1 **No evidence for large subglacial source of mercury from the southwestern margin of**
2 **the Greenland Ice Sheet.**

3

4 Christian Juncher Jørgensen[1*], Jens Søndergaard[1], Martin Mørk Larsen[1], Kristian Kjellerup Kjeldsen[2], Diogo Rosa[2], Sarah
5 Elise Sapper[3], Jesper Riis Christiansen[3] and Christian Nyrop Albers[2].

6 1: Aarhus University, Department of Ecoscience, Arctic Environment; Roskilde, Denmark

7 2: Geological survey of Denmark and Greenland; Copenhagen, Denmark

8 3: University of Copenhagen, Department of Natural Resource Management, Frederiksberg, Denmark.

9 *Corresponding author: cjj@ecos.au.dk

10 **Abstract**

11 In the current Matters Arising we present results from verifying control measurements of
12 dissolved mercury (Hg) in glacial meltwater from the Greenland Ice Sheet (GrIS), which
13 significantly challenges the conclusions of the recent publication by Hawkings et al. (2021)[1].
14 By direct measurements of meltwater in the same glacial catchment area, we demonstrate
15 that the input Hg concentration for the regional upscaling in[1] is likely vastly over-estimated
16 with major implications for the validity of the asserted extreme yield of Hg from the GrIS. In
17 addition, we present a plausible explanation for the high Hg concentration values in the
18 study, namely hitherto unidentified cross-contamination of water samples by mercury
19 chloride ($HgCl_2$), which was present and used for other purposes during field work[2].
20 Together, the result of our control study potentially invalidates the suggested implications of
21 geologically sourced Hg under the southwestern margin of the GrIS on the Arctic ecosystem
22 in both current and future climate conditions.

23 **Background and context**

24 Presence of elevated levels of dissolved mercury (Hg) in aquatic systems in Greenland is a
25 major concern due to its potential harmful environmental and health effects. Should a
26 hitherto undetected geological source of Hg exist, as suggested by[1], this could have wide
27 impacts on ecosystems with direct economic and societal consequences for Greenland,
28 including domestic food supplies, fishery export, and challenge the potential future export
29 sector of glacial ice and water.

30 In[1], the geology under the GrIS is indicated as the most likely source for the elevated Hg
31 concentrations in the water samples and the extreme Hg yield amounting to up to 10% of the
32 global riverine Hg export. Significant Hg deposits are often found associated with precious
33 metals (Ag, Au) in epithermal and Carlin-type deposits formed at shallow crustal levels[3,4].
34 However, the geology of West Greenland, in general, and of the Kangerlussuaq fjord area, in
35 particular, is not known to host such deposit types, which could release significant quantities
36 of Hg. This part of Greenland is dominated by Archean gneisses corresponding to deeply
37 eroded crustal levels, which are expected to extend to underneath the ice sheet[5,6].

38 Monitoring of Hg in the marine and freshwater ecosystems in Greenland has been performed
39 over several decades in Greenland under the Arctic Monitoring and Assessment Programme

40   (AMAP), the Greenland Ecosystem Monitoring programme (GEM), and various research
41   projects. Previous studies with direct relevance to the topic of Hawkings2021 include
42   riverine Hg export from the terrestrial to the marine environment at Kobbefjord near Nuuk in
43   West Greenland [7] and Zackenberg Research Station in Northeast Greenland [8,9]. Results from
44   these studies show that the baseline levels of dissolved Hg in riverine systems in Greenland
45   typically range between 0.2-0.6 ng/L corresponding to 1 – 3 pM dissolved Hg, as opposed to
46   the range of approximately 0-4000 pM (2015 data, "LG") and 250 to 1750 pM (2018 data,
47   "IS", "RG"," LG") in the proglacial river system presented by[1].

Summary of study design and results

49   During the melt season of 2021, we conducted a control study within the same proglacial
50   river system as[1] (Figure 1). The objective of the control study was to verify if the high
51   concentration range of dissolved Hg reported in[1] can be reproduced.
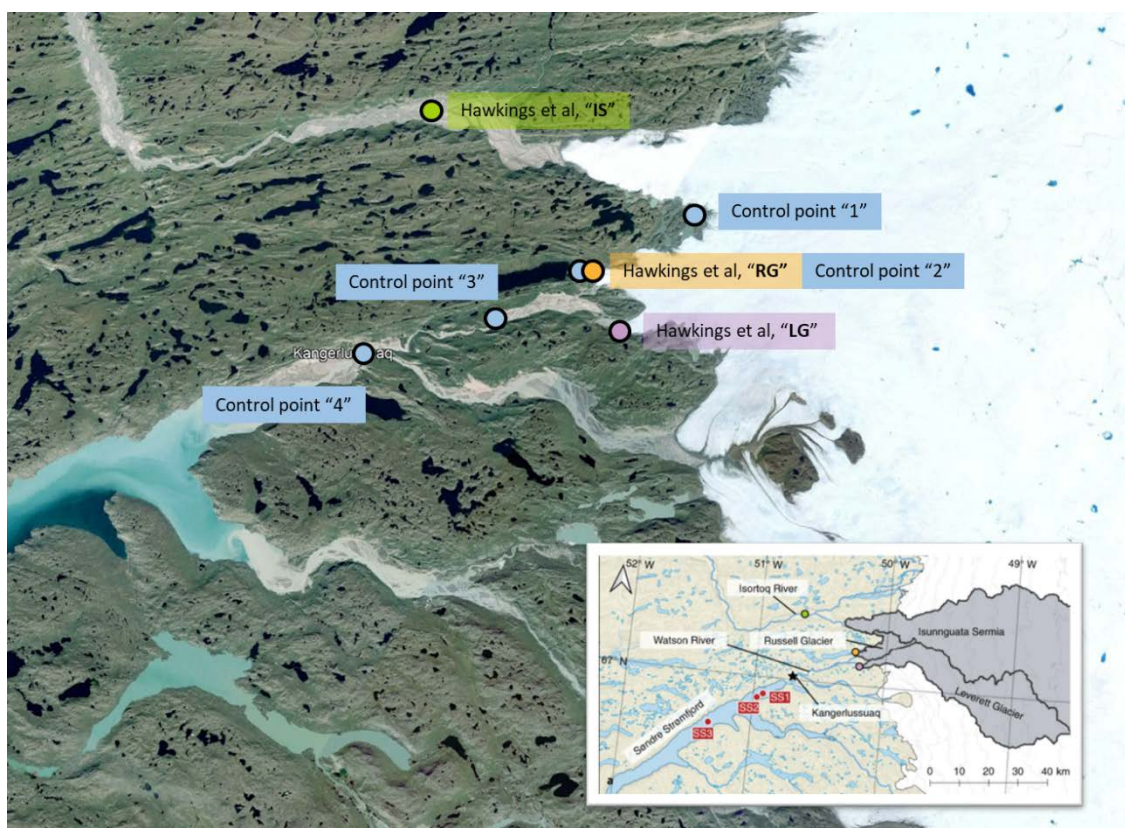
53   Figure 1 – Location of the four sampling stations of the control study (blue circles) near Kangerlussuaq, West
54   Greenland together with sampling stations of Hawkings et al., 2021 (green, orange, purple). Insert panel
55   displays meltwater catchment areas as shown in Hawkings et al., 2021. Source of base map: Google Earth,
56   2021.

57   A fundamental assumption for the control study is that, if the "*extremely high Hg yields*"
58   found by[1] is accurate and occupy potentially 10 % of the global riverine Hg flux, the high Hg
59   concentration range forming the basis for the upscaling model should be reproducible and
60   verifiable within the same hydrological catchment area. Seasonal variations in absolute Hg

61 concentrations due to different mixing ratio, induced by variations between melting of snow
62 and ice and between supra- versus subglacial meltwater routing are expected. However, the
63 same overall concentration range of dissolved Hg should be present in the meltwater from
64 year to year, as long as water samples are collected within the same hydrological catchment
65 area over the active melt season.

66 In the control study, we simultaneously sampled meltwater using two separate sets of
67 sampling equipment and sampling protocols. Each set of samples were then analyzed at two
68 separate accredited laboratories in Denmark (EUROFINS and Aarhus University).

69 Results from the control study show that concentration levels of dissolved Hg at all four
70 control sample stations were consistently below the analytical level of detection of 1 ng L^{-1} in
71 all water samples (n=8) analyzed at the commercial laboratory (EUROFINS). Results from
72 the samples analyzed at Aarhus University's research laboratory confirmed these findings,
73 with only three out of a total of 19 samples being above the AU lower limit of detection of
74 0.22 ng L^{-1} but lower than 1 ng L^{-1} (see table 1). Total Hg (i.e. particulate bound Hg) was
75 analyzed on a set of samples from all 4 control stations on July 29th ad August 25th 2021.
76 Total Hg concentrations in these samples (n=8) were below 1 ng L^{-1} (data not shown).

Date (DOY)	Control station	Dissolved Hg (ng L^{-1})	Analytical laboratory	Sampling protocol
29-07-2021 (210)	1,2,3,4	<1	Eurofins	G/E
29-07-2021 (210)	1,2,3,4	<0.22	Aarhus University	AU
05-08-2021 (217)	4	<0.22	Aarhus University	AU
08-08-2021 (220)	4	<0.22	Aarhus University	AU
13-08-2021 (225)	4	<0.22	Aarhus University	AU
17-08-2021 (229)	4	<0.22	Aarhus University	AU
20-08-2021 (232)	4	<0.22	Aarhus University	AU
23-08-2021 (235)	4	<0.22	Aarhus University	AU
25-08-2021 (237)	1,2,3,4	<1	Eurofins	G/E
25-08-2021 (237)	1,2,3,4*	<0.22	Aarhus University	AU
27-08-2021 (239)	4**	0.5	Aarhus University	AU
27-08-2021 (239)	4**	0.4	Aarhus University	AU
11-10-2021 (284)	2	0.3	Aarhus University	AU
12-10-2021 (285)	1	<0.22	Aarhus University	AU
13-10-2021 (286)	3	<0.22	Aarhus University	AU

77 Table 1: Dissolved Hg concentrations in meltwater samples from control stations 1, 2, 3 and
78 4. *sample from control station 4 lost during transportation. ** Control point 4 sampled twice
79 on the 27th August 2021 (09:00 and 18:45).

80

81 A fundamental requirement for the extrapolations made in[1] is a widespread occurrence of Hg
82 in Southwestern Greenland. In addition to samples collected in the Kangerlussuaq proglacial
83 rivers, we sampled six rivers carrying glacial meltwater in Southwest Greenland in late June
84 and again in early September 2021 (Extended Data Fig. 1). Similar to the samples from the

85 Kangerlussuaq area, all samples from these six sites were below the detection limit of 1 ng L⁻
86 ¹ total Hg.

87

Discussion

89 In contrast to the extremely high Hg concentrations in the proglacial river system presented
90 in[1] , the results from the control samples show concentration levels of dissolved Hg within
91 the same low order of magnitude as typically found in riverine environments in Greenland[7–9]
92 and other Arctic rivers[10–13].

93 One of the differences between[1] and the control study is the part of the melt season in which
94 the majority of the sampling is performed. Where meltwater sampling of [1] was performed
95 during seasonal increase in meltwater discharge (day of year (DOY) 135-210 in 2015 and
96 DOY 171-197 in 2018), the control study was conducted during seasonal decrease in
97 meltwater discharge (DOY 210-286). This difference in seasonality may produce some
98 variability in dissolved Hg as the mixing ratio between sub- and supraglacial meltwater will
99 vary over the season. However, since the dissolved Hg is postulated to originate from a
100 subglacial bedrock and thus be carried from the source to the proglacial rivers by subglacial
101 meltwater, the signal of elevated Hg concentrations should also be measurable during the part
102 of the season where the ratio between melting of snow and ice and routing of the meltwater is
103 different. Since the control study clearly shows that this is not the case, an alternative
104 explanation for the presence of dissolved Hg in the water samples of[1] must be investigated.

105 A major differences between[1] and the control study lies in the potential presence and use of
106 $HgCl_2$ for sample preservation during field work. While not directly mentioned in the
107 manuscript or included in the list of references of[1], the discharge curve presented in Figure 3c
108 in [1], was first published in Figure 2 of a study performed by the same research consortia[2].
109 Collection of water samples for both studies were thus performed by the same research
110 consortia in 2015 and 2018. An important methodological aspect mentioned in[2], but omitted
111 by[1], is the presence and use of mercuric chloride ($HgCl_2$) to 'poison' and preserve water
112 samples for later analysis of dissolved methane (CH_4) in meltwater (see also similar approach
113 in[14]) during the field work of at least 2015.

114 In[2], it is described that each sample was poisoned with 24 mg $HgCl_2$, equal to 93 µmole Hg.
115 By rough estimation, the absolute amount of Hg added to a single field sample following this
116 approach would take dilution of 47000 L water to reach a Hg concentration of 2000 pM. This
117 calculation demonstrates that only trace amounts of $HgCl_2$ are needed to accidentally pollute
118 pristine water samples to the level reported in[1] and that extreme care should take when
119 sampling and storing environmental samples for Hg analysis if at the same time using $HgCl_2$
120 for preservation in other samples during the same field campaign.

121 Instead of being of geological origin, we find it possible that the Hg present in the glacial
122 meltwater samples in[1] is a product of one or more of the following sources of error: 1)
123 accidental direct injection of $HgCl_2$ into the samples following sampling; 2) cross-

124   contamination of water samples by gaseous Hg volatized from $HgCl_2$ during long-term
125   storage of water samples in close proximity to concentrated $HgCl_2$ stock solutions or the
126   intentionally contaminated samples of[2] or; 3) usage of Hg polluted sampling equipment or
127   similar source of contamination linked to the presence and use of $HgCl_2$ in the field camp
128   and/or in the analytical laboratory.

Conclusion

130   Control samples of dissolved Hg sampled in 2021 within the same hydrological catchment
131   area cannot reproduce the extremely elevated Hg concentration levels of 2015 and 2018
132   reported by Hawkings *et. al.*[1] By contrast, the concentration levels of dissolved Hg in the
133   control study was consistently below 1 ng L^{-1}. Instead, the extremely elevated riverine Hg
134   concentrations of[1] could be due to accidental sample contamination by the presence of
135   mercuric chloride used for other purposes. A logical consequence of the lack of
136   reproducibility in concentration levels of dissolved Hg is that the main conclusion of[1]
137   concerning the magnitude of Hg yield from the Greenland Ice Sheet and potential
138   consequences for the public health and environment is most likely erroneous.

Extended Data

140   Sampling stations near Kangerlussuaq: Two independent sets of water samples ("Set 1" and
141   "Set 2") collected at four unique sampling stations (Control point "1","2","3" and "4") were
142   sampled on 29/07/2021 and 25/08/2021. A single set of samples were collected at all four
143   stations on 12/10/2021. Furthermore, single samples were collected at Control point "4" on 5,
144   8, 13, 15, 17, 20, 21 and 27 August 2021 to indicate temporal variability.

145   Control point "1" is located at the sample location of [14,15], which represent a minor glacial
146   outlet of the Isunnguata Sermia glacier. Control point "2" is identical to station "RG" of [1],
147   representing glacial runoff from Russel Glacier and the upstream environment. Control point
148   "3" is located downstream of the confluence point of the meltwater rivers draining Russel
149   Glacier and Leverett Glacier (station "LG" in[1]). Control point "4" is located at the river bend
150   immediately upstream of the Watson River bridge in Kangerlussuaq, representing the
151   combined meltwater input from Russel, Leverett and Isorlersuup glaciers.

152   By nature of design, each control point represents an incrementally increasing catchment area
153   of glacial discharge from the Greenland Ice Sheet. By increasing the catchment area and
154   mixing of water from different sources, annual variations in bed connectivity due to varying
155   development of the subglacial drainage channel network should be cancelled out.

156   Sampling and analytical protocol - GEUS/Eurofins (G/E): Water was sampled in 30 mL acid-
157   washed Amber glass vials with gas-tight Teflon-lined screw lids. For each sampling point
158   and time, water was sampled twice: One sample was taken by lowering a vial well below the
159   surface, shaking with the lid on, emptying and refilling to 90% of the volume of the vial
160   (non-filtered sample). A second vial was filled by passing water through a 0.45 µm filter (Q-
161   max PES membrane filter, Frisenette, Denmark) using a syringe that was thoroughly rinsed
162   in the river. The first few mL of the filtrate were discarded. Both vials were immediately

163   closed and stored cold and in the dark until arrival at the commercial laboratory (Eurofins
164   Denmark) within two weeks of the sampling date. Upon arrival to the laboratory,
165   hydrochloric acid was added to the vial and within another 7 days, the sample was analysed
166   by Cold Vapor Atomic Fluorescence Spectrometry (US EPA, 2005).

167   Sampling and analytical protocol - Aarhus University (AU): Discrete meltwater samples
168   were sampled in 250 ml glass bottles with Teflon lids before analysis. To obtain the water
169   sample, the rinsed bottle was fully submerged until full and capped underwater to avoid any
170   air bubbles in the bottle. Samples were kept cool and dark until analysis in the laboratory.

171   Water samples were analysed for THg following the US-EPA Method 1631, Revision E (US-
172   EPA, 2002). A drop of BrCl solution is added to the water sample to oxidise the Hg species
173   to Hg. The surplus of oxidants is removed by a drop of hydroxyl/ammonium, after which
174   Hg^{2+} is reduced by a $SnCl_2$ solution and the released $Hg(g)$ is driven by an Argon air current
175   to a gold trap, where Hg is pre-concentrated. After collection for a pre-set time, the Hg is
176   thermally desorbed into the atomic fluorescence detector (P.S. Analytical Millennium
177   Merlin, Kent, UK). Detection limits, calculated as three times the standard deviations on
178   blind samples, are typically 0.1–0.2 ng L.

179   The accredited method is validated by participation in the QUASIMEME proficiency testing
180   program, bi-yearly analyzing 3 unknown samples in the range 1 to 50 ng/l, and using
181   certified reference material BCR579 to ensure correct measurements.

182   At all sampling occasions following both sampling protocols, samples were obtained from
183   the bank of a free-flowing and well-mixed part of the meltwater stream. Fresh gloves were
184   worn during sampling.

185   Additional sampling stations: Using only the G/E sampling protocol, filtered and non-filtered
186   water was sampled and analysed from six additional meltwater rivers in South-West
187   Greenland. Two river received meltwater primarily from the ice sheet, while meltwater at the
188   four remaining rivers originate from local glaciers and ice caps. The rivers are located
189   between the towns of Nuuk and Paamiut (Extended Fig. 1.) and were sampled twice (late
190   June and early September).

191

192

193
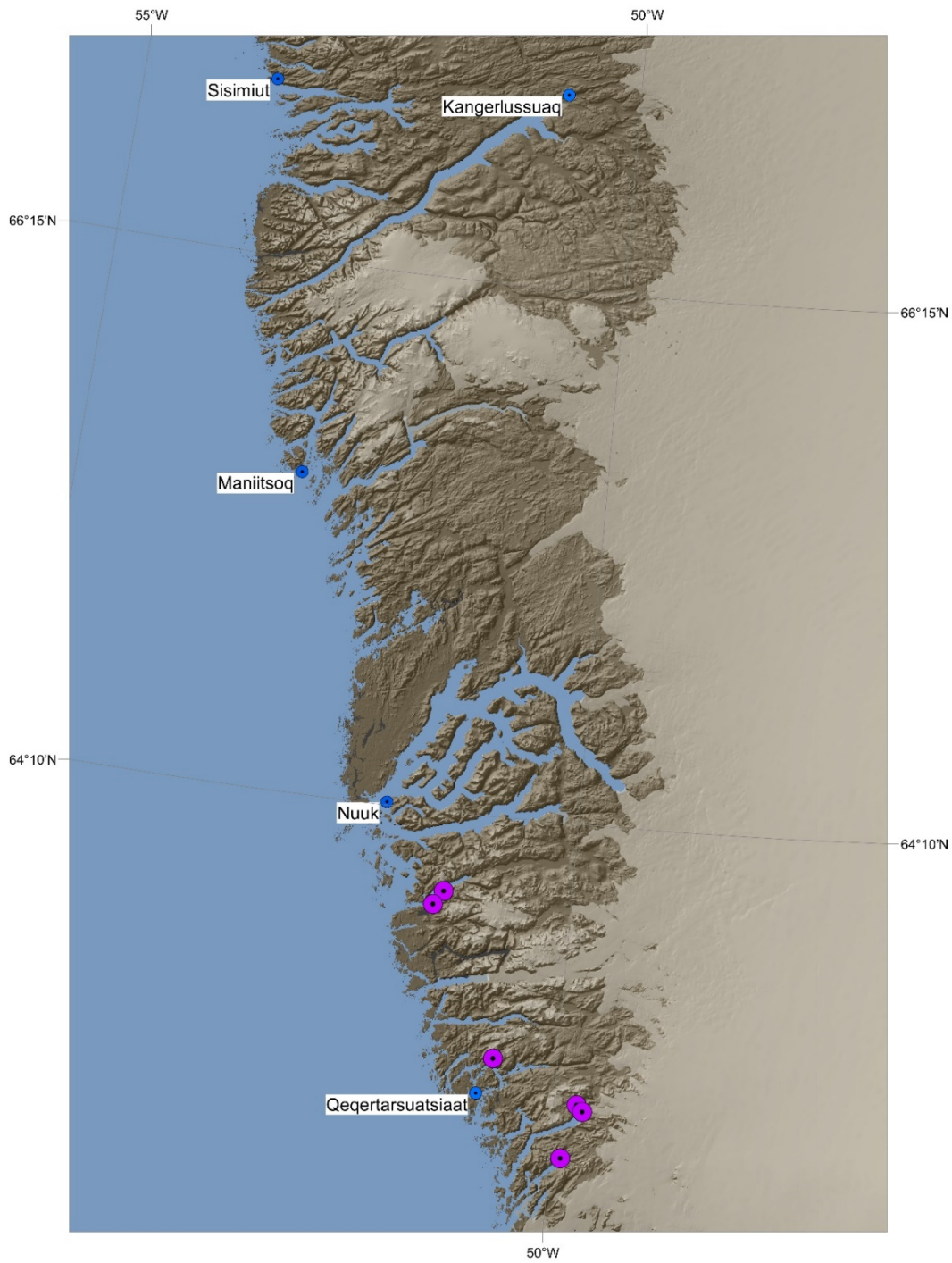
Extended Fig. 1. Location of the six additional rivers in South-West Greenland (purple circles). The two
southernmost rivers receive meltwater directly from the ice sheet, while the four other rivers receives meltwater
originating from local glaciers and ice caps.

197

Bibliography

1. Hawkings, J. R. *et al.* Large subglacial source of mercury from the southwestern margin of the Greenland Ice Sheet. *Nat. Geosci.* **14**, 496–502 (2021).

2. Lamarche-Gagnon, G. *et al.* Greenland melt drives continuous export of methane from its bed. *Nature* 73–77 (2018). doi:10.1038/s41586-018-0800-0

3. Hofstra, A. H. & Cline, J. Characteristics and Models for Carlin-Type Gold Deposits. in *SEG Reviews* 163–220 (2000). doi:10.5382/rev.13.05

4. John, D. A. *et al. Descriptive Models for Epithermal Gold-Silver Deposits. U.S. Geological Survey Scientific Investigations Report 2010–5070–Q* (2010).

5. Connelly, J. N. & Mengel, F. C. Evolution of Archean components in the Paleoproterozoic Nagssugtoqidian orogen, West Greenland. *Bull. Geol. Soc. Am.* **112**, 747–763 (2000).

6. Engström, J. & Klint, K. E. S. Continental collision structures and post-orogenic geological history of the kangerlussuaq area in the southern part of the nagssugtoqidian orogen, central west Greenland. *Geosci.* **4**, 316–334 (2014).

7. Rigét, F. *et al.* Mercury (Hg) transport in a high arctic river in northeast Greenland. *Water. Air. Soil Pollut.* **222**, 233–242 (2011).

8. Søndergaard, J. *et al.* Mercury exports from a High-Arctic river basin in Northeast Greenland (74°N) largely controlled by glacial lake outburst floods. *Sci. Total Environ.* **514**, 83–91 (2015).

9. Søndergaard, J., Rigét, F., Tamstorf, M. P. & Larsen, M. M. Mercury transport in a low-arctic river in Kobbefjord, West Greenland (64° N). *Water. Air. Soil Pollut.* **223**, 4333–4342 (2012).

10. Coquery, M., Cossa, D. & Martin, J. M. The distribution of dissolved and particulate mercury in three Siberian estuaries and adjacent Arctic coastal waters. *Water, Air, Soil Pollut. 1995 801* **80**, 653–664 (1995).

11. Emmerton, C. A. *et al.* Mercury export to the Arctic Ocean from the Mackenzie River, Canada. *Environ. Sci. Technol.* **47**, 7644–7654 (2013).

12. Outridge, P. M., Macdonald, E. R. W., Wang, G. F., Stern, G. A. & Dastoor, A. P. A mass balance inventory of mercury in the Arctic Ocean. *Environ. Chem* **5**, 89–111 (2008).

13. Sukhenko, S. A., Papina, T. S. & Pozdnjakov, S. R. Transport of mercury by the Katun river, West Siberia. *Hydrobiol. 1992 2281* **228**, 23–28 (1992).

14. Christiansen, J. R., Röckmann, T., Popa, M. E., Sapart, C. J. & Jørgensen, C. J. Carbon emissions from the edge of the Greenland Ice sheet reveal subglacial processes of methane and carbon dioxide turnover. *J. Geophys. Res. Biogeosciences* 1–13 (2021). doi:10.1029/2021jg006308

235   15.   Christiansen, J. R. & Jørgensen, C. J. First observation of direct methane emission to the
236   atmosphere from the subglacial domain of the Greenland Ice Sheet. *Sci. Rep.* **8**, 16623
237   (2018).

238

Author contributions

240   C.J.J., J.S., C.N.A., K.K.K. designed the control study. S.E.S., C.J.J., J.R.C., C.N.A.
241   collected field samples. M.M.L. analyzed water samples at Aarhus University. D.R.
242   performed the geological assessment. C.J.J. and C.N.A. wrote the manuscript with significant
243   contributions from all co-authors.

Competing interests.

245   The authors declare no competing interests.