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, Mongolia). 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 from Lake Baikal show that Hg enrichment commenced first in the south basin in the late-19th century, and then in the north basin in the mid-20th century. Hg flux was also 20-fold greater in the south basin compared to the north basin sediments. Hg enrichment was greatest in the Selenga Delta shallow lake (Enrichment Ratio (ER) = 2.3 in 1994 CE), with enrichment occurring in the mid- to late-20th century. Local sources of Hg are predominantly from gold 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 the region 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.

Keywords: Mercury, mining, atmospheric deposition, lake sediments

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 concentrations 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 (Fig. 1). Gold 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 gold from ore in a process of amalgamation and distillation. The first gold 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 (Lake Baikal's primary inflow) in 1841 CE (Misyurkeeva, 2009; Maruev, 2018). Between 1860-1890 CE 40% of all gold 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 gold 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, gold 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 (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 gold extraction activities (Brunello et al., 2012; Thorslund et al., 2012; 2016; Brumbaugh et al., 2013; Chalov et al., 2015; Jarsjö et al., 2017; Hampton et al., 2018).

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 in the water reservoir north of Irkutsk in the Baikal region (Koval et al., 1999). Analyses of the livers and muscle of the Baikal Seal (*Pusa sibirica*), have also shown Hg contamination within the lake's top consumer in the 1960s and 1970s, before declining to present (2013 CE) in response to reduced atmospheric Hg emissions from Europe and Russia (Ozersky et al., 2017).

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. Within

this study, we have undertaken the first Hg assessment for Lake Baikal in 20 years (Leermakers et al., 1996), and aim to address the following research questions: 1) is the Selenga River basin a major source of Hg into Lake Baikal, and (2) has there been Hg enrichment in the Selenga Delta and Lake Baikal since the onset of gold mining and development in the region?

2. Materials and Methods

2.1. Study sites and field collection

Lake Baikal can be divided into three main basins (south, central and north) 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).

The region around Lake Baikal became one of the most highly Hg polluted regions in Siberia, following industrialization of the catchment between the 1950s and 1990s (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, namely the Tuul, Orkhon and Kharaa rivers, respectively. In Russia, Ulan Ude and Selenginskii are situated along the Selenga River (Kasimov et al., 2017). Other major polluting cities and towns within Lake Baikal's catchment and

airshed include Irkutsk, Gusinoozersk and Severobaykalsk. 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 coal and 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).

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 S2). 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 S2).

144 Prior to water sample collection, bottles (120 mL PFA Savillex) were soaked in 5% Decon 90
145 solution for 24 hours, followed by multiple rinses of deionized water and then soaked in 1 M super
146 pure HCl for another 24 hours. This was then followed by extensive rinsing in deionized water and
147 double-bagging after drying. Unfiltered samples were acidified with 1.25 mL analytical grade HCl
148 (Romil Superpure 10M) and stored at 4ºC prior to analyses. Short sediment cores (< 65 cm) were
149 collected using an *UWITEC* gravity corer (UWITEC Ltd., Austria) fitted with a 6.3 cm internal
150 diameter Perspex® acrylic tube (UWITEC Ltd.) in August 2013 from BAIK13-10 (core: BAIK13-
151 10A, water depth = 66 m), BAIK13-19 (core: BAIK13-19B, water depth = 460 m), and in March
152 2014 from SLNG04 (core: SLNG04-C, water depth = 1.3 m) (Fig. 1; Table S1; S2). The sediment
153 cores were extruded in the field at 0.2 cm (BAIK13-10A and 19B) or 0.5 cm (SLNG04-C) intervals
154 using a vertical extruder. Extruded sediment samples were stored in Whirlpak® bags, shipped to
155 University College London (UCL), London, UK and University of Nottingham, UK, and stored at
156 -20°C until processing. Radiometric chronologies for sediment core BAIK13-10A and BAIK13-
157 19B have been previously published in Roberts et al. (2018), and for SLNG04-C in Adams et al.
158 (2018) (Fig. S1). These ^{210}Pb chronologies were constructed using the constant rate of supply
159 (CRS) dating model (Appleby, 2001), and independently verified using ^{137}Cs.
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2.2. Laboratory analysis of Hg concentrations in water samples

Hg in water samples was analysed at the Environmental Mercury Analytical Facility at UCL, UK. 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 gold 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

Sediment samples were freeze-dried using a Thermo Modulyo D freeze-drier in which samples were kept for several days at temperatures of -40°C until the pressure was < 100 mTorr. 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°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 & Discussion

3.1. Spatial patterns and modern Hg sources

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. 1). 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. 1). 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. 1), while near the Selenga Delta at BAIK13-10 the Hg concentration was 1.6 ng/L.

The spatial gradient from higher Hg concentrations in the upstream Selenga River to low concentrations in Lake Baikal is expected due to the mining activity along the Selenga River, and industrial activities in the cities of Ulan Ude and Selenginsk (Fig. 1). 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. 1). Single spot samples raise uncertainty regarding their spatial and temporal representativity and should be interpreted with caution. Nevertheless, the water Hg concentrations are likely indicating 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. 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).

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) are consistent with the suggestion that there is a nearby riverine source, however, there is no supporting evidence that the Upper Angara River is impacting the water Hg concentrations, through contamination from industry in the north basin catchment. The largest town in this area is Severobaykalsk, and the largest village settlement previously reported is Nizhneangarsk (Rose et al., 1998). The Baikal-Amur railroad 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. These sources have been demonstrated in past studies to contribute to the higher than expected spheroidal carbonaceous particle (SCP) concentrations in the north basin of Lake Baikal (BAIK28; Rose et al., 1998). 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).

3.2. Historic trends of sediment Hg contamination

Hierarchical cluster analysis indicates that sedimentary Hg concentrations at BAIK13-10 increase significantly at c. 1840 CE from 39 ng/g to 48 ng/g. At BAIK13-19, sedimentary Hg concentrations

253 increase towards the top of the core, with concentrations increasing significantly after 1920 CE
254 and remaining elevated to the surface (Fig. 2). While only two samples comprise the post-1940s
255 timeframe at BAIK13-19, they display similar concentrations of 53 and 51 ng/g. Hg concentrations
256 at SLNG04 showed a gradually increasing trend beginning c. 1950 CE, with a significant increase
257 in Hg concentration (c. 1960 CE) that continue to increase until a maximum concentration of 56
258 ng/g at c. 1990 CE. Sediment concentrations at SLNG04 then declined slightly after 1990 CE but
259 have remained relatively steady during the past two decades (Fig. 2). Sediment Hg concentrations
260 in Lake Baikal and the Selenga Delta are comparable with previous studies from Lake Baikal,
261 which reported values between c. 40 – 70 ng/g over a 16 cm sediment core depth, collected in 1990
262 CE (with no published sediment core chronology) (Leermakers et al., 1996).

263 Maximum and contemporary Hg concentrations show an approximate doubling of concentration
264 after 1945 CE across the sampled region, with recent concentrations close to 50 ng/g at all sites.
265 Sediments from BAIK13-10 show Hg enrichment, with Enrichment Ratios (ERs) ranging between
266 1.6 and 1.7 from 1910 CE to 2013 CE (Fig. 2). Similarly, the BAIK13-19 sediment core from
267 nearby the Upper Angara River in the north basin shows Hg enrichment in the upper sediments,
268 with ERs ranging between 1.2 and 1.5 from 1880 CE to 1960 CE (Fig. 2). Sediments from SLNG04
269 indicate little enrichment of Hg (ER c. 1.0) until the mid-20th century when Hg enrichment quickly
270 increased and was consistently > 1.4 between c. 1960 CE and 2013 CE (Fig. 2). Hg enrichment
271 peaks at c. 1990 CE at SLNG04 with an ER of 2.3, but declined to 1.9 by 2013 CE.

272 Total fluxes of Hg show higher values post-1850 CE, compared to pre-1850 CE, in both the south
273 basin (BAIK13-10) and north basin (BAIK13-19) sediment cores from Lake Baikal. However,
274 post-1850 CE Hg flux was 20-fold greater in the south basin compared to the north basin sediment
275 core (Fig. 2). In BAIK13-10, Hg fluxes ranged from 0.26 ng/cm^2/yr in 1910 CE to 6.32 ng/cm^2/yr

in 2013 CE (Fig. 2), 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 in 1880 CE to 0.43 ng/cm^2/yr in 2013 CE (Fig. 2)). Due to limitations of radiometric dating, 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. Since c. 1995 CE, Hg flux at SLNG04 has declined slightly to 8.1 ng/cm^2/yr (Fig. 2).

Both modern water samples and sedimentary records from Lake Baikal show that lakes in the Selenga Delta appear to retain Hg. In the sedimentary records this retention effect is apparent as Hg enrichment levels in Selenga Delta sediment core (SLNG04: mean post-1850 = 6.47 ± 3.01 ng/cm^2/yr) reach over 2-fold greater than baseline concentrations, which is a slightly higher range than in the south basin sediments (BAIK13-10: mean post-1850 = 2.85 ± 2.27 ng/cm^2/yr) in Lake Baikal close to the Selenga Delta system (Fig. 1), and 18-fold higher compared to in the north basin sediment core (BAIK13-19: mean post-1850 = 0.35 ± 0.09 ng/cm^2/yr) (Fig. 2). 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. It is important to note, however, that these enrichment levels are similar 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 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 drainage of industrial areas. Furthermore, Lake Baikal sediment records covering the last 6 million years show naturally elevated Hg concentrations in

299 the sediments during warmer climatic conditions (average Hg concentrations of 46 ± 11 ng/g
300 during warm periods and 27 ± 12 ng/g during cold periods), and anomalously high peaks in Hg
301 concentrations (between 210 – 420 ng/g) during volcanic events in the Baikal area (Gelety et al.,
302 2007). By comparison, Hg concentrations from BAIK13-10 and BAIK13-19 are only slightly
303 higher than the average Hg concentration during warmer periods (Gelety et al., 2007).

304 Hg enrichment levels are lower in the north basin (average post-1850 ER for BAIK13-19 = 1.3 ±
305 0.16) than the south basin (average post-1850 ER for BAIK13-10 = 1.6 ± 0.05) and Selenga Delta
306 lake (average post-1850 ER for SLNG04 = 1.6 ± 0.42). Moreover, ER results suggest an
307 enrichment of north basin (BAIK13-19) sediments after 1940 CE, whereas the south basin
308 (BAIK13-10) site near the Selenga Delta experienced enrichment much earlier at around 1910 CE.
309 Such temporal differences in the onset and overall magnitude of Hg enrichment between north and
310 south basins, and the Selenga Delta, suggest local scale sources of Hg contamination. Hg
311 enrichment of the south basin sediments in the early 1900s suggests the contribution of
312 contamination from local sources as a result of industrialization in the Lake Baikal catchment and
313 the adjacent areas drained by the Angara and Lena rivers. The mid-20th century onset of Hg
314 enrichment in the north basin is perhaps attributed to the development of the major town on the
315 north basin shores, Severobaykalsk, which was only founded in the 1970s and with the completion
316 of the Baikal-Amur Mainline railway.

317 All three sediment cores indicate increases in Hg flux in Lake Baikal post-1850 CE, but the
318 subsurface peak in SLNG04 Hg flux indicates a possible mid-1990s peak in the delivery of Hg to
319 the Selenga River/Lake Baikal system from both local and long-range sources. Adams et al. (2018)
320 recorded similar timing in decline of polycyclic aromatic hydrocarbons (PAHs), polychlorinated
321 biphenyls (PCBs), and dichlorodiphenyltrichloroethane (DDT) fluxes to SLNG04, while Rose et

al. (1998) recorded evidence of SCP concentration declines in Lake Baikal sediments after 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 1990s 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 the Selenga Delta 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). 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. The large differences in water column depths between the coring sites may also effect Hg fluxes, as within deeper water sites at BAIK13-10 (66 m) and BAIK13-19 (460 m) more particulate matter decomposition will occur within the water column, than in the shallow Selenga Delta site, SLNG04 (1.3 m). In deeper waters, more particulate-bound Hg will be released during particle-scavenged remineralization down the water column, as well as photo-reductive and photo-induced micro-biological processes, resulting in the evasion of Hg fluxes reaching deeper water sediments (O'Driscoll et al., 2003).

In summary, sedimentary profiles in the south and north basin of Lake Baikal are likely to reflect of both local sources and long-range atmospheric deposition of Hg, however the retention of Hg in the Selenga Delta reduces inputs to 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). Declines in Hg ER and flux at SLNG04 since the late-1900s indicates that long-range transport of Hg from elsewhere in Asia is likely to be an important contributor 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).

3.3 Implications for Lake Baikal

The 2013/2014 surveys of water Hg concentrations across Lake Baikal and the Selenga River basin 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 in Lake Baikal's catchment gives cause for concern with respect to future contamination by Hg.

For example, 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). 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. Hydro-climatic modelling studies for the Selenga River basin predict an increase in temperatures, precipitation and run off between 2010 – 2099 under a high greenhouse gas emission scenario (Törnqvist et al., 2014), which may lead to shifts in Hg loading as a result of altered hydrology and basin-scale permafrost degradation (Zhoa et al., 2010; Törnqvist et al., 2014). 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 (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 the region, including in Russian gold mining prior to 1950 CE and industrial practices, 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). These pressures, combined with the continued inputs of Hg from a variety of sources, put the Lake Baikal ecosystem at risk from Hg inputs into the future. Efforts need to be focussed on minimising Hg pollution to Lake Baikal and its catchment area, primarily 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 Minimata Convention need to continue, to reduce industrial release of Hg emissions into the atmosphere, which is likely a sizable contribution of contemporary Hg to Lake Baikal. Additionally, Hg levels need to be monitored on the freshwater ecosystems of the Selenga Delta itself, as it is an important Ramsar site for continental Eurasia, and demonstrates higher levels of Hg within the Lake Baikal catchment.

5. Conclusions

Mercury measurements from 2013/2014 demonstrate that the Selenga River is a major source of anthropogenic Hg contamination into the Selenga Delta region and Lake Baikal, as a result of the variety of sources of Hg within the Selenga River basin, including chemical (mainly the manufacturing of chlorine) and electrical plants where Hg is an element in the manufacturing process, metallurgical plants which produce Hg directly, coal and oil fired electric power plants, and current gold mining activity within the Mongolian Selenga River basin. The low Hg concentrations within Lake Baikal waters could be attributed to retention within the Selenga Delta system, which contains higher water Hg concentrations, and a result of dilution by the large volume of Lake Baikal. The highest water concentrations within Lake Baikal are seen at a north basin site near the Upper Angara River. Moreover, spatiotemporal differences in the timing of Hg enrichment in Lake Baikal and Selenga Delta sediments likely highlight key influences of local and regional sources of Hg to Lake Baikal during the 19^{th} and 20^{th} centuries. Recent moderate declines in ERs and fluxes may reflect declining local sources of Hg within the catchment.

However, as concentrations currently remain elevated above background levels in all sediment cores, long-range atmospheric sources likely continue to be a key contributor of Hg pollution in Lake Baikal. Moreover, Hg concentrations measured in the sediments are similar to measurements taken in the 1990s (Leermakers et al., 1996) and over warm climatic periods (Gelety et al., 2007). Thus, with the projected hydro-climatic changes in the region from previous modelling studies, there is a necessity to continue monitoring of Hg contamination 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 (Zhoa et al., 2010; Rose et al., 2012; Törnqvist et al., 2014) and greater fluvial inflows into connected rivers. These climate driven processes might increase the Hg loading within the Selenga River basin, and ultimately into pelagic Lake Baikal and its foodweb.

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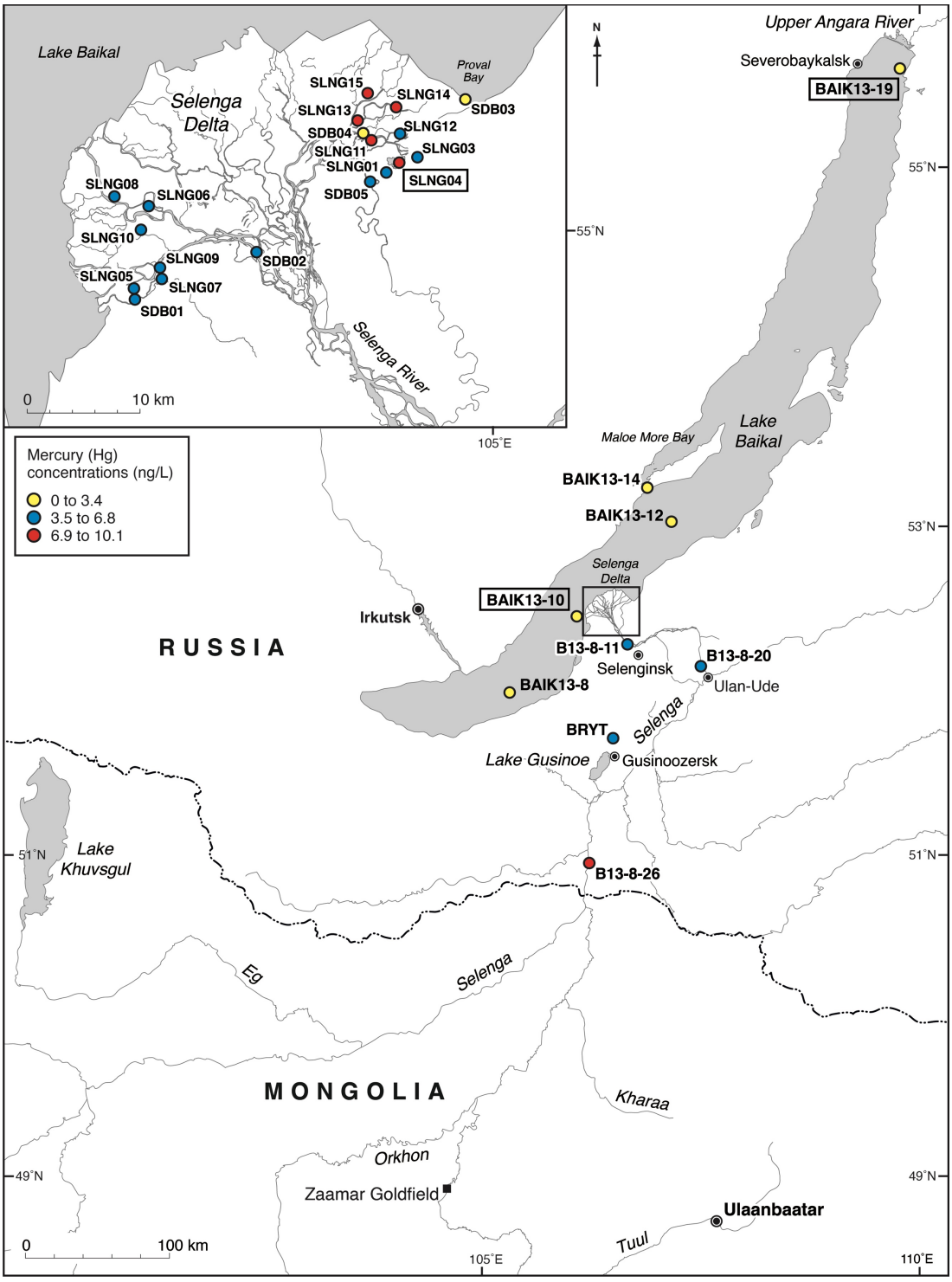

764 **Fig 1. Location of study sites and other key locations referred to in the text across Lake**
765 **Baikal and the Selenga River catchment. Mercury (Hg) concentrations (ng/L) in surface**
766 **water samples collected from the Selenga River, Selenga Delta and Lake Baikal.**

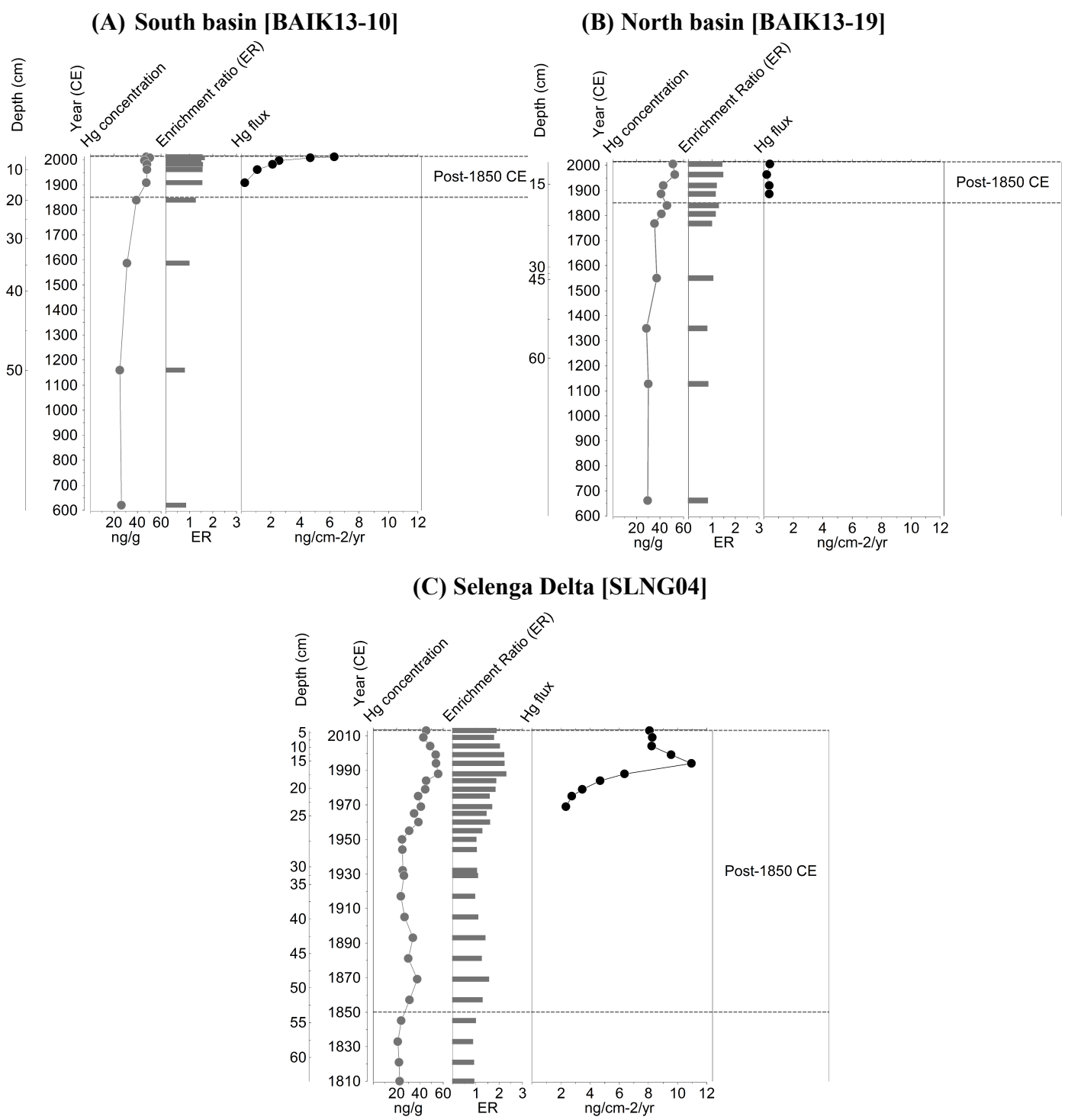

Fig 2. Sedimentary mercury (Hg) concentrations (ng/g), enrichment ratios (ER) and Hg fluxes (ng/cm^2/yr) profiles from the (A) south basin [BAIK13-10], (B) north basin [BAIK13-19] in Lake Baikal and (C) Selenga Delta [SLNG04]. For SLNG04 all the dates beyond c. 1945 are extrapolations of constant background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