Mercury loading within the Selenga River Basin and Lake Baikal, Siberia

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Abstract

Mercury (Hg) loading in Lake Baikal, a UNESCO world heritage site, is growing and poses a serious health concern to the lake's ecosystem due to the ability of Hg to transform into a toxic form, known as methylmercury (MeHg). Monitoring of Hg into Lake Baikal is spatially and temporally sparse, highlighting the need for insights into historic Hg loading. This study reports measurements of Hg concentrations from water collected in August 2013 and 2014 from across Lake Baikal and its main inflow, the Selenga River basin (Russia). We also report historic Hg contamination using sediment cores taken from the south and north basins of Lake Baikal, and a shallow lake in the Selenga Delta. Field measurements from August 2013 and 2014 show high Hg concentrations in the Selenga Delta and river waters, in comparison to pelagic lake waters. Sediment cores show temporal heterogeneity of Hg enrichment across Lake Baikal since the mid-19th century, increasing first in the southern basin in the late-19th century, and increasing in the north basin in the mid-20th century. Hg enrichment was greatest in the Selenga Delta shallow lake (ER = 2.3 in 1994 CE), with enrichment occurring in the mid- to late-20th century. Local sources of Hg are predominantly from gold (Au) mining along the Selenga River, which have been expanding over the last few decades. More recently, another source is atmospheric deposition from industrial activity in Asia, due to rapid economic growth across Asia since the 1980s. As Hg can bioaccumulate and biomagnify through trophic levels to Baikal's top consumer, the world's only truly freshwater seal (*Pusa sibirica*), it is vital that Hg input at Lake Baikal and within its catchment is monitored and controlled.

Sediment cores show greatest Hg enrichment in the Selenga Delta water body in the mid to late 20th century in response to gold mining and industrial activities along the Selenga River.

Keywords: Pollution, mining, long-range atmospheric deposition, lake sediments, Russia

1. Introduction

Mercury (Hg) is a global pollutant of concern and has both natural and anthropogenic sources. Once emitted, most inorganic Hg can remain in the atmosphere for up to 12 months (Corbitt et al., 2011) and can be transported across the world. Gaseous and particulate Hg emitted into the atmosphere is transformed into Hg (II), which is then deposited onto the landscape via wet and dry deposition (Bergan and Rodhe, 2001). Atmospherically emitted Hg will cycle between short-term stores (<10 years) in the atmosphere, terrestrial environments, and surface ocean waters, before being sequestered long-term into terrestrial soils and sediments, ocean margins and the deep ocean (Amos et al., 2014). Within aquatic environments, methylating bacteria can transform Hg (II) into a toxic organic form, known as methylmercury (MeHg). This organic form makes Hg especially harmful within aquatic ecosystems as it can bioaccumulate and biomagnify in foodwebs. Due to the toxicity of MeHg, the Minimata Convention was set up in 2017 to reduce the impact that human activities have on Hg releases to the environment (UN Environment, 2017). Hg cycling in aquatic environments may be affected by dissolved organic carbon (DOC), pH, temperature, redox conditions, sulfate concentrations and microbial activity, which control methylation (transformation of Hg into MeHg) and demethylation (transformation of MeHg into Hg) processes (Hintelmann et al., 1995; Kelly et al., 2003; French et al., 2014). Environmental changes associated with warming (e.g. increased weathering, temperature, productivity and organic loadings) can also affect Hg cycling, by stimulating methylation and inhibiting photodecomposition, due to increasing primary productivity and DOC which reduce light penetration in the water column (Hammerschmidt et al., 2006).

Lake Baikal is a UNESCO World Heritage Site and is internationally important for its high levels of water purity and endemism. The lake can be divided into three main basins (south, central and north) (Fig. 1) with the central basin separated from the south basin by the Buguldeika Ridge and the more than 20 km wide Selenga River Delta. The Selenga River, which is approximately 943 km long (Nadmitov et al., 2015), is the main tributary into Lake Baikal and contributes over 60% of annual flow into the lake. It originates in the Khangai Mountains, northern Mongolia, and accounts for over 80% (over 447,000 km^2) of Baikal's catchment (Nadmitov et al., 2015). The majority of the Selenga River basin is situated in Mongolia (282,349 km^2) rather than Russia (148, 060 km^2), with the basin covering almost 20% of the total land area in Mongolia (Nadmitov et al., 2015). The Selenga River branches into the Selenga Delta, the world's largest freshwater inland delta (Logachev, 2003), and a Ramsar-designated floodplain wetland, which is internationally important for high rates of biodiversity and migratory bird habitat (Scholz and Hutchinson, 2000).

1.1. Sources of Hg in the Lake Baikal region

Gold (Au) mining began in Lake Baikal's catchment with the discovery of the Ildikan deposit in the mid-1800s (Maruev, 2018). Small-scale gold mining operations use Hg to extract Au from ore in a process of amalgamation and distillation. The first Au extraction processes using Hg started along the Kharaa River, in the basin of the Amur River in 1837 CE (common era), and in the basin of the Selenga River in 1841 CE (Misyurkeeva, 2009; Maruev, 2018). Between 1860-1890 CE 40% of all Au in Russia was mined in the Baikal region, with Hg used in the extraction before being disposed in rivers and dispersed into the atmosphere (Maruev, 2018). Since the 1950s, the use of Hg in Au extraction has stopped in the Russian region of the Baikal catchment, but continues in the Mongolian Selenga River basin (Misyurkeeva, 2009). Over the last few decades, Au extraction along the Selenga River has increased, with over 700 mines currently in operation in the Baikal catchment within Mongolia (Brunello et al., 2004; Pietron et al., 2017), and the largest gold mining operation, the Zaamar Goldfield, situated within the Mongolian Selenga River basin

(Fig. 1) (Tumenbayer et al., 2000; Chalov et al., 2015; Pietron et al., 2017). Recent studies report the Lake Baikal catchment and Selenga River basin to be heavily polluted from these Au extraction activities (Brunello et al., 2004; Thorslund et al., 2012; 2016; Brumbaugh et al., 2013; Chalov et al., 2015; Jarsjö et al., 2017; Hampton et al., 2018).

The Lake Baikal catchment and Selenga River basin were heavily industrialised between the 1950s and the 1990s and became known as one of the most highly Hg polluted regions in Siberia (Koval et al., 1999). The largest cities and main industrial districts in Mongolia (Ulaanbaatar, Erdenet and Darkhan) are situated along the main tributaries of the Selenga River; Tuul, Orkhon and Kharaa rivers, respectively, and in Russia, Ulan Ude and Selenginskii are situated along the Selenga River (Kasimov et al., 2017), while the major cities and towns of Irkutsk, Gusinoozersk and Severobaykalsk are within Lake Baikal's catchment and airshed (Fig. 1). Notorious industrial Hg emitters in the region include metallurgical plants which produce Hg directly, chemical and electrical plants, where Hg is an element in the manufacturing process, and hydrocarbon/coal or oil fired thermal electric power plants, where Hg is recovered (Vasiliev et al., 1998). Chemical industries are prominent within the Irkutsk-Cheremkhovo industrial zone and are a major concern for Hg pollution (Koval et al., 1999). Other major regional Hg pollution sources include the Gusinoozersk State Regional Power Plant (a coal-fired power plant), and the Selenginsk Pulp and Cardboard Mill within the Selenga River basin, which began operating in 1974 CE and continued as an open system until 1990 CE (Pisarksy et al., 2005; Nikanorov et al., 2012; Nomokonova et al., 2013). Industrial activity around the shores of Lake Baikal began in the 20th century, and the Baikal Pulp and Paper Mill (BPPM), which was in operation between 1966 to 2013, was a suggested point source of Hg (Brunello et al., 2004).

1.2. Hg toxicity in Lake Baikal

Within the past decade, MeHg bioaccumulation has been observed in Baikal's pelagic foodweb (Perrot et al., 2010; 2012; Ciesielski et al., 2016). High Hg concentrations have been reported in fish from the Selenga River basin, which are above the recommended thresholds for human consumption (Kaus et al., 2017), and within fish from the Bratsk water reservoir in the Baikal region (Koval et al., 1999). Analyses on the livers and muscle of the Baikal Seal (*Pusa sibirica*), has also shown Hg contamination within the lake's top consumer in the 1960's and 1970's, before declining to present in response to reduced atmospheric Hg emissions from Europe and Russia (Ozersky et al., 2017).

1.3. Rationale and research questions

Recent and current levels of Hg contamination at Lake Baikal are largely unknown due to sparse records of Hg measurements and the lack of historical Hg loading records for the region. This study undertakes the first Hg assessment for Lake Baikal in 20 years (Leermakers et al., 1996). Herein, we report measurements of Hg concentrations from water samples collected in August 2013/2014 from across Lake Baikal and the Selenga River basin and establish historic Hg contamination records over the past c. 200 years using lake sediment cores. Moreover, we assess potential sources of contemporary and past Hg loading and transport within the catchment together with the relative importance of local vs. long-range sources of contamination.

2. Methodology

2.1. Study sites and field collection

Five sites were selected within Lake Baikal for surface water sampling to represent the main basins, including the south basin (BAIK13-8), the shallow waters off the Selenga Delta (BAIK13-10), the central basin (BAIK13-12), within Maloe More Bay off the central basin (BAIK13-14), and the Upper Angara River in the north basin (BAIK13-19) (Fig. 1; Table 1). Maloe More Bay is a vulnerable region of Lake Baikal, currently affected more than deeper water sites by anthropogenic influence (Timoshkin et al., 2016). Additionally, water samples at five sites from the Selenga Delta branches (SDB01 to SDB05), fourteen sites from Selenga Delta shallow water bodies (SLNG01, SLNG03-SLNG15), three sites from the Selenga River (B13-8-11, B13-8-20 and B13-8-26), and one shallow lake (Black Lake; BRYT) within the upstream section of the Siberian Selenga River basin were analysed for Hg (Fig. 1; Table 1).

Prior to water sample collection, bottles (120 mL Savillex) were soaked in 5% Decon 90 solution for 24 hours, followed by multiple rinses of deionized water and then soaked in 1 M super pure HCl for another 24 hours. This was then followed by extensive rinsing in deionized water and double-bagging after drying. Unfiltered samples were acidified with 1.25 mL analytical grade HCl (Romil Superpure 10M) and stored at 4ºC prior to analyses. Short sediment cores (< 65 cm) were collected using an *UWITEC* gravity corer (UWITEC Ltd., Austria) fitted with a 6.3 cm internal diameter Perspex® tube in August 2013 from BAIK13-10 (core: BAIK13-10A), BAIK13-19 (core: BAIK13-19B), and in March 2014 from SLNG04 (core: SLNG04-C) (Fig. 1; Table 1; Table S1). The sediment cores were extruded in the field at 0.2 cm (BAIK13-10A and 19B) or 0.5 cm (SLNG04-C) intervals using a vertical extruder. Extruded sediment samples were stored in Whirlpak® bags, shipped to University College London (UCL), London, UK and University of Nottingham, UK, and stored at -20°C until processing. Radiometric chronologies for sediment core BAIK13-10A and BAIK13-19B have been previously published in Roberts et al. (2018), and for SLNG04-C in Adams et al. (2018) (Fig. S1).

Table 1. Site code, geographical location and mercury (Hg) concentrations (ng/L) of water samples measured in August 2013 and 2014. (SB – south basin, SD – Selenga Delta, CB – central basin, MM – Maloe More Bay, NB – north basin, UAR – Upper Angara River) (Fig. 1).

Code	**Sample collection year**	**Location**	**North**	**East**	**Hg concentration (ng/L)**
BAIK13-8	2013	Lake Baikal (SB)	51º44’37.9”	105º18’52.4”	0.00
BAIK13-10	2013	Lake Baikal (SB/SD)	52º11’07.0”	106º05’38.0”	1.40
BAIK13-12	2013	Lake Baikal (CB)	52º47’53.3”	107º09’28.8”	1.40
BAIK13-14	2013	Lake Baikal (MM)	53º02’29.4”	106º56’29.5”	1.60
BAIK13-19	2013	Lake Baikal (NB/UAR)	55º38’57.8”	106º46’57.7”	3.20
SDB01	2014	Selenga Delta Branch	52º18’51.1”	106º44’23.3”	0.34
SDB02	2014	Selenga Delta Branch	52º17’11.1”	106º38’22.3”	1.92
SDB03	2014	Selenga Delta Branch	52º15’16.5”	106º38’07.3”	4.50
SDB04	2014	Selenga Delta Branch	52º09’14.8”	106º19’28.1”	5.50
SDB05	2014	Selenga Delta Branch	52º11’19.6”	106º29’37.5”	5.53
SLNG01	2014	Selenga Delta water body	52º15’23.0”	106º39’42.9”	6.48
SLNG03	2014	Selenga Delta water body	52º16’09.4”	106º42’10.1”	6.44
SLNG04	2014	Selenga Delta water body	52º15’52.5”	106º40’35.6”	7.93
SLNG05	2014	Selenga Delta water body	52º09’46.7”	106º19’59.6”	5.92
SLNG06	2014	Selenga Delta water body	52º13’49.0”	106º21’11.0”	6.18
SLNG07	2014	Selenga Delta water body	52º10’16.7”	106º22’06.6”	5.27
SLNG08	2014	Selenga Delta water body	52º14’12.8”	106º18’27.6”	5.78
SLNG09	2014	Selenga Delta water body	52º10’51.6”	106º21’56.8”	5.81
SLNG10	2014	Selenga Delta water body	52º12’38.3”	106º20’33.3”	6.05
SLNG11	2014	Selenga Delta water body	52º16’52.8”	106º38’26.6”	8.17
SLNG12	2014	Selenga Delta water body	52º17’17.3”	106º40’45.8”	6.00
SLNG13	2014	Selenga Delta water body	52º17’56.1”	106º37’27.7”	8.17
SLNG14	2014	Selenga Delta water body	52º18’32.9”	106º40’27.0”	10.14
SLNG15	2014	Selenga Delta water body	52º19’12.6”	106º38’26.6”	8.17
B13-8-11	2013	Selenga River	52º03’02.6”	106º40’20.0”	6.00
B13-8-20	2013	Selenga River	51º08’15.9”	107º29’21.7”	6.10
B13-8-26	2013	Selenga River	50º31’49.1”	106º16’16.7”	8.10
BRYT	2014	Selenga River Basin Lake	51º24’14.2”	106º29’25.5”	4.16

2.2. Laboratory analysis of Hg concentrations in water samples

0.25 mL concentrated HCl (Romil, pure grade) and 0.25 mL 0.1 N BrO^{3-}/Br^- (purified) was added to each 45 mL water sample, which was then sealed for 30 minutes, had 15 µg/L 12% NH_2OH-HCl added, and diluted to 50 mL. Hg concentrations were analysed using Au trap cold vapour-atomic fluorescence spectrometry (CV-AFS) following reduction with $SnCl_2$ (US EPA, 2002). Detection limit is 0.4 ng/L; measurement errors for the Hg concentrations of less than 4 ng/L were 0.4 ng/g, and 10% for concentrations greater than 4 ng/L. Standard solutions and quality control blanks were measured after every three samples to monitor measurement stability.

2.3. Laboratory analysis of Hg concentrations in sediments

Freeze-dried sediment samples were analysed at a temporal resolution of 5 – 20 years for BAIK13-10A and BAIK13-19B. For SLNG04, samples were analysed through the core at a temporal resolution of approximately 15 years. Hg analyses on sediment samples followed procedures in Yang et al. (2010a). For each sample, approximately 0.2 g fine powdered freeze-dried sediment, was digested with 8 mL of a 1:3 mixture of HNO_3 and HCl (aqua regia) at 100^{o}C on a hotplate for 2 hours in rigorously acid-leached 50 mL Teflon digestion tubes. Following digestion, samples were diluted to 50 mL with deionized water, capped and mixed. Digested solutions were then analysed for Hg using cold vapour-atomic fluorescence spectrometry (CV-AFS), following reduction with $SnCl_2$. Standard reference material (GBW07305; certified Hg value of 100 ± 10.0 ng/g and measured mean value is 104 ng/g, with RSD = 4.3 ng/g (n=3)), and sample blanks were digested with every 20 samples.

2.4. Hg enrichment and total fluxes

To examine trends in Hg loading over time, total Hg fluxes were calculated using the radiometrically-derived sedimentation rates (Fig. S1). Standard enrichment factors could not be calculated as lithogenic element data (for example Al, Li and Ti; Ribeiro et al., 2018) were not available for the cores. Instead, Hg enrichment ratios (ER) were calculated by normalising Hg concentrations in sediments deposited after 1850 CE, as determined from the age-depth model, by the natural baseline (mean Hg concentrations prior to 1850 CE) (BAIK13-10A baseline mean = 30.4 ± 6.4 ng/g; BAIK13-19B = 35.5 ± 6.6 ng/g; SLNG04-C = 22.6 ± 1.2 ng/g). The calculated ER therefore represent a comparative ratio of background vs post-1850 Hg concentrations (Yang et al., 2010b). A baseline date of 1850 CE was chosen to take into account global atmospheric contamination from industrialisation, despite the main regional development and expansion in the Lake Baikal catchment region beginning in the 1900s (Brunello et al., 2004). An ER of > 1.4 demonstrates that post-1850 Hg concentrations are in exceedance of baseline by 2 SD, suggesting post-1850 anthropogenic pollution. To examine trends in Hg loading, constrained cluster and broken stick analyses were conducted on Hg concentration profiles from the three sediment cores, to determine points of significant change, using the rioja package in R (version 3.5.2; R Core Team, 2018) (Juggins, 2017).

3. Results

3.1. Spatial distribution of Hg concentrations

Water Hg concentrations ranged between 5.3 and 10.1 ng/L in the Selenga Delta shallow water bodies and between 0.3 and 5.5 ng/L in the Selenga Delta branches with a decreasing trend from the Selenga River to the mouth of the delta (Fig. 2 and 3). Along the Selenga River, Hg concentrations ranged from 6.0 to 8.1 ng/L with highest values at the furthest upstream locations near the town of Ust-Kyakhta (B13-8-26) (Fig. 1). Black Lake (BRYT), within the Selenga River basin, had the lowest Hg concentration of the shallow lakes, at 4.2 ng/L (Fig. 2). In the waters of Lake Baikal, Hg concentrations reached 3.2 ng/L at the one site (BAIK13-19) in the north basin, near the Upper Angara and ranged from below the limit of detection to 1.6 ng/L in the south and central basin lake waters. (Fig. 2), while near the Selenga Delta at BAIK13-10 the Hg concentration was 1.6 ng/L.

3.2. Historic trends of Hg contamination

Hierarchical cluster analysis indicates that Hg concentrations at BAIK13-10 increase significantly at c. 1840 CE. At BAIK13-19, Hg concentrations increase towards the top of the core, with concentrations increasing significantly post-1920 CE and remaining elevated to the surface (Fig. 4). While only two samples comprise the post-1940s timeframe at BAIK13-19, they display similar concentrations of 53 and 51 ng/g. Hg concentrations at SLNG04 showed a gradually increasing trend beginning c. 1950 CE, with a significant increase in Hg concentration (c. 1960 CE) that continue to increase until a maximum concentration of 56 ng/g is reached at c. 1990 CE. Concentrations at SLNG04 then declined slightly post-1990 CE but have remained relatively steady during the past two decades (Fig. 4).

Maximum and contemporary Hg concentrations show an approximate doubling of concentration after 1945 CE across the sampled region, with recent concentrations close to 50 ng/g at all sites. Sediments from BAIK13-10 show Hg enrichment, with ERs ranging between 1.6 and 1.7 between 1910 CE and 2013 CE (Fig. 4). Similarly, the BAIK13-19 sediment core from nearby the Upper Angara River in the north basin show Hg enrichment in the upper sediments, with ER’s ranging between 1.2 and 1.5 from 1880 CE to 1960 CE (Fig. 4). Sediments from SLNG04 indicate little enrichment of Hg (ER c. 1.0) until the mid-20th century when Hg enrichment quickly increased and was consistently > 1.4 between c. 1960 CE and 2013 CE (Fig. 4). Hg enrichment peaks at SLNG04 in c. 1990 CE with an ER of 2.3 has declined to 1.9 by 2013 CE.

Total fluxes of Hg show higher values post-1850 CE, compared to pre-1850 CE, in both the south basin (BAIK13-10) and north basin (BAIK13-19) sediment cores from Lake Baikal. However, post-1850 CE Hg flux was 20-fold greater in the south basin compared to the north basin sediment core (Fig. 4). In BAIK13-10, Hg fluxes ranged from 0.26 ng cm^{-2} yr^{-1} in 1910 CE to 6.32 ng cm^{-2} yr^{-1} in 2013 CE (Fig. 4), whereas in the north basin (BAIK13-19) a smaller range in Hg flux is recorded in the sediments over the post-1850 CE period (from 0.38 ng cm^{-2} yr^{-1} in 1880 CE to 0.43 ng cm^{-2} yr^{-1} in 2013 CE (Fig. 4). Due to limitations of radiometric, SLNG04 Hg flux can only be calculated from the mid-20th century, but fluxes show a distinct increase between c. 1945 CE and c. 1995 CE, from 2.3 to 11.0 ng cm^{-2} yr^{-1}. Since c. 1995 CE, Hg flux at SLNG04 has declined slightly to 8.1 ng cm^{-2} yr^{-1} (Fig. 4).

4. Discussion

4.1 Spatial patterns and modern Hg sources

Mercury concentrations in surface waters span a spatial gradient from higher concentrations in the upstream Selenga River to low concentrations in Lake Baikal. This pattern is expected due to the mining activity along the Selenga River, and industrial activities in the cities of Ulan Ude and Selenginsk (Fig. 1). There is a caveat regarding the interpretation of these single spot samples in 2013/2014, due to the uncertainty in whether these single measurements are representative of the whole year and lake/drainage basin. With the exception of SLNG07, concentrations in the Selenga Delta shallow lakes are consistently higher than in the Selenga Delta branches, and are higher than concentrations found in Lake Baikal. Mercury concentrations are at their highest and most variable in lakes on the east side of the Delta but are similar amongst lakes on the west side (Fig. 2). River deltas are known hotspots for geochemical retention and transformations, which may be controlled by seasonal and hydrological factors, including sediment load and flow (Lychagin et al 2015; Chalov et al 2016). As most of the Hg in rivers is particle-bound, much of it will tend to deposit in the smaller branches and shallow water bodies of the Selenga Delta, as flow decreases (Amos et al., 2014). However, the fraction of the suspended particle load in rivers that is buried is highly variable depending on freshwater discharge rates and the physical characteristics of different deltas (Amos et al., 2014). Therefore, it is likely that the lakes of the Selenga Delta are acting as retention ponds for Hg contamination within the Selenga River basin and preventing it from entering Lake Baikal. The retention effect of the Selenga Delta is also apparent from the sedimentary records, as Hg fluxes are 2-fold higher in the Selenga Delta sediment core (mean post-1850 =6.47 ±3.01 ng/cm^2/yr) compared to in the south basin (mean post-1850 =2.85 ±2.27 ng/cm^2/yr) and 18-fold higher compared to in the north basin sediment core (mean post-1850 =0.35 ±0.09 ng/cm^2/yr) (Fig. 4). The higher sedimentary Hg fluxes in these Selenga Delta lakes compared to Lake Baikal is also expected due to their closer proximity to the sources of Hg pollution within the Selenga River area.

Lake Baikal surface water Hg concentrations in August 2013 (mean 1.52 ±1.14 ng/L) were higher than previously published values of 0.14 – 0.77 ng/L in June 1992 – 1993 (Meuleman et al., 1995; Baeyens et al., 2002). The slightly elevated Hg concentration observed in the north basin at BAIK13-19 (3.2 ng/L) also highlights the importance of the Upper Angara River as a source, with contamination from industry in the north basin catchment. The largest town in this area is Severobaykalsk, and the largest village settlement is Nizhneangarsk (Rose et al., 1998). The Baikal-Amur rail-road also travels through this region. The main Hg sources in Severobaykalsk are from fossil-fuel combustion facilities, waste incineration processes and chemical or electrical industries. Alongside anthropogenic sources, another possible source of Hg into Lake Baikal is from the hydrothermal vents at the bottom of the lake, which form as a result of the active tectonic rift boundary (Crane et al., 1991; Kipfer et al., 1996). This geothermal activity mainly occurs in the north basin of Lake Baikal and releases Hg into the sediments and water column via the hydrothermal waters which are enriched in metals (Crane et al., 1991; Kipfer et al., 1996). Isotope ratios of Hg can be used to distinguish between sources; however, it has been suggested that hydrothermal discharge along fault lines at the bottom of Lake Baikal causes only a minor impact on the lake water chemistry (Granina et al., 2007).

4.2 Decadal-scale trends

Sedimentary Hg concentrations in Lake Baikal and the Selenga Delta are comparable with previous studies from Lake Baikal, which reported values between c. 40 – 70 ng/g over a 16 cm sediment core depth, collected in 1990 CE (with no published sediment core chronology) (Leermakers et al., 1996). Both modern water samples and sedimentary records from Lake Baikal show that lakes in the Selenga Delta appear to be acting as Hg filters. In the sedimentary records this filter effect is apparent as Hg enrichment levels in SLNG04 sediments reach over 2-fold greater than baseline concentrations, which is a slightly higher range than BAIK13-10A sediments in Lake Baikal close to the Selenga Delta system (Fig. 2 and 3). It is important to note, however, that these enrichment levels are not dissimilar to those found in remote lakes in Uganda, North America, Europe and Arctic Alaska, where Hg concentrations were up to 3-fold higher than those in the pre-industrial period (Swain et al., 1992; Fitzgerald et al., 2005; Engstrom et al., 2007; Yang et al, 2010a), which indicates that Hg loading at Lake Baikal is not greater than the global background Hg enrichment levels. These enrichment levels in the above remote lakes (Swain et al., 1992; Fitzgerald et al., 2005; Engstrom et al., 2007; Yang et al, 2010a) relate to atmospheric deposition sources and not riverine draining industrial areas. Furthermore, it is interesting to consider that Lake Baikal sediment records covering the last 6 million years show naturally elevated Hg concentrations in the sediments during warmer climatic conditions (average Hg concentrations of 46 ±11 ng/g during warm periods and 27 ±12 ng/g during cold periods), and anomalously high peaks in Hg concentrations (between 210 – 420 ng/g) during volcanic events in the Baikal area (Gelety et al., 2007). By comparison, Hg concentrations from BAIK13-10 and BAIK13-19 are only slightly higher than the average Hg concentration during warmer periods and fall within the range over the last 6 million years (Gelety et al., 2007).

In the north basin sediments, the Hg enrichment levels are lower (average post-1850 ER for BAIK13-19 = 1.3 ± 0.16) than the south basin (average post-1850 ER for BAIK13-10 = 1.6 ± 0.05) and Selenga Delta lake (average post-1850 ER for SLNG04 = 1.6 ± 0.42). ER results also suggest an enrichment of north basin (BAIK13-19) sediments post 1940 CE, whereas the south basin (BAIK13-10) site nearby the Selenga Delta experienced enrichment much earlier at around 1910 CE. Mercury enrichment of these sediments in the south basin in the early 1900s suggests the contribution of contamination from local sources as a result of industrialisation in the Lake Baikal catchment and the adjacent areas drained by the Angara and Lena rivers. In contrast to the south basin, north basin sediments show a later onset in the mid-20th century of Hg enrichment, perhaps because the major town on the north basin shores, Severobaykalsk, was only founded in the 1970's and with the completion of the Baikal-Amur Mainline (BAM).

All three Lake Baikal cores indicate increases in Hg flux in Lake Baikal post-1850 CE, but the subsurface peak in SLNG04 Hg flux indicates a rise in the sedimentation rate and a possible mid-1990s peak in the delivery of Hg to the Selenga River/Lake Baikal system from both local and long-range sources. Adams et al. (2018) recorded similar timing in decline of PAH, PCB, and DDT fluxes to SLNG04, while Rose et al. (1998) recorded evidence of SCP concentration declines in Lake Baikal sediments post-1990, likely indicating a regional decline in industrial coal and oil combustion in southeast Siberia. The timing of this observed decline in anthropogenic contamination in the Lake Baikal region ties in with the economic recession in the early 1990's following the collapse of the former Soviet Union (Khanin, 2003; Adams et al. 2018). However, the decline in Hg flux at SLNG04 is not large and remains elevated relative to pre- c. 1950 CE levels. Differences in Hg flux between Lake Baikal and SLNG04 are also likely due to the high affinity of Hg for organic matter; Hg binds to DOC and the Selenga Delta lakes receive a higher input of catchment derived DOC than the pelagic regions of Lake Baikal (Yoshioka et al., 2002). Other factors which affect Hg cycling in aquatic environments are temperature, redox conditions, pH and microbial activity, which influence the Hg species transformation via methylation and demethylation processes and biological uptake of MeHg (Hintelmann et al., 1995; French et al., 2014). Thus, the higher input of DOC bound Hg into the Selenga Delta lakes could be a contributing factor to the elevated levels of Hg enrichment seen in these lakes in comparison to Lake Baikal. Alternatively, the Selenga Delta might be receiving greater impacts from local sources than Lake Baikal, as a result of more sediments being deposited in the SLNG04 location, and therefore SLNG04 is actually more highly contaminated by Hg inputs.

In summary, sedimentary profiles in the south basin of Lake Baikal are likely to be largely a reflection of both local sources and long-range atmospheric deposition of Hg, however the filtration effect of the Selenga Delta reduces the input of Hg pollution entering Lake Baikal from the Selenga River. As Hg can remain within the atmosphere for up to a year, an important anthropogenic source of Hg to Lake Baikal and its catchment area is likely to be atmospherically transported Hg from industrial centres, from other urban areas in Russia and across the globe (Gelety et al., 2007; UNEP Global mercury assessment, 2013). Air pollution controls and mitigation efforts in North America and Europe have helped to reduce their Hg emissions from industrial activity. However, in Asia (mainly China and India), Hg emissions have been rising since the 1990s due to the marked economic expansion (Pacyna et al., 2016; Sundseth et al., 2017). Thus since the late-1900's, long-range transport of Hg from elsewhere in Asia is likely to be contributing to the enrichment at Lake Baikal; lake sediment cores from remote regions in China show a marked increase in China's metal air pollution from 1990 CE (Wan et al., 2019) continuing to present day (Yang et al., 2010b; UNEP Global mercury Assessment, 2013).

4.3 Implications for Lake Baikal

The 2013/2014 surveys of Hg concentrations across Baikal and the Selenga River basin area show elevated levels of Hg in the Selenga River waters, in comparison to Lake Baikal waters, most likely linked to gold mining and location of industrial centres (Brunello et al., 2004; Thorslund et al., 2012; 2016; Brumbaugh et al., 2013; Chalov et al., 2015; Jarsjö et al., 2017). However, although the Selenga Delta reduces the extent of Hg pollution entering the south and central basins of Lake Baikal, the current state of the environment around Lake Baikal and its catchment gives cause for concern with respect to future contamination by Hg.

For example, alongside present atmospheric deposition of Hg, it is also important to take into consideration the effect of legacy Hg on the landscape. Re-emission of legacy Hg stores has become another important source of Hg pollution to the landscape, which can be released via soil erosion and permafrost thaw (Yang, 2015). Legacy Hg input into Lake Baikal and the Selenga River basin is likely to increase with regional climate warming, as permafrost underlays a large proportion of the catchment area. Modelling of current Hg reservoirs by Amos et al. (2013) indicated that up to 60% of present-day atmospheric deposition of Hg is legacy-derived, re-emitted from surface reservoirs. Moreover, recent increases in Hg concentrations within the lake sediments could be impacted by permafrost thaw in the Lake Baikal basin (Hampton et al., 2008; Moore et al., 2009) and catchment loading of Hg from the subsequent increased erosion of catchment soils (Yang, 2015). In western Europe, changes to the climate system in recent years have also led to increased storm events, causing further increased instability of catchment soils, increasing the mobility of particulate-bound Hg across the terrestrial landscape (Yang and Smyntek, 2014). Thus, Hg which has previously been deposited and stored within the lake catchment can also act as a source of anthropogenic Hg to the lake system (Yang et al., 2002; Rose et al., 2012). Hg pollution in Lake Baikal and the Selenga River basin area could therefore be a result of the continuing Hg use in gold extraction processes in Mongolia, plus historical legacy of past Hg used in Russian gold mining prior to 1950 CE, as well as long-range transport of atmospheric Hg from regional and international industrial centres, from metal smelters, chemical and electrical industries, coal combustion facilities and waste incineration plants.

Lake Baikal is increasingly facing pressures from shoreline anthropogenic nutrient pollution from inadequate sewage treatment (Timoshkin et al., 2016), as well as pressures from recent atmospheric warming since the 1950s which has been driving limnological and ecosystem changes (Hampton et al., 2008; 2014; 2015; Moore et al., 2009; Izmest'eva et al., 2016; Silow et al., 2016; Roberts et al., 2018). All these pressures combined put the Lake Baikal ecosystem at continued risk from Hg inputs into the future. Efforts need to be focussed on minimising Hg pollution to Lake Baikal and its catchment area, by eliminating the current use of Hg in the extraction process of small-scale gold mining operations in Mongolia. Furthermore, global efforts, in accordance with the new international treaty for the Minimata Convention need to continue, to reduce industrial release of Hg emissions into the atmosphere. Mercury levels need to be monitored on the freshwater ecosystems of the Selenga Delta itself, as it is an important Ramsar site for continental Eurasia.

5. Conclusions

Mercury measurements from 2013/2014 suggest that the Selenga River is a major source of anthropogenic Hg contamination into the Selenga Delta region and Lake Baikal, due to the chemical (mainly the manufacturing of chlorine) and electrical plants where mercury is an element in the manufacturing process, metallurgical plants which produce mercury directly, hydrocarbon/coal or oil fired electric power plants and gold mining activity within the Mongolian Selenga River basin. The low Hg concentrations within the lake waters could be attributed to the retention effect of the Selenga Delta system and a result of dilution by large volume of Lake Baikal and retention within the Selenga Delta. However, it is interesting that the highest concentrations in the pelagic lake water are seen at a north basin site near the Upper Angara River. Sediments by the Upper Angara River show Hg enrichment post-1940, but sediments near the Selenga Delta showed evidence of enrichment above background levels much earlier, post-1850 CE. Hg concentrations measured in the sediments are similar to measurements taken in the 1990’s (Leermakers et al., 1996) and over warm climatic periods (Gelety et al., 2007). Although there is evidence of contamination in the Selenga Delta sediments (ERs over 1.4 in SLNG04), the pollution levels are also modest. Thus, the current levels of Hg contamination within the Selenga River basin highlight the necessity for the protection of Lake Baikal and the Selenga catchment, to reduce Hg pollution of this unique aquatic ecosystem and the deterioration of a globally important freshwater resource.

With rising unregulated mining activity along the Selenga River, it is vital to monitor Hg pollution across the Baikal catchment, especially as MeHg has already been found to bioaccumulate within

Lake Baikal's pelagic foodweb (Ciesielski et al., 2016). Furthermore, recent and future climate warming is likely to increase the transfer of different forms of Hg, such as Hg bound DOC across the terrestrial landscape, from thawing permafrost and soil erosion (Rose et al., 2012) and greater fluvial inflows into connected rivers. These climate driven processes will increase the Hg loading within the Selenga River basin, and ultimately into pelagic Lake Baikal and its foodweb.

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Fig 1. Location of study sites and other key locations referred to in the text across Lake Baikal and the Selenga River catchment.

Fig 2. Mercury (Hg) concentrations (ng/L) in water samples collected from the Selenga River, Selenga Delta and Lake Baikal.

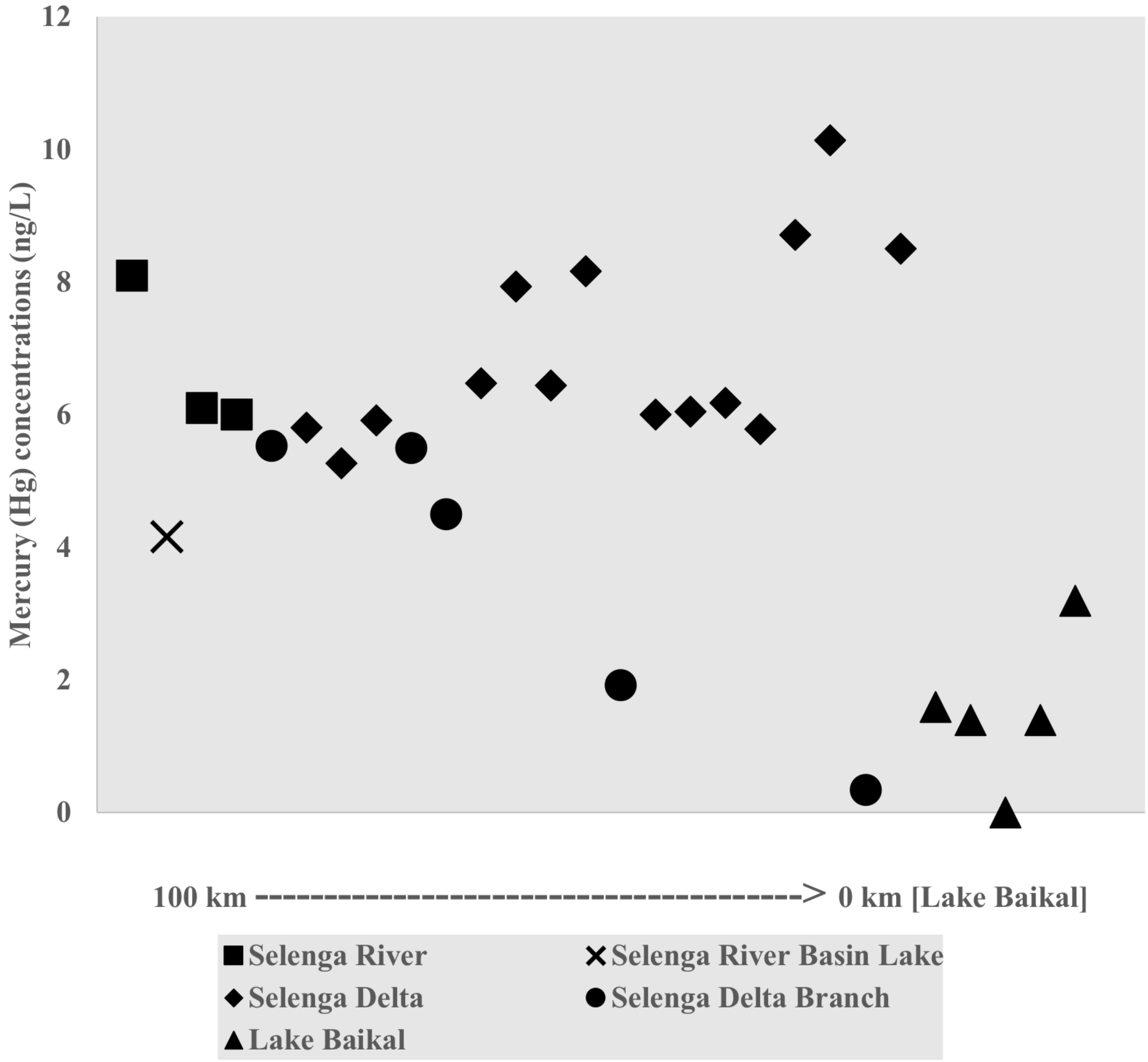
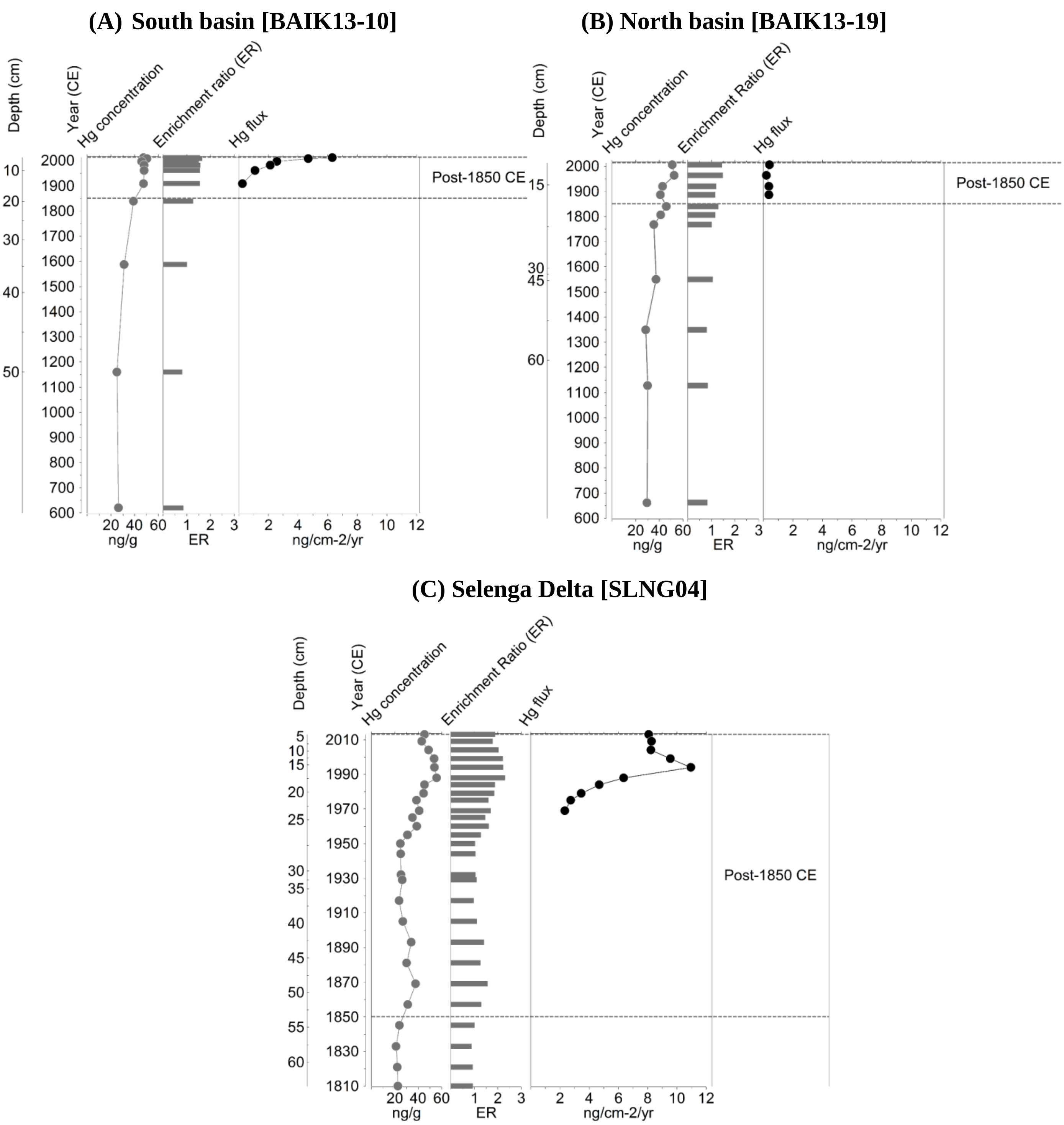


Fig 3. Mercury (Hg) concentrations (ng/L) in water samples collected at each site (grouped by Selenga River, Selenga River Basin Lake, Selenga Delta, Selenga Delta Branch and Lake Baikal) plotted along a distance gradient from the Selenga River to Lake Baikal.



(A) South basin [BAIK13-10]

(B) North basin [BAIK13-19]

(C) Selenga Delta [SLNG04]

Fig 4. Sedimentary mercury (Hg) concentrations (ng/g), enrichment ratios (ER) and Hg fluxes (ng/cm^2/yr) profiles from the (A) south basin [BAIK13-10], (B) north basin [BAIK13-19] in Lake Baikal and (C) Selenga Delta [SLNG04]. For SLNG04 all the dates beyond c. 1945 are extrapolations of constant background sedimentation rates pre-1980.

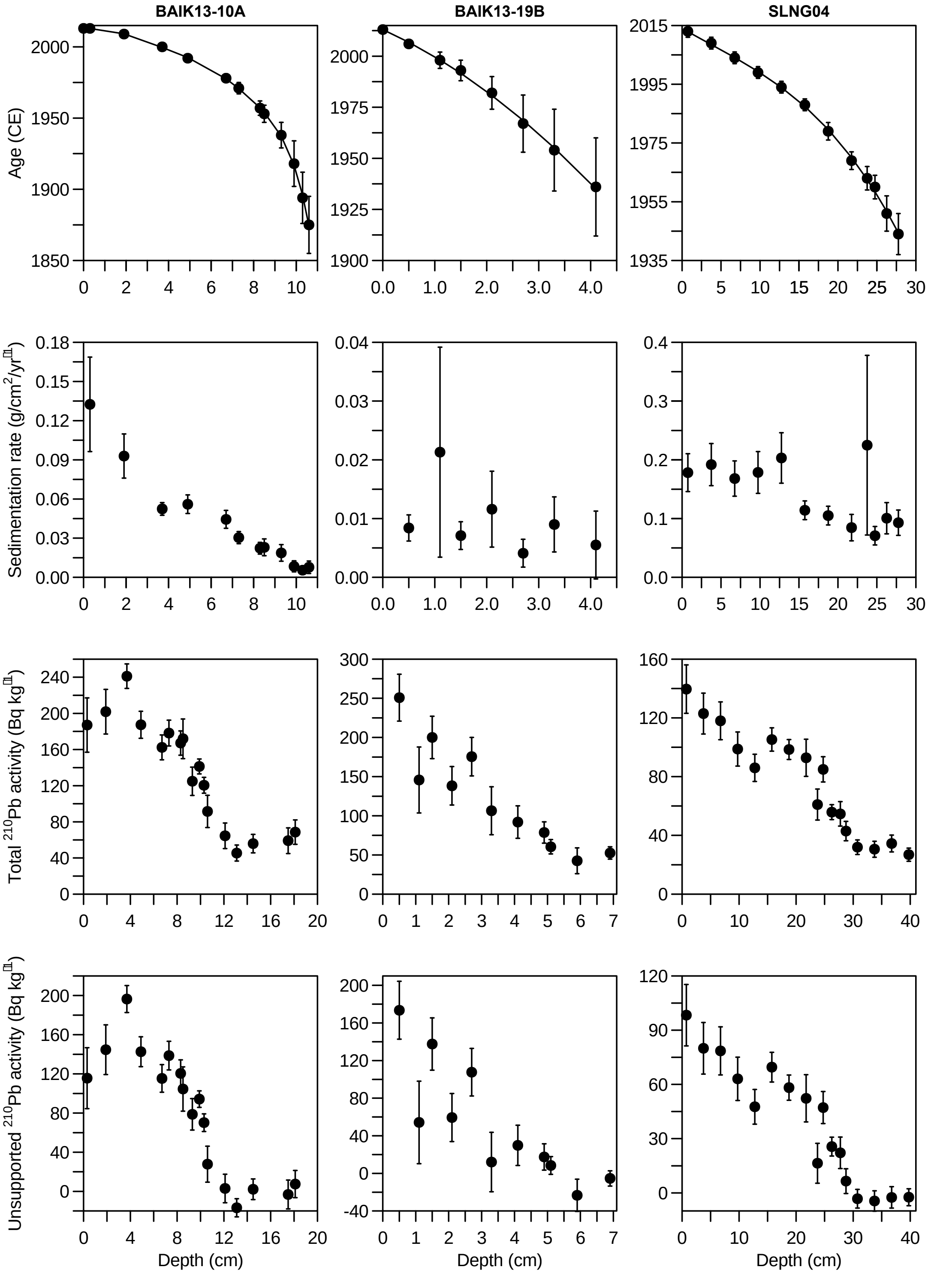


Fig S1. ^{210}**Pb chronology and sedimentation rates for BAIK13-10A (south basin), BAIK13-19B (north basin) (Roberts et al., 2018) and SLNG04 (Selenga Delta) (Adams et al., 2018) sediment cores.**