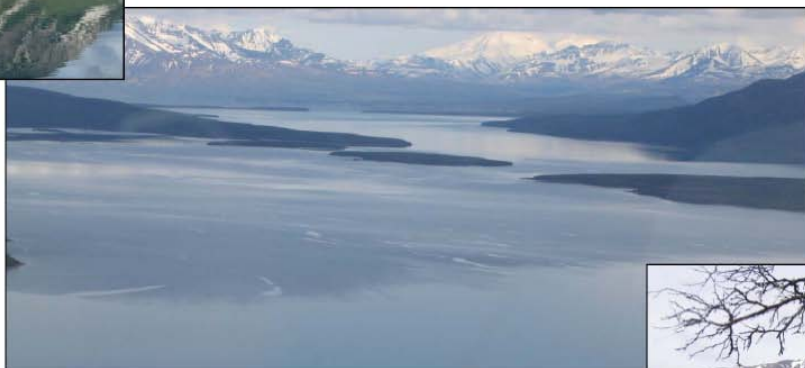




Historical Trace Element Trends Recorded in Lake Sediment Cores from the Southwest Alaska Network of Parks

Natural Resource Technical Report NPS/SWAN/NRTR—2010/395



ON THE COVER

Photographs of Brooks Lake, Naknek Lake and Kijik Lake in the Southwest Alaska Network
Photographs by: Brian Cohn and LeeAnn Munk, University of Alaska Anchorage

Historical Trace Element Trends Recorded in Lake Sediment Cores from the Southwest Alaska Network of Parks

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LeeAnn Munk
University of Alaska Anchorage
Department of Geological Sciences
3101 Science Drive
Anchorage, Alaska 99508

Brian Cohn
University of Alaska Anchorage
Environment and Natural Resource Institute
3151 Alumni Loop
Anchorage, AK 99508

Bruce Finney
Idaho State University
Department of Biological Sciences
921 S. 8th Ave., Stop 8007
Pocatello, ID 83209-8007

November 2010

U.S. Department of the Interior
National Park Service
Natural Resource Program Center
Fort Collins, Colorado

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Munk, L.A., B. Cohn, and B. Finney. 2010. Historical trace element trends recorded in lake sediment cores from the Southwest Alaska Network. Natural Resource Technical Report NPS/SWAN/NRTR—2010/395. National Park Service, Fort Collins, Colorado.

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Abstract

A study of trace element concentrations and accumulation rates in sediment cores from five lakes from southwest Alaska (Southwest Alaska Network (SWAN) of the National Park Service) was undertaken to establish historical trends in trace elements from anadromous and non-anadromous lake systems. Sediment cores were collected within the last ten years by various coring methods. All cores were sub-sampled at 0.5 to 1.0 cm intervals for standard core analyses. Additionally, samples were analyzed for mercury by atomic absorption (AA). A sub-sample of the sediment was digested in ultra-pure H_2O_2 and HNO_3 and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for major and trace elements including aluminum (Al), arsenic (As), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), and zinc (Zn). The longest record is preserved in the sediment core from Naknek Lake which extends back to 1284 AD. It appears that the anadromous lakes contain higher (up to 250 ppb in Brooks Lake) Hg concentrations than the non-anadromous lakes (averaging ~ 25 ppb Hg). However, both major and trace element accumulation rate trends indicate that all five lakes are dominated by landscape processes which seem to be the primary contributor of most elements to the lakes. The concentrations of trace elements vary from lake to lake depending on the overall landscape contributions (ie. glacial melt-water fed or not). Idavain Lake, which is non-anadromous and non-glacial appears to have the least disturbed sediment record of trace element accumulation over time and also indicates an increase in Hg from 24 ppb to 45 ppb at ~mid-1700s A.D. Other trace elements including Zn, Cu, Pb, and Cr also indicate an approximate 50% increase at that time probably from volcanic ash sources but other atmospheric contributions cannot be ruled out. Trace element concentrations also nearly double around the time of the Mount Katmai 1912 eruption but then recover to levels similar to those around mid-1700s. The lake sediment cores from Naknek Lake and Lake Clark (anadromous and glacial fed) indicate an approximate 50% increase in most major and trace elements since pre-1800 A.D. likely indicating that these systems are dominated by landscape weathering over time. The sediment core from Kontrashibuna Lake (non-anadromous and glacial) shows significant variability in trace and major element concentrations throughout the core, likely the result of the frequent landslide disruptions that were identified in the core.

Acknowledgments

This research was made possible by funding from the National Park Service Southwest Alaska Network (NPS SWAN). Special thank you to the Environmental Geochemistry Laboratory at Michigan State University for conducting the total Hg analyses on the sediment samples and to Andrea Krumhardt at the University of Alaska Fairbanks for providing access to the necessary sediment core samples. Also, the authors are grateful for the cooperation and interest of Jeff Shearer and Michael Shephard from the National Park Service.

Introduction

As land use changes occur within and near the boundaries of the NPS SWAN, and in light of the potential of atmospheric and salmon-vector transport from outside park boundaries, it is essential to establish a baseline for naturally occurring chemical elements and or compounds that may be introduced to these environments by human activity in the present and near future. This type of baseline data and information will provide a framework in which to assess and compare any future data and studies on the occurrence and distribution of trace metals and other trace elements. Some examples of common inorganic elements and compounds that may exist naturally but may also be introduced from anthropogenic sources in these environments include trace metals (mercury, zinc, lead, copper, etc.) and other trace elements (arsenic, selenium) which can be utilized as micronutrients in aquatic systems. In addition, many of the lakes in the SWAN are anadromous and semelparous and therefore support large runs of sockeye salmon (*Oncorhynchus nerka*) today, however, they may or may not have in the past. Thus it is of interest to compare trace element occurrence with historical salmon abundance. Although a direct comparison between salmon abundance and contaminants cannot be made, it is possible to compare the $\delta^{15}\text{N}$ signature as a proxy for marine derived nutrients (i.e. salmon) to the trends of potential contaminants preserved in lake sediment cores. In particular, this study focuses on mercury because salmon are known carriers (vectors) of mercury that bioaccumulate this heavy metal in the ocean (more than 95% of salmon biomass is accumulated in the marine environment over 1-4 years). During spawning migrations, Pacific salmon likely transfer bioaccumulated mercury from the northern Pacific Ocean to freshwater and terrestrial ecosystems.

Although the role of Pacific salmon in transferring nutrients from the ocean to their natal lakes and streams has received considerable attention (e.g. Schmidt et al., 1998) it may also be that they contribute to the metal load of the sediments.

Potential sources of mercury and other trace metals to the aquatic lake systems include 1) the natural weathering of bedrock including volcanic deposits such as tephra and subsequent transport through surface water and groundwater, 2) historic anthropogenic sources of metals from atmospheric deposition from the smelting of metallic sulfide ores and burning of fossil fuels that are transported to the Arctic and subarctic, and 3) salmon returning to freshwater environment.

To date there has been limited research done to indicate the natural vs. anthropogenic sources of mercury or other trace metals in most Alaskan environments including the SWAN. Most work has focused on organic contaminants such as polychlorinated biphenols (PCBs) which have been shown to be transported from ocean environments by salmon to terrestrial ecosystems (Krummel et al., 2003) in addition to the transport and deposition by ocean and atmospheric currents. Smith et al. (2006) reported that a range of trace metals are detectable in recent lake sediments in Katmai National Park as part of a study to determine metal accumulation in freshwater mussels.

Previous and current work in the SWAN by Finney (2006) has focused on reconstructing the paleolimnology of several lakes within the parks. The main goal of this work is to decipher past trends in salmon abundance from lake sediment cores, primarily through utilizing the $\delta^{15}\text{N}$ stable isotope signature input to the lakes from the marine environment carried by sockeye salmon. In general the marine $\delta^{15}\text{N}$ signature is approximately 10 ‰ higher than the non-marine signatures input from the landscape and therefore provides an excellent tool for estimating relative salmon abundance through time as preserved in the lake sediments. Recent work by Cohn (2009) in non-anadromous lake systems of the SWAN suggests that changes in watershed vegetation type and abundance and disturbance (volcanic eruption) influence erosion and thus the delivery of nutrients, micro-nutrients and minerals to the aquatic system. Several lines of evidence also suggested potential contributions from atmospheric sources into the aquatic ecosystems of the SWAN.

Study Objectives

The overall goal of the proposed work is to determine historical trends of mercury and other trace metals and the accumulation of these elements within the lake environments of the SWAN. This will provide information on the geogenic and possible anthropogenic sources of these elements in the Parks and therefore establish a baseline from which to assess future changes in the geochemistry of these aquatic systems. Specifically the objectives of the work are to:

- 1) determine the total mercury concentrations from bulk sediment samples from lakes of high importance as determined by the National Park Service (Lake Clark, Naknek, Brooks, Kontrashibuna, and Idavain, Figure 1),
- 2) utilize the total concentrations of other environmentally significant elements, such as copper, lead, and zinc, from the same lake sediment cores to help decipher mercury trends and assess anthropogenic vs. geogenic sources as a function of time, and
- 3) assess the possible influence salmon have on transporting mercury (i.e. $\delta^{15}\text{N}$ vs. mercury) and other metal concentrations in the lakes as preserved in the sediment record .



Figure 1. Shaded relief map of the study area illustrating the five lakes from which sediment cores were collected and utilized for this study.

Methods

Sediment cores that were previously collected from the SWAN Tier 1 and other lakes (Finney, 2006) were used for this study. Five different sediment cores from four different classifications of lakes were used in this pilot study as listed below:

- 1) Non Anadromous, non-glacial lake

Idavain Lake – Katmai National Park and Preserve

- 2) Non Anadromous, glacial lake

Kontrashibuna Lake – Lake Clark National Park and Preserve

- 3) Anadromous, non-glacial lake

Brooks Lake – Katmai National Park and Preserve

4) Anadromous, glacial lakes

Naknek Lake – Katmai National Park and Preserve Lake Clark – Lake Clark National Park and Preserve

Sediment samples were selected at appropriate intervals from the length of each sediment core for both total mercury and trace metal analysis. The sample interval at the tops of the cores was 0.5 to 1 cm but is larger in the lower parts of the cores due to sampling limitations to stay within budget for this pilot study and based on availability of processed sediment. The sediment core from Naknek Lake was an exception and was sampled about every 10 cm in the upper part of the core then at varying intervals below because of its greater length and limits on the number of samples that could be analyzed. In addition, after the Hg analysis was completed there was not enough sample material remaining for several of the Lake Clark intervals and therefore, there are some intervals that were not analyzed for other trace elements. Table 1 illustrates the exact samples that were analyzed for each core in this study. A split of each sample was weighed, digested and analyzed by ICP-MS for metals at the University of Alaska Anchorage and the other split was sent to the Applied Geochemistry Laboratory at Michigan State University for total mercury analysis performed on a Lumex RA-915+ Zeeman Corrected Atomic Absorption (AA) analyzer with the Thermal Decomposition (TD) R-91C attachment. This allows for the analysis of mercury in freeze-dried sediment rather than liquid analysis which is most appropriate for solid samples.

The stable isotopes of nitrogen in lake sediments were determined on freeze dried, finely ground, homogenized samples by elemental analysis-isotope ratio mass spectrometry (EA-IRMS, Carlo Erba Elemental Analyzer coupled with a Finnigan Delta V Plus Mass Spectrometer at the University of Alaska, Fairbanks and EA-IRMS, Carlo Erba Elemental Analyzer coupled with a Finnigan Delta ^{XP} Plus Mass Spectrometer at the University of Alaska, Anchorage). ¹⁵N is expressed in δ notation, indicating the difference between a sample and a standard (Peterson and Fry 1987):

$$\delta^{15}\text{N} (\text{‰}) = [\text{R}_{\text{sample}} - \text{R}_{\text{standard}}] \times 1000$$

Where R is the ratio of ¹⁵N/¹⁴N. All isotope results were expressed relative to the international standards: atmospheric N₂ (AIR) for δ¹⁵N. Analytical precision associated (SD) with the EA-IRMS for δ¹⁵N was typically 0.2 ‰ or less. Precision was typically lower for replicate (n ≥ 4) analyses.

Core chronologies were developed using a combination of both radiometric (¹⁴C [radiocarbon] and ²¹⁰Pb analysis) and tephrochronologic (tephra stratigraphy) methods. The ²¹⁰Pb method is commonly used to determine the accumulation rate of sediments in lakes and oceans over the past 100 – 150 years. The chronology of individual lake records was based on vertical down-core profiles of excess ²¹⁰Pb in sediments. One cubic centimeter samples of sediment were freeze-dried, homogenized, and analyzed for ²¹⁰Pb age determination using alpha-spectrometric analysis by Flett

Research Ltd., Winnipeg, Manitoba, Canada. From the accumulation rate calculations, the age of sediment from a particular depth in the sediment column can be estimated. Sediment ages and chronological errors were estimated by using the constant rate of supply (CRS) method based on excess or unsupported ^{210}Pb activity (Appleby and Oldfield 1978; Binford 1990). All dates are reported as year After Dominion (AD). Typically, accumulation rate over a period of 80 -100 years were obtained. Ages of sediments beyond the maximum obtainable ^{210}Pb analyses were estimated by a combination of extrapolation of mass accumulation rates or radiocarbon dating and tephra identification depending on the core stratigraphy, sedimentation rate and availability of organic matter in core.

Where radiocarbon dates were used, they were calibrated and converted to Years AD or Years BP (Before Present) using the CALIB radiocarbon calibration program (e.g., Stuiver and Reimer, 1993; Stuiver et al., 1998). Radiocarbon samples were submitted to the Center for Accelerator Mass Spectrometry (CAMS), Lawrence Livermore National Laboratory. Tephra layers common in these cores given the close proximity to active volcanoes were critical in refining chronologies based on known events. Tephrochronology also assisted in dating and between lake correlation.

Data analysis includes comparison of total mercury and other metal concentrations with depth (age) in the sediment cores. In addition, the total mercury and the $\delta^{15}\text{N}$ signal are examined as a function of age as well as compared to each other through basic regression analysis.

Results and Discussion

Trace element results for both anadromous and non-anadromous lake systems in both glacial and non-glacial systems were examined for this study. Figures 2-6 illustrate the trace element trends for all sediment cores as well as aluminum concentration for comparison. Aluminum is a conservative element that can be used as a control for comparing non-conservative trace element behavior in natural systems. In other words if trace elements vary in a similar pattern to aluminum, the trace elements are considered to be geogenic in origin and in the case of this study likely represent landscape contributions to the lakes. This is particularly important in the SWAN environment because of the abundance of high-silica volcanic rocks that contain appreciable aluminum.

Non-Anadromous Lakes

Idavain Lake represents a non-anadromous, non-glacial lake system. Because of the lack of salmon and glaciolacustrine input, its trace metal record may best preserve a background record of trace element accumulation over time (Figure 2). The deeper part of the core has fewer samples that were analyzed for trace elements, but does indicate a relative steady input of trace elements to the system. The upper part of the core is dominated by the pulse of ash from the 1912 Mt. Katmai eruption. Initially,

concentrations of most elements are reduced likely reflecting the high glass content of the ash. Subsequently, concentrations of most elements nearly double and then recover to the pre-1912 concentrations near the top of the core. The sudden input of fresh, easily weathered volcanic ash can contribute a pulse of major and trace elements into the lake system. According to the Idavain Lake sediment core it apparently takes 75-100 years for the lake sediments to recover to the pre-volcanic disruption state.

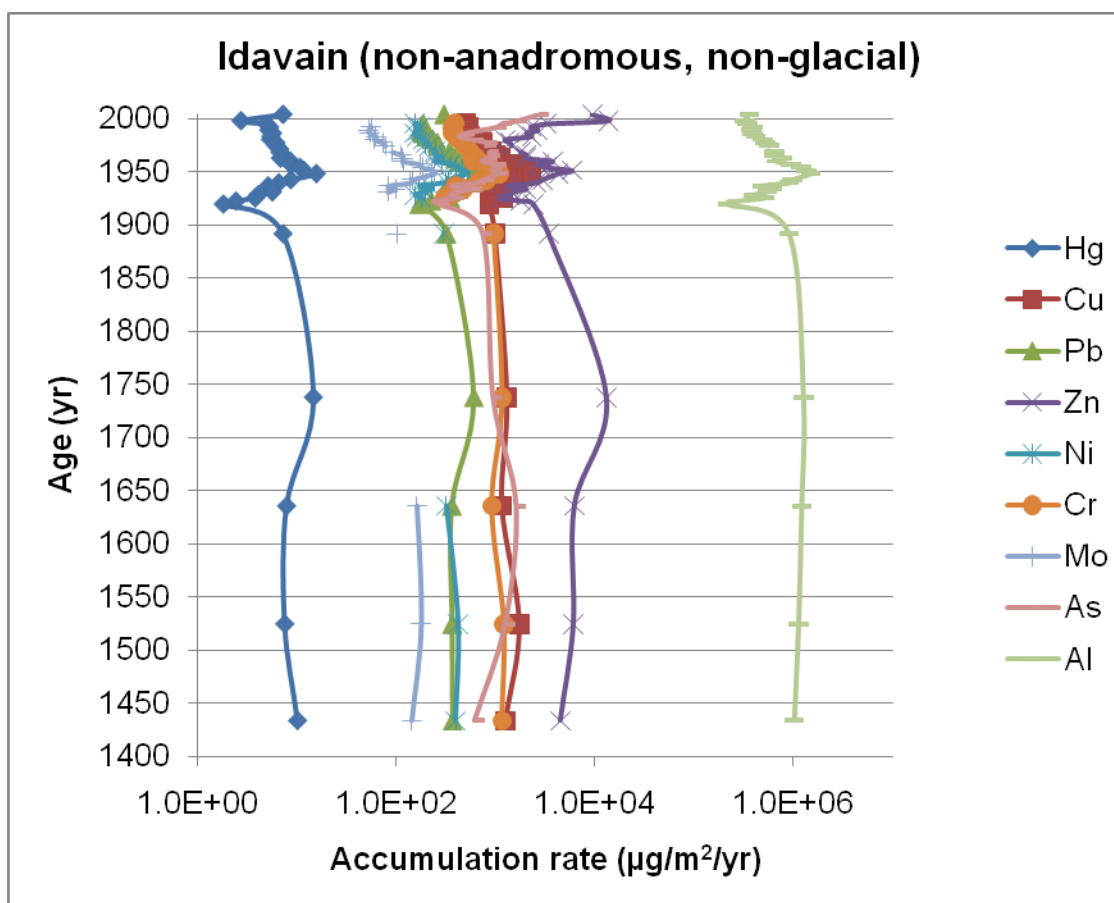


Figure 2. Idavain Lake sediment core historical accumulation rate trace element trends.

The majority of the trace elements have the same trend as Al indicating that the landscape contributions from weathering of the surrounding bedrock and/or from pulses of volcanic ash deposition are the dominant processes controlling the inputs of trace and major elements to Idavain Lake. The only elements that have a different trend in the upper part of the core are As and Zn which increase at the top of the sediment column and to some extent Hg, which also increases. There are numerous possibilities that could explain these trends. For example, As is a redox sensitive element and is more mobile under reducing conditions. Therefore, this could explain the increase in As in the top part of the core. It has a complex cycle in lake systems and can also be mobilized at the sediment-water interface, or could reflect anthropogenic contributions.

Zinc is a common micronutrient and may be concentrated at the top of the sediment core where the organic matter content is higher.

The other non-anadromous lake included in this study was Kontrashibuna Lake. The sediment core from Kontrashibuna Lake (non-anadromous, glacial) shows significant variability in trace and major element concentrations throughout the core (Figure 3). This was expected because the lake receives most of its water from glacial meltwater resulting in a comparatively higher sedimentation rate setting, and also due to frequent landslide disruptions that were identified in the core by the presence of intervals with coarsening upward sequences. This results in disturbances in the sediment accumulation and therefore, subtle patterns in trace element concentrations are difficult to decipher. However, this core is of value because it does indicate relatively constant long-term trends in the trace metals over the past ~ 700 years.

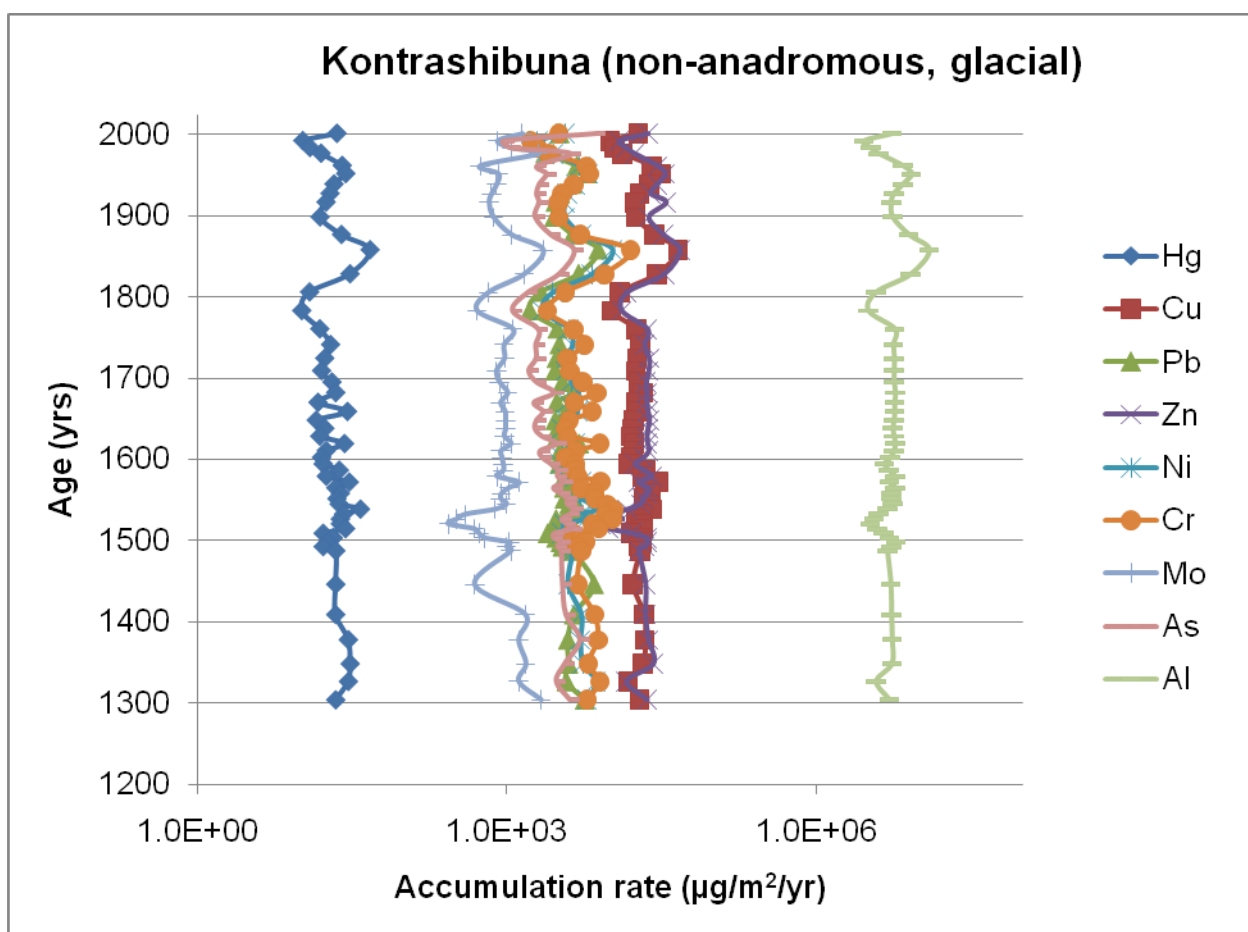


Figure 3. Kontrashibuna Lake sediment core historical accumulation rate trace element trends.

Anadromous Lakes

Figure 4 illustrates that major and trace elements in the sediment core from Brooks Lake have a relatively constant accumulation rate until just prior to 1600 A.D., followed by a relatively steady decrease to the present, with a spike in accumulation rates

Also of note is that the sediment core from Brooks Lake has the highest concentrations of Hg (up to 250 ppb) as compared to the other cores. For comparison, a study of Hg in lake sediments from northern Canada indicates that mean Hg concentrations range from 23 to 155 ppb in post 1950s age sediments and that mean Hg concentrations in pre 1950s sediment range from 15.8 to 130 ppb (Lockhart et al., 1998). The lake sediments in the SWAN fall within these ranges, with the exception of Brooks Lake which has elevated Hg concentrations at depth as well as in the upper parts of the sediment core. However, the source of Hg in the Canadian lakes is interpreted to be atmospheric rather than geogenic and/or from salmon contributions as may be the case for Brooks Lake.

The anadromous and glacial-fed lakes include Naknek Lake and Lake Clark. These lakes indicate an approximate 50% increase in most trace element accumulation since pre-1800 A.D. (Figures 5 and 6). However, they also show this trend for major elements likely indicating that these systems are primarily controlled by landscape contributions over time with some exceptions, mainly Hg (addressed in the next section) and some of the more redox sensitive elements that may have less predictable trends in particular in the upper part of the cores.

Our assessment from the Hg/Al data for Lake Clark and Naknek Lake is no trend in Lake Clark and increasing over time in Naknek Lake based on a graphical comparison. We feel this is consistent with a salmon source, as there are larger contributions of salmon nutrients in Naknek.

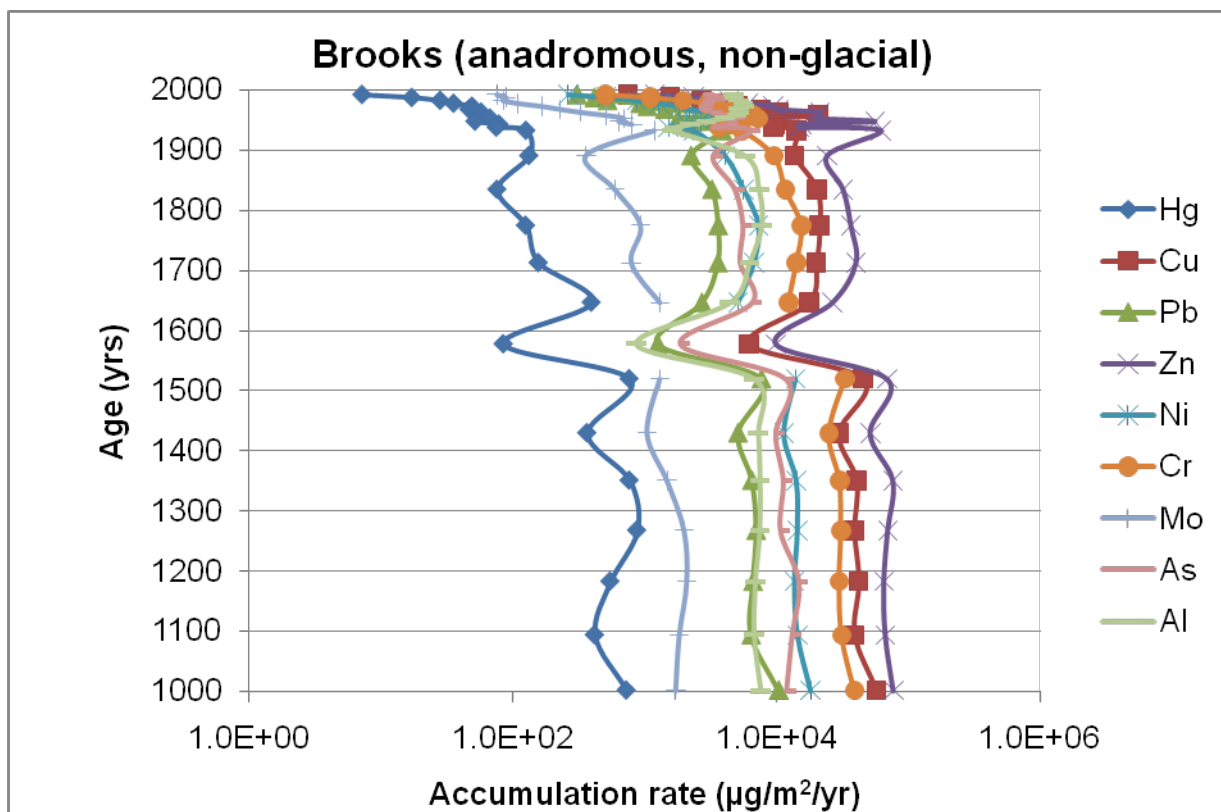


Figure 4. Brooks Lake sediment core historical accumulation rate trace element trends.

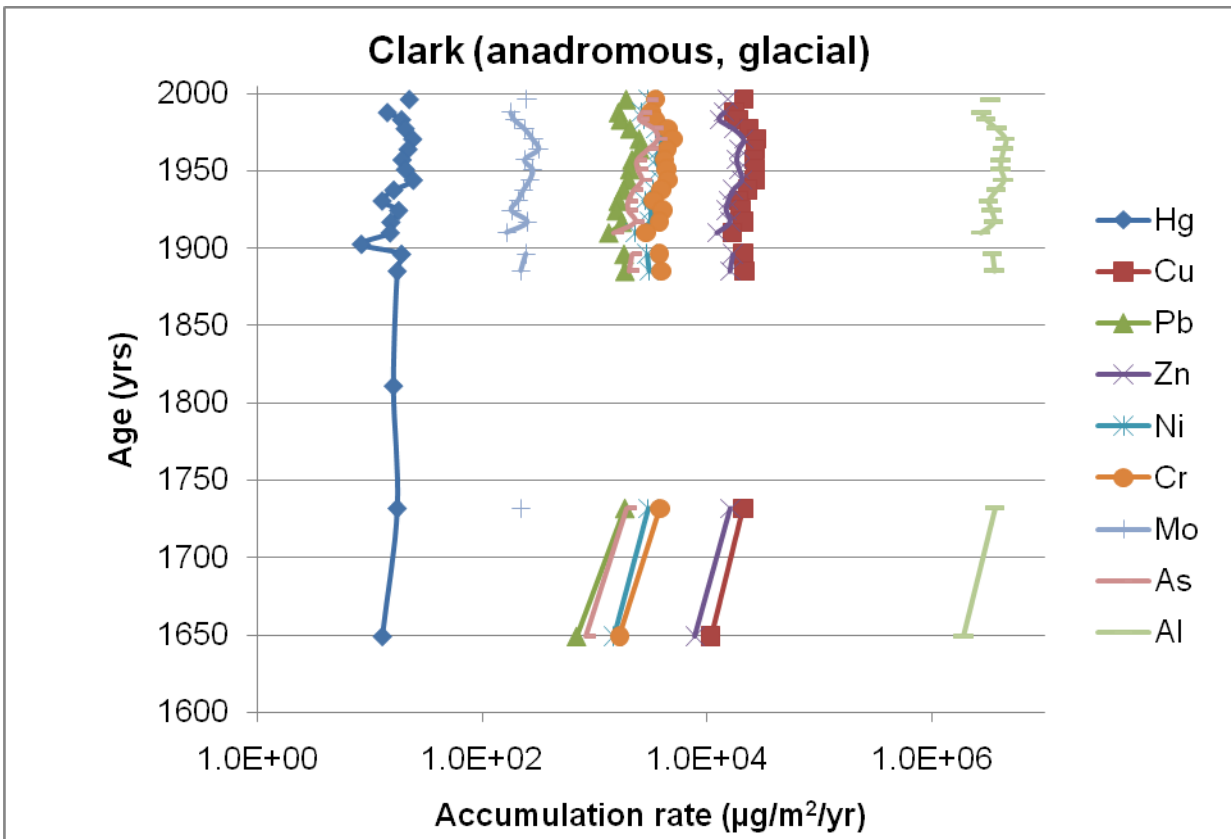


Figure 5. Lake Clark sediment core historical accumulation rate trace element trends.

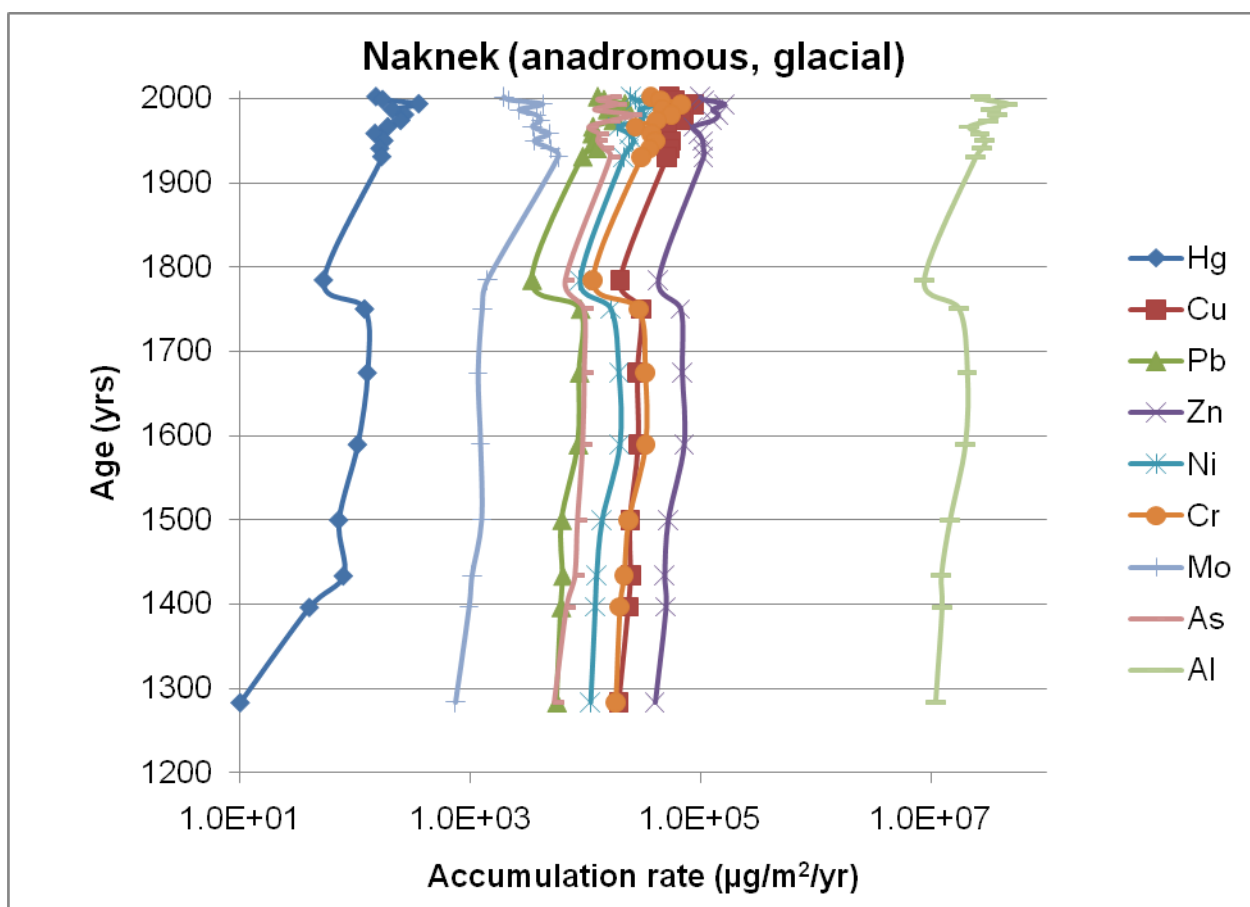


Figure 6. Naknek Lake sediment core historical accumulation rate trace element trends.

$\delta^{15}\text{N}$ and Hg

Because of the relatively elevated Hg concentrations in the anadromous lakes it is of interest to further investigate any possible relationship between Hg and marine derived nutrients (i.e. the $\delta^{15}\text{N}$ proxy). Figures 7-11 illustrate the $\delta^{15}\text{N}$ and Hg accumulation rates as a function of age (depth) in the cores as well as a basic regression analysis to test the possibility of a correlation between $\delta^{15}\text{N}$ and Hg in each system. Additionally, because of the pristine nature of the SWAN lake environments it is of interest to try to further understand potential sources of certain trace elements, particularly Hg.

As expected there is no correlation between the $\delta^{15}\text{N}$ signature and Hg based on the down-core comparison of $\delta^{15}\text{N}$ and Hg accumulation rates in the non-anadromous lakes. The $\delta^{15}\text{N}$ signature does not reflect a marine signature. There is a slight negative correlation for Idavain Lake and slight positive correlation for Kontrashibuna Lake. R-squared values are 0.0234 and 0.0013 for Idavain Lake and Kontrashibuna Lake respectively, but these are statistically insignificant.

The same comparisons made for the anadromous lakes are similar but with relatively stronger R-squared values. Brooks Lake has a negative correlation with an R-squared value of 0.1897, Lake Clark has a positive correlation with an R-squared value of 0.1247, and Naknek Lake has a negative correlation with the strongest R-squared value of 0.3037, however, these R-squared values are still low. Based on $\delta^{15}\text{N}$ as a proxy for nitrogen loading Naknek has the highest values of all the lakes and it has the highest Hg accumulation near the top of the core. One hypothesis would be that increasing amounts of Hg in salmon in more modern times has resulted in this increased Hg accumulation compared to about 200 years ago. An additional hypothesis is that reductions in sedimentation load into Naknek Lake has resulted in more concentrated accumulation within the sediment profile in the recent past in contrast to higher sedimentation rates during the Little Ice Age.

Therefore, the relationships between salmon (i.e., $\delta^{15}\text{N}$) and Hg are likely complicated by changes over time in Hg concentrations in salmon. Salmon take on most of their biomass (and trace elements) while feeding in the North Pacific ocean, and it is likely that Hg concentrations in this region have increased since the 20th century from increased sources such as atmospheric input from Asia. Therefore, as the Hg burden of returning salmon is not constant over time, $\delta^{15}\text{N}$ vs. Hg relationships over time are not constant. The fact that there are higher Hg concentrations in anadromous lakes suggests possible salmon contribution, but this contribution would vary over time in response to factors such as salmon escapement and Pacific Ocean Hg concentrations. It is also likely that there is spatial variability in ocean Hg levels, and thus salmon migration pathways could also be an important consideration. Negative Hg vs. $\delta^{15}\text{N}$ correlations could result from recent increases in ocean Hg levels, coupled with constant or decreasing escapement levels; constant or fewer salmon could transport more Hg if their burdens are higher.

Further regression analysis of concentration data indicate that Hg is only weakly correlated with AI whereas most other trace elements have a relatively strong correlation with AI just as the accumulation rate data show. This would also support the hypothesis that the Hg cycle in these lakes is more complicated than that of other trace elements prompting further study of Hg in the aquatic system and perhaps in both resident fish and salmon.

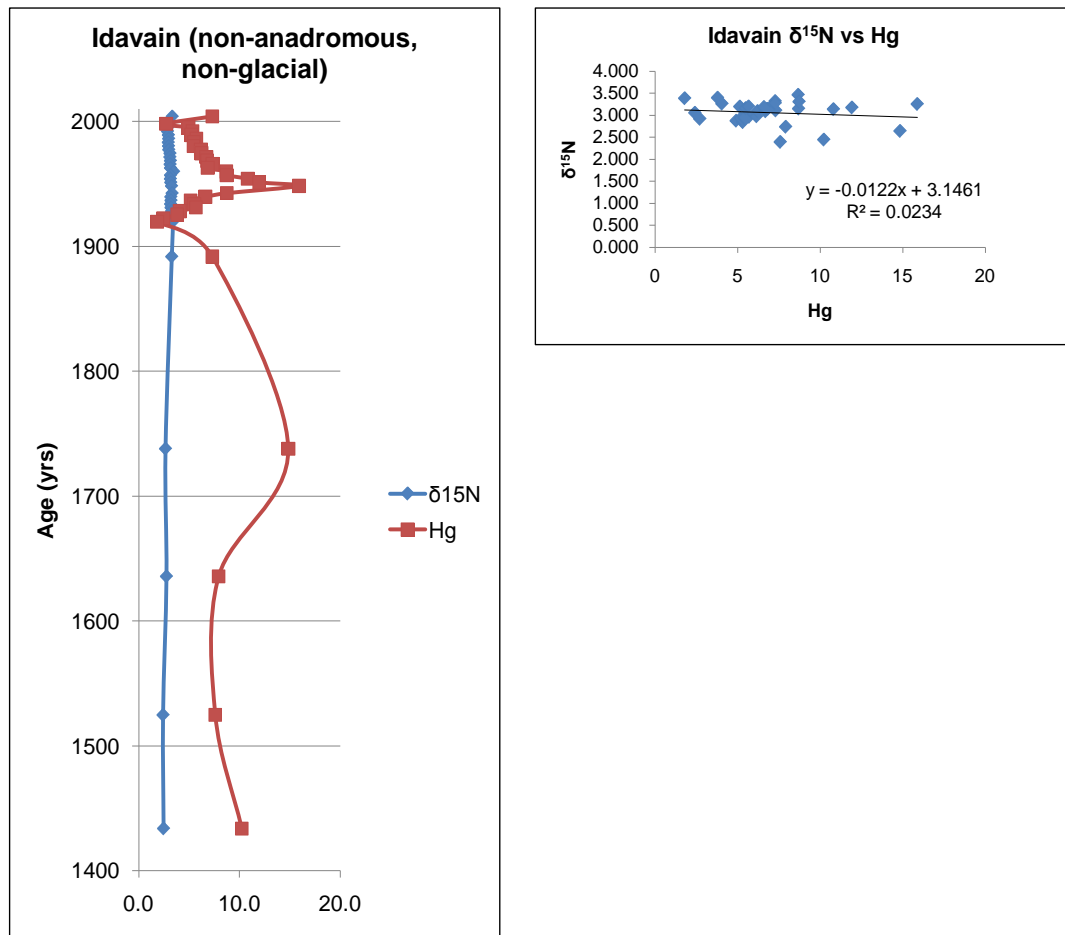


Figure 7. $\delta^{15}\text{N}$ vs Hg for Idavain Lake. Units for $\delta^{15}\text{N}$ are ‰ and for Hg are $\mu\text{g}/\text{m}^2/\text{yr}$.

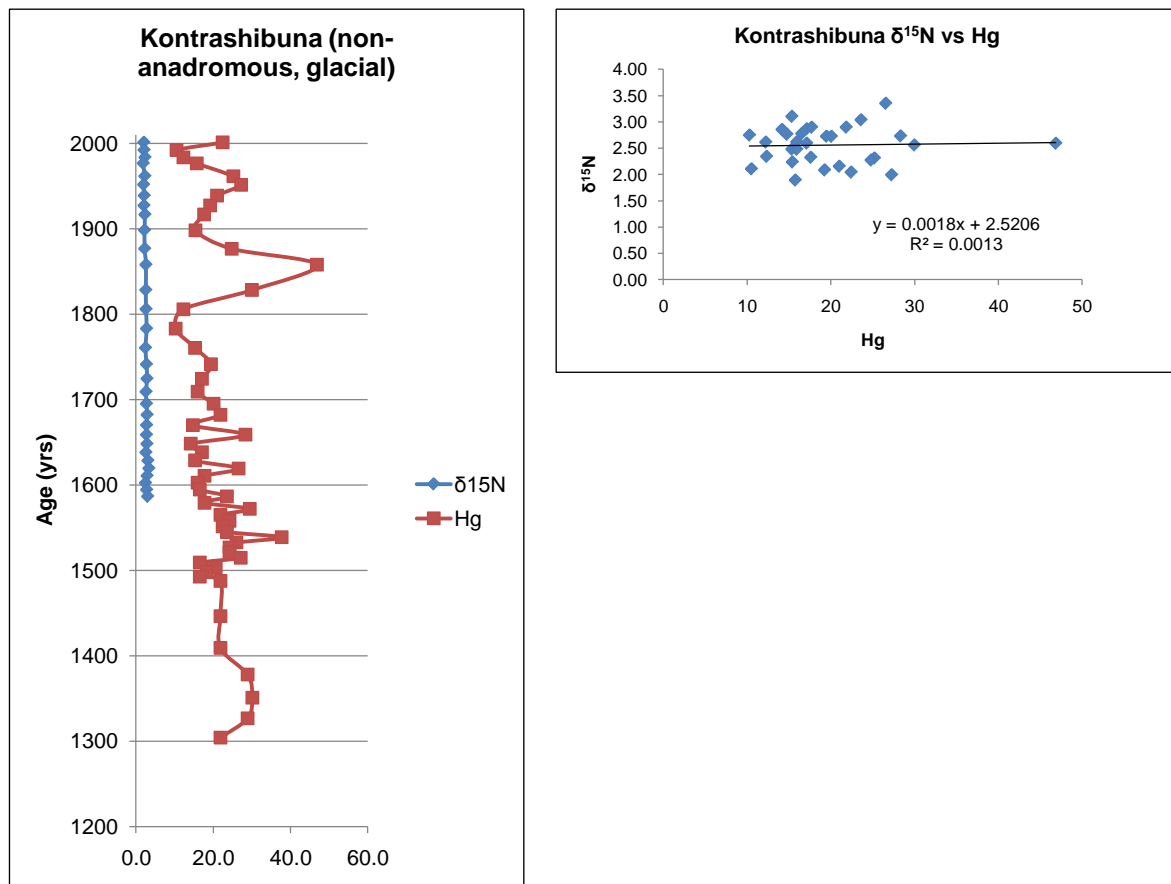


Figure 8. $\delta^{15}\text{N}$ vs Hg for Kontrashibuna Lake. Units for $\delta^{15}\text{N}$ are ‰ and for Hg are $\mu\text{g}/\text{m}^2/\text{yr}$.

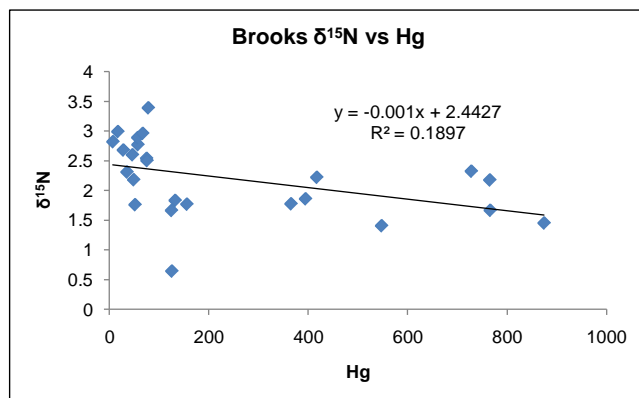
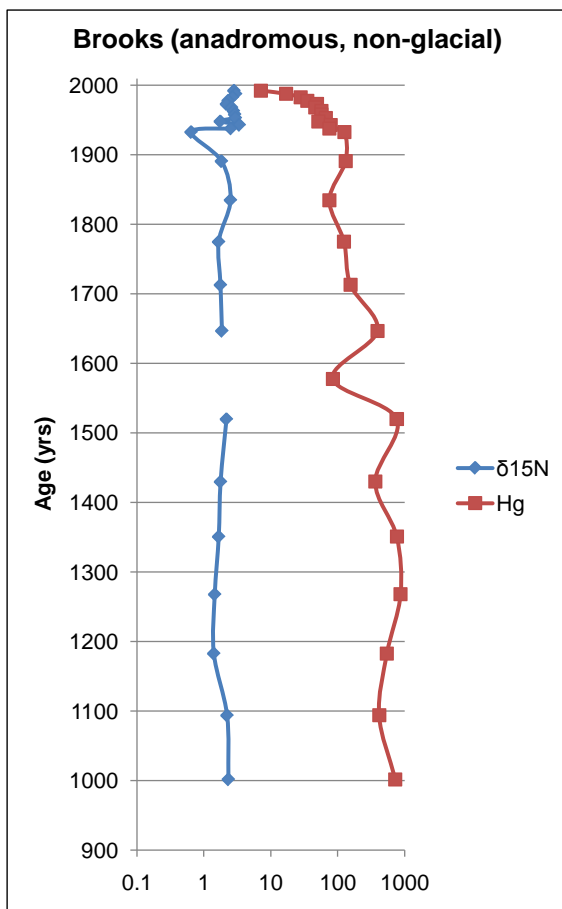


Figure 9. $\delta^{15}\text{N}$ vs Hg for Brooks Lake. Units for $\delta^{15}\text{N}$ are ‰ and for Hg are $\mu\text{g}/\text{m}^2/\text{yr}$.

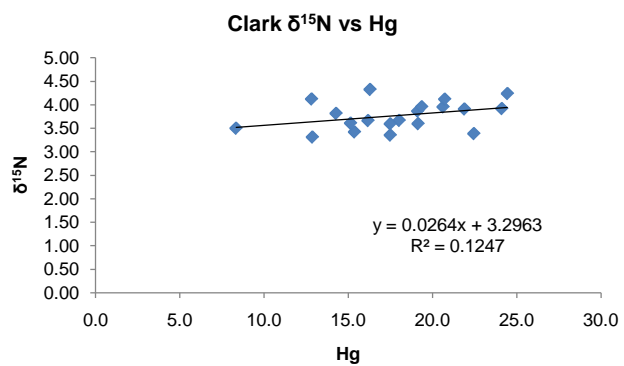
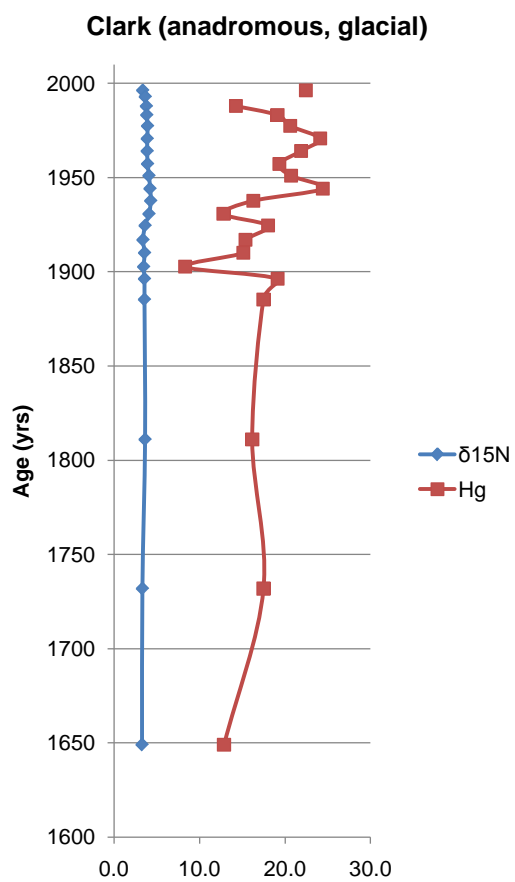


Figure 10. $\delta^{15}\text{N}$ vs Hg for Lake Clark. Units for $\delta^{15}\text{N}$ are ‰ and for Hg are $\mu\text{g}/\text{m}^2/\text{yr}$.

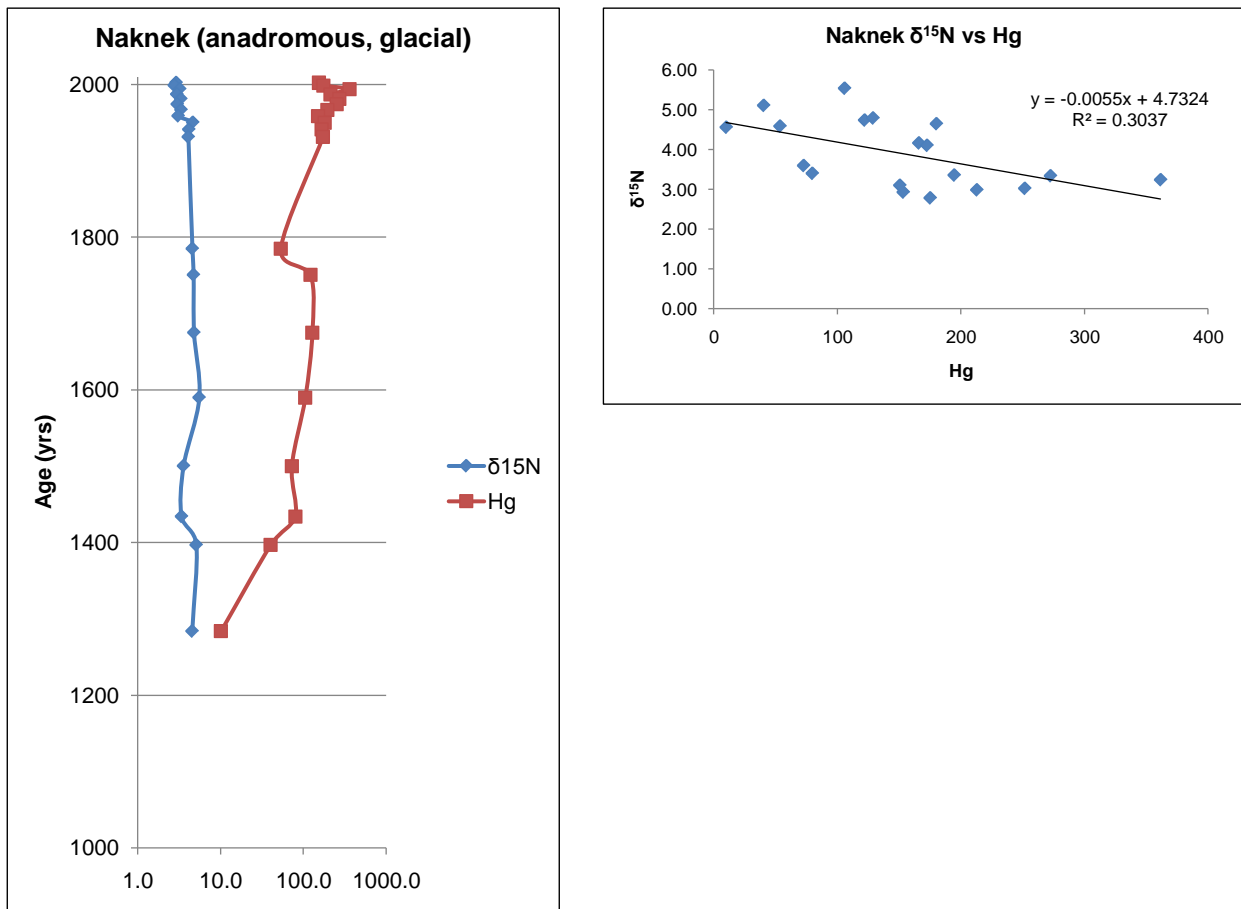


Figure 11. $\delta^{15}\text{N}$ vs Hg for Lake Naknek. Units for $\delta^{15}\text{N}$ are ‰ and for Hg are $\mu\text{g}/\text{m}^2/\text{yr}$.

Comparison of SWAN lakes to Western Airborne Contaminant Assessment Project (WACAP) Alaskan Lakes

The major and trace element lake sediment accumulation rates and trends from these five lakes can be compared to lakes included in the WACAP study (Landers et al, 2008). WACAP was a six year study focused primarily on determining which contaminants are present in seven Western National Parks and their potential to cause negative ecological effects. Three primary parks in Alaska (Denali, Gates of the Arctic, and Noatak) were included. In addition, there were three secondary parks (Glacier Bay, Katmai, Wrangell-St.Elias) included in the study. One of the data sets gathered in this study included contaminant distribution which used lake sediment cores to assess trace element accumulation rates. A brief comparison of the results from this study and the results from Alaska parks including Denali (DENA), Gates of the Arctic (GAAR) and Noatak (NOAT) will be presented in this section. WACAP only provides data on trace elements from DENA, GAAR, and NOAT.

One of the key elements of interest in this study and the WACAP study was Hg. Overall the Hg sediment accumulation rates for DENA, GAAR and NOAT are in the range of $< 10 \mu\text{g}/\text{m}^2/\text{y}$ as compared to the SWAN lakes which range from >10 to $1,000\text{s } \mu\text{g}/\text{m}^2/\text{y}$, with the highest accumulation rate in Brooks Lake. Other trace metals to be compared from the two studies include Cu, Ni, Pb, and Zn. In general these element accumulation rates in the SWAN lakes range from 100s to $10,000\text{s } \mu\text{g}/\text{m}^2/\text{y}$ as compared to 10s to $1,000\text{s } \mu\text{g}/\text{m}^2/\text{y}$ in DENA, GAAR and NOAT. However, because of the relatively rapid sedimentation rates of glacial lakes, this comparison could be biased. It would be better to compare concentration data, but that was not available for the WACAP study. It is likely that the elevated accumulation rates in the SWAN lakes are related to much higher bulk sedimentation rates as well as the recent and current glacial and volcanic activity, and perhaps salmon input. This type of geologic activity is lacking in DENA, GAAR and NOAT (at least in the area of the lakes studied) and therefore those environments may represent more of an overall background signal for trace elements in Alaska. However, further comparisons of the two data sets should be carried out to more fully understand why there is such variation.

The WACAP work specifically targeted lakes to get background signals for trace elements. It would be much better here to contrast the Idavain core with the cores from DENA, GAAR, and NOAT. This comparison may also allow for speculation on the Hg, As, and Zn signals from Idavain and whether those same signals are seen in the other lakes. After comparisons with Idavain, then it may be appropriate to contrast the results from the other 4 lakes with the DENA, GAAR and NOAT lakes.

Summary

- 1) This study provides a thorough baseline of trace elements in the SWAN parks through a historical perspective of accumulation rates of trace elements in lake sediments.
- 2) The anadromous lakes studied in SWAN contain higher concentrations of Hg vs. non-anadromous lakes within their historical and modern lake bed sediments. And Idavain Lake displays a relatively steady accumulation rate of most trace elements as compared to the other four lakes.
- 3) There are elevated concentrations of Hg in the Brooks Lake sediment record with the highest concentration occurring at approximately 1250 AD and the modern lake bed sediments contain approximately 100 ppb Hg.
- 4) All five lakes appear to be dominated by landscape contributions (natural weathering of bedrock) of trace elements, with exceptions to the Hg pattern.
- 5) Analysis of $\delta^{15}\text{N}$ and Hg accumulation rates in all sediment cores showed either a slight positive or negative correlation with low R-squared values indicating that there is not a decipherable pattern relating Hg to marine derived nutrient signals. The lack of a simple pattern is likely due to changing concentrations of Hg in salmon over time, as a result of anthropogenic influence in the North Pacific ocean.
- 6) In comparison to DENA, GAAR, and NOAT the SWAN lakes have on average two to three orders of magnitude higher accumulation rates of trace elements likely because of overall higher sediment accumulation and recent and modern volcanic activity in and nearby the lakes. See earlier note: It is better to primarily make comparisons with Idavain.

Recommendations for further study

- 1) Conduct watershed level studies in Brooks Lake to measure trace elements in water and sediments from major drainages flowing into lake systems.
- 2) Collect fresh surface cores from Brooks Lake for methyl mercury determination.
- 3) Trace element and mercury study of plankton, trout, salmon etc. to examine source and sinks in aquatic food web.
- 4) GIS analysis of bedrock geology to further assess linkages between geogenic sources and accumulation rates of trace elements in the SWAN as well as a comparative study in DENA, GAAR, and NOAT.
- 5) Comparison of trace element concentrations in fish from the SWAN lakes to DENA, GAAR and NOAT.

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Table 1. Ages, accumulation rates ($\mu\text{g}/\text{m}^2/\text{y}$) and $\delta^{15}\text{N}$ (‰) signatures for Idavain Lake sediment core.											
Sediment Sample Interval	Age (AD)	Al	As	Cr	Cu	Hg	Mo	Ni	Pb	Zn	$\delta^{15}\text{N}$
ISC-1 0.5cm	2004	361883.2	2768.9	BD	BD	7.3	BD	BD	301.7	9477.8	3.3
ISC-1 1.5cm	1998	327320.7	1682.4	BD	BD	2.7	BD	BD	BD	13754.1	2.9
ISC-1 2cm	1995	348101.1	1179.5	390.3	508.9	4.9	BD	153.9	188.0	3312.0	2.9
ISC-1 2.5cm	1992	391318.9	1038.2	376.7	533.0	5.3	56.2	173.9	179.3	2300.0	2.8
ISC-1 3cm	1989	377646.1	720.3	367.1	526.4	5.2	52.8	164.7	176.5	2670.3	2.9
ISC-1 3.5cm	1986	391779.8	494.5	370.6	519.9	5.7	54.4	152.4	186.6	2090.4	3.0
ISC-1 4cm	1983	421133.5	429.0	403.2	555.7	5.5	62.9	163.8	202.1	2315.9	2.9
ISC-1 4.5cm	1980	497229.5	600.9	446.4	621.8	5.4	60.6	187.3	234.6	1270.5	2.9
ISC-1 5 cm	1977	523073.2	832.8	476.5	748.0	6.2	73.8	197.6	258.4	1406.7	3.0
ISC-1 5.5cm	1975	569980.5	811.5	504.7	752.2	6.2	77.7	216.4	267.6	1454.5	3.1
ISC-1 6cm	1972	NA	NA	NA	NA	6.7	NA	NA	NA	NA	3.1
ISC-1 6.5cm	1969	646633.0	864.4	555.1	923.7	6.8	91.5	248.2	339.4	1815.6	3.1
ISC-1 7cm	1966	646928.1	885.1	571.8	997.1	7.3	113.7	246.5	364.0	2073.3	3.1
ISC-1 7.5cm	1963	768271.2	843.0	646.6	1114.2	6.8	116.8	291.0	391.6	2021.4	3.1
ISC-1 8cm	1960	676947.1	741.3	597.5	1092.2	8.7	117.5	241.4	427.6	3789.6	3.5
ISC-1 8.5cm	1957	952395.0	1035.5	779.9	1562.1	8.7	173.0	358.9	627.8	2716.6	3.1
ISC-1 9cm	1954	1202929.9	946.1	895.8	1911.1	10.8	184.7	404.8	681.9	3308.2	3.1
ISC-1 9.5cm	1951	1362406.1	931.1	877.1	2050.2	11.9	230.6	464.4	867.2	5960.7	3.2
ISC-1 10cm	1948	1497835.0	1065.6	1108.5	2311.9	15.9	242.5	526.1	932.5	4320.8	3.3
ISC-1 11cm	1943	986175.0	765.1	812.7	1534.4	8.7	145.2	340.9	657.6	3001.1	3.3
ISC-1 11.5cm	1940	908920.9	635.9	673.7	1366.2	6.6	139.9	320.0	545.5	2591.3	3.2
ISC-1 12cm	1937	486714.8	355.4	399.8	867.2	5.1	83.4	172.4	325.0	1351.5	3.2
ISC-1 12.5cm	1934	611867.7	579.8	471.2	1112.8	5.5	98.7	231.3	422.6	2048.0	3.2
ISC-1 13cm	1931	545891.1	378.4	383.5	1021.0	5.7	82.3	194.8	351.7	1496.2	3.2
ISC-1 13.5cm	1928	404548.1	348.1	344.8	964.4	4.1	BD	154.4	319.5	1391.3	3.3
ISC-1 14cm	1925	513111.5	385.9	314.5	1202.8	3.8	BD	181.3	347.8	1113.1	3.4
ISC-1 14.5cm	1923	279955.2	235.6	BD	873.8	2.4	BD	BD	224.9	1817.2	3.1
ISC-1 15cm	1920	220889.7	269.0	BD	869.8	1.8	BD	BD	171.0	2416.8	3.4
ISC-1 20cm	1892	907022.2	746.3	967.4	992.4	7.3	101.9	302.3	318.6	3443.3	3.3
ISC-1 50cm	1738	1269683.6	949.2	1177.9	1308.2	14.9	BD	BD	602.0	13189.1	2.6

ISC-1 70cm	1636	1221396.0	1628.4	925.7	1167.0	7.9	161.7	321.1	362.2	6271.9	2.7
ISC-1 89cm	1525	1133453.7	1259.8	1228.5	1739.2	7.6	178.6	423.9	365.4	6136.3	2.4
Table 1. (cont.)											
IA D-1 99cm	1434	1029609.3	615.7	1166.1	1268.4	10.2	143.4	397.2	369.6	4525.6	2.4
NA = not available, BD = below detection											

Table 2. Ages, accumulation rates ($\mu\text{g}/\text{m}^2/\text{y}$) and $\delta^{15}\text{N}$ (‰) for Kontrashibuna Lake sediment core.											
Sediment Sample Interval	Age (AD)	Al	As	Cr	Cu	Hg	Mo	Ni	Pb	Zn	$\delta^{15}\text{N}$
KL HC-2 0 cm	2001	5430095.6	7269.6	3178.9	18911.4	22.4	1411.1	3702.4	3264.8	23333.2	2.0
KL HC-2 0.5 cm	1992	2913671.6	940.0	1693.1	10074.0	10.5	810.9	1985.7	1683.5	12314.8	2.1
KL HC-2 1 cm	1984	3375876.3	1092.1	2027.1	11134.1	12.3	1111.8	2311.7	1971.0	14300.3	2.3
KL HC-2 1.5 cm	1977	4050366.7	4165.0	2584.5	13241.6	15.8	2023.8	2814.7	2366.9	17201.7	1.9
KL HC-2 2.5 cm	1962	6920046.6	1972.6	5928.1	25320.1	25.2	553.3	5100.4	4798.2	28759.1	2.3
KL HC-2 3 cm	1952	8364013.1	2421.5	6341.8	31079.7	27.3	826.5	6025.4	6023.3	34331.1	2.0
KL HC-2 3.5 cm	1939	6882605.3	2056.4	4443.4	24102.0	21.0	794.3	4652.9	4312.8	28763.7	2.2
KL HC-2 4 cm	1927	5639310.6	1940.6	3436.7	19387.5	19.2	710.3	3829.8	3296.8	24838.3	2.1
KL HC-2 4.5 cm	1917	5325002.2	2044.7	3153.9	17539.4	17.6	672.1	3663.6	2974.7	35075.1	2.3
KL HC-2 5 cm	1898	5506973.6	1886.3	3194.2	17751.5	15.4	741.8	3647.4	2881.3	23711.6	2.2
KL HC-2 5.5 cm	1877	7903972.2	2674.6	5115.0	26753.2	24.8	1107.8	5309.2	4360.8	33082.1	2.3
KL HC-2 6 cm	1858	12430791.4	4509.7	15779.8	45483.2	46.9	2243.9	10536.0	7731.5	47615.3	2.6
KL HC-2 7 cm	1828	8248638.4	3212.8	8762.0	28378.7	30.0	1467.5	6673.3	4982.5	33655.7	2.6
KL HC-2 8 cm	1806	3800762.2	1612.5	3695.3	12484.6	12.2	664.2	2800.3	2136.0	14601.9	2.6
KL HC-2 9 cm	1783	3210217.3	1135.4	2459.8	10271.8	10.3	513.9	2245.4	1674.5	12933.0	2.7
KL HC-2 10 cm	1761	5787301.8	2017.9	4440.1	17984.6	15.3	1143.7	3984.3	3101.1	23019.2	2.5
KL HC-2 11 cm	1741	5583513.9	1909.9	5684.9	19570.7	19.5	936.2	4326.1	3239.2	21604.8	2.7
KL HC-2 12 cm	1724	5710853.5	1924.9	3861.0	18226.9	17.1	946.6	3811.8	3035.7	23937.8	2.9
KL HC-2 13 cm	1709	5666570.4	1629.5	4078.0	17673.1	15.9	791.5	3745.9	2942.1	23721.5	2.6
KL HC-2 14 cm	1695	5668355.6	1941.0	5446.0	18879.7	20.1	849.9	4195.6	3479.7	22447.5	2.7
KL HC-2 15 cm	1682	5856236.2	2870.1	7435.9	20948.2	21.8	1013.8	4952.0	4417.2	22736.1	2.9
KL HC-2 16 cm	1670	5737679.6	1836.2	4494.6	17963.5	14.8	869.6	3869.1	3055.1	22744.5	2.8
KL HC-2 17 cm	1659	5758835.9	2248.6	6742.7	18694.9	28.3	962.4	4842.4	3790.9	23287.5	2.7
KL HC-2 18 cm	1648	5653117.3	1936.9	3991.3	16905.6	14.2	968.2	3669.4	2959.6	24048.4	2.9
KL HC-2 19 cm	1638	5529206.9	1870.3	3679.7	16620.6	17.1	970.7	3452.9	3119.8	23229.7	2.6
KL HC-2 20 cm	1629	5667470.5	2186.2	3899.5	16121.3	15.3	942.5	3578.6	3104.0	22769.6	3.1

[illegible]

Table 3 . Ages, accumulation rates ($\mu\text{g}/\text{m}^2/\text{y}$) and $\delta^{15}\text{N}$ (‰) for Brooks Lake sediment core.

[illegible]

Table 4. Ages, accumulation rates ($\mu\text{g}/\text{m}^2/\text{y}$) and $\delta^{15}\text{N}$ (‰) for Naknek Lake sediment core.											
Sediment Sample Interval	Age (AD)	Al	As	Cr	Cu	Hg	Mo	Ni	Pb	Zn	$\delta^{15}\text{N}$
Naknek HC-2 2 cm	2002	27134792.2	16923.6	37063.8	53594.7	153.4	1969.1	24893.0	12721.2	100100.0	2.9
Naknek HC-2 10 cm	1999	29180612.0	12815.8	44951.7	59210.7	175.2	2171.6	27528.9	14440.2	108125.5	2.8
Naknek HC-2 21cm	1994	46025060.7	19156.0	67590.8	88647.3	361.6	4278.1	42215.7	21916.9	162251.1	3.2
Naknek HC-2 31 cm	1987	33008993.8	12065.9	46743.9	61665.9	212.9	2678.5	29666.6	15526.7	128111.8	3.0
Naknek HC-2 41cm	1981	37996817.1	25827.8	55874.5	71671.8	272.5	3766.7	32632.4	17533.1	143734.9	3.3
Naknek HC-2 51 cm	1974	31404998.9	16488.8	41494.4	68193.7	251.7	4109.9	29202.9	17430.2	127320.8	3.0
Naknek HC-2 61cm	1967	21372936.0	10725.3	27173.6	46232.2	194.6	3490.7	19268.4	11586.9	86068.0	3.4
Naknek HC-2 71 cm	1959	26751957.9	13131.1	37807.7	51029.4	150.6	4871.7	24026.8	11440.7	97213.0	3.1
Naknek HC-2 81 cm	1950	29437811.1	12834.0	40483.5	55901.7	180.2	3618.4	26178.1	11898.6	104399.3	4.7
Naknek HC-2 91cm	1941	27819411.0	14500.8	36115.0	54230.3	166.0	4987.0	23997.9	12574.8	105971.5	4.2
Naknek HC-2 101cm	1931	24462287.6	16577.8	30791.0	51054.1	172.6	5846.2	21430.0	9444.7	106278.4	4.1
Naknek HC-1 111 cm	1785	8756930.7	6661.7	11607.6	20122.4	53.6	1415.1	8952.7	3427.5	42658.7	4.6
Naknek HC-1 131 cm	1750	17555906.9	9703.8	28941.8	30490.6	122.1	1274.2	16644.1	9045.6	67002.6	4.7
Naknek HC-1 171cm	1675	20691808.9	9758.4	33198.6	28432.6	128.9	1173.1	19527.2	8862.0	69122.6	4.8
Naknek HC-1 211 cm	1590	19877581.0	9466.6	33455.8	28866.5	105.9	1233.1	19922.3	8644.4	71891.3	5.5
Naknek PC-1 250 cm	1500	14636338.0	8519.9	23821.4	24593.2	72.8	1258.0	13919.5	6241.9	52045.4	3.6
Naknek PC-1 275 cm	1434	12307460.0	8098.5	21685.4	24772.1	79.8	1035.7	12445.6	6369.4	48536.9	3.4
Naknek PC-1 290 cm	1397	12486916.2	6830.6	19937.7	23732.6	40.4	978.5	12104.9	6147.3	49723.1	5.1
Naknek PC-1 330 cm	1284	10989497.8	5328.2	18369.8	19609.7	10.1	745.9	11047.7	5636.2	40066.0	4.6

Table 5. Ages, accumulation rates ($\mu\text{g}/\text{m}^2/\text{y}$) and $\delta^{15}\text{N}$ (‰) for Lake Clark sediment core.											
Sediment Sample Interval	Age (AD)	Al	As	Cr	Cu	Hg	Mo	Ni	Pb	Zn	$\delta^{15}\text{N}$
L.C. H-3 ES 0cm	1996	3294034.1	2999.7	3487.6	21273.7	22.4	248.2	2990.9	1911.9	15200.9	3.4
L.C. H-2 ES 0.5cm	1993	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.7
Lake Clark H-3 ES 1 cm	1988	2746610.5	2651.3	3179.4	17383.5	14.3	180.7	2632.2	1629.4	14165.3	3.8
L.C. H-3 ES 1.5 cm	1983	3018250.2	2535.2	3420.9	18759.2	19.1	195.2	2769.6	1701.1	12905.3	3.9
L.C. H-3 ES 2cm	1977	3730976.0	3382.1	4434.1	23677.6	20.6	240.4	3513.2	2065.1	17284.9	4.0
L.C. H-3 ES 2.5 cm	1971	4470956.7	3654.2	4932.3	27469.5	24.1	282.9	3982.8	2503.2	21238.2	3.9
L.C. H-3 ES 3cm	1964	4291914.0	2990.9	4425.1	26907.9	21.9	318.2	3779.5	2538.2	19283.6	3.9
L.C. H-3 ES 3.5 cm	1957	4072108.9	2398.0	4183.3	26323.4	19.3	240.6	3537.6	2153.6	18414.0	4.0
L.C. H-3 ES 4 cm	1951	4059917.2	2425.1	4377.8	26806.9	20.7	282.4	3808.6	2058.7	19442.8	4.1
L.C. H-3 ES 4.5 cm	1944	4316103.5	2642.5	4452.1	26710.3	24.4	266.5	3897.2	2000.3	20430.1	4.2
Lake Clark H-3 ES 5cm	1938	3704035.4	2235.3	3934.5	23062.9	16.3	233.5	3327.8	1806.2	17052.3	4.3
Lake Clark H-3 ES 5.5cm	1931	3185335.9	1998.4	3341.5	19185.6	12.8	209.6	2787.3	1626.1	15480.4	4.1
L.C. H-3 ES 6cm	1925	3361086.2	1999.5	4016.6	20027.2	18.0	183.0	3184.4	1559.4	14874.9	3.7
L.C. H-3 ES 6.5cm	1917	3527957.7	2293.7	3771.1	21045.2	15.4	253.4	3081.1	1755.1	16061.2	3.4
L.C. H-3 ES 7cm	1910	2708956.5	1481.2	2852.7	16841.7	15.1	166.2	2305.5	1334.4	12265.5	3.6
L.C. H-3 ES 7.5 cm	1903	NA	NA	NA	NA	8.3	NA	NA	NA	NA	3.5
L.C. H-3 ES 8 cm	1896	3421998.5	2155.7	3764.4	21001.0	19.1	246.1	2929.7	1827.4	17034.2	3.6
Lake Clark H-3 ES 10cm	1885	3575606.9	2038.4	3919.6	21491.8	17.5	222.2	3050.6	1862.8	16052.3	3.6
L.C. H-3 12cm	1811	NA	NA	NA	NA	16.2	NA	NA	NA	NA	3.7
Lake Clark H-3 ES 16cm	1732	3613158.0	1935.9	3788.8	20809.4	17.5	222.5	2998.8	1858.7	16147.4	3.4
Lake Clark H-3 ES 20 cm	1649	1906407.6	841.3	1661.6	10771.9	12.9	BD	1470.0	685.7	7812.9	3.3

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

NPS 953/105979, November 2010

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Natural Resource Program Center
1201 Oakridge Drive, Suite 150
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