocarbons (Long, Robertson et al. 1996) are shown in Tables 5, 6 and 7. Effects Range Low (ERL) and Effect Range Median (ERM) are provided. For trace metals only As exceeds the ERL, which is not uncommon for Alaska marine sediments due to the presence of arsenopyrite in many Alaskan geological formations (Dasher, 2013). Arsenic concentrations for individual stations are shown in Figure 4.

[4] The CTD mean is a weighted mean based on binning results at 0.5 meter intervals and weighing based on number of sampled points in each bin.

Table 5: Sediment Grain Size

Sediment Grain Size	N	Min	Max	Mean	SD	CV
Gravel %	20	0.00%	0.98%	0.13%	0.25%	2.00
Sand %	20	29.50%	96.40%	58.70%	20.70%	0.35
Silt %	16	21.20%	64.80%	42.90%	13.00%	0.30
Clay %	16	4.07%	9.15%	6.31%	1.52%	0.24
Mud %	20	3.59%	70.50%	41.20%	20.70%	0.50

Table 6: Sediment Trace Metals

Sediment Variable	N	Min	Max	Mean	SD	CV	ERL	ERM
Ag mg/kg dry	20	0.15	0.63	0.26	0.11	0.43	1.0	3.7
Al mg/kg dry	20	3989	10066	7507	1584	0.21		
As mg/kg dry	20	7.82	12.38	10.50	1.26	0.12	8.2	70.0
Ba mg/kg dry	20	206	327	279	31	0.11		
Cd mg/kg dry	20	0.12	1.05	0.71	0.24	0.34	1.2	9.6
Cr mg/kg dry	20	4.64	20.90	11.40	3.68	0.32	81.0	370.0
Cu mg/kg dry	17	0.48	8.78	3.78	1.99	0.53	34.0	270.0
Fe mg/kg dry	20	8814	20023	15406	3039	0.20		
Mn mg/kg dry	20	36	173	92	40	0.43		
Ni mg/kg dry	20	1.60	24.23	6.50	4.59	0.71	20.9	51.6
Pb mg/kg dry	20	4.96	9.07	7.52	1.21	0.16	46.7	218.0
Se mg/kg dry	20	4.44	8.45	6.03	1.05	0.17		
Zn mg/kg dry	20	35.33	81.21	63.83	13.77	0.22	150.0	410.0
Total Carbon %	20	0.21%	4.35%	2.88%	1.14%	0.40		
Total Organic Carbon %	20	0.21%	4.30%	2.84%	1.13%	0.40		
THg µg/kg dry	20	0.012	0.117	0.045	0.023	0.52	0.15	0.71

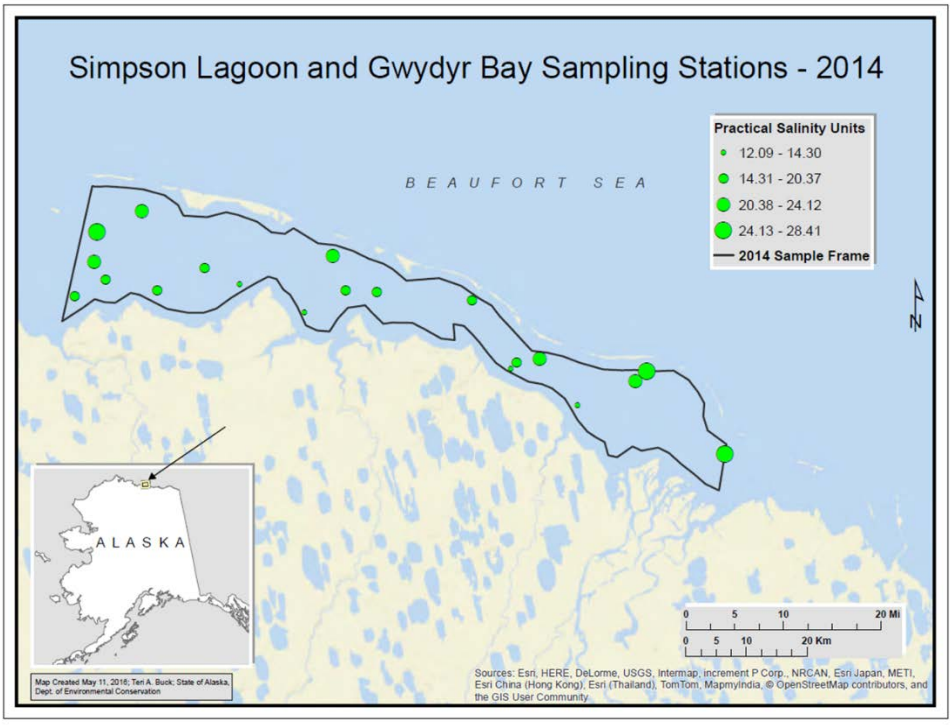

Figure 3 **–** PSU levels across Simpson Lagoon. Waters closer to freshwater inlets have lower PSU levels and waters closer to Beaufort Sea inputs have higher PSU levels.

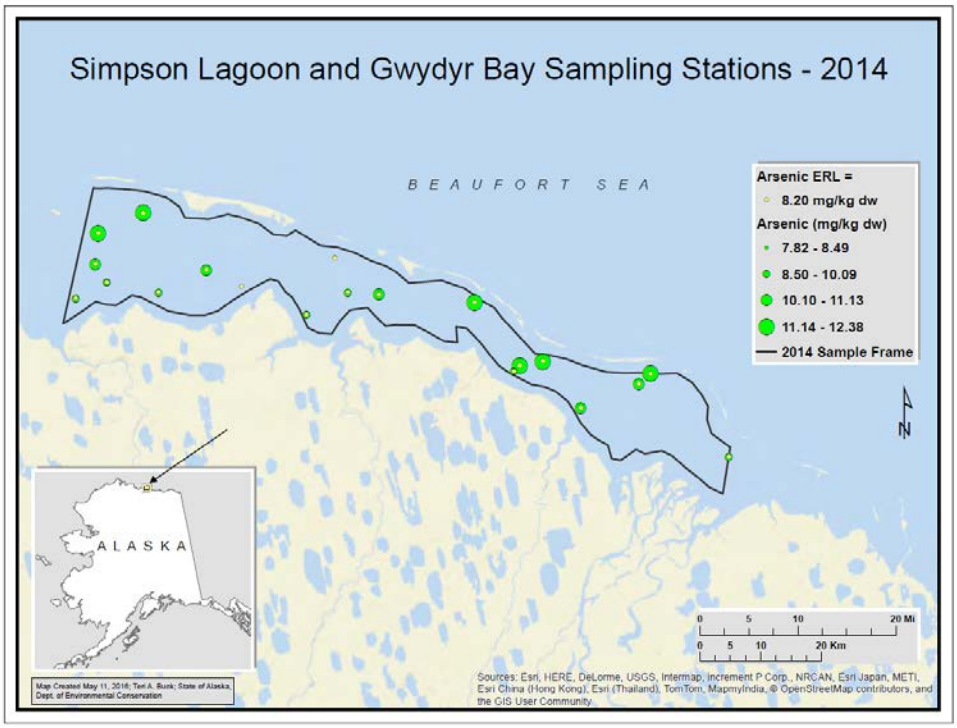

Figure 4 – ERL for arsenic concentrations are exceeded at all but two stations.

Sediment polycyclic aromatic hydrocarbon data is shown in Table 7 for hydrocarbons with ERL and ERM guideline concentrations. None of the ERL or ERM values were exceeded, distribution of NOAA National Status and Trends (NT&S) total polycyclic aromatic hydrocarbons (TPAH) set and naphthalene are shown in Figure 5 and 6.

Table 7: Sediment Polycyclic Hydrocarbons[5]

Sediment PAH	N	Min	Max	Mean	SD	CV	ERL	ERM
Total NS&T PAHs	20	63.46	444.6	256	106.6	0.416	4022	44792
Naphthalene	20	8.82	60.4	22.78	11.91	0.523	160	2100
Acenaphthylene	20	0.14	0.86	0.52	0.217	0.418	44	640
Acenaphthene	20	0.11	1.1	0.706	0.311	0.441	16	500
Fluorene	20	1.03	7.64	4.847	2.009	0.415	19	540
Phenanthrene	20	3.66	39.61	22.98	10.52	0.458	240	1500
Anthracene	20	0.41	2.41	1.256	0.541	0.431	85.3	1100
Fluoranthene	20	0.66	8.21	4.494	2.124	0.473	600	5100
Pyrene	20	0.81	11.75	6.211	3.133	0.504	665	2600
Chrysene	20	2.01	20.8	12.26	5.655	0.461	384	2800
Benzo(a)pyrene	20	0.33	3.51	1.753	0.883	0.504	430	1600

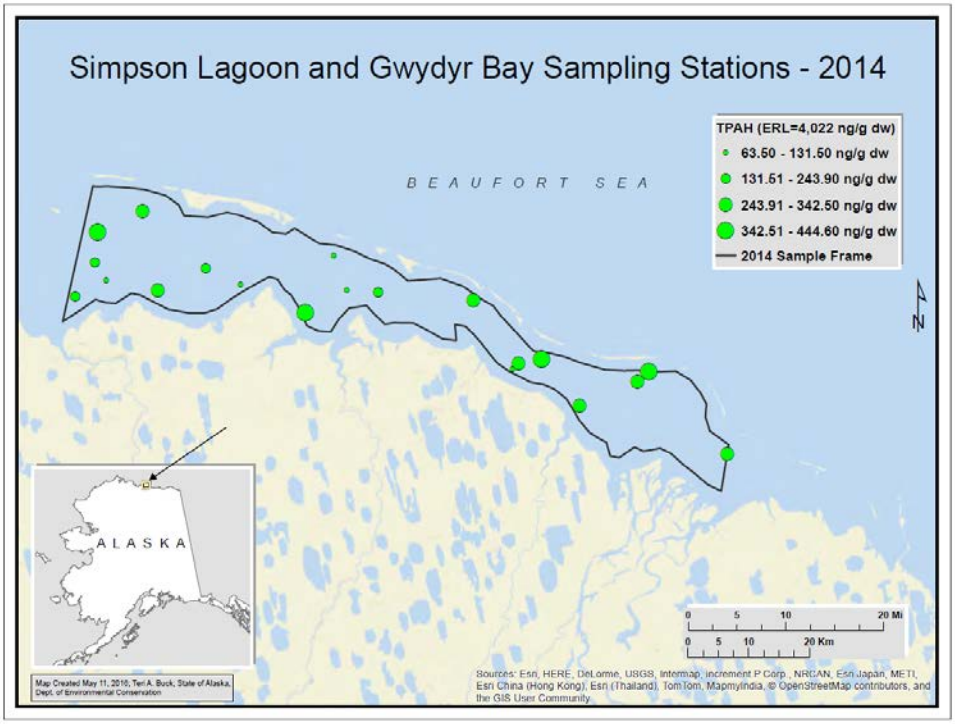

Figure 5 – TPAH Concentrations at Stations

[5] Only those are show that had ERL/ ERM values.

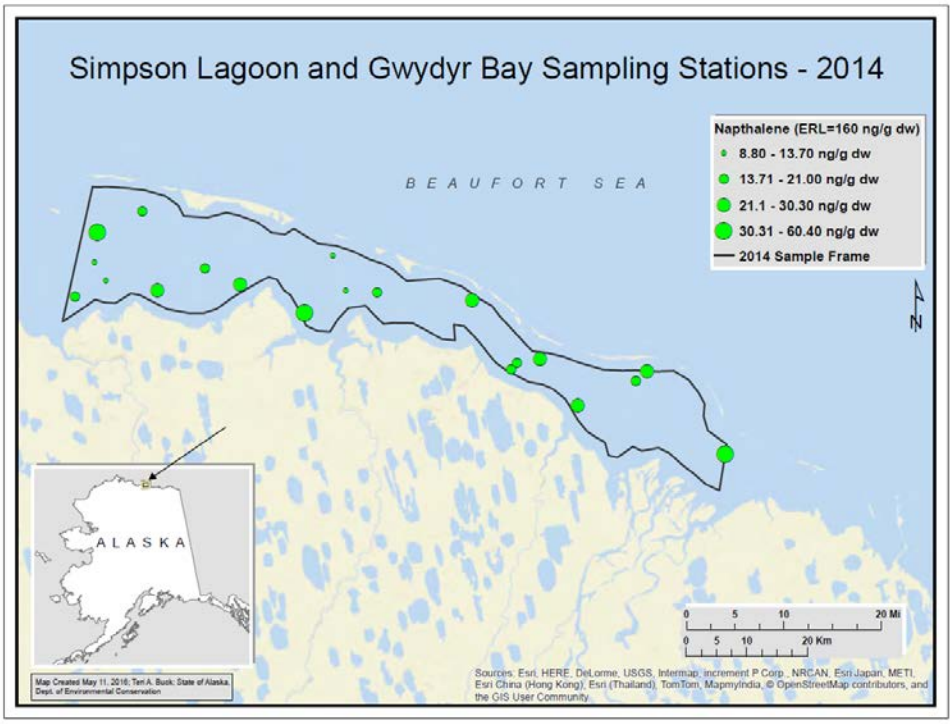

Figure 6 – Naphthalene Concentrations at Stations

Macroinvertebrates

Sediment macroinvertebrates were collected on 1 mm sieves and taxonomic data was provided for baseline use. Taxonomic results may have been biased by the storm surge due to physical disturbance of surficial sediment layers.

Baseline Comparison with 1977 Data Set

Simpson Lagoon saw little environmental study until oil and gas development began at Prudhoe Bay in the early 1970s. Sediment trace metals in Simpson Lagoon were assessed in a 1977 study that concluded trace metal concentrations were at a natural pre-development baseline. There has not been a similar study of trace metals until this project in 2014. Significant oil and gas development has occurred in the watersheds draining into the Simpson Lagoon region over the last 40 years. We compare 1977 and 2014 sediment trace metal data and consider effects of the 2014 storm surge in Chapter 2. Conclusions from this comparison are that 2014 concentrations are depleted compared to 1977 because of the storm surge.

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Chapter 2: Effects of a Storm Surge on Sediment Trace Metal Concentrations in an Arctic Lagoon: A Case Study Comparing 1977 and 2014 Data

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Introduction

The coastal region of the Alaskan Beaufort Sea, adjacent to the North Slope of Alaska, is dominated by a chain of barrier islands which shelter landward a series of lagoon-estuarine system. Simpson Lagoon and Gwydyr Bay (both hereafter referred to as Simpson Lagoon) which are a shallow part of this system were subjected to little environmental study until oil and gas development at Prudhoe Bay in the early 1970s. The earliest known baseline studies on sediment trace metals in the Simpson Lagoon were in early 1970s (Alexander et al., 1975; Naidu, 1989). Those studies concluded that the trace metal concentrations provide a natural pre-development baseline (Sweeney, 1984; Sweeney and Naidu, 1989). Later the National Oceanic and Atmospheric Administration (NOAA) and the US Bureau of Land Management (BLM) conducted an Environmental Assessment of the Alaskan Continental Shelf (ARLIS, 2016), including Beaufort coastal lagoons. Subsequently, post-development monitoring on sediment trace metals were conducted by Boehm et al. (1987), Naidu et al.(2012), and the Alaska Department of Environmental Conservation (DEC 2016). Significant oil and gas development has occurred in the watersheds draining into the North Slope and the adjacent coastal region over the last 40 years (Figure 7). However, all time-interval assessments of the region suggest little change in the baseline trace metal concentrations over the past four decades.

A salient feature of the nearshore environment of north arctic Alaska is the occurrence of occasional storms which, in ice free season, can develop threshold wave intensity (8 m s^{-1}) to suspend particles from shallow bottoms (Larsen, 1980). In August 2014 a storm event struck the North Slope region, which encompassed Simpson Lagoon. The mean wind speed during this storm was 14 m s^{-1} with gusts up to 67 m s^{-1} (NOAA Deadhorse weather station) with estimated wave height of one to two meters (Dasher, unpublished results). The consequent substrate reworking on sediment trace metal concentrations for the study area is unknown and knowledge on other storm impacted nearshores are few (Kalnejais et al., 2007; Warren et al., 2011). This prompted us to compare the sediment trace metals chemistry of baseline and post-storm periods, of 1977 and 2014 respectively, in Simpson Lagoon. The resulting information will provide data to better understand the fate of deposited contaminants following storms and, thus, useful in environmental monitoring strategies in the above region. We hypothesize that the storm-induced wave-current action would preferably resuspend and advect the hydro dynamically lighter and metal-rich mud fraction, ensuing in depletion of trace metals from the original depositional site.

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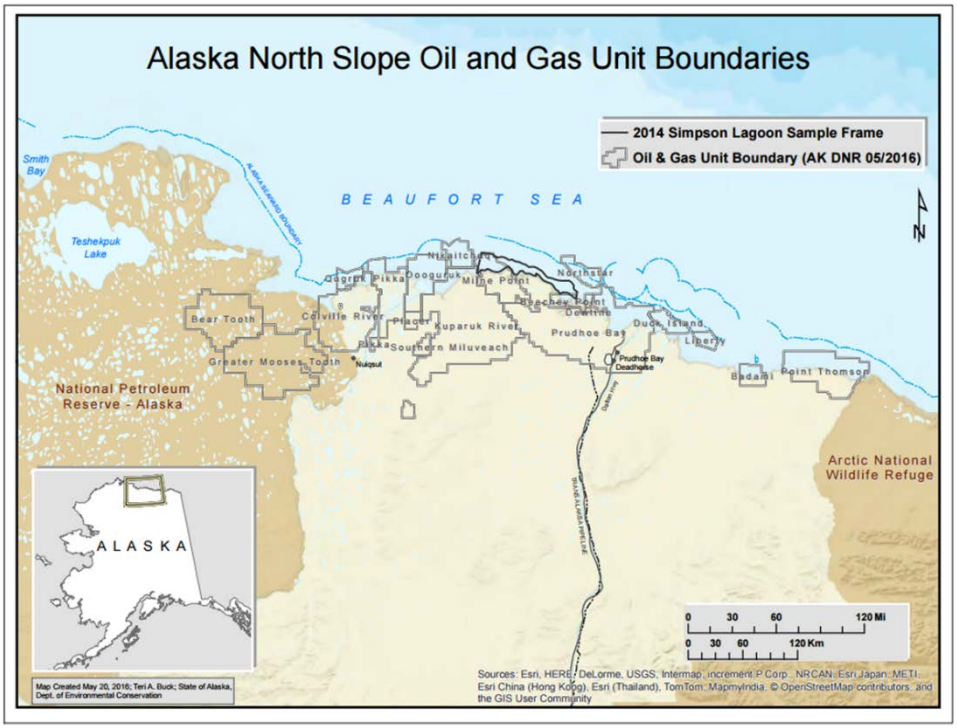


Figure 7- Oil and Gas Development

Environmental Setting

Simpson Lagoon is an island protected lagoon system of the Beaufort Sea that receives freshwater and sediment inputs from the Colville, Kuparuk, Sagavanirktok, and other smaller rivers in the watershed (Figure 7 -8). Simpson Lagoon is approximately 35 km long and 1 to 6 km wide, with a maximum depth around 3 meters, about 65% is deeper than 1.8 meters (Dunton et al., 2006; Sweeney, 1984; and Tucker, 1973). The lagoon is subject to annual ice cover for approximately 8-9 months a year and much of the lagoon is covered with land-fast ice (Sweeney, 1984). Bottom sediments are typically poorly sorted and consist of muddy sand or gravelly, sandy mud (Naidu et al., 1984). Beaufort Sea lagoon circulation patterns are characterized by wind and wave induced currents, typically a westward current generated by prevailing northeast winds. Fall storms bring west winds and reverse the current flow. (Alexander et al., 1975; Hanna et al., 2014). Winter ice restricts general circulation patterns. In the coastal region of the Beaufort Sea astronomical tides only have an average range of 0.15 meters, which are typically overshadowed by wind effects (Reimnitz and Maurer, 1979).

During summer estuarine and brackish salinities range from 4 to 20 PSU with water temperatures in the 0 to 12°C range (Sweeney, 1984). Estuarine mixing zone have salinities as low as 1.5 PSU with a temperature ~12°C (Alexander et al., 1975). Brine concentrate released from the creation of sea ice results in pockets of hypersaline waters along the bottom with measurements up to 65.9 PSU (Schell and Hall, 1972; Alexander et al., 1975).

Water column dissolved oxygen (DO) suggest well oxygenated waters are present (Alexander et al., 1975). Although levels of DO decrease under the ice, anoxic conditions were never observed (Alexander et al., 1975).

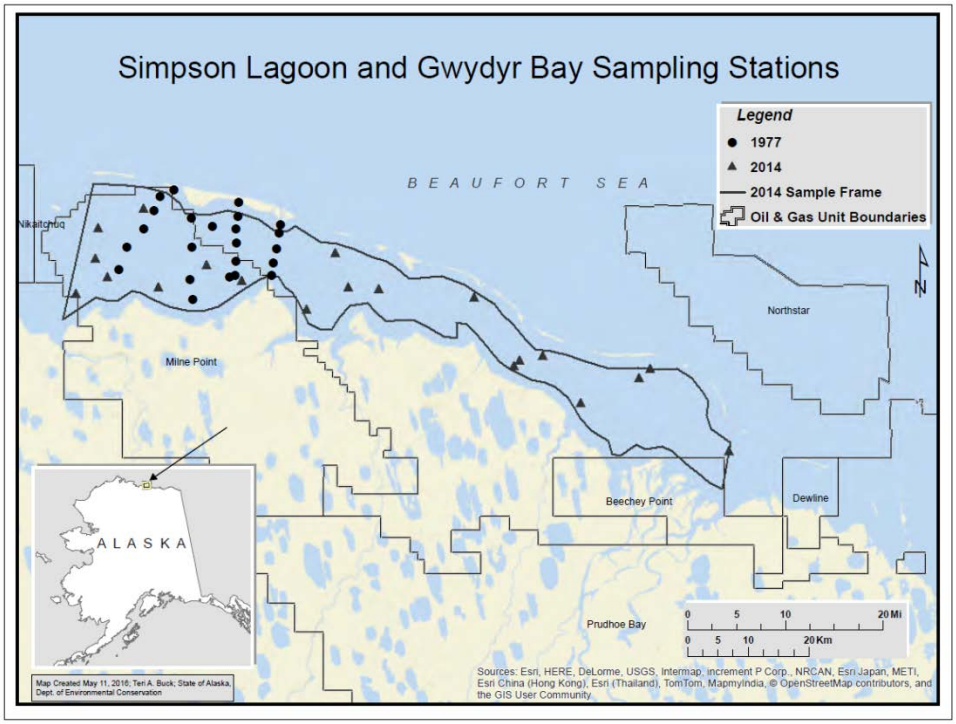


Figure 8 - 1977 and 2014 Simpson Lagoon Stations

August 2014 Storm surge

August 5-17, 2014, a storm brought sustained high winds out of the northeast. The NOAA Prudhoe Bay, Alaska, tide station (ID 9497645), recorded tides as low as - 0.37 m below the mean sea level (Figure 9). Estimated mean wind speed was 14 m s^{-1} with gusts up to 67 m s^{-1} (Figure 10). The record remains incomplete as the weather station was damaged from August 11-15th. Wave height estimates in the nearshore Beaufort were one to two meters (personal observations Dasher) while in the open Beaufort wave heights reached nearly four meters (Smith and Thompson 2016).

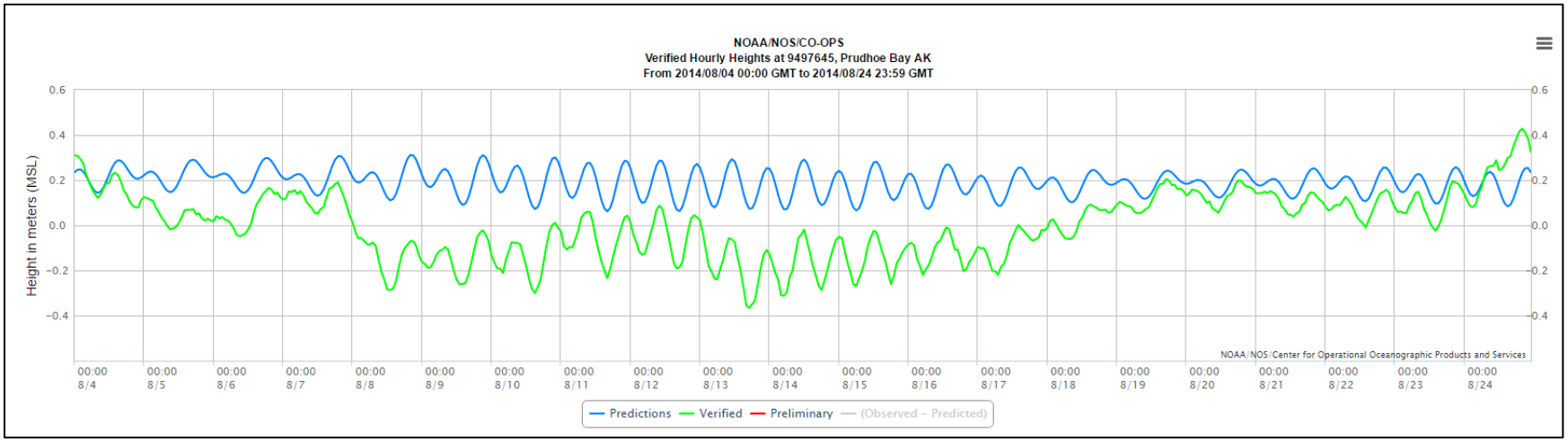


Figure 9 – 2014 Storm Surge Sea Level Observations

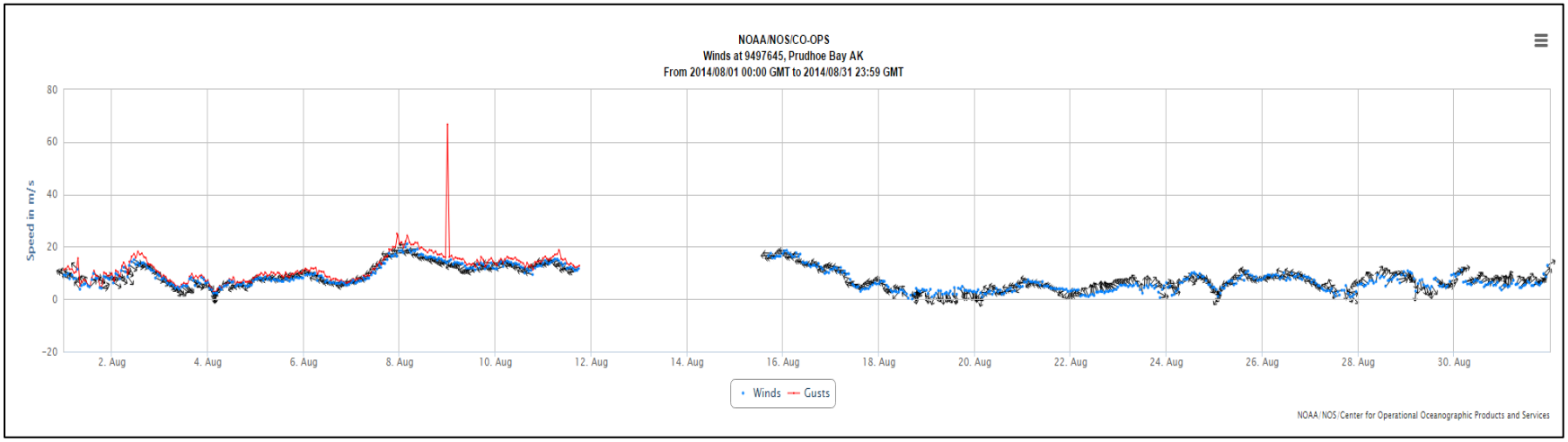


Figure 10 – 2014 Storm Surge Wind Speed and Direction

Selection of Sample Sites & Trace Metals for Analysis

1977

Five transects were selected in this study to help assess the sediment trace metal distribution along the coast and the potential deposition of sediments from rivers entering Simpson Lagoon (Sweeny and Naidu, 1989). Only 1977 study locations located within the 2014 sample frame were included in this analysis (Figure 8).

Trace metals sampled in 1977 were V, Cr, Co, Cu, Ni, Zn as well as major metals Fe and Mn. These trace metals were selected because of their association with anthropogenic enrichment from domestic and industrial wastewater point and non-point source activities. Iron and Mn are of interest because of their ability to scavenge certain trace metals and to assess sediment redox status (Du Laing, 2009). Other parameters that contribute to the understanding of trace and major metal distribution in sediments, such as grain size, carbonate, and total organic carbon were also analyzed.

2014

AKMAP conducted a randomized survey, similar to the EPA National Aquatic Resource Surveys (EPA, 2016a), to estimate the spatial distribution of environmental parameters such as sediment trace metal concentrations, within a defined area of Simpson Lagoon (Figure 2). The sampling design was done utilizing ArcGis™ and the spSurvey R package (Kincaid et al., 2015).

Trace metals sampled mirrored those of other marine AKMAP surveys (As, Ba, Cd, Cr, Cu, Pb, Li, Ni, Se, and Zn). Major metals Al, Fe and Mn were also included. Similar to the 1977 study these trace and major metals were selected because of their potential for anthropogenic enrichment and their ability to act as scavengers and normalizers for the trace metals. Other parameters that contribute to the understanding of trace and major metal distribution in sediments, such as grain size, carbonate, and total organic carbon were also analyzed.

Field Methods

1977

Sediment samples were collected using a 0.02m^2 Ekman grab sampler. The samples were stored in clean polyethylene bags or plastic boxes stored at 5°C in the field before shipping to the University of Alaska Fairbanks Institute of Marine Science (IMS) laboratory. They were stored frozen until analyzed.

2014

A stainless steel 0.05 m^2 Ponar grab sampler was used to collect surficial surface sediment samples. A stainless steel scoop was used to collect the top (0-2cm) layer from the Ponar. Due to the small collection area of the Ponar and at times hard substrate the samples were composited to obtain adequate mass. Recovered sediments were placed in a stainless steel bucket and mixed before being removed with a stainless steel spoon and placed into the appropriate sample container. Sampling equipment was washed down with sea water and cleaned with Alconox and alcohol wipes between each sampling event. Between sampling events the cleaned equipment was stored in plastic bags.

Trace metal sediment samples were placed in 125 ml I-Chem bottles. Total Organic Carbon (TOC) samples were combined with the sediment hydrocarbon samples in 500 ml I-Chem bottles and sediment grain size samples were stored in Whirl-pak™ bags. Chemistry samples were frozen after collection at -20°C and sediment grain size samples were stored at 4°C. Samples for trace metals, TOC and hydrocarbon analysis were shipped to the Texas A&M Geochemical and Environmental Research Group (GERG) laboratory for analysis.

Analytical Methods

1977

Sediment samples for trace and major elements were dried at 60°C, disaggregated, ground to fine powder with an agate mortar and pestle, and stored in vials. Samples were collected for both partial-extraction and total metals, but only total extraction methods are detailed for comparison with the 2014 study. For total extraction the powdered samples were ashed in platinum crucibles, transferred to Teflon dishes, and then digested to dryness with 48% hydrofluoric and 70% nitric acids. Metals were quantified using atomic absorption spectrometry calibrated with standards in similar composition to the sample digestion. U.S. Geological Survey (USGS) AGV-1 and BCR-1 Standard Rock Powders were used to check the analytical method. Two duplicate samples were also run.

Sediment grain size fractions were determined by sieving the gravel and sand followed by pipette techniques to determine the silt and clay fraction following methods described by Naidu et al. 1971. Total carbon and carbonate were determined by an automatic carbon induction furnace and manometric techniques (Sweeny, 1984). Total organic carbon was calculated as the difference between total and carbonate-carbon.

2014

Total digestion of sediment was followed by trace metal analysis of the samples for trace metals , except for total Hg, by inductively coupled plasma mass spectrometry (ICP-MS). Atomic Absorption method was used to determine sediment THg. Selenium and arsenic were determined using anhydrous ammonia as a reaction gas in the Dynamic Reaction Cell to improve sensitivity of the ICP-MS for these elements. Standard reference material sediments from an independent source were used to evaluate analytical accuracy and were required with each set of 20 or fewer samples.

Carbon concentrations on dried sediment/soil were determined using a LECO Model 523-300 induction furnace, an infrared detector, and an integrator. Total carbon (TC) is determined from an unmodified dry sample, while total organic carbon (TOC) is determined after sample acidification. Total inorganic carbon (TIC) is calculated as the difference between total carbon and total organic carbon.

Sediment grain size was determined by wet and dry sieving for gravel and sand fractions, silt and clay fraction were determined using the pipette method based on Folk (1974) and US EPA (2016b).

Dataset Comparability 1977 and 2014

Although the trace metal analytical instrumentation differs between the two periods the laboratory protocols, precision and accuracy checks using National Institute of Standards and Technology or USGS reference standards support comparisons of trace metal results.

Statistical Analysis

Statistical calculations from exploratory, correlations, scatterplots, box-plots, and linear regression were carried out using ProUCL 5.1 (Singh, A. and Singh, A.K., 2016) and R (R Core Team, 2016). Statistical analysis techniques consisted of descriptive characteristics, graphical presentation of notched box plots, non-parametric one-way ANOVA, Spearman Rank Correlation Matrix, and ordinary least square linear regression.

Linear regression is a parametric method that is based on the assumptions that the residuals or differences between predicted and actual values used to construct the model are normally distributed; residuals do not have non-linear patterns; residuals exhibit homoscedasticity or equal variance; and that there is a significant correlation and linear relationship between the normalizing factor and the trace metal (Hector, 2015). A linear regression line is established between the y-axis or dependent response variable and the x-axis or predictor or normalization variable (Trefry et al., 2003; Summers et al., 1996; Schropp et al., 1990).

The linear regression model utilized was the lm function found in the basic R statistical package. Results were evaluated using the linear regression diagnostics in R and in the Companion to Applied Regression (CAR) R package (Fox and Weisberg, 2011). The graphics were done within the R ggplot2 package (Wickham, 2009). Linear regressions were run with no transformations of the data and then, with single and double square root and log transformations for each trace metal. Graphic diagnostics were done by observing residual versus fitted, Normal Q-Q, scale-location, and residual versus leverage plots (Kim, 2016). Normality was also examined using the Shapiro and Wilk's W statistic in the basic R statistical set while homoscedasticity was examined using the ncvTest in the R CAR package. The model fit was examined with lmfit in R, which includes the model intercept and slope, adjusted R^2, p-values, and other information to assess the model fit. Residual versus leverage plots were closely examined to see if potential outliers should be removed.

Results & Discussion

Water Column Characteristics

In 2014 weighted water column salinity averaged 19.6 ± 4.6 PSU with a range from 12.9 to 28.4 PSU. The 2014 water column weighted average temperature was 4.1 ± 1.1°C with a range from 0.97 to 5.23°C.

Sediment Characteristics

Descriptive characteristics of the sampled sediments in 1977 and 2014 are summarized in Table 8. Average sand and mud percentages were 42.9% and 56.2% in 1977, and 58.7% and 41.2% in 2014. The average mud fraction contained 41.2% silt and 15% clay in 1977 compared with 42.9% silt and 6.3% clay in 2014. Average TOC percentage in 1977 was 1.04% and 2.84% in 2014. The TIC percentage in 1977 was 7.86%, but only 0.04% in 2014. A nonparametric (Kruskal-Wallis Test) one-way ANOVA was carried out to determine if the sediment properties

mean/median values of the 1977 and 2014 sediment are comparable with significance determined at a p-value ≤ 0.05. Except for silt, all other measured sediment characteristics were significantly different between the sampling years.

Simpson Lagoon has an average depth less than three meters and the threshold wind velocity required to induce wave-current resuspension of bottom sediments is eight cm s^{-1}, based on time-series plots correlating wind speed and water column suspended solids concentration (Naidu et al., 1979). Applying the following linear regression equation from Alexander et al., 1975

$$Y \text{ (water current cm } s^{-1}) = 10.1 + 0.78*X \text{ (wind speed, m } h^{-1})$$

the average wind speed observed during the 2014 storm surge of 14 m s^{-1} may have produced water current velocities of 34 cm s^{-1} or greater.

A study of six Simpson Lagoon cores by x-radiography revealed highly interbedded sediments, suggesting a lagoon sedimentation regime dominated by depositional (seasonal flooding) and physical reworking (storm event) layers (Hanna et al., 2014). The modern sedimentation accumulation rate (0.07 cm y^{-1}) compared to the rate integrated over the last 1,500 years (0.15 cm y^{-1}) for the six sediment cores from Simpson lagoon suggest that modern sediment is being re-suspended and removed from the lagoon at an increased rate compared to the past. During other storm surges in the region anecdotal evidence supports the concept that large amounts of bottom sediment are suspended in the water column (Reimntiz and Maurer, 1979). Previous studies have provided indications that a majority of the sediments input to the lagoon are being re-suspended and transported out of the lagoon system (Hanna et al., 2014; Naidu et al., 1984; Hume and Schalk, 1967).

Descriptive Trace Metal Concentrations

Major and trace metal concentrations in sediment are presented in Table 9, and presented graphically as notched box plots in Figures 11,12 and 13. The notched box plots were plotted using $\log_{10}$ to reduce the data skew in the raw data and to provide a more normal distribution (Reimann et al., 2008). The notches provide an estimate of the 95 percent confidence interval around the median allowing a graphical comparison of medians between years somewhat like the more formal t-test. Comparisons of trace metal sediment concentrations between 1977 and 2014 show a consistent depleted Cr, Cu, Fe, Mn, Ni and Zn in the 2014 sediments compared to 1977. The notched box plots also suggest that the trace metal sediment concentrations are not comparable between years as supported by the earlier Kruskal-Wallis Test.

Table 8 – 1977 and 2014 Sediment Characteristics

Variable	N	Minimum	Maximum	Mean	SD	CV
Gravel (1977)	23	0.00%	5.50%	0.98%	1.71%	1.74
Gravel (2014)	20	0.00%	0.98%	0.13%	0.25%	2.00
Sand (1977)	23	7.70%	98.00%	42.90%	25.50%	0.59
Sand (2014)	20	29.50%	96.40%	58.70%	20.70%	0.35
Silt (1977)	23	0.70%	79.50%	41.20%	20.70%	0.50
Silt (2014)	16	21.20%	64.80%	42.90%	13.00%	0.30
Clay (1977)	23	1.00%	25.30%	15.00%	6.51%	0.43
Clay (2014)	16	4.07%	9.15%	6.31%	1.52%	0.24
Mud (1977)	23	1.70%	92.30%	56.20%	25.90%	0.46
Mud (2014)	20	3.59%	70.50%	41.20%	20.70%	0.50
TC (1977)	23	1.56%	14.00%	8.90%	3.71%	0.42
TC (2014)	20	0.21%	4.35%	2.88%	1.14%	0.40
TOC (1977)	23	0.08%	2.50%	1.04%	0.69%	0.67
TOC (2014)	20	0.21%	4.30%	2.84%	1.13%	0.40
TIC (1977)	23	1.40%	12.60%	7.86%	3.22%	0.41
TIC (2014)	20	0.003%	0.094%	0.036%	0.019%	0.52

Table 9 - 1977 and 2014 Sediment Trace Metals mg/kg dry weight

Variable	N	Minimum	Maximum	Mean	SD	Median	CV
Cr (1977)	23	16	70	47.78	15.08	54	0.32
Cr (2014)	20	4.64	20.90	11.40	3.68	11.11	0.32
Cu (1977)	23	6.3	33	17.53	6.703	18	0.38
Cu (2014)	20	0.48	8.78	3.78	1.99	3.53	0.53
Fe (1977)	23	8500	29200	20204	5878	22500	0.29
Fe (2014)	20	8814	20023	15406	3039	15371	0.20
Mn (1977)	23	115	554	283.3	121.1	268	0.43
Mn (2014)	20	36.19	173.20	91.54	39.66	80.60	0.43
Ni (1977)	23	8.4	32	23.93	7.082	27	0.30
Ni (2014)	20	1.60	24.23	6.50	4.59	5.18	0.71
Zn (1977)	23	28	120	76.09	23.78	83	0.31
Zn (2014)	20	35.33	81.21	63.83	13.77	65.97	0.22

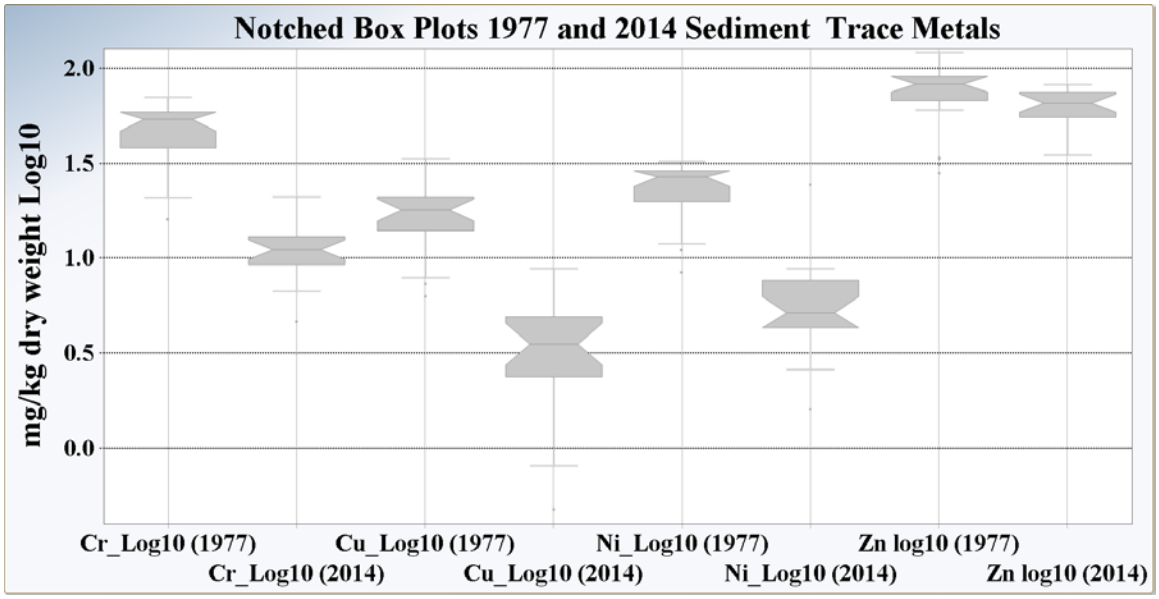


Figure 11 - 1977 and 2014 Cr, Cu, Ni, and Zn

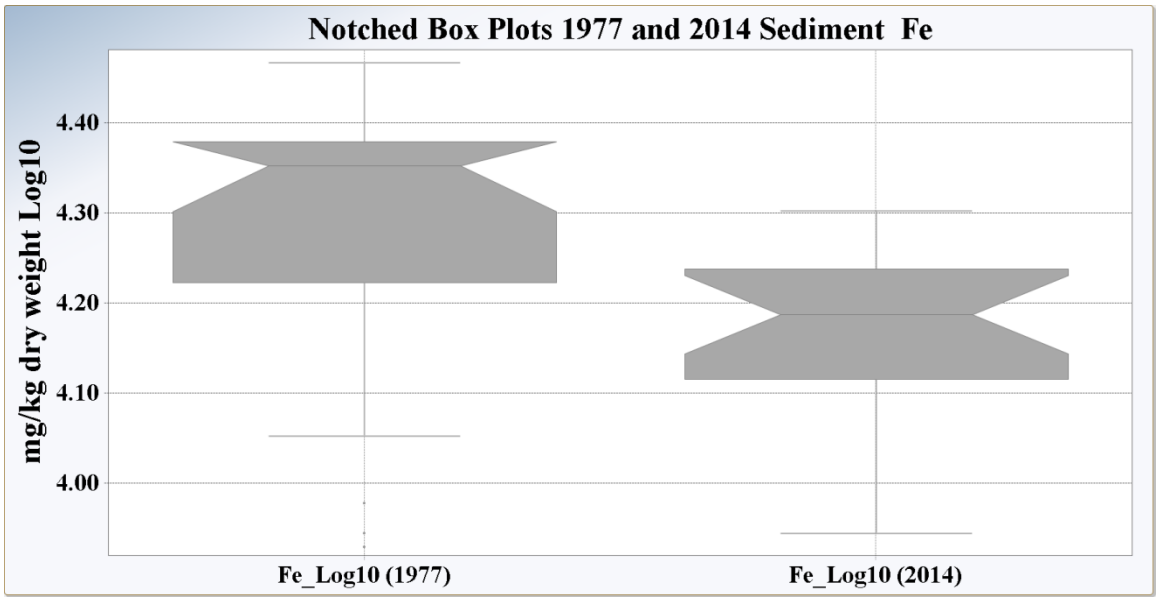


Figure 12 – 1977 and 2014 Sediment Fe

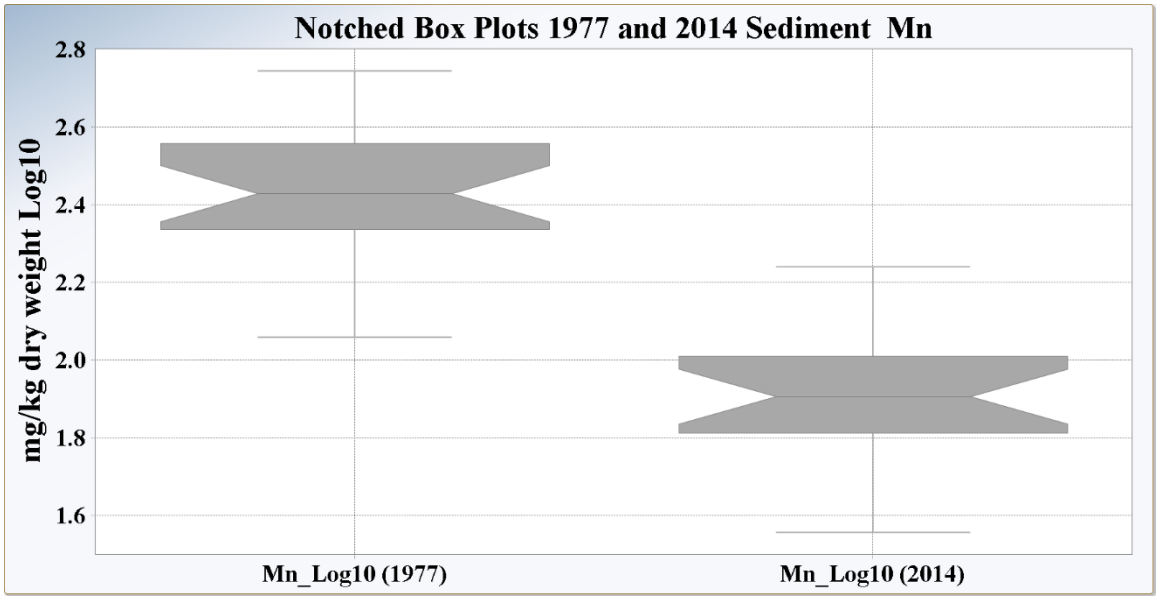


Figure 13 - 1977 and 2014 Manganese

Sediment Baseline Comparison of 1977 to 2014 Results

Because natural sediment trace metal concentrations vary with grain size, any comparison of trace metal concentrations between stations requires some form of normalization or compensation for grain size texture differences between samples (Windom et al., 1989; Summers et al., 1996; Trefry et al., 2003). Normalization methods usually fall into the two following groups:

1. A granulometric approach either by sieving the sample to provide only the mud fraction (< 63µm) for analysis or directly normalizing the trace metal data analyzed on the total sediment by the percentage mud in the bulk sample (Horowitz, 1985).

2. A geochemical approach using "conservative" elements that are considered to have a uniform regional crustal-rock source, high natural concentration, minimal anthropogenic input, and exhibits a linear correlation with the trace elements in the sediment fine grains (Schropp et al, 1990; Aloupi and Angelidis, 2001; Trefry et al., 2003).

Utilization of the grain size mud fraction (≤ 63µm, silt+clay component) is used here as a normalizing factor with the assumption that most of the trace metals are found in the mud fraction (Horowitz, 1985). Aluminum, frequently used as a reference element in assessing metal concentrations in coastal regions (Trefry et al., 2003; Windom et al., 1988), was not analyzed in 1977 and could not be used a normalizing factor. Iron in some coastal regions may be used as a reference element (Schiff and Weisberg, 1999). Due to potential chemical reactions promoting dissolution or precipitation of iron in sediments, this metal was not an ideal normalizing element for Simpson Lagoon.

Table 10 - 1977 Simpson Lagoon Sediment Trace Metal Correlations

	Cr	Cu	Fe	Mn	Ni	Zn	Sand	Mud	TOC
Cr	1.00	***	***	**	***	***	***	***	***
Cu	0.76	1.00	***	**	***	**	***	**	***
Fe	0.88	0.67	1.00	***	***	***	***	***	***
Mn	0.62	0.60	0.80	1.00	***	***	***	***	***
Ni	0.93	0.71	0.96	0.78	1.00	***	***	***	***
Zn	0.87	0.62	0.89	0.73	0.90	1.00	***	***	***
Sand	-0.90	-0.68	-0.89	-0.68	-0.92	-0.79	1.00	***	***
Mud	0.87	0.63	0.90	0.72	0.92	0.80	-0.99	1.00	***
TOC	0.71	0.74	0.70	0.66	0.76	0.79	-0.65	0.65	1.00

Table 11 - 2014 Simpson Lagoon Sediment Trace Metal Correlations

	Cr	Cu	Fe	Mn	Ni	Zn	Sand	Mud	TOC
Cr	1	***	.	**	**				
Cu	0.93	1		***	**				
Fe	0.4	0.23	1			***	***	***	***
Mn	0.63	0.71	-0.2	1	*	.	*	*	**
Ni	0.65	0.65	0.03	0.52	1				
Zn	0.29	0.1	0.91	-0.38	-0.09	1	***	***	***
Sand	-0.22	-0.03	-0.86	0.45	0.05	-0.93	1	***	***
Mud	0.22	0.03	0.86	-0.45	-0.05	0.93	-1	1	***
TOC	0.06	-0.15	0.69	-0.57	-0.21	0.87	-0.9	0.9	1

Degree of significance of the correlation indicated by stars
*** very high significance ($p<0.001$); ** high significance ($0.001 \leq p < 0.01$);
* significance ($0.01 \leq p < 0.05$); **.** weak significance ($0.05 \leq p < 0.10$); No symbol for no significance ($p \geq 0.10$).
Note: Spearman Rank Correlation - Raw Data - Only 1977 data within the 2014 sampling frame used.

Correlation Analysis

Because not all trace elements or sediment characteristics were normally distributed, a Spearman Rank Correlation on the raw non-transformed 1977 data set was used with $p \leq 0.05$ (Table 10). The results support the use of mud % as a normalizing factor in the linear regression model. The correlation matrix for the comparable sediment trace elements and mud for 2014 are shown in Table 11. Contrasted with the 1977 correlation matrix, the 2014 correlation matrix shows no significant correlations between Fe and Cr, Cu, Mn, Ni, or Zn and mud % .

1977 Baseline Linear Regression Model

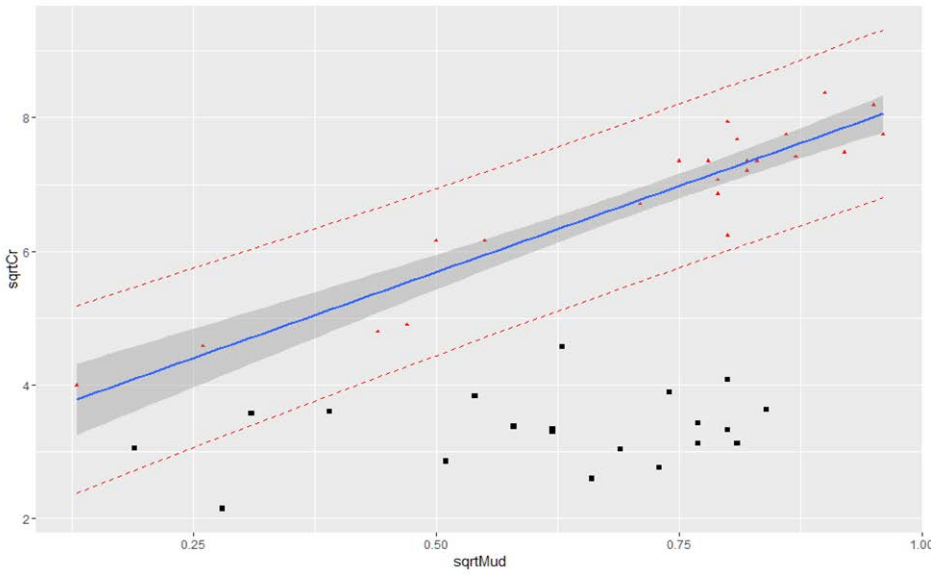
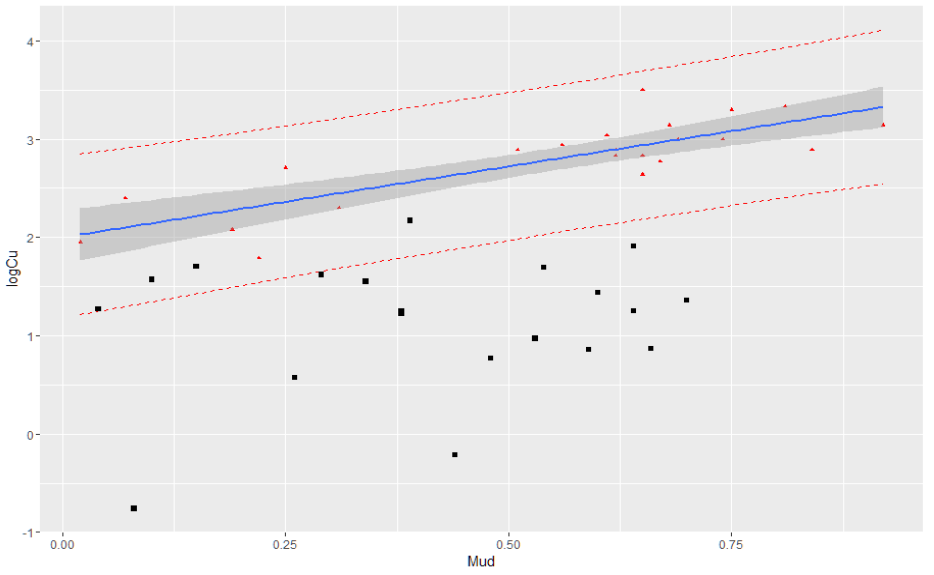
Results of the linear regressions are shown in Table 12. Single outliers were removed for each of the following trace metals, Cu, Fe and Zn. All of the slope coefficients were positive and significantly different from zero ($p < 0.01$). The adjusted R^2 for Cr, Fe, Ni, and Zn suggests that over 80% of the variance in the dependent variable (y) can be explained by the predictor (Mud) variable. Only 66% of the variation in Cu and Mn were explained by the regression model, due to the somewhat greater degree of scatter in the datasets at the upper end of the plot.

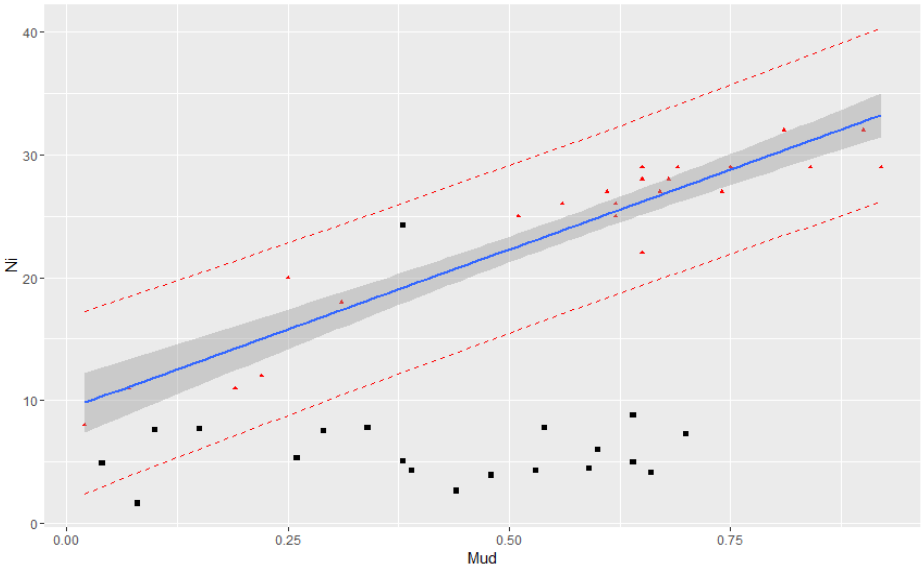
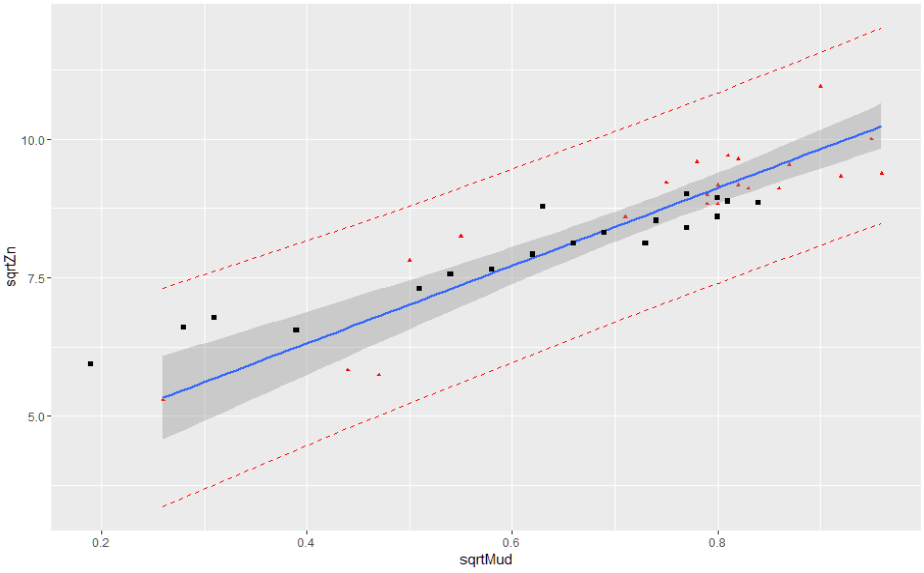
Table 12 – Transformations and results of regressions that were applied to the 1977 Simpson Lagoon Mud versus trace metal data. Correlations between all trace metals and mud were significant ($p < 0.01$) (Adjusted R^2=coefficient of determination, RSE = Residual Standard Error).

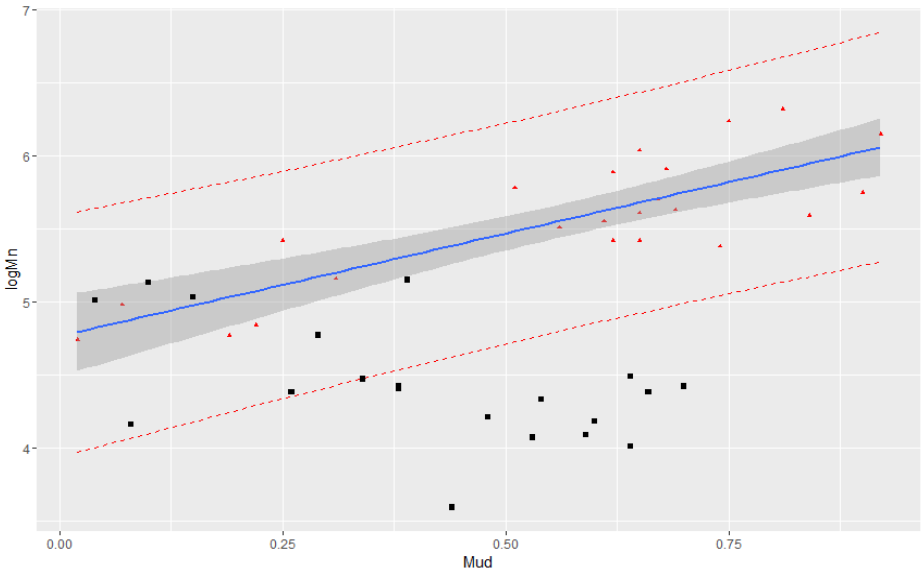
Metal	Transformation	N	Adjusted R^2	RSE	Slope	Intercept
Cr	√Y, √X	23	0.88	0.42	5.14	3.12
Cu	ln(Y)	22	0.66	0.26	1.44	2.00
Fe	None	22	0.86	2026	20003	9167
Mn	ln(Y)	23	0.66	0.26	1.41	4.76
Ni	None	23	0.89	2.35	26.01	9.29
Zn	√Y, √X	22	0.85	0.59	7.01	3.51

Observing the linear regression graphs (Figure 14 a-f), 2014 sediment trace metals Cr, Cu, Mn, and Ni primarily plot below the models 99% lower prediction interval. Four of the 2014 Ni sediment concentrations plotted between the 99% prediction intervals with three below and one above the regression line. This data presents an interesting case of anomalous low or depleted 2014 sediment concentrations for the Cr, Cu, Mn and Ni versus the 1977 dataset used to construct the model.

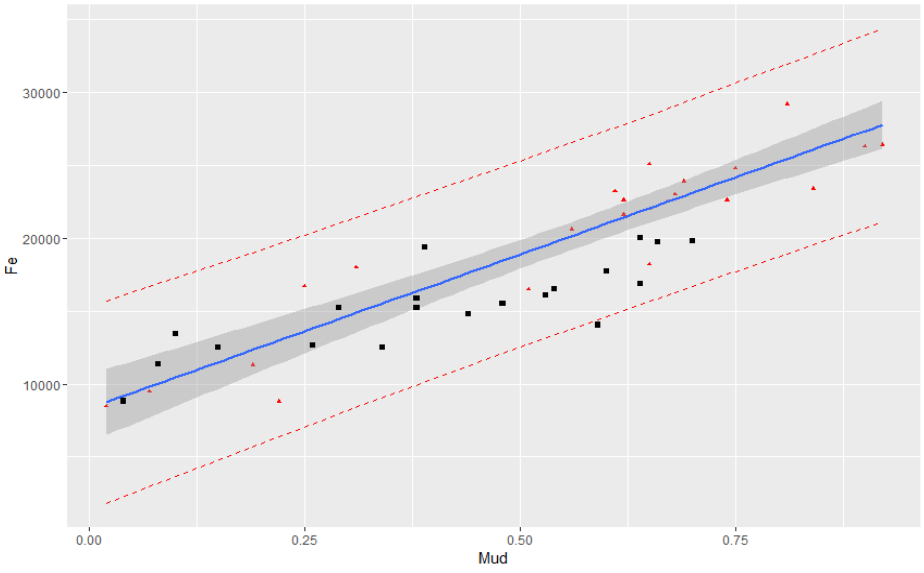
Realizing the limitations in the AKMAP 2014 Simpson Lagoon survey, which was not intended to directly investigate the effects of storm surges on nearshore sediment physical and trace metal composition, a few possible mechanisms are offered for the depletion of sediment trace metals in 2014 compared to 1977.

 sqrtCr 8 6 4 2 0.25 0.50 0.75 sqrtMud	14. (a)
 logCu 4 3 2 1 0 -1 0.00 0.25 0.50 0.75 Mud	14. (b)

 Ni Mud 0 10 20 30 40 0.00 0.25 0.50 0.75	14. (c)
 sqrtZn sqrtMud 5.0 7.5 10.0 0.2 0.4 0.6 0.8	14. (d)



14. (e)



14. (f)

Figure 14 – Mud versus Cr (a), Cu (b), Ni (c), Zn (d), Mn (e), and Fe (f). Red dashed lines represent the linear regression models 99% prediction interval, shaded area represents 95% confidence interval and blue line is the regression line. The 1977 data used to build the model are represented by small red triangles and the 2014 data is represented by the black squares. 2014 data was not included in the regression calculations used to develop the model.

Grain size fraction sorting by the 2014 storm surge suspended much of the clay fraction into the water column and provided a mechanism for the physical removal of trace metals associated with the clay fraction (Huang et al., 2012; Kalnejais et al., 2007). Due to the greater surface area and adsorption properties of clays their loss from the sediment removes significant portions of many trace metals present in the sediment, especially those metals most closely held in the residual phase, such as Cr, Cu and Ni (Suh et al., 2005; Trefry et al., 2003: Schropp et al., 1990). The 2014 Simpson Lagoon Al average concentration of 7,394 ± 1,552 mg kg^{-1} is much lower than that observed in the Beaufort Sea shelf adjacent Simpson Lagoon (Trefry et al., 2003) of 39,300 ± 16,300 mg kg^{-1}. The 2014 Simpson Lagoon Fe average concentration of 15,194 ± 3,019 is also higher than the Al concentration. Overall the 2014 Simpson Lagoon sediment low Al and Fe > Al values is an anomalous condition for marine sediments suggesting a dynamic physical alteration of the sediment grain size fraction composition due to storm surge (Trefry et al., 2003). In the adjacent Beaufort Shelf waters, 1999 sediment grain size fractions had been reported as being dramatically altered by a previous storm surge (Brown et al., 2004).

Chromium, Cu, and Ni 2014 average concentrations were around 22-27% of the 1977 averages. Average 2014 clay was about 42% of the 1977 clay and average 2014 sand was about 136% higher than 1977. The combination of low clay content and higher sand content, which acts as a diluting agent for these trace metals, in the bulk sediment samples could reasonably account for the depleted 2014 sediment trace metal concentrations compared to 1977. Iron and Zn were somewhat depleted with average concentrations being respectively 76% and 84% of the 1977 concentrations. The affinity of iron hydroxides and manganese oxides for Zn (Schiff and Weisberg, 1999; Balkis et al., 2010) and distribution throughout the other bulk sediments fractions, such as silt and sand, could account for the lesser depletion of these metals compared to 1977. Manganese average concentration in 2014 was only 32% of the average 1977 concentration. Mn removal during the storm surge may have been driven by salinity changes and redox changes in the upper few millimeters of sediments.

Water chemistry and physical processes occurring in the lagoon system are another factor in variability of sediment trace metal concentrations. Seasonal cycles of ice cover and open water, resuspension of sediments into the water column caused by storm events, low salinity to hypersaline waters, anoxic to oxic conditions, pH changes, and variations in organic carbon inputs are just some of the factors that can affect the biogeochemical cycle of trace metals in sediments (Huang et al., 2012; Du Laing et al., 2009). For example, trace metals can be absorbed or mobilized from sediments with changes in salinity and likely undergo cycling from one phase to the other during the seasonal salinity cycles in Simpson Lagoon. Since these changes can occur relatively rapidly, the system is rarely in an equilibrium state (Sweeny, 1984). Any significant decrease in summer sea ice and corresponding increase in open water fetch and wave energy (Smith and Thompson, 2016) could enhance the dynamics of sediment re-suspension and transport in Beaufort Sea coastal lagoon systems like Simpson Lagoon. Re-suspended sediments may remain in suspension for hours or longer during a storm event and be transported outside of the lagoon (Kalnejas et al., 2007; Hanna et al., 2014). The resuspension of sediment can result in increases in dissolved and fine particulate trace metals in the water column which may increase bioavailability of these elements and compounds (Eggleton and Thompson, 2004). Sediments may adsorb hydrocarbons and trace metals in oil spill events, it is unclear the impacts of storm

surges on these sediments. Increased loading of re-suspended sediments, especially clay, in the water column can potentially absorb to the suspended sediments and sink to the bottom as observed in a San Francisco oil spill (Larsen, 1980).

Conclusions

The 2014 sediment Cr, Cu, and Ni trace metal concentrations in Simpson Lagoon were depleted when compared to the 1977 datasets. This is believed to be primarily due to a storm surge that occurred just before and continued during the 2014 sampling. The storm surge was strong enough to re-suspend fine grained sediments and resulted in removal of these trace metal resources from the sampled sediments. Re-suspended sediments may remain in suspension for hours or longer during a storm event and be transported outside of the lagoon (Kalnejas et al., 2007; Hanna et al., 2014). Re-suspension of sediments can also result in increases in dissolved and fine particulate trace metals or other contaminants in the water column which may increase bioavailability of these elements and compounds (Eggleton and Thompson, 2004). Sediments may adsorb hydrocarbons and trace metals in oil spill events, the impacts of storm surges on these sediments is unclear. Increased loading of re-suspended sediments, especially clay, in the water column can potentially absorb to the suspended sediments and sink to the bottom as observed in a San Francisco oil spill (Larsen, 1980). Environmental monitoring of these nearshore lagoon systems utilizing sediments to will need to take these dynamics into consideration.

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