



Historical Trends in Mercury Deposition as Recorded in Lake Cores near Glacier Bay National Park and Preserve, Alaska

Natural Resource Report NPS/SEAN/NRR—2019/1928





ON THIS PAGE

Cliff Lake

Photo credit: UAS/ SONIA NAGORSKI

ON THE COVER

Rectangle Lake

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Historical Trends in Mercury Deposition as Recorded in Lake Cores near Glacier Bay National Park and Preserve, Alaska

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Abstract

Sediment cores were collected from four lakes on Chichagof Island in southeast Alaska in May, 2015 for the purpose of obtaining profiles of total mercury deposition over multiple centuries. Core sections were analyzed for organic content and dry density, age dated using ^{210}Pb isotopes and constant rate of supply dating models, and for three of the cores, analyzed for total mercury (Hg) and stable isotopes of mercury ($\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$). The three cores with full analyses (single cores from Rectangle, Sapsucker, and Goldeneye Lakes (unofficial names)) were age dated as far back as the 11th century. Total mercury fluxes to each lake were fairly constant prior to the 18th century, followed by sharp increases in two of the lakes (Rectangle and Goldeneye) in the mid-19th centuries, at the start of the Industrial Revolution. Rectangle and Sapsucker Lakes then show their strongest deposition increases in the mid-20th centuries, with peak flux values during 1990s-2000, perhaps reflecting increased coal burning in Asia and global small scale gold mining operations. Modern fluxes of Hg to the lakes are 2-4 times higher than during preanthropogenic (pre-year 1500) times. Mercury flux profiles also track closely with those in a regional ice core that exhibits sharp increases late in the 20th century. Differences in profiles between the lakes, as well as some incongruence of profiles from the same lakes in 2003, highlight the need to obtain multiple cores per lake and multiple lakes in order to track fine-scale local changes in sediment accumulation rates and atmospheric mercury deposition. Variations among cores and lakes are likely attributable to heterogeneous timing of release and sourcing in the watershed from geogenic and atmospheric sources. Lake cores such as these, especially if augmented by larger sample sizes, are excellent archives of long term Hg wet and dry deposition to remote areas such as those in the Southeast Alaska Network of National Park units.

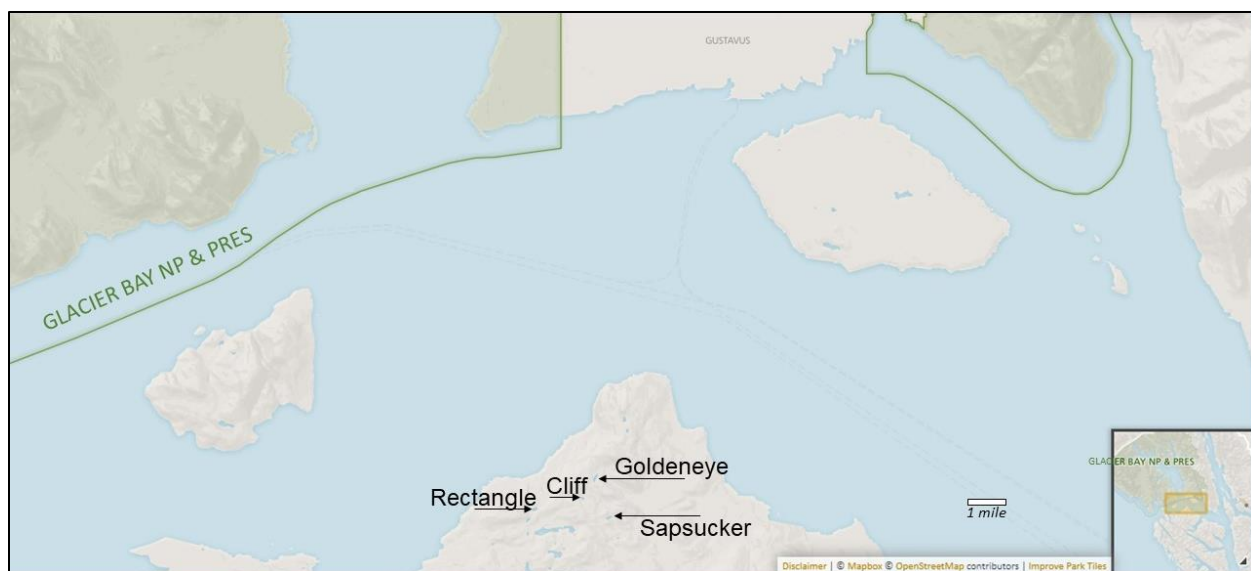


Figure 1. Location of the four unofficially named lakes sampled near Point Adolphus on Chichagof Island, Southeast Alaska, across from the southern end of Glacier Bay National Park and Preserve. Base map derived from <https://www.nps.gov/glba/planyourvisit/maps.htm>.

Acknowledgments

We thank the Science Museum of Minnesota for providing the age dating analyses and the USGS Mercury Research Lab for providing the total mercury and mercury isotope analyses on the sediment cores. Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

List of Terms

CH_3Hg^+ : Monomethylmercury

CVAFS: Cold vapor atomic fluorescence spectroscopy

DMAR: Dry mass accumulation rate

Hg: Mercury

Hg_T : total mercury

$\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$: Nomenclature for mass dependent fractionations and odd- mass independent fractions imposed on Hg isotopes, “fingerprinting” markers for isotopic signatures of mercury

LOI: Loss on Ignition

MC-ICPMS: Multicollector-inductively coupled plasma mass spectrometer

NIST: National Institute of Standards and Technology

NPS: National Park Service

Pb: Lead

SEAN: Southeast Alaska Network of the National Park Service

SCWRS: St. Croix Watershed Research Station

UAS: University of Alaska Southeast

USGS: United States Geological Survey

Introduction

Lake sediments provide reliable archives for long-term global mercury (Hg) deposition trends and rates (Biester et al., 2007). Dated lake sediment cores in the northern hemisphere have yielded detailed profiles of Hg deposition over multiple centuries and track a sharp rise, leading to a ~3-5 fold increase, in Hg deposition since the beginning of the Industrial Revolution (Bindler et al., 2001; Engstrom et al., 2014; Fitzgerald et al., 2005). Moreover, lake sediment cores in the Midwestern U.S. record a decline in Hg deposition since the 1970s, corresponding to regional reductions in Hg emissions (Engstrom et al., 2007). Yet unlike the Hg profiles in lake sediments in the Midwest, the few cores that exist from Alaska show continued increases in Hg deposition through the end of the 20th century, indicating that Hg deposition to Alaska went unabated at least until then (Engstrom and Swain, 1997; Engstrom et al., 2014).

The recorded increased Hg loading through the end of the 20th century (Engstrom et al., 2014), coupled with the recent acceleration of coal-burning activity in Asia (Pacyna et al., 2010), and the onset of mercury fish consumption advisories in Alaska in the last decade (Hamade, 2014), have motivated the question of whether transport and deposition to the region has continued to climb since the retrieval of the most recent lake sediment cores (in 2003, by Engstrom et al (2014)). The industrialization of Asia—primarily China and India—in the past 1-2 decades has been rising sharply, fueled largely by energy from coal-burning power plants that can emit significant mercury without proper abatement technology (Pacyna et al., 2010). However, while marked increase in mercury emissions are evident in Asia and India (Zhang et al., 2016), globally this increase is largely balanced by notable decreases in the developed regions of North America and Europe where steady declines in emissions and atmospheric total gaseous mercury are observed. These recent observations of diverging trends in atmospheric mercury concentrations bring into question some of the long-held assumptions about a mixed global pool of mercury in the atmosphere and expected responses to local and regional emission rules. Much of the mercury emissions from Asia are carried atmospherically to the north coast of North America, as indicated by atmospheric models and west coast measurements (Durnford et al., 2010; Jaffe et al., 2005; Kirk et al., 2012). Mercury pollution is also sourced from chlor-alkali plants, cement production, and large and small scale mining of both mercury and gold and silver, and other currently active industrial activities (UNEP, 2013).

Mercury is a volatile metal that travels as an uncharged gaseous element once released into the atmosphere, and is subsequently deposited by wet or dry deposition (Schroeder and Munthe, 1998). Mercury deposition to Alaska appears to be similar in magnitude to that in temperate latitudes although local sources are minimal and scarce (Fitzgerald et al., 2005; Lamborg et al., 2013). Deposited inorganic mercury can become methylated (converted to CH_3Hg^+) in marine and freshwater environments and bioaccumulated in fish, wildlife, and ultimately humans (Gilmour et al., 1992; Ullrich et al., 2001; Wolfe et al., 1998). Mercury in northern latitudes shows significant concentration increases over the last few decades, as shown in that mercury in the bodies of otters, whales, seals, bears, eagles, and indigenous people who rely on subsistence harvests show increasing trends over the last few decades (Braune et al., 2014; Dietz et al., 2013).

Placing current and recent Hg deposition to southeastern Alaska into historical and geographic contexts is of interest to the National Park Service (NPS) Southeast Alaska Network's monitoring of the "Freshwater Contaminants" vital sign, one of their indicators of park land health, in order to inform the design of an environmental contaminants monitoring program. Mercury pollution has been identified as an issue of concern to the network (Eckert et al., 2006). With this project, the NPS cooperated with the St. Croix Watershed Research Station, the USGS Mercury Research Laboratory, and University of Alaska Southeast to revisit sites in 2015 on Chichagof Island that were last cored, dated, and measured for mercury in 2003. The goal of this work was to obtain the most recent record of mercury deposition in order to evaluate the magnitude of deposition in the context of previous decades and centuries. In addition, recent discoveries of mercury isotopic signatures (e.g. coal vs. geogenic) and advances in analytical capabilities have opened new opportunities to provide information on the geographic source of mercury contamination (Sonke and Blum, 2013). In this report, we present the mercury profiles in cores collected from three lakes in 2015. Isotopic Hg interpretations are being prepared in a separate journal manuscript, as these results are meaningful in the context of isotopic profiles from other cores from around the world (Engstrom et al., 2017).

Methods

Sediment cores were collected in May, 2015, from the same four lakes sampled in 2003 (Engstrom et al. 2014). The study lakes are located near Point Adolphus on Chichagof Island in southeastern Alaska. (Table 1 and Figure 1).

Table 1. Locations of the sampling sites at the four study lakes. AC/AL indicates the ratio of catchment area: lake area.

Lake	Elevation (m)	Latitude	Longitude	Area (km ²)	Ac/AL	Depth (m) of lake at coring location (+/- 0.2 m)
Rectangle	240	N 58.23584	W 135.87704	8.7	16.0	10.8
Goldeneye	329	N 58.24701	W 135.83340	15.1	17.8	11.3
Sapsucker	266	N 58.23287	W 135.82262	4.3	9.5	6.1
Cliff	336	N 58.24015	W 135.84224	11.6	17.1	14.4

The selected lakes (all names unofficial) occur in a relatively tight cluster, within three kilometers of one another. The sites were selected by the researchers conducting the 2003 coring due to their location within a close distance (25 km) of precipitation mercury and ²¹⁰Pb precipitation collectors that were set up at the time in Bartlett Cove, Glacier Bay National Park and Preserve headquarters (Lamborg et al., 2013). The lakes were also chosen due their relatively small watershed sizes, which was favored in order to maximize the direct atmospheric Hg signal relative to watershed inputs of Hg initially deposited to vegetation and soils. This location contains no permafrost, which has been recently discovered to be a large source of atmospheric mercury in arctic Alaska. (Schuster et al., 2018).

Local vegetation around the lakes is comprised of undisturbed coastal rainforest (Sitka spruce, western hemlock) and open muskeg (peatlands) on more gently sloping surfaces. GIS analyses were used to determine precise surface areas, bathymetry, and catchment characteristics. Watershed maps for the four lakes are provided, along with coring locations from both the 2003 and 2015 sampling campaigns (Figures 2-5).

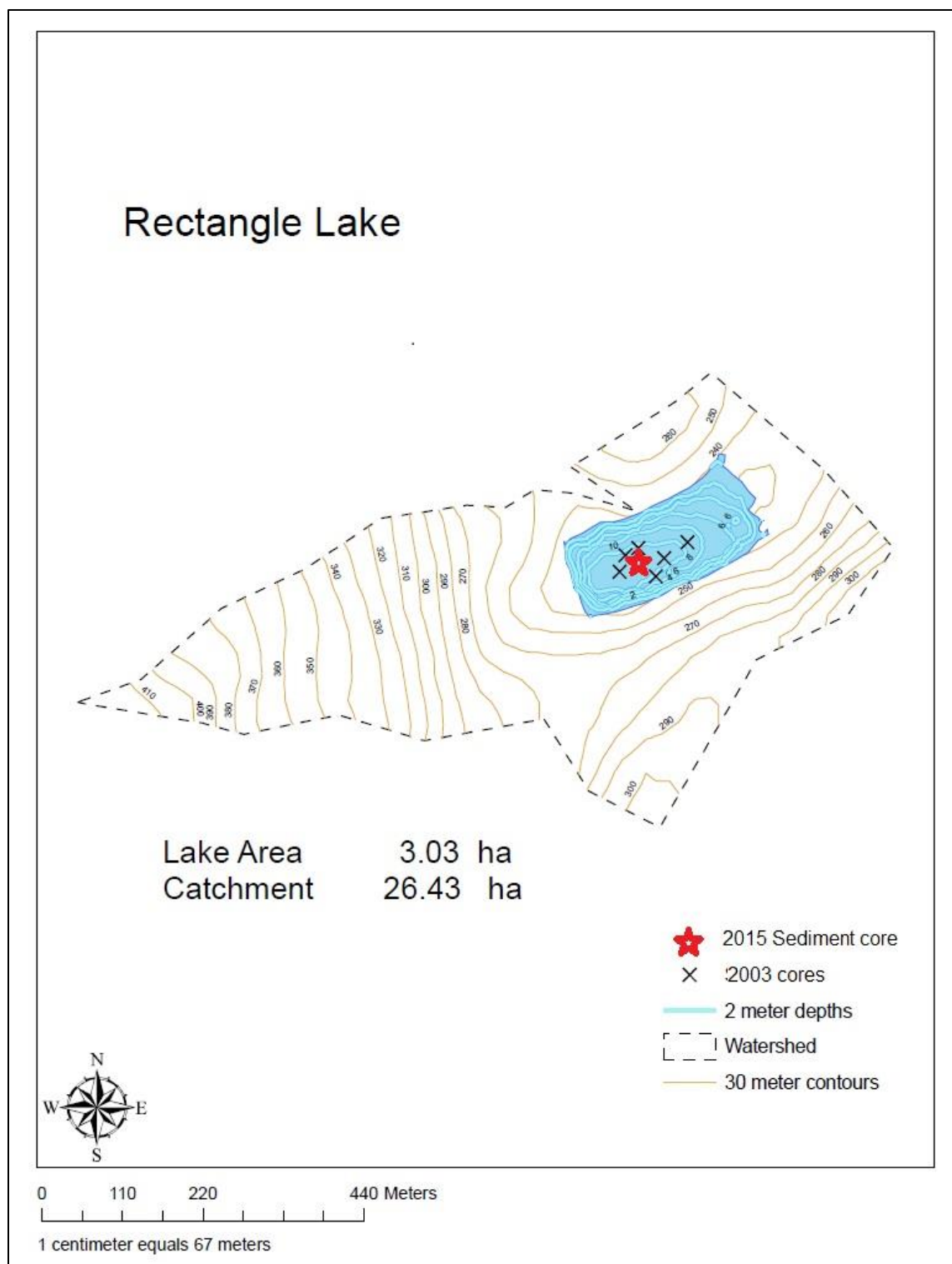


Figure 2. Map of Rectangle Lake with coring locations from 2003 and 2015.

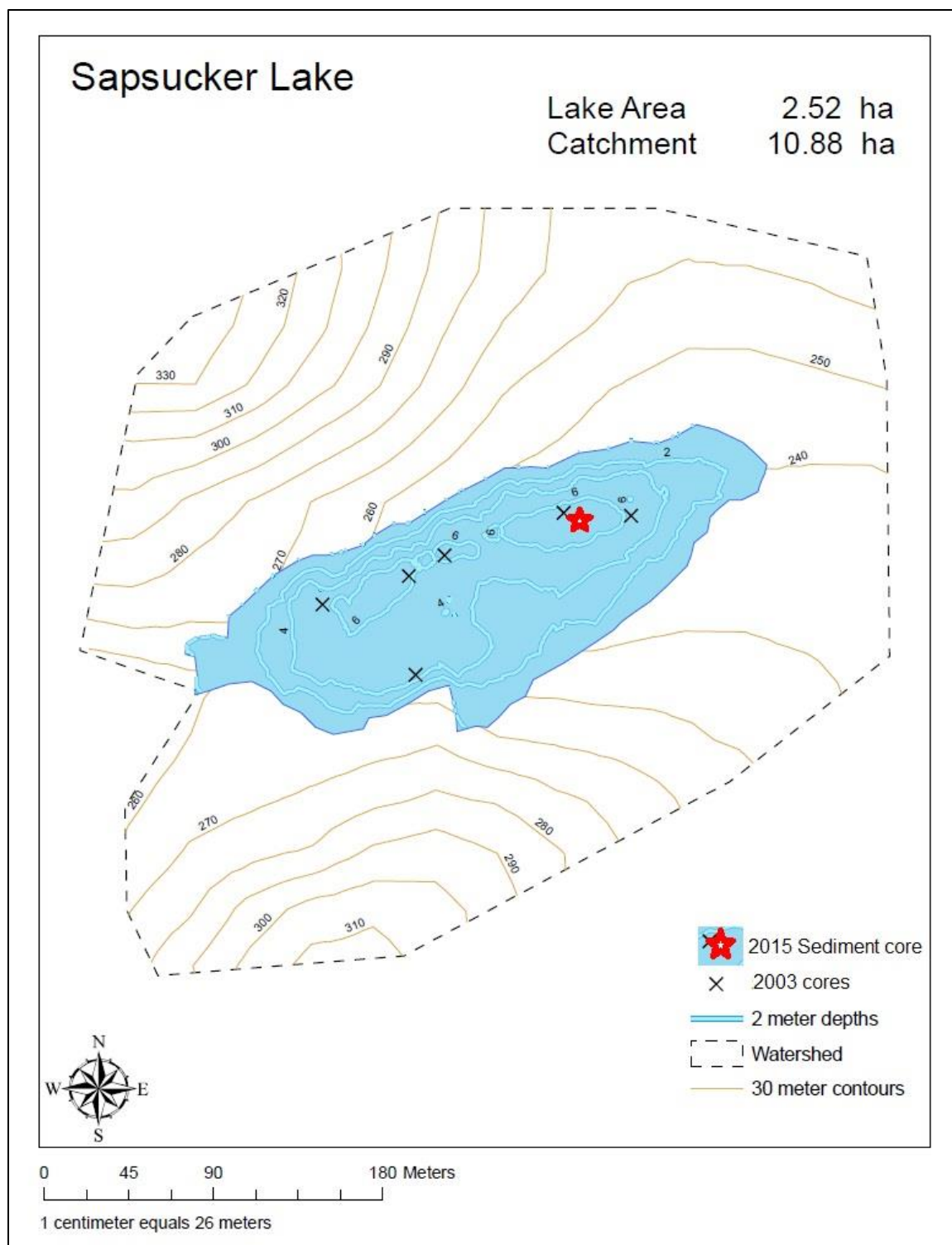


Figure 3. Map of Sapsucker Lake with coring locations from 2003 and 2015.

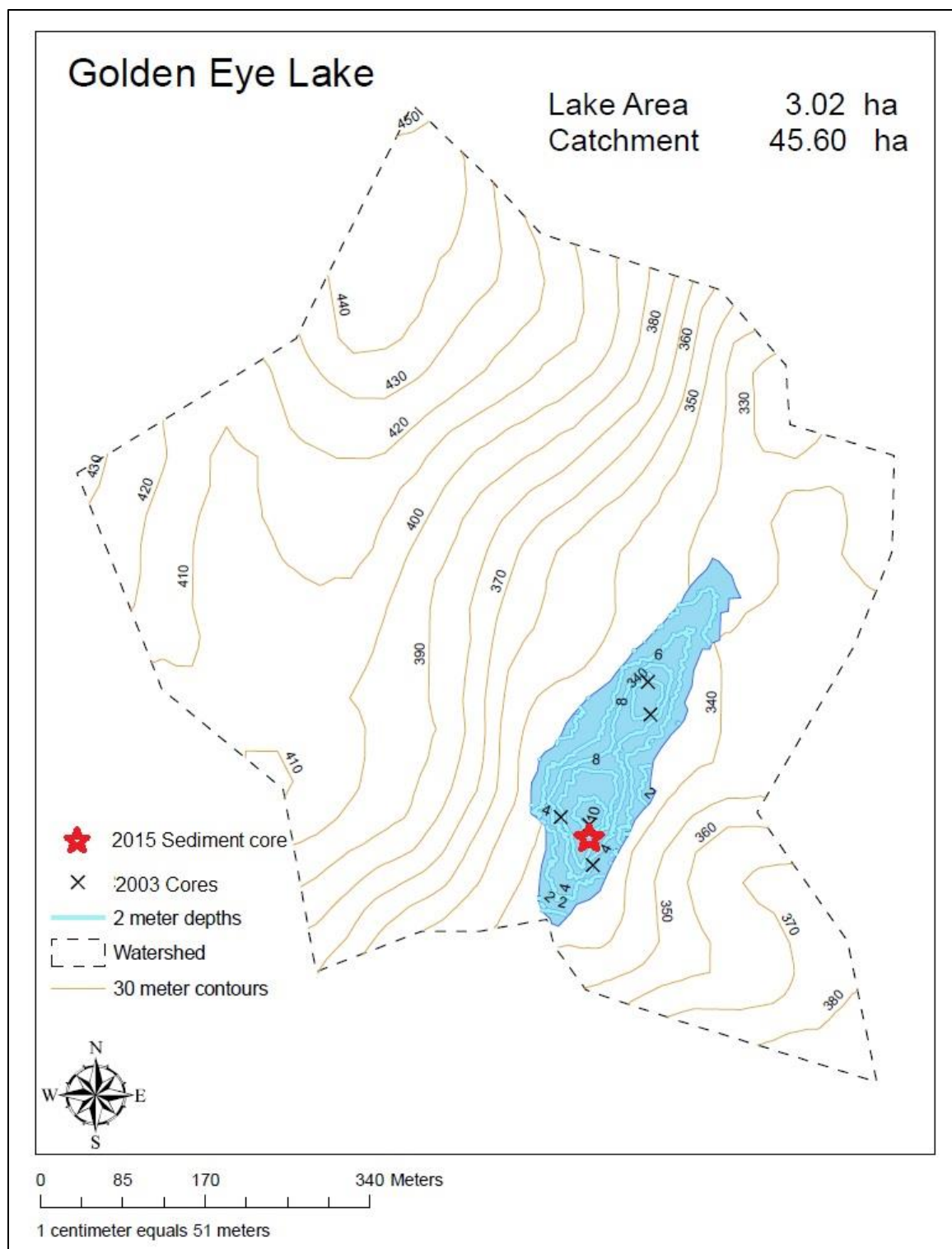


Figure 4. Map of Goldeneye Lake with coring locations from 2003 and 2015.

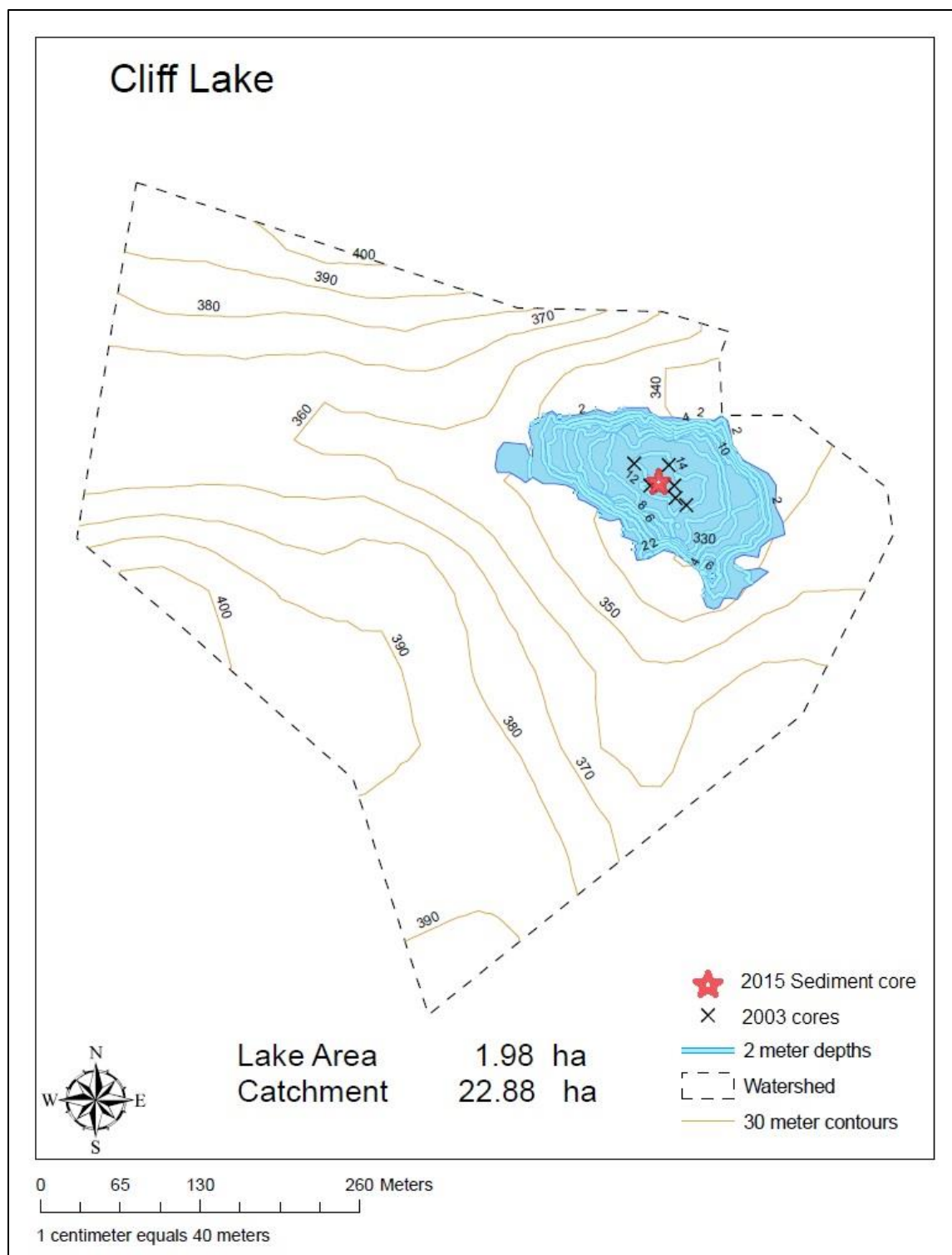


Figure 5. Map of Cliff Lake with coring locations from 2003 and 2015.

The coring was accomplished from a small Zodiac inflatable boat powered by an electric trolling motor. Two sediment cores were obtained from closely spaced locations in the deeper region of each lake by means of a HTH-Teknik gravity corer equipped with 7-cm polycarbonate core tubes. Tubes were kept upright and undisturbed during transport.

At the University of Alaska Southeast (UAS) Natural Science Laboratory, the cores were sectioned into 0.5-1 cm increments into polypropylene plastic cups within two days of collection. Within two weeks, water content, bulk density, and loss-on-ignition (LOI) were measured at the UAS. Briefly, a well-mixed $\sim 1 \text{ cm}^3$ subsamples of each core segment were heated progressively at 105° C (for 12 hours) and 550° C (for 1.25 hours) in crucibles to sequentially drive off their water and organic content. Samples were weighed at each stage of the sequential ignition to 0.1 mg in order to obtain precise profiles of the density, water content, and organic content of the core sections.

Core sections were shipped to the St. Croix Watershed Research Station (SCWRS) labs (MN), where additional subsamples they were freeze-dried and then analyzed for ^{210}Pb dating. Age dating was conducted using ^{210}Pb isotope-dilution, alpha spectrometry, and the constant rate of supply dating model (Appleby, 2002; Eakins and Morrison, 1978).

Subsamples of freeze-dried sediment samples were analyzed for total mercury (Hg_T) and Hg stable isotopes by high-throughput methods at the USGS Mercury Research Lab in Middleton, WI. Samples were acid digested overnight at 90° C with Hg_T analysis of the solution using reduction, Au amalgamation and CVAFS detection (USEPA, 2002). Reference materials for Hg_T were within 95-100% (average 98.1%, standard deviation 0.9%) of the reported values. Spike recovery for Hg_T concentrations averaged 98.9% (std dev=6.4%). Each water sample was run in duplicate for Hg_T , and the average difference between runs was 6.3%. Sediment digest duplicates ($n=7$) were between 2-10% (average 7%) of each other.

Hg isotopes were measured directly on the digests with a custom gas liquid separator, connected to an Apex Q (Tl generator) set to free flow mode. Detection of the isotope ratios were performed on a Neptune Plus MC-ICPMS. Analytical Q/A included: secondary standards (UM-Almaden), triplicate digests when possible, standard reference material IAEA SL1 and delta determination followed standard sample bracketing using NIST–sample–NIST. More thorough descriptions of the instrument setup and QA/QC protocols can be found elsewhere (Lepak et al., 2015; USGS-MRL, 2016; Yin et al., 2016).

Results and Discussion

Loss on ignition

Lake sediment profiles show a general increase in bulk density and decrease in percent organic matter with depth, particularly within the first 0-10 cm of the core, likely due to compaction and corresponding decreasing pore space and decomposition of organic matter (Figures 6-9). Profile trends in the 2015 cores were compared to those from the 2003 cores and matched up very closely (Figures 6-9). One pronounced anomaly in the otherwise smooth trend included a sharp and discrete drop in % organic matter and spike in bulk density in the 20-21cm zone of the Sapsucker core. A distinct light colored silt layer was clearly visible at this core depth, explaining the drop in organic matter.

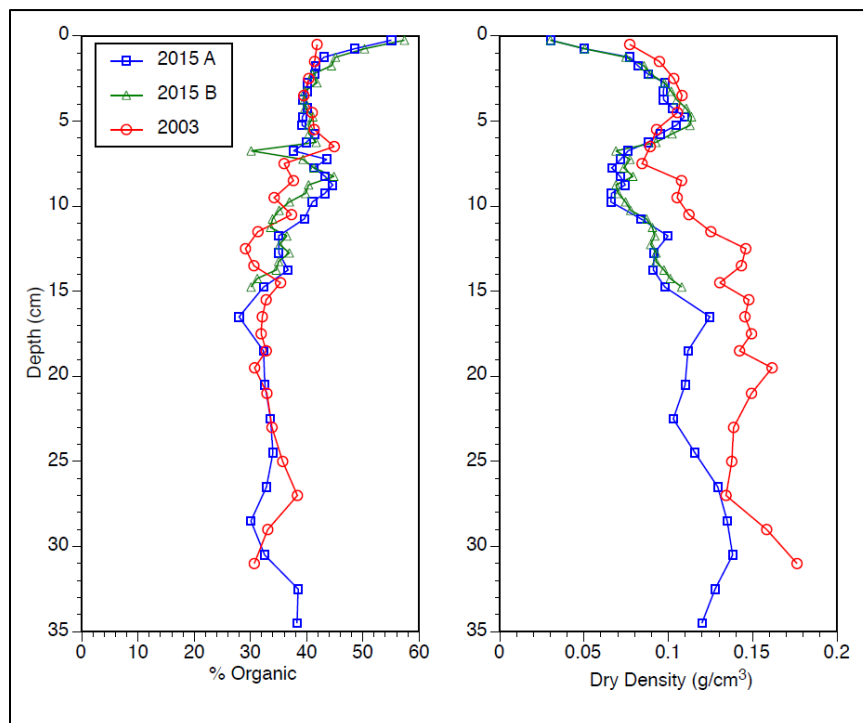


Figure 6: Percent organic content and dry density profiles in the two lake cores collected from Rectangle Lake, shown overlain with the Rectangle Lake core profile from 2003.

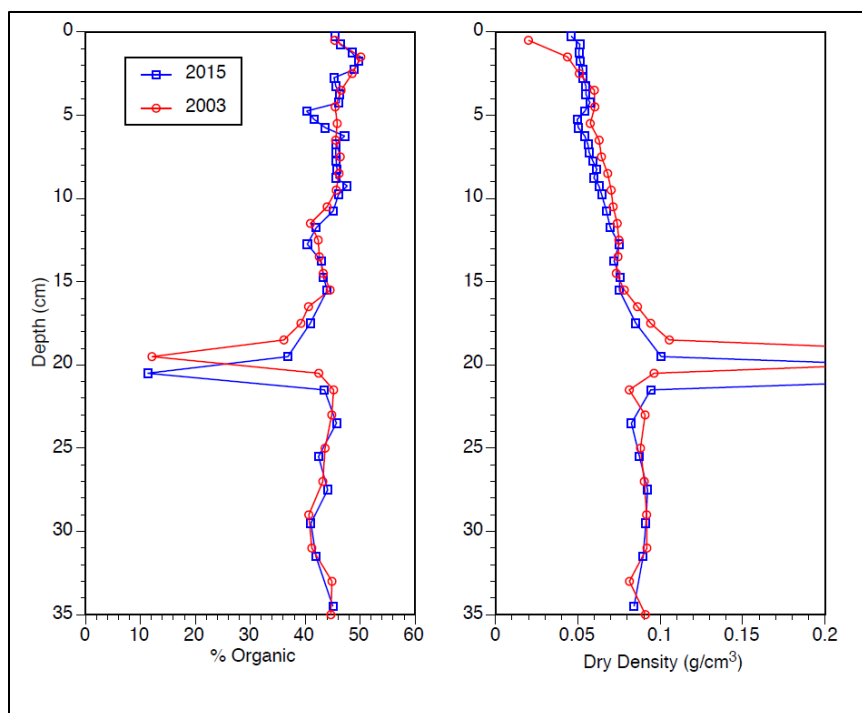


Figure 7: Percent organic content and dry density profiles in the lake cores collected from Sapsucker Lake, shown overlain with the Sapsucker Lake core profile from 2003.

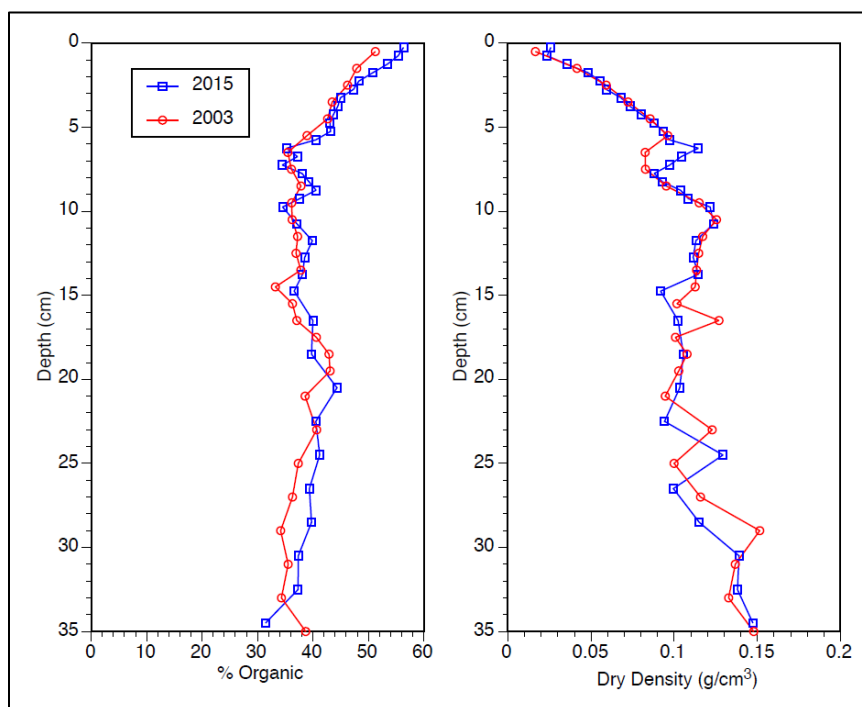


Figure 8: Percent organic content and dry density profiles in the lake cores collected from Goldeneye Lake, shown overlain with the Goldeneye core profile from 2003.

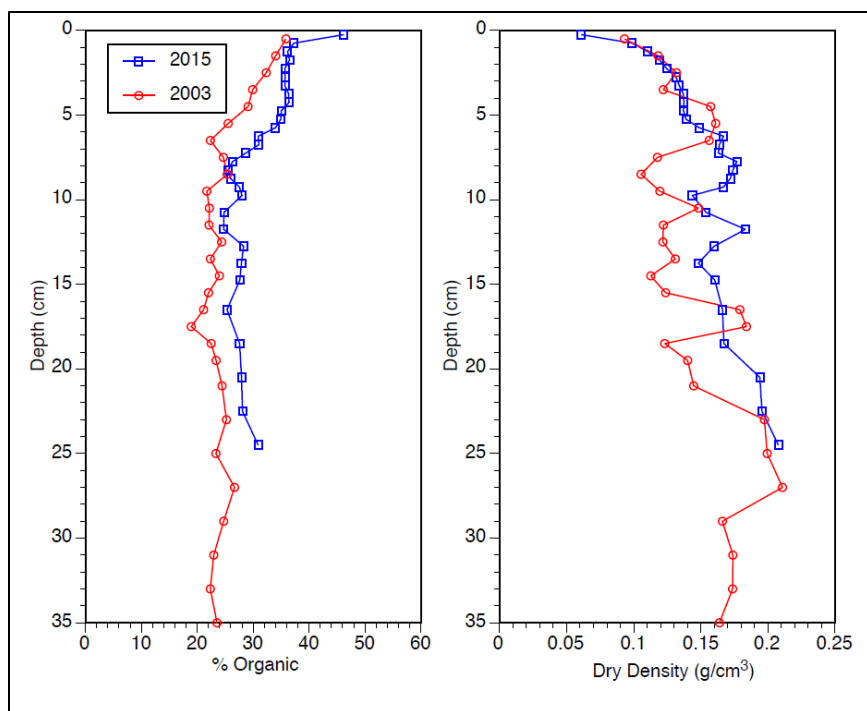


Figure 9: Percent organic content and dry density profiles in the lake cores collected from Cliff Lake, shown overlain with the Cliff core profile from 2003.

Age dating and sediment accumulation rates

It was possible to age-date the lake core sections using ^{210}Pb over the uppermost 6.0-11.5 cm of the cores (Figure 10), and results show ages in those intervals extending back to the early 1800s, just prior to the beginning of the Industrial Revolution (Figure 11, Tables 2-5). Sediment chronologies prior to the oldest ^{210}Pb dates were extrapolated based on cumulative dry mass (g cm^{-2}) and mean mass accumulation rate ($\text{g cm}^{-2} \text{yr}^{-1}$) for each core (see Engstrom et al., 2014).

The lowest sections of the cores are calculated to represent the years approximately 1300, 1100, and 1040 for Rectangle, Sapsucker, and Goldeneye, respectively. (The core from Cliff Lake was age dated using ^{210}Pb to the year 1829 at 6 cm depth. Further calculations were not done on this core, as it was not included in total Hg and Hg isotopic analyses.) The uppermost sample slice of each core, 0.5 cm thick, represent about 4-7 years of deposition. Hence, the top 1-2 sample intervals encompass the new record added since the 2003 cores.

Sediment accumulation rates (Figure 12) were relatively uniform (except Cliff), as indicated by the near-exponential activity profiles for ^{210}Pb and the near-constant mercury concentrations prior to the year ~1800 (see next section). The determination of near-constant sediment accumulation rates allow for the reliable extrapolation of dates prior to the oldest explicit ^{210}Pb date. Dating uncertainly for an extrapolated date of 1500 averaged $+63/-44$ years ($\pm 1 \sigma$).

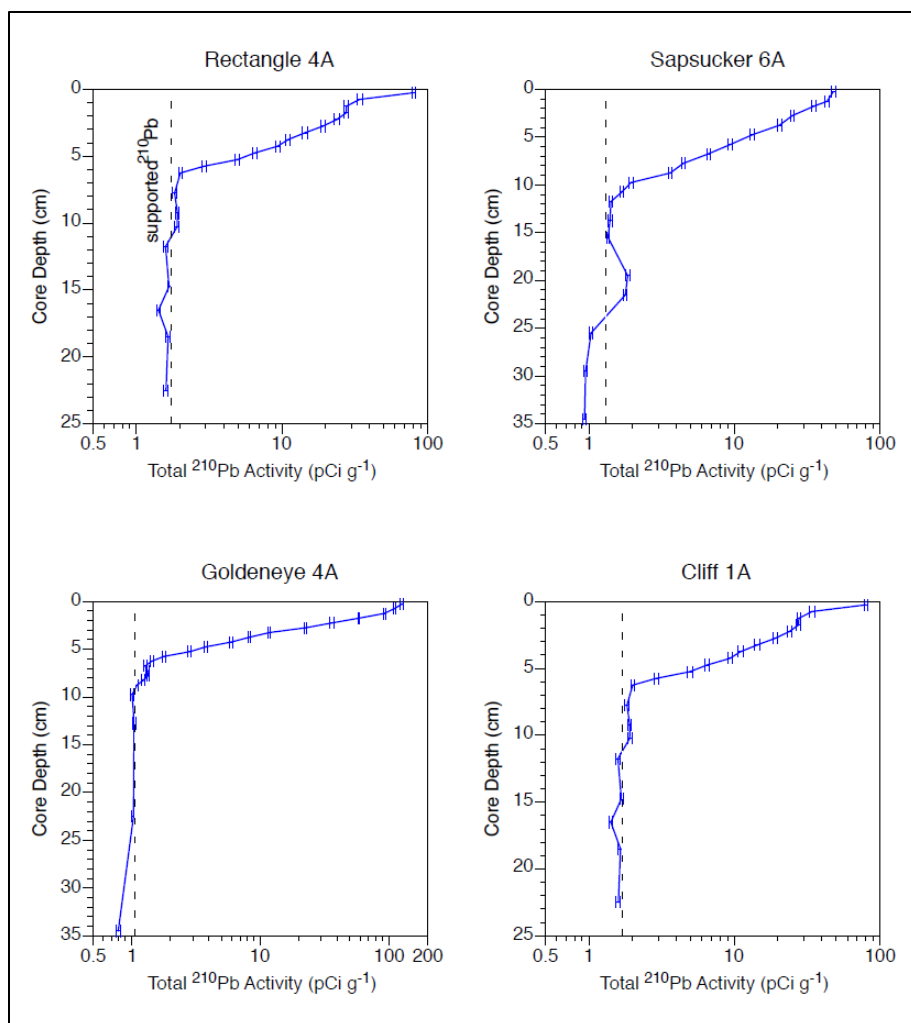


Figure 10: Profiles of total ^{210}Pb activity vs. core depth for the four study lakes. The depth at which ^{210}Pb activity becomes constant represents supported ^{210}Pb and the limit of ^{210}Pb dating.

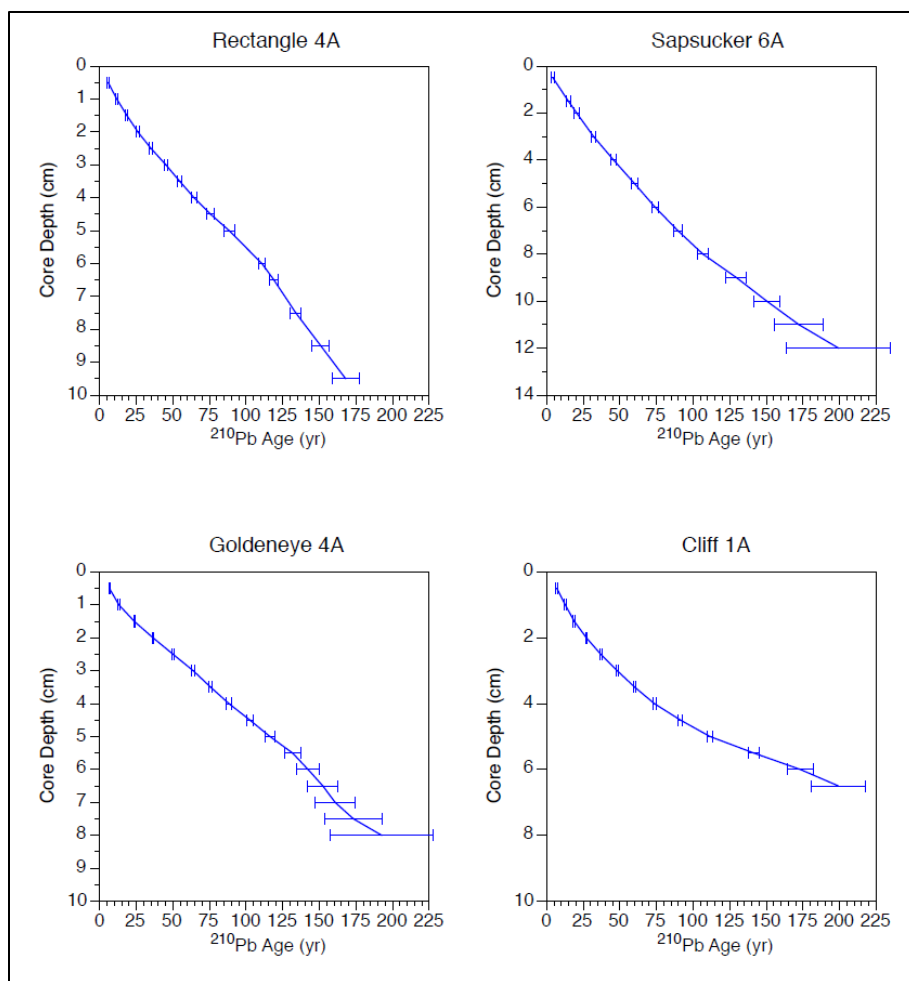


Figure 11: Age-depth profile of the core sections as calculated using ^{210}Pb ; error bars represent ± 1 s.d. determined by first-order propagation of analytical uncertainty.

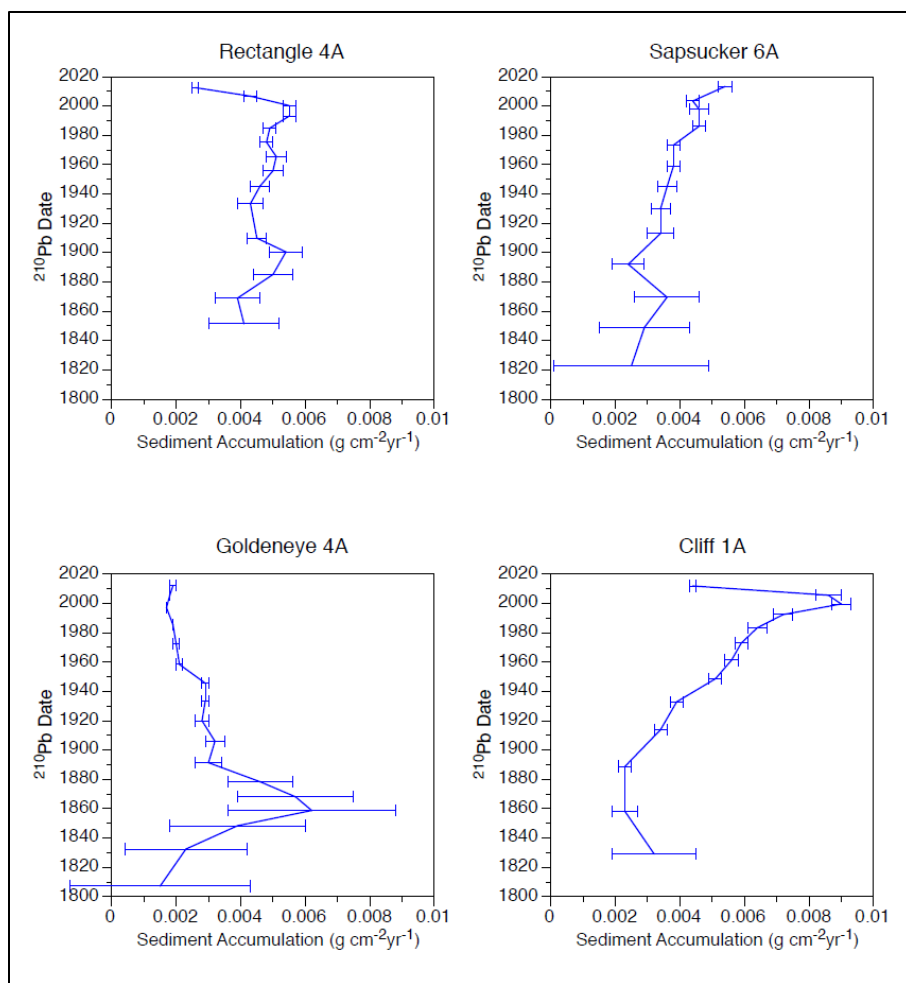


Figure 12. Sediment accumulation rate with ^{210}Pb age in the four lake cores; error bars represent ± 1 s.d. determined by first-order propagation of analytical uncertainty.

Table 2. Rectangle Lake core intervals with corresponding ^{210}Pb age dates, error values, and corresponding age dates (and errors) for interval midsections and bases, and dry mass accumulation rates (DMAR).

Top of Interval (cm)	Base of Interval (cm)	Mid of Interval (cm)	Total ^{210}Pb (pCi/g)	Error of Total Pb ($\pm$ s.d.)	Cum. Dry Mass (g/cm ²)	Unsup. ^{210}Pb (pCi/g)	Error of Unsup Pb ($\pm$ s.d.)	Age: Base of Int. (yr)	Error of Age ($\pm$ s.d.)	Date: Base A.D.	Date: Mid A.D.	Sediment DMAR (g/cm ² yr)	Error of DMAR ($\pm$ s.d.)
0	0.5	0.25	105.625	3.349	0.015	104.954	3.349	5.76	0.65	2009.6	2012.5	0.0026	0.0001
0.5	1	0.75	54.185	1.870	0.040	53.513	1.870	11.61	0.69	2003.8	2006.7	0.0043	0.0002
1	1.5	1.25	34.699	1.166	0.079	34.028	1.166	18.56	0.75	1996.8	2000.3	0.0055	0.0002
1.5	2	1.75	28.064	1.039	0.120	27.393	1.040	26.00	0.83	1989.4	1993.1	0.0055	0.0002
2	2.5	2.25	24.396	0.884	0.164	23.724	0.885	34.95	0.95	1980.4	1984.9	0.0049	0.0002
2.5	3	2.75	18.763	0.640	0.213	18.092	0.641	45.14	1.17	1970.2	1975.3	0.0048	0.0002
3	3.5	3.25	13.147	0.489	0.261	12.476	0.490	54.60	1.45	1960.8	1965.5	0.0051	0.0003
3.5	4	3.75	10.225	0.324	0.310	9.554	0.326	64.41	1.89	1951.0	1955.9	0.0050	0.0003
4	4.5	4.25	8.141	0.190	0.361	7.469	0.193	75.64	2.62	1939.7	1945.4	0.0046	0.0003
4.5	5	4.75	6.154	0.216	0.416	5.482	0.219	88.38	3.82	1927.0	1933.4	0.0043	0.0004
5.5	6	5.75	3.160	0.105	0.515	2.488	0.111	110.76	2.18	1904.6	1909.9	0.0045	0.0003
6	6.5	6.25	2.245	0.071	0.559	1.574	0.079	118.97	2.76	1896.4	1900.5	0.0054	0.0005
7	7.5	7.25	1.705	0.056	0.634	1.033	0.066	133.88	3.64	1881.5	1885.1	0.0050	0.0006
8	8.5	8.25	1.482	0.048	0.706	0.810	0.059	150.97	5.90	1864.4	1869.0	0.0039	0.0007
9	9.5	9.25	1.118	0.031	0.773	0.446	0.047	167.92	9.15	1847.5	1851.5	0.0041	0.0011

Table 3. Sapsucker Lake core intervals with corresponding ^{210}Pb age dates, error values, and corresponding age dates for interval midsections and bases, and dry mass accumulation rates (DMAR).

Top of Interval (cm)	Base of Interval (cm)	Mid of Interval (cm)	Total ^{210}Pb (pCi/g)	Error of Total Pb ($\pm$ s.d.)	Cum. Dry Mass (g/cm ²)	Unsup. ^{210}Pb (pCi/g)	Error of Unsup Pb ($\pm$ s.d.)	Age: Base of Int. (yr)	Error of Age ($\pm$ s.d.)	Date: Base A.D.	Date: Mid A.D.	Sediment DMAR (g/cm ² yr)	Error of DMAR ($\pm$ s.d.)
0	0.5	0.25	47.974	1.667	0.023	46.826	1.671	4.24	1.18	2011.1	2013.3	0.0054	0.0002
1	1.5	1.25	43.521	1.462	0.072	42.373	1.466	14.88	1.39	2000.5	2003.4	0.0044	0.0002
1.5	2	1.75	35.437	1.381	0.098	34.289	1.386	20.50	1.56	1994.9	1997.7	0.0046	0.0003
2.5	3	2.75	25.074	0.808	0.151	23.926	0.816	32.03	1.60	1983.3	1986.3	0.0046	0.0002
3.5	4	3.75	20.474	0.804	0.205	19.326	0.812	45.73	2.03	1969.6	1973.3	0.0038	0.0002
4.5	5	4.75	13.320	0.406	0.260	12.172	0.422	60.00	2.04	1955.4	1959.0	0.0038	0.0002
5.5	6	5.75	9.464	0.331	0.311	8.316	0.350	73.95	2.35	1941.4	1944.9	0.0036	0.0003
6.5	7	6.75	6.636	0.163	0.365	5.488	0.200	89.55	2.97	1925.8	1929.9	0.0034	0.0003
7.5	8	7.75	4.455	0.116	0.424	3.307	0.163	106.71	3.78	1908.7	1913.1	0.0034	0.0004
8.5	9	8.75	3.634	0.096	0.483	2.486	0.150	129.60	7.03	1885.8	1892.1	0.0024	0.0005
9.5	10	9.75	1.951	0.058	0.547	0.803	0.129	150.29	8.79	1865.1	1869.6	0.0036	0.0010
10.5	11	10.75	1.684	0.054	0.613	0.536	0.127	172.23	16.36	1843.1	1849.0	0.0029	0.0014
11.5	12	11.75	1.421	0.044	0.682	0.273	0.123	199.34	35.48	1816.0	1823.0	0.0025	0.0024

Table 4. Goldeneye Lake core intervals with corresponding ^{210}Pb age dates, error values, and corresponding age dates for interval midsections and bases, and dry mass accumulation rates (DMAR).

Top of Interval (cm)	Base of Interval (cm)	Mid of Interval (cm)	Total ^{210}Pb (pCi/g)	Error of Total Pb ($\pm$ s.d.)	Cum. Dry Mass (g/cm ²)	Unsup. ^{210}Pb (pCi/g)	Error of Unsup Pb ($\pm$ s.d.)	Age: Base of Int. (yr)	Error of Age ($\pm$ s.d.)	Date: Base A.D.	Date: Mid A.D.	Sediment DMAR (g/cm ² yr)	Error of DMAR ($\pm$ s.d.)
0	0.5	0.25	127.736	3.713	0.013	126.789	3.713	6.64	0.43	2008.7	2012.1	0.0019	0.0001
0.5	1	0.75	110.797	2.324	0.025	109.850	2.325	13.11	0.46	2002.3	2005.5	0.0018	0.0000
1	1.5	1.25	92.588	1.834	0.042	91.641	1.835	23.59	0.51	1991.8	1997.1	0.0017	0.0000
1.5	2	1.75	58.504	0.963	0.066	57.557	0.966	36.40	0.63	1979.0	1985.4	0.0019	0.0000
2	2.5	2.25	36.028	1.293	0.094	35.081	1.295	50.06	0.64	1965.3	1972.2	0.0020	0.0001
2.5	3	2.75	22.665	0.396	0.124	21.718	0.402	63.83	0.86	1951.5	1958.4	0.0021	0.0001
3	3.5	3.25	11.855	0.228	0.158	10.908	0.238	75.72	1.15	1939.7	1945.6	0.0029	0.0001
3.5	4	3.75	8.232	0.180	0.194	7.286	0.193	88.25	1.62	1927.1	1933.4	0.0029	0.0001
4	4.5	4.25	5.945	0.188	0.235	4.999	0.200	102.53	2.40	1912.8	1920.0	0.0028	0.0002
4.5	5	4.75	3.786	0.095	0.279	2.840	0.117	116.26	3.59	1899.1	1906.0	0.0032	0.0003
5	5.5	5.25	2.849	0.082	0.325	1.903	0.107	131.65	5.68	1883.7	1891.4	0.0030	0.0004
5.5	6	5.75	1.789	0.052	0.374	0.842	0.087	142.26	7.79	1873.1	1878.4	0.0046	0.0010
6	6.5	6.25	1.437	0.037	0.431	0.491	0.079	152.35	10.50	1863.0	1868.1	0.0057	0.0018
6.5	7	6.75	1.282	0.035	0.483	0.335	0.078	160.74	13.45	1854.6	1858.8	0.0062	0.0026
7	7.5	7.25	1.334	0.037	0.532	0.388	0.079	173.24	19.60	1842.1	1848.4	0.0039	0.0021
7.5	8	7.75	1.353	0.035	0.576	0.406	0.078	192.49	35.34	1822.9	1832.5	0.0023	0.0019
8	8.5	8.25	1.238	0.040	0.622	0.292	0.080	223.89	92.81	1791.5	1807.2	0.0015	0.0028

Table 5. Cliff Lake core intervals with corresponding ^{210}Pb age dates, error values, and corresponding age dates for interval midsections and bases, and dry mass accumulation rates (DMAR).

Top of Interval (cm)	Base of Interval (cm)	Mid of Interval (cm)	Total ^{210}Pb (pCi/g)	Error of Total Pb ($\pm$ s.d.)	Cum. Dry Mass (g/cm ²)	Unsup. ^{210}Pb (pCi/g)	Error of Unsup Pb ($\pm$ s.d.)	Age: Base of Int. (yr)	Error of Age ($\pm$ s.d.)	Date: Base A.D.	Date: Mid A.D.	Sediment DMAR (g/cm ² yr)	Error of DMAR ($\pm$ s.d.)
0	0.5	0.25	80.374	2.255	0.030	78.740	2.256	6.97	0.62	2008.4	2011.9	0.0044	0.0001
0.5	1	0.75	34.284	1.357	0.080	32.650	1.359	12.68	0.64	2002.7	2005.6	0.0086	0.0004
1	1.5	1.25	27.844	0.929	0.135	26.210	0.931	18.85	0.68	1996.5	1999.6	0.0090	0.0003
1.5	2	1.75	27.695	1.068	0.195	26.062	1.070	27.13	0.72	1988.2	1992.4	0.0072	0.0003
2	2.5	2.25	23.906	0.894	0.257	22.272	0.897	36.91	0.77	1978.5	1983.4	0.0064	0.0003
2.5	3	2.75	19.130	0.740	0.323	17.497	0.743	48.16	0.83	1967.2	1972.9	0.0059	0.0002
3	3.5	3.25	14.383	0.577	0.390	12.749	0.581	60.12	0.90	1955.3	1961.3	0.0056	0.0002
3.5	4	3.75	11.058	0.416	0.458	9.425	0.422	73.54	1.05	1941.8	1948.6	0.0051	0.0002
4	4.5	4.25	9.348	0.332	0.527	7.714	0.339	91.35	1.37	1924.0	1932.9	0.0039	0.0002
4.5	5	4.75	6.506	0.249	0.595	4.872	0.258	111.56	2.00	1903.8	1913.9	0.0034	0.0002
5	5.5	5.25	4.949	0.195	0.665	3.315	0.206	141.38	3.91	1874.0	1888.9	0.0023	0.0002
5.5	6	5.75	2.904	0.101	0.739	1.270	0.122	173.19	9.09	1842.2	1858.1	0.0023	0.0004
6	6.5	6.25	2.005	0.051	0.823	0.372	0.086	199.16	18.20	1816.2	1829.2	0.0032	0.0013

Total mercury concentrations and accumulation

Concentrations of mercury in the core sections (Table 6, Figure 13) were multiplied by the DMAR to yield total mercury fluxes to each lake (Figure 14, Tables 6-8).

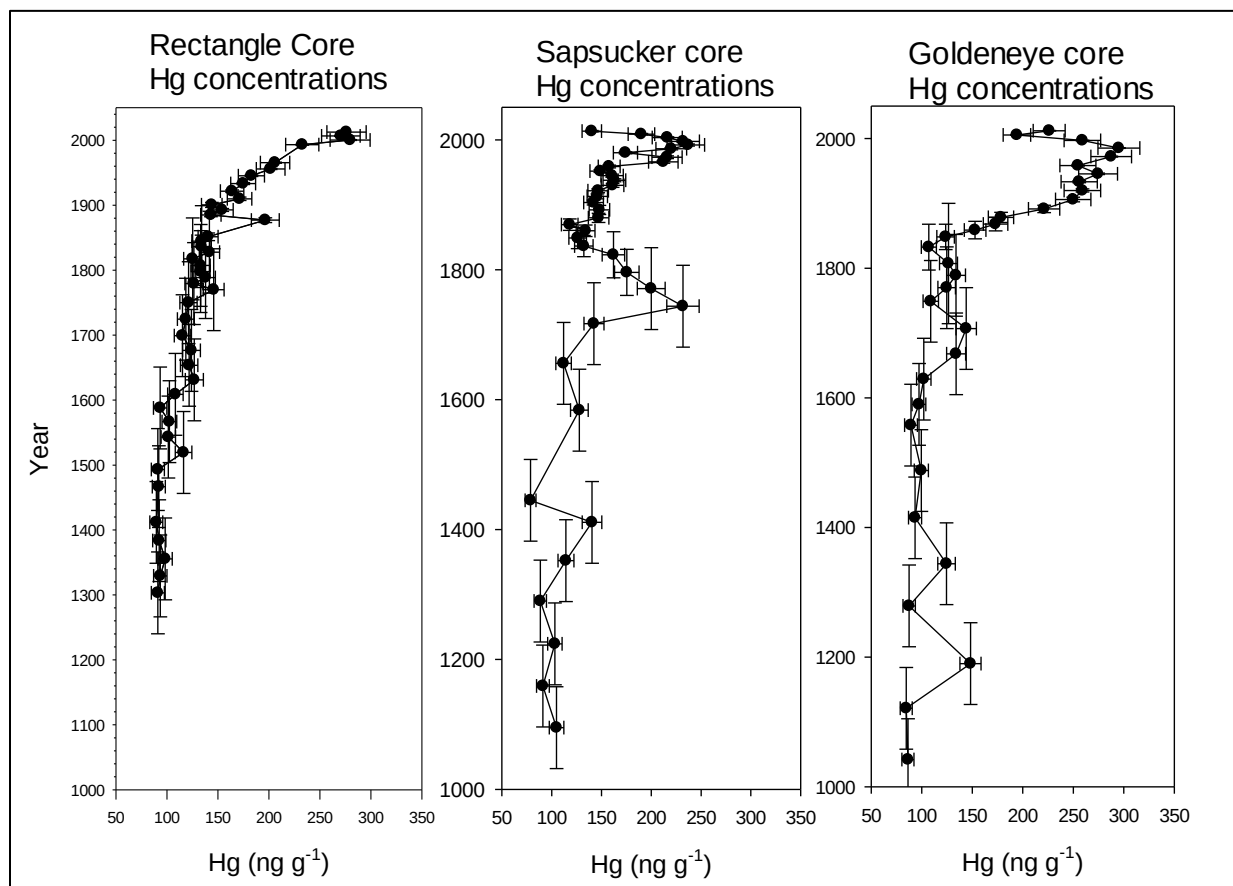


Figure 13. Lake core profiles of total mercury concentrations in Rectangle, Sapsucker, and Goldeneye Lakes over the past 7-10 centuries. Error bars in Hg concentration are based on the 7% average difference between the sediment digestion duplicates, the largest source of analytical variability.

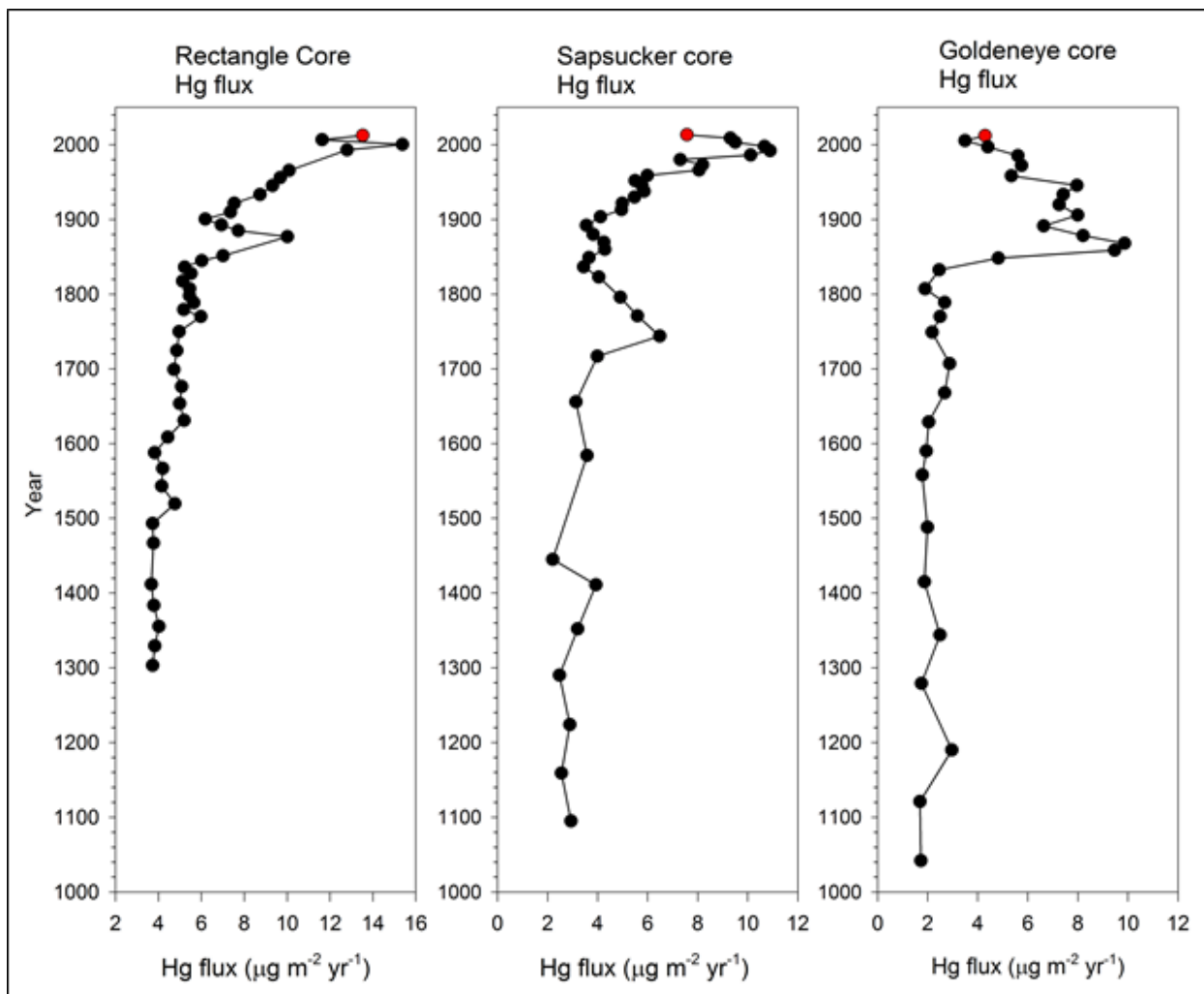


Figure 14. Lake core profiles of total mercury flux to Rectangle, Sapsucker, and Goldeneye Lakes over the past 7-10 centuries. The most recent datapoint is in red.

Table 6. Age dates (calculated using ^{210}Pb and extrapolations via the constant rate of supply model), total Hg concentrations, total Hg deposition, and Hg isotope concentrations along depth intervals of the Rectangle Lake core.

Top (cm)	Base (cm)	Mid- Date	Organic content (%)	Sediment DMAR (g/cm ² yr)	Hg conc. (ng/g)	Hg dep. μg/m ² /yr	Isotopes δ ²⁰² Hg	Δ ¹⁹⁹ Hg
0.0	0.5	2012.5	55.08	0.0049	276.0	13.52	-1.550	-0.130
0.5	1.0	2006.7	48.52	0.0043	270.5	11.63	-1.840	-0.250
1.0	1.5	2000.3	43.08	0.0055	279.6	15.38	-1.920	-0.250
1.5	2.0	1993.1	41.57	0.0055	232.6	12.79	-1.980	-0.240
3.0	3.5	1965.5	40.15	0.0049	206.0	10.09	-2.210	-0.330
3.5	4.0	1955.9	39.22	0.0048	201.6	9.68	-2.040	-0.320
4.0	4.5	1945.4	40.13	0.0051	182.7	9.32	-1.850	-0.310
4.5	5.0	1933.4	39.23	0.005	174.7	8.74	-2.010	-0.370
5.0	5.5	1921.6	39.20	0.0046	163.8	7.53	-1.780	-0.350
5.5	6.0	1909.9	41.37	0.0043	171.1	7.36	-2.040	-0.380
6.0	6.5	1900.5	39.97	0.0043	143.9	6.19	-2.100	-0.390
6.5	7.0	1892.8	37.68	0.0045	154.1	6.93	-2.040	-0.440
7.0	7.5	1885.1	43.57	0.0054	143.0	7.72	-1.760	-0.250
7.5	8.0	1877.0	41.28	0.0051	196.4	10.02	-1.870	-0.350
9.0	9.5	1851.5	43.22	0.005	140.3	7.02	-2.020	-0.430
9.5	10.0	1845	41.03	0.0045	133.8	6.02	-1.900	-0.420
10.0	10.5	1836	–	0.0039	134.0	5.23	-1.900	-0.340
10.5	11.0	1828	39.58	0.0039	141.6	5.52	-2.040	-0.380
11.0	11.5	1817	–	0.0041	125.1	5.13	-2.000	-0.330
11.5	12.0	1807	35.00	0.0041	133.0	5.45	-2.070	-0.410
12.0	12.5	1798	–	0.0041	132.9	5.45	-1.850	-0.320
12.5	13.0	1789	35.05	0.0041	137.8	5.65	-2.010	-0.380
13.0	13.5	1779	–	0.0041	126.3	5.18	-1.920	-0.400
13.5	14.0	1770	36.71	0.0041	145.8	5.98	-2.180	-0.410
14.5	15.0	1750	32.35	0.0041	121.1	4.97	-1.920	-0.350
15.0	16.0	1725	–	0.0041	118.5	4.86	-1.970	-0.490
16.0	17.0	1699	27.97	0.0041	115.2	4.72	-2.030	-0.410
17.0	18.0	1676	–	0.0041	124.0	5.08	-1.950	-0.480
18.0	19.0	1654	32.31	0.0041	121.7	4.99	-1.970	-0.390
19.0	20.0	1631	–	0.0041	126.8	5.20	-2.010	-0.390

Table 6 (continued). Age dates (calculated using ^{210}Pb and extrapolations via the constant rate of supply model), total Hg concentrations, total Hg deposition, and Hg isotope concentrations along depth intervals of the Rectangle Lake core.

Top (cm)	Base (cm)	Mid- Date	Organic content (%)	Sediment DMAR (g/cm ² yr)	Hg conc. (ng/g)	Hg dep. μg/m ² /yr	Isotopes δ ²⁰² Hg	Δ ¹⁹⁹ Hg
20.0	21.0	1609	32.57	0.0041	108.2	4.44	-2.180	-0.400
21.0	22.0	1588	—	0.0041	93.3	3.83	-2.050	-0.370
22.0	23.0	1567	33.57	0.0041	102.4	4.20	-2.160	-0.440
23.0	24.0	1543	—	0.0041	101.3	4.15	-2.110	-0.430
24.0	25.0	1520	34.00	0.0041	116.2	4.76	-2.110	-0.400
25.0	26.0	1493	—	0.0041	91.0	3.73	-2.120	-0.400
26.0	27.0	1467	32.84	0.0041	91.9	3.77	-2.020	-0.420
28.0	29.0	1412	30.08	0.0041	89.5	3.67	-1.860	-0.330
29.0	30.0	1384	—	0.0041	92.4	3.79	-2.020	-0.450
30.0	31.0	1355	32.53	0.0041	98.2	4.03	-2.090	-0.370
31.0	32.0	1329	—	0.0041	93.4	3.83	-2.170	-0.400
32.0	33.0	1303	38.49	0.0041	91.0	3.73	-2.020	-0.360

Table 7. Age dates (calculated using ^{210}Pb and extrapolations via the constant rate of supply model), total Hg concentrations, total Hg deposition, and Hg isotope concentrations along depth intervals of the Sapsucker Lake core.

Top (cm)	Base (cm)	Mid- Date	Organic content (%)	Sediment DMAR (g/cm ² yr)	Hg conc. (ng/g)	Hg dep. μg/m ² /yr	Isotopes δ ²⁰² Hg	Δ ¹⁹⁹ Hg
0	0.5	2013.3	56.35	0.0054	140.2	7.57	-1.518	-0.314
0.5	1	2008.7	55.38	0.0049	190.0	9.31	-1.509	-0.266
1	1.5	2003.4	53.43	0.0044	216.0	9.50	-1.546	-0.260
1.5	2	1997.7	50.85	0.0046	232.0	10.67	-1.571	-0.182
2	2.5	1992.1	48.31	0.0046	236.8	10.89	-1.629	-0.201
2.5	3	1986.3	47.31	0.0046	220.0	10.12	-1.559	-0.164
3	3.5	1980.1	44.96	0.0042	174.0	7.31	-1.555	-0.229
3.5	4	1973.3	44.50	0.0038	215.8	8.20	-1.663	-0.298
4	4.5	1966.1	43.69	0.0038	212.0	8.06	-1.531	-0.215
4.5	5	1959.0	43.08	0.0038	157.7	5.99	-1.469	-0.299
5	5.5	1951.9	43.19	0.0037	148.7	5.50	-1.406	-0.305
5.5	6	1944.9	40.53	0.0036	160.7	5.78	-1.596	-0.358

Table 7 (continued). Age dates (calculated using ^{210}Pb and extrapolations via the constant rate of supply model), total Hg concentrations, total Hg deposition, and Hg isotope concentrations along depth intervals of the Sapsucker Lake core.

Top (cm)	Base (cm)	Mid- Date	Organic content (%)	Sediment DMAR (g/cm ² yr)	Hg conc. (ng/g)	Hg dep. μg/m ² /yr	Isotopes δ ²⁰² Hg	Δ ¹⁹⁹ Hg
6	6.5	1937.7	35.25	0.0036	162.9	5.86	-1.521	-0.352
6.5	7	1929.9	37.22	0.0034	161.1	5.48	-1.643	-0.438
7	7.5	1921.6	34.47	0.0034	146.6	4.98	-1.599	-0.367
7.5	8	1913.1	38.03	0.0034	145.7	4.95	-1.245	-0.220
8	8.5	1903.6	39.31	0.0029	141.9	4.12	-1.653	-0.379
8.5	9	1892.1	40.57	0.0024	147.8	3.55	-1.693	-0.405
9	9.5	1879.9	37.61	0.0026	147.0	3.82	-1.653	-0.405
9.5	10	1869.6	34.53	0.0036	118.0	4.25	-1.779	-0.455
10	10.5	1860.0	—	0.0032	134.0	4.29	-1.742	-0.474
10.5	11	1849.0	37.12	0.0029	126.0	3.65	-1.819	-0.513
11	11.5	1836.6	—	0.0026	132.3	3.44	-1.751	-0.504
11.5	12	1823	39.90	0.0025	161.9	4.05	-1.768	-0.540
12.5	13	1796	38.51	0.0028	175.3	4.91	-1.735	-0.431
13.5	14	1771	38.13	0.0028	199.9	5.60	-1.745	-0.255
14.5	15	1744	36.62	0.0028	231.7	6.49	-1.648	-0.393
15	16	1717	—	0.0028	142.4	3.99	—	—
17	18	1656	39.99	0.0028	111.9	3.13	-1.867	-0.421
19	20	1584	39.74	0.0028	127.7	3.58	-1.529	-0.337
20	21	1445	44.34	0.0028	78.7	2.20	-1.381	-0.392
21	22	1411	40.53	0.0028	140.4	3.93	-1.801	-0.377
23	24	1352	41.22	0.0028	114.2	3.20	-1.821	-0.407
25	26	1290	39.36	0.0028	88.5	2.48	-1.681	-0.455
27	28	1224	39.75	0.0028	103.1	2.89	-1.787	-0.389
29	30	1159	37.36	0.0028	91.2	2.55	-1.510	-0.366
31	32	1095	37.32	0.0028	104.8	2.93	-1.793	-0.523

Table 8. Age dates (calculated using ^{210}Pb and extrapolations via the constant rate of supply model), total Hg concentrations, total Hg deposition, and Hg isotope concentrations along depth intervals of the Goldeneye Lake core.

Top (cm)	Base (cm)	Mid- Date	Organic content (%)	Sediment DMAR (g/cm ² yr)	Hg conc. (ng/g)	Hg dep. µg/m ² /yr	Isotopes $\delta^{202}\text{Hg}$	$\Delta^{199}\text{Hg}$
0	0.5	2012.1	45.48	0.0019	226.2	4.3	-1.204	-0.187
0.5	1	2005.5	46.37	0.0018	194.2	3.5	-1.047	-0.111
1	1.5	1997.1	48.54	0.0017	259.0	4.4	-1.252	-0.145
1.5	2	1985.4	49.79	0.0019	295.1	5.6	-1.445	-0.114
2	2.5	1972.2	48.94	0.0020	287.6	5.8	—	—
2.5	3	1958.4	45.25	0.0021	254.6	5.3	-1.593	-0.195
3	3.5	1945.6	45.58	0.0029	274.6	8.0	-1.518	-0.200
3.5	4	1933.4	46.29	0.0029	255.8	7.4	-1.566	-0.226
4	4.5	1920.0	46.17	0.0028	259.1	7.3	-1.577	-0.263
4.5	5	1906.0	40.27	0.0032	249.9	8.0	-1.535	-0.343
5	5.5	1891.4	41.62	0.0030	221.1	6.6	-1.524	-0.231
5.5	6	1878.4	43.66	0.0046	178.5	8.2	-1.342	-0.135
6	6.5	1868.1	47.17	0.0057	173.1	9.9	—	—
6.5	7	1858.8	45.62	0.0062	152.8	9.5	-1.081	-0.350
7	7.5	1848.4	45.58	0.0039	123.7	4.8	-1.150	-0.250
7.5	8	1832.5	45.64	0.0023	107.0	2.5	-1.240	-0.343
8	8.5	1807.2	45.80	0.0015	126.5	1.9	-1.361	-0.310
8.5	9	1789	45.60	0.0020	134.0	2.7	-1.538	-0.326
9	9.5	1770	47.66	0.0020	124.7	2.5	-1.577	-0.340
9.5	10	1749	46.08	0.0020	108.9	2.2	-1.473	-0.260
10.5	11	1707	45.09	0.0020	144.0	2.9	-1.719	-0.299
11.5	12	1668	42.03	0.0020	134.0	2.7	-1.540	-0.263
12.5	13	1629	40.39	0.0020	102.0	2.0	-1.451	-0.323
13.5	14	1590	42.91	0.0020	97.3	1.9	-1.332	-0.314
14.5	15	1558	43.34	0.0020	89.4	1.8	-1.327	-0.339
16	17	1488	40.92	0.0020	99.6	2.0	-1.268	-0.298
18	19	1415	36.85	0.0020	93.4	1.9	-1.282	-0.336
20	21	1344	43.51	0.0020	124.6	2.5	-1.242	-0.372
22	23	1279	45.69	0.0020	87.5	1.8	-1.240	-0.331

Table 8 (continued). Age dates (calculated using ^{210}Pb and extrapolations via the constant rate of supply model), total Hg concentrations, total Hg deposition, and Hg isotope concentrations along depth intervals of the Goldeneye Lake core.

Top (cm)	Base (cm)	Mid-Date	Organic content (%)	Sediment DMAR (g/cm ² yr)	Hg conc. (ng/g)	Hg dep. µg/m ² /yr	Isotopes $\delta^{202}\text{Hg}$	$\Delta^{199}\text{Hg}$
24	25	1190	42.43	0.0020	148.3	3.0	-1.619	-0.339
26	27	1121	44.10	0.0020	84.6	1.7	-1.179	-0.335
28	29	1042	41.05	0.0020	86.4	1.7	-1.362	-0.374

Grouping of core intervals into 25-100+ year averages (Table 9) reveals that flux values doubled in Goldeneye and tripled in Rectangle and Sapsucker Lakes, between the pre-1500 period and the most recent time interval (1990-2015). (Pre-1500 is designated as pre-anthropogenic because large scale use of mercury began in the late 1500s in colonial South American silver mines (Cooke et al., 2009; Guerrero, 2016). Assuming that pre-1500 age Hg fluxes to the lake are due to natural geogenic sources in the watershed and natural atmospheric deposition, the increase during the recent three centuries above background can be attributed to enhanced deposition from anthropogenic activity such as coal combustion, metal smelting, and industrial processes within the air shed of these lakes.

Table 9. Grouped time intervals from the Rectangle, Sapsucker, and Goldeneye sediment cores, with averaged values of percent organic matter, Hg concentration, Hg flux, and Hg isotopes.

Lake	Time interval (year)	%Org	Hg conc. ng/g	Hg flux µg/m ² /yr	Hg isotopes $\delta^{202}\text{Hg}$	$\Delta^{199}\text{Hg}$	Hg flux ratio* m/p
Rectangle	1990-2015	47.1	265	13.3	-1.82	-0.22	3.5
	1950-1990	39.7	204	9.9	-2.13	-0.33	—
	1900-1950	40.0	167	7.8	-1.96	-0.36	—
	1850-1900	41.4	158	7.9	-1.92	-0.37	—
	1800-1850	38.5	134	5.5	-1.98	-0.38	—
	1700-1800	34.7	130	5.3	-1.98	-0.39	—
	1500-1700	32.1	112	4.6	-2.06	-0.41	—
	pre-1500	33.5	92	3.8	-2.04	-0.39	—
Sapsucker	1990-2015	52.9	203	9.6	-1.55	-0.24	3.3
	1950-1990	44.5	188	7.5	-1.53	-0.25	—
	1900-1950	37.5	153	5.2	-1.54	-0.35	—
	1850-1900	37.6	137	4.0	-1.72	-0.43	—
	1800-1850	38.5	140	3.7	-1.78	-0.52	—
	1700-1800	37.8	187	5.2	-1.71	-0.36	—

*m/p= modern to pre-anthropogenic (pre-1500) Hg flux ratio

Table 9 (continued). Grouped time intervals from the Rectangle, Sapsucker, and Goldeneye sediment cores, with averaged values of percent organic matter, Hg concentration, Hg flux, and Hg isotopes.

Lake	Time interval (year)	%Org	Hg conc. ng/g	Hg flux $\mu\text{g}/\text{m}^2/\text{yr}$	Hg isotopes $\delta^{202}\text{Hg}$	$\Delta^{199}\text{Hg}$	Hg flux ratio* m/p
Sapsucker (cont.)	1500-1700	39.9	120	3.4	-1.70	-0.38	–
	pre-1500	40.0	103.0	2.9	-1.7	-0.42	–
Goldeneye	1990-2015	46.8	226	4.1	-1.17	-0.15	2.0
	1950-1990	48.0	279	5.6	-1.52	-0.15	–
	1900-1950	44.6	260	7.7	-1.55	-0.26	–
	1850-1900	44.5	181	8.5	-1.32	-0.24	–
	1800-1850	45.7	119	3.1	-1.25	-0.30	–
	1700-1800	46.1	128	2.6	-1.58	-0.31	–
	1500-1700	42.2	106	2.1	-1.41	-0.31	–
	pre-1500	42.1	103	2.1	-1.3	-0.34	–

*m/p= modern to pre-anthropogenic (pre-1500) Hg flux ratio

The 2.0-3.5 fold increases in mercury flux to the lake sediments between pre-anthropogenic and modern periods in these Chichagof lakes matches well with flux ratios revealed in lakes from Arctic Alaska, Newfoundland, and other regions remote from emission sources (Engstrom et al. 2014). Pre-anthropogenic to modern flux ratios are higher (6-20 fold) in areas closer to local sources such as in near Hg-mining districts in South America and in urban areas of the US (Engstrom et al., 2007).

In Rectangle Lake, Hg flux increased with each progressive grouped time interval shown (Table 9), with the largest relative increase in the 1990-2015 section relative to 1950-1990 (flux increase from 9.9 to 13.3 $\mu\text{g m}^{-2} \text{yr}^{-1}$). In both Rectangle and Sapsucker Lakes, the highest average Hg flux was in the most recent sections (1990-2015). Although not analyzed for Hg in this study, Cliff Lake's sediment cores collected in 2003 showed a similar sharp and unabated rise in Hg fluxes in the late 20th century (Engstrom et al. 2014). In Goldeneye, peak Hg flux occurred much earlier—in the 1850-1900 core section, with declines since then but with the most recent (1990-2015) section's average flux still doubling the pre-1500 value. It is notable that all three cores show increases in Hg flux starting around 1850 and then declining toward about 1900, but the magnitude of this increase and the time period over which it is sustained is different (least for Sapsucker and greatest for Goldeneye). Whether this is due to known large mercury uses associated with the Gold Rush in North America is not certain, but it is well timed with that event. Differences among lakes in absolute mercury flux are likely due to variations in sediment focusing within each, as well as differences in the export of atmospherically derived Hg from catchment vegetation and soils.

In Rectangle and Goldeneye, the most recent sediment layer (core section mid-date 2012 and 2015, respectively) show 15-20% increases in calculated flux values compared with the second most recent interval (core section mid-date 2005 and 2007), reversing a downward trend in Hg flux in

these cores. In Rectangle, the highest Hg deposition was in year 2000 (core section mid-date), with $15.4 \mu\text{g m}^{-2} \text{yr}^{-1}$, which is 4.1 times higher than the pre-1500 background (Table 6). The sample above that (core section mid-date 2007) had a lower flux ($11.6 \mu\text{g m}^{-2} \text{yr}^{-1}$), but the most recent segment (top 0.5 cm of the core, section mid-date 2012) has a flux of $13.5 \mu\text{g m}^{-2} \text{yr}^{-1}$. Although 20th century Hg flux to Goldeneye was highest in 1945 and has generally (with some fluctuation) declined since then, it shows an increase in Hg flux (3.5 to $4.3 \mu\text{g m}^{-2}/\text{yr}$, or 20%) between the 2005 to 2012 intervals (Table 8). In contrast, the uppermost core section from Sapsucker Lake follows a trend of consistent decrease in Hg flux since the peak in the mid-1990s, when the maximum value was 3.7-fold higher than the pre-1500 background level (Table 7).

Profiles from Rectangle and Sapsucker closely match profiles obtained in the same lakes in 2003 (Engstrom et al. 2014). However, the profile in the Goldeneye core is substantially different from those from cores taken in 2003, in that it shows an earlier Hg flux peak (around 1850-1900) rather than in the late-20th century. A likely reason for the discrepancy is that in the current study, only a single core per lake was analyzed, whereas the 2003 study integrated 6 widely-spaced individual cores from each lake. This indicates that within-site variability in lakes may be substantial and therefore multiple cores/lake are needed in order to accurately track decadal-scale temporal trends.

The general trend in the 2015 Chichagof lake cores follows closely the Hg temporal profiles shown in a Mt Logan (Yukon, Canada) ice core collected in 2002, the only other published long-term Hg archive in the region (Beal et al., 2015). In that core, the first major rise in Hg fluxes is seen in the late 19th century and is attributed to activities associated with North American silver and gold mining and European Hg production during that time. Late 19th century increases in Hg fluxes are also seen in the Rectangle and Goldeneye (but not Sapsucker) lake sediment profiles. In both the Mt Logan ice core and in the Rectangle Lake sediment core, however, this Gold Rush signal is small and brief compared with the late-20th century rise. However, Goldeneye's maximum Hg flux during the late 1900s is more pronounced, illustrating the between-lake heterogeneity and the importance of obtaining cores from multiple lakes in order to obtain more certain regional trends. In Beal et al. (2015) ice core, Hg fluxes rise well above background levels from about 1940-1975 (maximum in 1960), followed by a decline in the 1980s and then a rise through the 1990s. Beal et al. (2015) also suggest that the most recent rise in Hg deposition is may reflect recent growth in Asian coal burning.

Stable isotopes of mercury may be informative for delineating sources of mercury, elucidating regional differences in mercury deposition and cycling, and site-specific controls on mercury inputs to lakes. The results of the mercury stable isotopes measurements on the Chichagof lake core will be reported and interpreted in a separate manuscript in the context of data from multiple other lake core sites around the world. Generally, however, the patterns apparent from the Chichagof data indicate a slight positive trending of $\Delta^{199}\text{Hg}$ with inputs of anthropogenic Hg over time, as well as asynchronous variations (among cores) in $\delta^{202}\text{Hg}$, which may be attributable to variable mechanisms of Hg fractionation in the watersheds and inputs to the lakes (Engstrom et al., 2017).

Conclusions

Cores obtained from lakes on north Chichagof Island are excellent archives of historical mercury deposition to the region over multiple centuries and help place modern fluxes in the context of historical background levels. The mercury flux data indicate a relatively steady level of Hg deposition (average $2.1\text{--}3.8\ \mu\text{g m}^{-2}\ \text{yr}^{-1}$) to the lakes prior to the 17th century, with some higher fluxes in the 18th and 19th centuries, and in two of the cores, a 3- to 4-fold increase over pre-anthropogenic values in the most recent couple of decades. In two of the lakes (Rectangle and Goldeneye), the uppermost core interval (top 0.5 cm of the cores), representing the most recent 5-8 years, shows a reversal (15-20% increase over the next older interval) of a prior, short duration downward trend of Hg flux to the lakes at the end of the 20th century. Recoring the lakes in a few decades would help elucidate if this trend holds as a reflection of recently elevated emissions from industrial Asian nations, (despite global declines otherwise), or if it is only a temporary variation of mercury deposition rates or export from the catchment. Differences among the lakes need to be considered in that the lake catchment areas may be routing, storing, and releasing mercury to the lakes by different processes that may include heterogeneous mercury storage and release, non-uniform contributions by geologic sources in the catchments, and heterogeneous isotopic fractionation of the stable mercury isotopes as a result of *in situ* processes, resulting in profile variations within and among cores. For the purpose of planning future monitoring of mercury deposition to the region, it is advisable that multiple cores be collected at each of the four lakes. Any additional information on the timing, magnitude, and fractionation of mercury as it is routed through the catchments into the lakes would also help explain variations in the profiles. Overall, these cores provide valuable information on long-term mercury deposition to the region, and their coastal, remote location make them appropriate surrogates for atmospheric deposition from global sources to the SE Alaska region in general.

Literature Cited

- Appleby, P.G. (2002). Chronostratigraphic Techniques in Recent Sediments. In *Tracking Environmental Change Using Lake Sediments*, W.M. Last, and J.P. Smol, eds. (Dordrecht: Kluwer Academic Publishers), pp. 171–203.
- Beal, S.A., Osterberg, E.C., Zdanowicz, C.M., and Fisher, D.A. (2015). Ice Core Perspective on Mercury Pollution during the Past 600 Years. *Environ. Sci. Technol.* **49**, 7641–7647.
- Biester, H., Bindler, R., Martinez-Cortizas, A., and Engstrom, D.R. (2007). Modeling the Past Atmospheric Deposition of Mercury Using Natural Archives. *Environ. Sci. Technol.* **41**, 4851–4860.
- Bindler, R., Renberg, I., Appleby, P.G., Anderson, N.J., and Rose, N.L. (2001). Mercury Accumulation Rates and Spatial Patterns in Lake Sediments from West Greenland: A Coast to Ice Margin Transect. *Environ. Sci. Technol.* **35**, 1736–1741.
- Braune, B., Chételat, J., Amyot, M., Brown, T., Claydon, M., Evans, M., Fisk, A., Gaden, A., Girard, C., Hare, A., et al. (2014). Mercury in the marine environment of the Canadian Arctic: Review of recent findings. *Sci. Total Environ.*
- Cooke, C.A., Balcom, P.H., Biester, H., and Wolfe, A.P. (2009). Over three millennia of mercury pollution in the Peruvian Andes. *Proc. Natl. Acad. Sci.* **106**, 8830–8834.
- Dietz, R., Sonne, C., Basu, N., Braune, B., O'Hara, T., Letcher, R.J., Scheuhammer, T., Andersen, M., Andreassen, C., Andriashek, D., et al. (2013). What are the toxicological effects of mercury in Arctic biota? *Sci. Total Environ.* **443**, 775–790.
- Durnford, D., Dastoor, A., Figueras-Nieto, D., and Ryjkov, A. (2010). Long range transport of mercury to the Arctic and across Canada. *Atmospheric Chem. Phys.* **10**, 6063–6086.
- Eakins, J.D., and Morrison, R.T. (1978). A new procedure for the determination of lead-210 in lake and marine sediments. *Int. J. Appl. Radiat. Isot.* **29**, 531–536.
- Eckert, G., Hood, E., Nagorski, S., and Talus, C. (2006). Assessment of coastal water resources and watershed conditions at Glacier Bay National Park and Preserve, Alaska (Water Resources Division, National Park Service).
- Engstrom, D.R., and Swain, E.B. (1997). Recent Declines in Atmospheric Mercury Deposition in the Upper Midwest. *Environ. Sci. Technol.* **31**, 960–967.
- Engstrom, D.R., Balogh, S.J., and Swain, E.B. (2007). History of mercury inputs to Minnesota lakes: Influences of watershed disturbance and localized atmospheric deposition. *Limnol. Oceanogr.* **52**, 2467–2483.

- Engstrom, D.R., Fitzgerald, W.F., Cooke, C.A., Lamborg, C.H., Drevnick, P.E., Swain, E.B., Balogh, S.J., and Balcom, P.H. (2014). Atmospheric Hg Emissions from Preindustrial Gold and Silver Extraction in the Americas: A Reevaluation from Lake-Sediment Archives. *Environ. Sci. Technol.* 48, 6533–6543.
- Engstrom, D.R., Fitzgerald, W.F., Hurley, J.P., Janssen, S., Krabbenhoft, D.P., Lepak, R., Nagorski, S.A., Yin, R., and Zhu, C. (2017). Historic change in mercury sources and cycling reconstructed from isotopic records in a globally distributed suite of lake core sediments. In 13th International Conference on Mercury as a Global Pollutant, (Providence, RI), p.
- Fitzgerald, W.F., Engstrom, D.R., Lamborg, C.H., Tseng, C.-M., Balcom, P.H., and Hammerschmidt, C.R. (2005). Modern and Historic Atmospheric Mercury Fluxes in Northern Alaska: Global Sources and Arctic Depletion. *Environ. Sci. Technol.* 39, 557–568.
- Gilmour, C.C., Henry, E.A., and Mitchell, R. (1992). Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* 26, 2281–2287.
- Guerrero, S. (2016). The history of silver refining in New Spain, 16c to 18c: back to the basics. *Hist. Technol.* 32, 2–32.
- Hamade, A.K. (2014). Fish consumption advice for Alaskans: A risk management strategy.
- Jaffe, D., Prestbo, E., Swartzendruber, P., Weisspenzias, P., Kato, S., Takami, A., Hatakeyama, S., and Kajii, Y. (2005). Export of atmospheric mercury from Asia. *Atmos. Environ.* 39, 3029–3038.
- Kirk, J.L., Lehnherr, I., Andersson, M., Braune, B.M., Chan, L., Dastoor, A.P., Durnford, D., Gleason, A.L., Loseto, L.L., Steffen, A., et al. (2012). Mercury in Arctic marine ecosystems: Sources, pathways and exposure. *Environ. Res.* 119, 64–87.
- Lamborg, C.H., Engstrom, D.R., Fitzgerald, W.F., and Balcom, P.H. (2013). Apportioning global and non-global components of mercury deposition through 210Pb indexing. *Sci. Total Environ.* 448, 132–140.
- Lepak, R.F., Yin, R., Krabbenhoft, D.P., Ogorek, J.M., DeWild, J.F., Holsen, T.M., and Hurley, J.P. (2015). Use of Stable Isotope Signatures to Determine Mercury Sources in the Great Lakes. *Environ. Sci. Technol. Lett.* 2, 335–341.
- Pacyna, E.G., Pacyna, J.M., Sundseth, K., Munthe, J., Kindbom, K., Wilson, S., Steenhuisen, F., and Maxson, P. (2010). Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmos. Environ.* 44, 2487–2499.
- Schroeder, W.H., and Munthe, J. (1998). Atmospheric mercury—An overview. *Atmos. Environ.* 32, 809–822.

- Schuster, P.F., Schaefer, K.M., Aiken, G.R., Antweiler, R.C., Dewild, J.F., Gryziec, J.D., Gusmeroli, A., Hugelius, G., Jafarov, E., Krabbenhoft, D.P., et al. (2018). Permafrost Stores a Globally Significant Amount of Mercury: Permafrost Stores a Globally Significant Amount of Mercury. *Geophys. Res. Lett.* *45*, 1463–1471.
- Ullrich, S.M., Tanton, T.W., and Abdrashitova, S.A. (2001). Mercury in the Aquatic Environment: A Review of Factors Affecting Methylation. *Crit. Rev. Environ. Sci. Technol.* *31*, 241–293.
- USEPA (2002). Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (US Environmental Protection Agency Office of Water).
- USGS-MRL (2016). Analysis of Total Mercury in Sediments, Soils, and Plants by Cold Vapor Atomic Fluorescence Detection with the Brooks-Rand “MERX” Automated Mercury Analytical System (U.S. Geological Survey).
- Wolfe, M.F., Schwarzbach, S., and Sulaiman, R.A. (1998). Effects of mercury on wildlife: a comprehensive review. *Environ. Toxicol. Chem.* *17*, 146–160.
- Yin, R., Krabbenhoft, D.P., Bergquist, B.A., Zheng, W., Lepak, R.F., and Hurley, J.P. (2016). Effects of mercury and thallium concentrations on high precision determination of mercury isotopic composition by Neptune Plus multiple collector inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* *31*, 2060–2068.
- Zhang, Y., Jacob, D.J., Horowitz, H.M., Chen, L., Amos, H.M., Krabbenhoft, D.P., Slemr, F., St. Louis, V.L., and Sunderland, E.M. (2016). Observed decrease in atmospheric mercury explained by global decline in anthropogenic emissions. *Proc. Natl. Acad. Sci.* *113*, 526–531.

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