



Mercury exports from a High-Arctic river basin in Northeast Greenland (74°N) largely controlled by glacial lake outburst floods



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HIGHLIGHTS

- Hg concentrations and exports in the Zackenberg River were assessed from 2009–2013.
- Hg in snow, soil and permafrost was measured within the river basin (ZRB).
- Hg yields from the ZRB were among the highest reported from Arctic river basins.
- Glacial lake outburst floods accounted for up to >31% of the annual Hg export.
- Winter snowfall and summer temp. were also found to be important indirect controls.

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ABSTRACT

Riverine mercury (Hg) export dynamics from the Zackenberg River Basin (ZRB) in Northeast Greenland were studied for the period 2009–2013. Dissolved and sediment-bound Hg was measured regularly in the Zackenberg River throughout the periods with running water (June–October) and coupled to water discharge measurements. Also, a few samples of snow, soil, and permafrost were analysed for Hg. Mean concentrations of dissolved and sediment-bound Hg in the river water (\pm SD) were 0.39 ± 0.13 and $5.5 \pm 1.4 \text{ ng L}^{-1}$, respectively, and mean concentrations of Hg in the river sediment were $0.033 \pm 0.025 \text{ mg kg}^{-1}$. Temporal variations in river Hg were mainly associated with snowmelt, sudden erosion events, and outburst floods from a glacier-dammed lake in the upper part of the ZRB. Annual Hg exports from the 514 km² ZRB varied from 0.71 to > 1.57 kg and the majority (86–96%) was associated with sediment-bound Hg. Hg yields from the ZRB varied from 1.4–3.1 g Hg km⁻² yr⁻¹ and were among the highest yields reported from Arctic river basins. River exports of Hg from ZRB were found to be largely controlled by the frequency, magnitude and timing of the glacial lake outburst floods, which occurred in four of the five years in July–August. Floods accounted for 5 to > 10% of the annual water discharge, and up to >31% of the annual Hg export. Also, the winter snowfall and the summer temperatures were found to be important indirect controls on the annual Hg export. The occurrence and timing of glacial lake outburst floods in the ZRB in late summer at the time of maximum soil thaw depth, the location of the glacier in the upper ZRB, and increased thawing of the permafrost in Zackenberg in recent years leading to destabilisation of river banks are considered central factors explaining the high fraction of flood-controlled Hg export in this area.

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1. Introduction

Mercury (Hg) is a well-known contaminant of concern to top predators and the human population in the Arctic (AMAP, 2011). Riverine exports of Hg from river basins to the ocean constitutes an important

part of the Arctic Hg cycle, but relatively few studies have attempted to quantify the sizes and controls of Arctic river exports. Previous studies that have examined Hg exports from Arctic rivers include studies from Siberia (Coquery et al., 1995), Canada (Semkin et al., 2005; Leitch et al., 2007; Hare et al., 2008; Kirk and St. Louis, 2009; Schuster et al., 2011; Emmerton et al., 2013) and Greenland (Rigét et al., 2011; Søndergaard et al., 2012). Sources of Hg from river basins in the Arctic include Hg from recent atmospheric deposition, and Hg stored in soil, permafrost and glacier ice (Douglas et al., 2012; Stern et al., 2012; Zdanowicz et al., 2013). The contribution of Hg from these sources

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may be significantly influenced by climate variability and change, and there is a concern that warming in the Arctic may lead to increased future mobilization and riverine export of Hg to the marine environment (Schuster et al., 2011; Fisher et al., 2012; Stern et al., 2012). To increase the knowledge on the controls of Arctic riverine Hg export, and to establish a baseline that can be used for comparison with future conditions, there is a need for more studies on Hg export dynamics from Arctic river basins.

Thus, the aim of this study was to investigate the size and controls of the riverine Hg exports and yields from the Zackenberg River Basin (ZRB) in Northeast Greenland (74° N). The ZRB represents a relatively small river basin of 514 km² and is not influenced by ground water. Therefore, Hg released from snow, ice, soil or rain to water within the river basin was expected to be measured at a measuring station near the river mouth within a relatively short time. This makes ZRB ideal for studying small-scale processes and controls for riverine Hg exports. Glacial outburst floods have regularly been observed in Zackenberg River since the Zackenberg Research Station was established in 1996. The overall hypothesis of the study was that the frequency, magnitude, and timing of these floods and variations in meteorological variables such as temperature and precipitation were likely to have a high impact on the riverine Hg budget. To examine this, high-time-resolution water samples were taken from the Zackenberg River during 5 years from 2009 to 2013 throughout the periods with running water and coupled to continuous water discharge measurements. Both dissolved Hg and sediment-bound Hg were measured in the water samples. Data on air temperature, snow depth, and precipitation from the Zackenberg Research Station were used to examine controls. In addition to the above, a limited amount of snow samples from the ZRB was collected during spring to evaluate atmospheric deposition of Hg to snow, and snow as a source of riverine Hg. Also, a limited amount of soil and permafrost samples was analysed for total Hg to assess concentrations. Finally, data from the Zackenberg River was compared against published data from a range of other Arctic river studies. A minor part of the data (river data from 2009) was previously published in Rigét et al. (2011).

2. Site description

The sampling locations were situated in the Zackenberg River Basin (Fig. 1 and Supplemental Information (SI) Fig. SI 1, Photographs SI 1–4 and Table SI 1) located near the Zackenberg Research Station in Northeast Greenland (78°28'12"N; 20°34'23"W). The ZRB covers an area of approximately 514 km² of which 106 km² are covered by glacier ice (Jensen et al., 2013). The A.P. Olsen Glacier is the headwaters for ZRB and the basin includes St. Sødal Valley, Lindeman Valley and Zackenberg Valley. The altitude of the ZRB is between 0–1450 metres above sea level (m.a.s.l.) and the ZRB is not connected to the Greenland Ice Sheet.

Lowland is dominated by Quaternary non-calcareous sandy sediment and the rest of the basin is composed of areas of Caledonian gneissic and granitic bedrock to the west, and Cretaceous and Tertiary sedimentary rocks and basalts to the east (Ineson et al., 2006). Most vegetated surfaces are located in the Zackenberg Valley below 300 m.a.s.l. and in the lowest lying areas in St. Sødal Valley. Vegetation covers around 40% of the Zackenberg Valley and dominant vegetation types are dry and moist dwarf shrub heath (*Dryas integrifolia*, *Cassiope tetragona*, *Salix arctica*), grasslands (e.g., *Arctagrostis latifolia*), and fen areas (e.g., *Eriophorum scheuchzeri*) (Elberling et al., 2008).

The ZRB has continuous permafrost and only the upper 45–80 cm of the soil thaws every summer (Christiansen et al., 2008). The climate is High-Arctic with an annual mean air temperature of −9.0 °C (1996–2013), and only June, July, August and September have average monthly temperatures above 0 °C. The mean annual precipitation is 211 mm (1996–2013) of which most falls as snow during the 8–9 month winter period. Selected climate data from 2009–2013 is shown in Table 1 and described in detail in Jensen et al. (2013).

3. Methods and instrumentation

3.1. Water sampling and discharge measurements

Depth-integrated water samples for Hg analyses were taken at the location of a hydrometric station (78°28'07"N; 20°34'46"W) close to

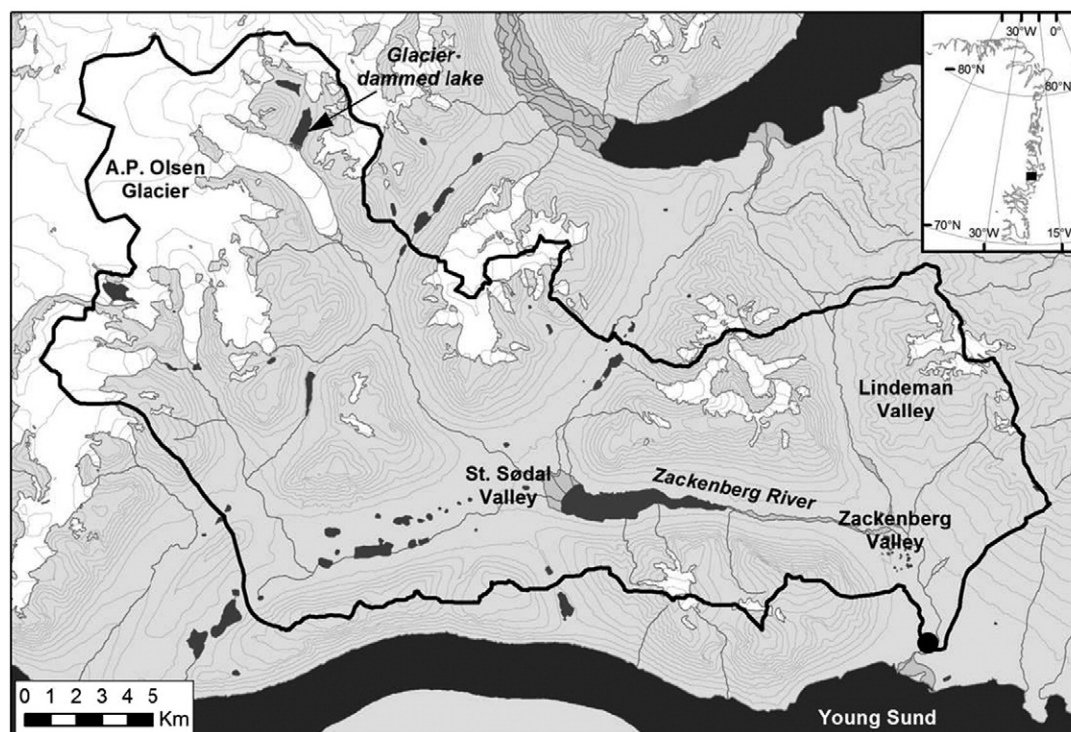


Fig. 1. The Zackenberg River Basin and location of major valleys, A.P. Olsen Glacier and the glacier-dammed lake. River water was sampled at the hydrometric station (marked with dot) located just before the Zackenberg River enters Young Sound in the lower right part of the area.

Table 1
Selected climate data from the meteorological station at Zackenberg during the 2009–2013 period.

Year	Mean summer air temp. (June–August) (°C)	Maximum snow depth (m) ^a	Summer precipitation (June–August) (mm water eq.)
2009	4.7	0.2	60
2010	4.2	0.7	16
2011	4.6	0.4	40
2012	5.9	1.3	13
2013	5.2	0.1	85

^a Measured during the previous winter period i.e., the 2008/2009 winter period for the year 2009 etc.

the river mouth of the Zackenberg River (Fig. 1; Photographs SI 1–2). Samples were taken using a 1 L water bottle connected to a pole and the bottle was moved up and down in the water column until it was filled. Samples were taken at one spot each time aimed to have an approximately average depth of the river profile. Waders were used when sampling and care was taken not to re-suspend sediment from the river bottom into the water column when sampling. Samples were taken throughout the periods with running water during the summers 2009 to 2013. A total of 42 to 95 samples were taken each summer, typically with 2–3 day intervals but with a higher sampling frequency during flood events (usually every second hour). Increased water sampling during the flood events was initiated as soon as the floods were observed and continued until the water level was normal again. The water level was logged at 15 min intervals at the hydrometric station and these data were used to confirm that the entire flood events were sampled at higher frequency. Apart from the flood events, sampling was performed at 8 AM. The sampling time of 8 AM for water sampling at Zackenberg River has been part of the monitoring programme at the Zackenberg Research Station since 1996. The sampling time was chosen because earlier studies showed that the water composition at this time of day was found to provide a good average for the day. For the Hg measurements, approximately 250 mL of water was filtered through Nuclepore 0.45 µm pore size filters into acid-rinsed borosilicate glass bottles and the sediment-containing filters were air-dried. The filtered water samples were filled to the top and water samples and filters were kept cool and subsequently sent to Denmark for analyses.

The water discharge in the Zackenberg River was continuously measured at the hydrometric station during the period 2009–2013 as part of the regular ClimateBasis and GeoBasis monitoring programmes at the Zackenberg Research Station. Sediment discharge was also determined as part of the programmes based on filtering of water samples taken every day at 8 AM during the entire period with running water. For the sediment concentration measurements, a 1 L water sample was filtered through a 0.45 µm filter and the sediment concentration in the water was determined by weighting the dried filter before and after filtration.

3.2. Snow, soil and permafrost sampling

Snow samples for Hg analysis were taken in the early spring during 2010 ($n = 11$), 2012 ($n = 26$) and 2013 ($n = 6$) either from the top of the snowpack or down through a profile, where samples were collected with 20 cm intervals. Samples were taken in 2 L polyethylene bottles and the snow was thawed at room temperature. The water was then filtered through Nuclepore 0.45 µm pore size filters into acid-cleaned borosilicate glass bottles. The bottles were filled to the top and kept cool until analyses.

Sampling of soil and permafrost was based on excavation of 16 pits down to the permafrost table, followed by drilling to obtain intact permafrost cores. Additional 3 deeper bore holes were made and samples analysed for Hg at a fen site (peat at 31 depths intervals), a grassland site (9 depths) and a dry dwarf heath site (22 depths). Sampling locations are shown in Fig. SI 1 and Table SI 1. Permafrost cores were

collected using either a metal core hammer or by using motorised hand-drilling equipment consisting of a Stihl drilling engine. Samples were packed in plastic bags in the field and immediately stored in a freezer box. Samples were kept below -5 °C at the Zackenberg Research Station and during transportation.

3.3. Chemical analyses

All Hg analyses were performed at the accredited trace element lab at the Department of Bioscience, Roskilde, Denmark. Filtered water samples were acidified to a concentration of 1 mL Suprapure nitric acid per L sample for a minimum of 24 h prior to analyses. All samples were analysed for total Hg using a Millennium Merlin analyser (P.S. Analytical, Kent, UK) following the US-EPA Method 1631, Revision E (US-EPA, 2002). In short, the procedure was: a volume of 50 µL of BrCl was added to the water sample to oxidize all Hg species to Hg^{2+} . The surplus of oxidants was removed by 50 µL of hydroxyl/ammonium after which Hg^{2+} was reduced by a SnCl_2 solution. The released Hg gas was driven by an argon flow to a gold trap where Hg was pre-concentrated. After collection for a pre-set time, the Hg was thermally desorbed into an atomic fluorescence detector. Detection limits using this procedure, calculated as 3 standard deviations on laboratory blank samples (milliQ water), were typically around 0.1 ng Hg L^{-1} . The method was checked using a certified quality control sample at 1.85 to 5.00 ng Hg L^{-1} (diluted NRCC ORMS-3 to 5 or direct JRC-IRMM BCR-579 (Kramer et al., 1998)). The certified quality control sample was analysed after calibration and after every approximately 10 samples. Further, the method was compared with others by bi-annual participation in QUASIMEME proficiency testing rounds (www.quasimeme.org). Results were presented in Rigét et al. (2011).

To verify the stability of the storage method, a transport blank, a natural seawater sample ($0.81 \pm 0.17\text{ ng Hg L}^{-1}$, $n = 4$), and a QUASIMEME seawater sample (QTM161SW: $4.61 \pm 0.75\text{ ng Hg L}^{-1}$) were put in borosilicate glass bottles at the laboratory in Denmark and sent to Zackenberg and returned together with the rest of the samples. Subsequent analyses showed that the transport blanks were all within the concentration range of the laboratory blanks (0.00 ± 0.09 , $n = 5$) and that Hg concentrations in the seawater sample ($0.87 \pm 0.20\text{ ng Hg L}^{-1}$; $n = 4$) and in the QUASIMEME sample ($4.85 \pm 0.12\text{ ng Hg L}^{-1}$, $n = 5$) were not significantly different from the concentrations in the original samples (T-test, $\alpha = 0.05$). The QUASIMEME sample was acidified, whereas both the natural seawater sample and the blank sample were not. Addition of acid to the samples was therefore avoided to exclude any potential contamination from the acid. The stability of the method is in accordance with Guevara and Horvat (2013) who showed that natural low level Hg in fresh water samples was stable in borosilicate containers during their 10-day measuring period without acid conservation. All analysis and handling was performed in a cleanroom.

Filtered river sediment, soil and permafrost samples (50–100 mg) were all freeze-dried and analysed for total Hg using a solid sample atomic absorption spectrometer, AMA-254 (LECO Advanced Mercury Analyser-254). Using this technique, the sample is led through a combustion/catalyst tube that decomposes the sample in an oxygen-rich environment and removes interfering elements. The released Hg is collected at a gold amalgamator trap, then released by flash heating and finally measured by UV absorption. The analytical quality of the analyses was continuously checked by analysing blanks, duplicates, and the certified sediment reference material MESS-3 (www.nrc-nrc.gc.ca) along with the samples. The measured recovery percentage on MESS-3 was $99 \pm 7\%$ and the detection limit (calculated as 3 SD on blank samples) was 0.004 mg kg^{-1} .

3.4. Data treatment

Hg exports from ZRB were calculated based on measured concentrations of Hg in the water samples (measured every 2–3 days) multiplied

with the daily water discharge. Hg in the water samples was separated into dissolved Hg (Hg contained in filtered water samples) and sediment-bound Hg (Hg contained in the filter). For days when Hg concentrations were not measured, mean Hg concentrations of the two nearest measurements (before and after) were used. The total suspended sediment (TSS) export was calculated based on sediment concentrations in water samples taken daily as part of the GeoBasis monitoring programme at Zackenberg multiplied with the daily water discharge. Hg exports data during the 2009 flood event originally published in Rigét et al. (2011) were recalculated and found to be overestimated. At 6 August 2012, a flood flushed away the hydrometric station, caused substantial erosion of the river banks and changed the river cross profile markedly. Consequently, the discharge during the flood in 2012 could not be accurately assessed. The discharge after the flood in 2012 was estimated based on manual water level readings and a discharge/water level relationship established during the summer 2013. Hg and TSS yields from ZRB were calculated as the total annual export divided by the basin area.

Differences in Hg concentration in spring snow among years were tested by the non-parametric Kruskal–Wallis rank sum test. A loess (local polynomial regression fitting) smoother was applied to graphically interpret possible seasonal patterns in sediment-bound and dissolved Hg concentrations. The statistical package R (R Core Team, 2013) was used for the statistical analysis.

4. Results and discussion

4.1. Hydrology and sediment transport of the Zackenberg River

Data from the Zackenberg River from 2009, 2010, 2011, 2012 and 2013 is presented in Table 2, Figs. 2 and SI 2–5. Periods with running water in the river typically lasted from June to October. In the beginning of the season, water came mainly from melting of the snow cover from the previous winter precipitation within the ZRB and thawing of the upper soil layer. Melting of glacier ice from the A.P. Olsen Glacier contributed more to the water flow in Zackenberg River later in the season when the temperatures increased and the snow cover had melted. Summer precipitation events did not contribute markedly to the water discharge of the Zackenberg River because of the sparse amount of summer precipitation and because of the relatively large input of water from the melting of snow and glacier ice. Sudden glacial outburst floods caused by drainage of a glacier-dammed lake near the A.P. Olsen Glacier (Fig. 1) occurred during July–August in 2009, 2011, 2012 and 2013 (Table 2). Typical water discharges in Zackenberg River during the summer were 10–60 m³ s⁻¹. During the glacial lake outburst floods, water discharges were estimated to be up to 400 m³ s⁻¹ (on 11–12 August 2009) and accounted for 5–10% of the total annual water discharges. On 6 August 2012, a major glacial lake outburst flood occurred

that completely flushed away the hydrometric station. Consequently, discharges during the flood in 2012 could not be measured and values for 2012 should be regarded as a minimum estimate. The 2012 flood was the largest ever observed at Zackenberg and caused large erosion of the river banks of Zackenberg River (Photographs SI 3–4). During the years from 2009 to 2013, total water discharges ranged from 0.146 to >0.231 km³ yr⁻¹ corresponding to 2.84 to >4.49 × 10⁵ m³ km⁻² yr⁻¹ within the ZRB.

Sediment concentrations in the Zackenberg River were typically in the range of 50 to 500 mg L⁻¹, but concentrations up to 4000 mg L⁻¹ were observed during the glacial lake outburst floods. Peaks of sediment concentrations were observed several times during the seasons and were considered the result of sudden erosion events of the river banks and slopes. Total sediment exports from Zackenberg River ranged from 2.4 to >5.0 × 10⁴ t year⁻¹, which corresponded to a sediment yield of 46 to >97 t km⁻² yr⁻¹ within the ZRB. In the years when flood events occurred (excluding 2012 when the flood could not be measured), 25–48% of the annual sediment discharge was associated with the glacial lake outburst floods.

A comparison with river data from other Arctic rivers is listed in Table 3. As shown, mean sediment concentrations in Zackenberg River (136 to >306 mg L⁻¹ yr⁻¹) were relatively high, only exceeded by those published from Mackenzie and Yukon Rivers in Canada. Similarly, the TSS yield from ZRB (46 to >97 t km⁻² yr⁻¹) was high and near-similar to those from Mackenzie and Yukon River basins. Although a detailed comparison between ZRB and those other Arctic river basins cannot be made to large differences in scale, physiography, geology, latitude etc. the high sediment yield from ZRB is evident of a very dynamic landscape. This is mainly considered the result of a highly variable topography, a loose character of the bedrock, the glacial influence and the sudden glacial lake outburst floods causing significant erosion of the river banks. However, observed thawing of the permafrost within the ZRB at a rate of more than 1 cm⁻¹ yr⁻¹ since 1997 (Elberling et al., 2013; Lund et al., 2014) may also play an important role as it exposes more soil material for erosion at slopes and river banks, which may subsequently be transported as river sediment.

4.2. Hg concentrations in soil, permafrost and snow within the Zackenberg River Basin

Depth-specific samples of soil and permafrost were taken from 3 locations representing the three dominant vegetation types within the lower ZRB area, including fen, grassland, and heath. Additional spatially distributed top-permafrost samples were taken from 16 sites (Fig. SI 1). Surface snow was collected within the ZRB during spring in 2010, 2012, and 2013. Hg concentrations measured in the snow, soil, and permafrost samples are presented in Table 4.

Table 2
Hg data from Zackenberg River during the period 2009–2013.

Year	Occurrence and timing of glacial lake outburst floods	Water discharge (km ³ yr ⁻¹)	Sediment export (10 ⁶ t yr ⁻¹)	Hg concentrations ^a				Hg river export (kg yr ⁻¹)	Flood-controlled annual discharge/Hg export				
				Hg _D (ng L ⁻¹)		Hg _P (mg Kg ⁻¹)			Hg _D (kg yr ⁻¹)	Hg _P (kg yr ⁻¹)	Hg _T (kg yr ⁻¹)	Water discharge (%)	Sediment discharge (%)
2009	Yes (11–12 August)	0.146	0.045	0.34	0.15	0.042	0.034	0.046	1.05	1.10	10	48	31
2010	No	0.173	0.024	0.53	0.43	0.036	0.014	0.140	0.85	0.99	No flood	No flood	No flood
2011	Yes (22–23 July)	0.198	0.038	0.53	0.20	0.026	0.023	0.088	0.81	0.90	6	26	29
2012	Yes (6 August)	>0.231 ^b	>0.050	0.25	0.18	0.028	0.013	>0.074	>1.50	>1.57	ND ^c	ND ^c	ND ^c
2013	Yes (10 July)	0.147	0.035	0.29	0.21	0.025	0.023	0.036	0.67	0.71	5	25	15

^a Hg_D = total dissolved Hg (Hg in water filtered to <0.45 μm); Hg_P = total sediment-bound Hg (>0.45 μm); Hg_T = Hg_D + Hg_P.

^b On 6 August 2012, a major flood flushed away the hydrometric station, caused significant erosion of river banks and changed the river cross profile. Consequently, it was not possible to accurately estimate the discharge and exports during the 2012 flood and numbers should be regarded as a minimum only.

^c Not determined but is considered higher than the other four years with respect to relative water, sediment and Hg discharge.

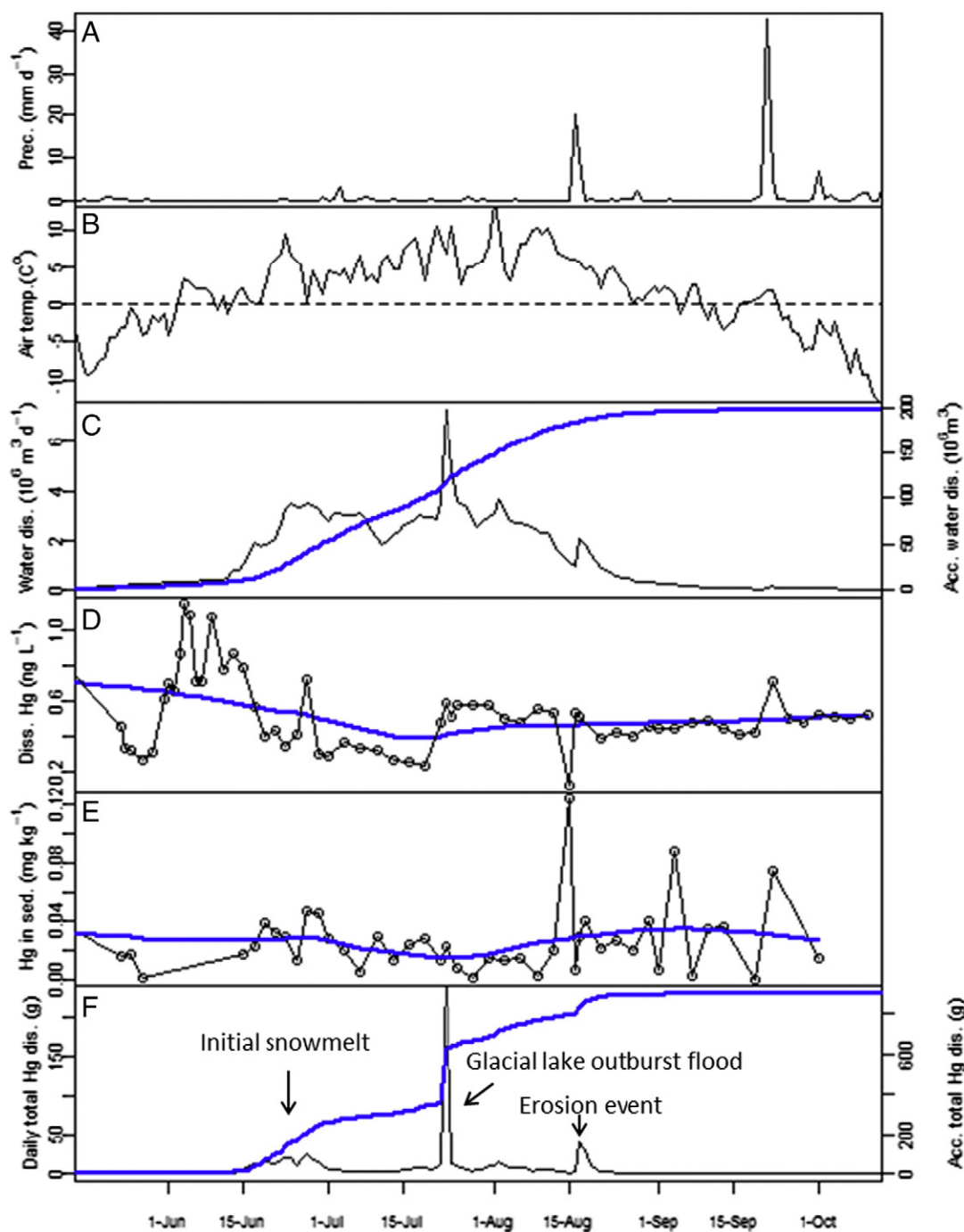


Fig. 2. Zackenberg River data and meteorological data from a typical year (2011) during the 2009–2013 period. A) Precipitation; B) Air temperature in 2 m; C) Daily (thin black line) and accumulated (bold blue line) water discharge; D) Dissolved Hg concentration (thin black line with symbols) and a loess (local polynomial regression fitting) smoother trend line (bold blue line); E) Hg concentrations in river sediment (thin black line with symbols) and a loess (local polynomial regression fitting) smoother trend line (bold blue line) and; F) Daily total Hg discharge (thin black line) and accumulated total Hg discharge (bold blue line) with events indicated. Similar data from 2009, 2010, 2012 and 2013 is shown in Figs. SI 2–5.

Total soil-Hg in peat soils ranged from 0.037 to 0.13 mg kg⁻¹ and total soil-Hg in the permafrost profiles ranged from 0.011 to 0.034 mg kg⁻¹. Total soil-Hg in the spatially distributed top-permafrost samples ranged from 0.008 to 0.039 mg kg⁻¹. Concentrations of dissolved Hg in the snow samples ranged from 0.08 to 0.84 ng L⁻¹. Almost similar concentrations were measured in 2010 and 2013 (0.45 ± 0.13 and 0.49 ± 0.20 ng L⁻¹, respectively) while concentrations in 2012 samples were significantly lower (0.22 ± 0.09 ng L⁻¹) than in 2010 and 2013 (*p* < 0.05).

Spring snow was collected to evaluate atmospheric deposition of Hg in snow within the ZRB and estimate the contribution to Hg in

Zackenber River. In recent years, there has been focus on a phenomenon called atmospheric Hg depletion events (MDEs) where gaseous elemental Hg is transformed and removed from the atmosphere in Arctic areas during short periods in spring (Schroeder et al., 1998). High spring-time Hg concentrations up to 373 ng L⁻¹ have been measured in surface snow associated with MDEs (Dommergue et al., 2010). The low Hg concentrations measured in surface snow in this study suggest that any contribution of a MDE to the net Hg deposition within ZRB is limited or at least undetectable at the scale of our sampling. The lower dissolved Hg concentrations measured in 2012 compared to 2010 and 2013 could be due to variations in the amount and distribution of

Table 3
Comparison of Hg data from the Zackenberg River with data from other Arctic rivers.

River/year	Location/sampling latitude	Basin area (10 ³ km ²)	Water discharge (km ³ yr ⁻¹)	TSS export (10 ⁶ t yr ⁻¹) ^a	Mean sediment conc. (mg L ⁻¹ yr ⁻¹) ^b	Mean Hg conc. ^c		Hg export					Hg and TSS yield		Ref.
						Hg _D (ng L ⁻¹)	Hg _P (mg kg ⁻¹ sEd.)	Hg _P (ng L ⁻¹)	Hg _T (ng L ⁻¹)	Hg _D (kg yr ⁻¹)	Hg _P (kg yr ⁻¹)	Hg _T (kg yr ⁻¹)	Hg _T (g km ⁻² yr ⁻¹)	TSS (t km ⁻² yr ⁻¹)	
Yenisei (1993)	Russia (70–72° N)	2590	620	5.9	10	0.30	0.05	–	–	410	310	720	0.28	2.3	f
Ob (1993)	Russia (69–73° N)	2550	429	17	38	0.56	0.05	–	–	530	820	1350	0.53	6.5	f
Lena (1991)	Russia (71–73° N)	2490	525	18	34	1.0	0.12	–	–	1150	2900	4050	1.63	7.1	f
Mackenzie (2003–2005)	Canada (61–69° N)	1780	330	125	379	2.8	0.01 ^d	3.7	7.2	530	1640	2170	1.21	70.2	g
Mackenzie (2007–2010)	Canada (61–69° N)	1780	320	–	–	1.6	–	13	15	369	2730 ^e	3099	1.74	–	h
Nelson (2003–2007)	Canada (56–57° N)	892	112	–	–	–	–	–	0.9	–	–	113	0.13	–	i
Nelson (2005–2007)	Canada (56–57° N)	892	94	0.74	8	1.9	0.04 ^d	0.33	2.2	179	31	210	0.24	0.8	g
Yukon (2001–2005)	Canada (60–68° N)	854	203	61	300	1.9	–	13	15	353	4003	4372	5.17	71.4	j
Churchill (2003–2007)	Canada (58° N)	281	17	–	–	–	–	–	2.0	–	–	37	0.13	–	i
Churchill (2005–2007)	Canada (58° N)	281	21	0.18	9	3.3	0.02 ^d	0.13	3.5	69	2.7	71	0.25	0.6	g
Hayes (2005–2007)	Canada (57° N)	108	19	–	–	1.8	–	1.1	2.9	34	20	54	0.24	–	g
Zackenberg (2009–2013)	NE Greenland (74° N)	0.514	0.144–>0.231	0.024–>0.050	136–>306	0.25–0.53	0.03–0.04	4.1–7.2	4.5–7.5	0.036–>0.140	0.67–>1.50	0.90–>1.57	1.4–>3.1	46–>97	k
Kobbefjord (2009–2010)	SE Greenland (64° N)	0.032	0.019–0.039	–	–	–	–	–	0.26–0.46	–	–	0.06–0.014	0.20–0.45	–	l

^a TSS = total suspended sediment.

^b Mean sediment concentrations are here calculated as the annual TSS export divided by the annual water discharge.

^c Hg_D = total dissolved Hg (Hg in water filtered to <0.45 μm); Hg_P = total sediment-bound Hg (>0.45 μm); Hg_T = Hg_D + Hg_P.

^d Mean Hg_P concentration is here calculated as the annual Hg_P export divided by the TSS discharge.

^e Hg_P export here determined as bulk Hg export (Hg_T) minus dissolved Hg export (Hg_D).

^f Coquery et al. (1995).

^g Hare et al. (2008).

^h Emmerton et al. (2013).

ⁱ Kirk and St. Louis (2009).

^j Schuster et al. (2011).

^k This study.

^l Søndergaard et al. (2012).

Table 4

Dissolved Hg measured in spring snow during 2010, 2012 and 2013, mean sediment-bound Hg in the river sediment in Zackenberg River during 2009–2013 and total soil-Hg in soil and permafrost from selected sites within the Zackenberg River Basin (Fig. S1 1).

	Hg concentrations		Total sediment-bound Hg or soil-Hg (mg kg ⁻¹)	
	Hg _D (ng L ⁻¹)		Mean	SD
	Mean	SD		
Spring surface snow, 2010 (n = 11)	0.49	0.20	–	–
Spring surface snow, 2012 (n = 26)	0.22	0.09	–	–
Spring surface snow, 2013 (n = 6)	0.45	0.13	–	–
Mean river sediment (2009–2013, n = 324)	–	–	0.033	0.025
Top peat soil profile (0–22 cm, n = 22)	–	–	0.109	0.030
Lower peat soil profile (23–31 cm, n = 9)	–	–	0.047	0.008
Permafrost at a grassland site (95–323 cm, n = 9)	–	–	0.020	0.008
Permafrost at a heath site (58–252 cm, n = 22)	–	–	0.023	0.008
Spatially distributed top-permafrost samples (n = 16)	–	–	0.025	0.013

Hg_D = total dissolved Hg (Hg in water filtered to <0.45 μm).

atmospheric Hg deposition. Further, 2012 was a year with record high snow fall (Table 1), which may have resulted in a dilution or covering of any atmospheric deposited Hg during the winter/spring of 2012.

The limited amount of soil and permafrost samples was collected to assess soil and permafrost Hg concentrations within ZRB and to compare with other Arctic sites. Notable, the entire catchment area cannot be presented by the limited amount of soil/permafrost samples. The soil and permafrost samples were collected as part of a carbon-survey of the lower Zackenberg Valley (Palmtag et al., in press). The 16 top-permafrost samples as well as permafrost cores represent contrasting soil types within the area downstream from the ice-dammed lake where the flooding and the associated erosion is considered most important for sediment transport in the Zackenberg River. Few studies have previously measured Hg concentrations in permafrost (Givelet et al., 2004; Outridge and Sanei, 2010). Those studies reported Hg concentrations in permafrost of peat sites ranging from ~0.010 to 0.050 mg kg⁻¹, which is within the Hg concentration range measured in this study.

4.3. Hg concentrations in the Zackenberg River

Mean concentrations of total dissolved and total sediment-bound Hg in river water (±SD) were 0.39 ± 0.13 ng L⁻¹ and 5.4 ± 1.3 ng L⁻¹, respectively (Table 2). During all years, there was a tendency towards higher spring concentrations of dissolved Hg in the river water typically in the range 0.5–1.0 ng L⁻¹ decreasing to below 0.5 ng L⁻¹ later in the season (Figs. 2 and SI 2–5). Concentrations of Hg bound in sediment were typically in the range 0.02–0.05 mg kg⁻¹, but some peaks up to 0.20 mg kg⁻¹ were measured during the seasons. Concentrations of Hg in the sediment did not display any consistent variation correlating with season, year, rain, erosion or flood events.

Dissolved Hg concentrations in Zackenberg River during spring were higher than the average dissolved Hg concentrations in spring snow measured during 2010, 2012 and 2013 (Table 4). The higher dissolved Hg concentrations in spring may be solely due to an outwash of ions from the snow pack, a well-known phenomenon from Arctic areas known as the 'ionic pulse' (Rasch et al., 2000), but Hg from thawing of the upper soil layer cannot be excluded. In 2009, a range of other metals and major ions (Ca, Mg, Na etc.) were analysed in the river water and these data showed that there was an ionic pulse due to initial snowmelt in the beginning of the spring period (Rigét et al., 2011). A mass calculation of the Hg amount melting from the snowpack, however, was beyond the

scope of this study as it would require an estimation of the total volume of snow melting from ZRB during the season, which we cannot make using the available data. The lack of consistent variation in sediment-bound Hg in Zackenberg River indicates that the source contributions of Hg-containing sediment from ZRB is not changing significantly during the season, between years or following erosion- or flood events. Presumably, the peak Hg concentrations in sediment observed during the seasons represent outwash of Hg-rich topsoil from within the ZRB but no data exists to confirm that.

Compared to other Arctic river studies, concentrations of dissolved Hg in the Zackenberg River were at the low end and closest to Yenisei and Ob River in Russia (Table 3). Concentrations of Hg in sediment and concentrations of sediment-bound Hg in the river water were more typical to those previously reported from other Arctic rivers. The large fraction of sediment-bound Hg in Zackenberg River was consistent with observations from the Mackenzie and Yukon Rivers, where 88–92% of the Hg export was associated with Hg bound to sediment (Schuster et al., 2011; Emmerton et al., 2013). However, there is a large variation in reported fractions of sediment-bound Hg exports from different rivers. Hare et al. (2008) reported as little as 4% sediment-bound Hg export in Churchill River, which is mainly a result of low sediment concentrations in the Churchill River.

4.4. Hg exports from the Zackenberg River Basin and important controls

Daily riverine exports of Hg varied markedly during the seasons and peaks were mostly associated with initial snowmelt, sudden erosion events and the glacial lake outburst floods (Figs. 2 and SI 2–5). Erosion events were identified as days with unusual high sediment concentrations in the river water. The glacial lake outburst floods occurred during four of the five years (2009, 2011, 2012 and 2013), and accounted for up to more than 31% of the total annual Hg (Table 2). Rain events during the summer did not contribute markedly to the Hg exports from ZRB, presumably due to the sparse summer precipitation, and the relatively higher water input from melting of snow and glacier ice. Hg export varied markedly between years and the majority (86–96%) of the Hg export was associated with sediment-bound Hg. The total annual exports of Hg in Zackenberg River ranged from 0.71 (in 2013) to >1.57 kg (in 2012) corresponding to a Hg yield from the ZRB of 1.4 to >3.1 g km⁻² yr⁻¹. No flood occurred in 2010 and the Hg export of 0.90 kg was the second lowest during the period.

The year 2012, which had the highest Hg export, was a year with record high snowfall and summer temperatures (Table 1), and the glacial lake outburst flood came relative late that year on 6 August. In contrast, the year 2013, which had the lowest Hg export, was a year with very low snowfall and the flood came early on 10 July. The year 2010, which had the second lowest Hg export, the lowest summer temperatures and no floods occurred, had the second highest snowfall during the period. Consequently, the following factors are considered key controls for the Hg export from ZRB: 1) the amount of winter snowfall (affecting the water discharge and outwash of surface soil during spring); 2) the summer temperatures (influencing thawing of snow, ice and soil and degradation/transport of Hg-containing organic matter); and finally, 3) the frequency, magnitude and timing of the glacial lake outburst floods (affecting the impact of the floods and the volume of thawed soil exposed for erosion at river banks). The location of the glacier-dammed lake high up in the ZRB near the boundary of the basin is considered a major reason for the high impact of the floods in ZRB as the water from the floods affects a relatively large area before it enters the ocean.

Table 3 shows Hg data from other Arctic rivers in comparison with ZRB. Comparing data from ZRB to other larger river basins in the Arctic, however, should be treated with caution due to large differences in scale, physiography, geology, latitude etc. As shown, Hg yields from the ZRB were among the highest reported from rivers in the Arctic only exceeded by Hg yields reported from Yukon River Basin (Table 3). Mean Hg concentrations in river sediment in Zackenberg River were

within the range of Hg observed in soil and permafrost samples within ZRB (Table 4). This indicates that the high riverine Hg exports in Zackenberg River during flood events can solely be explained by soil being eroded from the river banks (see Photographs SI 3–4 for river bank erosion). The soil transport from ZRB is considered influenced by ongoing freeze–thaw cycles as well as an increasing maximum soil active layer thickness within the ZRB (Elberling et al, 2013; Lund et al., 2014). Consequently, the high Hg yields from ZRB compared to other sites is considered due to Hg in soil and permafrost being eroded at high rates due to flood events, annual thawing and during the study period also increasing thawing compared to previous years.

The climate is warming in Zackenberg and in other areas of the Arctic and there are concerns about how this will impact the river exports. Schuster et al. (2011) hypothesized that thawing of permafrost containing stored Hg could be a reason for the high yield observed from the Yukon River Basin. Long-term thawing of the permafrost is likely to have an impact on the Hg budget of ZRB because as the permafrost thaws, more soil becomes exposed to erosion on slopes and river banks, thus potentially increasing the Hg export. High daily Hg exports from Zackenberg River were observed in 2009 and 2011 due to sudden erosion events, which could be influenced by the increased thawing within the ZRB. Also, thawing of the permafrost is likely to influence the water content and water flow within the thawed soil layer and an increase in soil temperatures will lead to increased decomposition of Hg-rich organic material within the active soil layer. All this may potentially lead to increased Hg mobilization and Hg concentrations, exports and yields but further studies are required to assess that. Further, it is not known how increasing temperatures will impact the frequency, magnitude and timing of the glacial lake outburst floods in ZRB as long as the glaciers still exist. Nevertheless, data show that a combination of high snow fall, high summer temperatures, a major flood and timing of the flood late in the season at the time of maximum thaw depth will result in a very high riverine Hg export. Glacial lake outburst floods as those in ZRB are well-known phenomena associated with glacial systems and known to occur in other places in Greenland e.g., at Kangerlussuaq in West Greenland (Russels et al., 2011). Most of the river basins around the entire 44,000 km coastline of Greenland are influenced by glaciers. However, as only a fraction of these basins are monitored, it was not possible to estimate how common such glacial lake outburst floods are in Greenland as well as in the rest of the Arctic.

5. Conclusion

This study investigated riverine exports of Hg from a High-Arctic river basin the Zackenberg in Northeast Greenland during a 5-year period from 2009–2013. The majority of the Hg export was found to be associated with sediment-bound Hg, and exports were mainly linked to snowmelt, sudden erosion events and floods from a glacier-dammed lake. The frequency, magnitude, and timing of the glacial lake outburst floods, as well as the summer temperatures, and the amount of snowfall the previous winter were found to be key controlling factors for the Hg export in Zackenberg River. Currently the climate is warming, and permafrost is thawing in the Zackenberg River Basin, and other areas of the Arctic, and there are concerns regarding how this, and a change in precipitation patterns will impact the river exports. Besides highlighting processes and controls for riverine Hg exports from a High-Arctic river basin, this study provides important baseline data that can be used for comparison with future conditions to improve our knowledge on the Arctic Hg cycle.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.01.097>.

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