Electronic Supplementary Material (ESI) for Metallomics.

Supporting Information for

Natural Hg isotopic composition of different Hg compounds in mammal tissues as a proxy for *In vivo* breakdown of toxic methylmercury

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Description of the Samples, Sampling and Storing Procedures. Beluga whales (*Delphinapterus leucas*) occur throughout northern and western Alaska and are an important subsistence resource for Alaska native people. Beluga liver samples come from the Alaska Marine Mammal Tissue Archival Project (AMMTAP), led by the National Biomonitoring Specimen Bank (NBSB) at the National Institute of Standards and Technology (NIST, Charleston, SC, USA). This project began in 1987 and consists in sampling and archiving mammal tissues collected from stranding or Inuit subsistence hunting in the Alaskan Arctic. For this study, we disposed of 11 beluga livers from the Eastern Chukchi Sea stock sampled at Point Lay, North Alaska (**Figure S1a**). All the belugas have been harvested during the feeding season from June 30th through July 11th of 1990, 1996 and 1999.A very strict sampling protocol followed by cryogenic homogenization has been undertaken to minimize contaminations[1]. Once received, samples were stored in -80°C freezer until their analysis. Age of beluga individuals has been estimated counting growth rings in a thin longitudinal section taken from the middle of the mandibular tooth. The following samples were analysed: MM 15L 055C, MM 11L 420, MM 04L 146 , MM 11L 444, MM 04L 125, MM 11L 455, MM 04L 134, MM 15L 070C, MM 11L 440, MM 04L 137, MM 15L 058C. For better readability of the text and figures/tables, the sample codes for Beluga whale samples were abbreviated as B-xxx, with “B” replacing the official code “MM XXL’” as recommended by NIST.

Seal tissues (*Phoca sibirica*) were collected from seals sampled in the southern and central basins of Lake Baikal in 2008-2010 (**Figure S1b**). Four seals of the age 1-1.5 months (P-8, P-10, P-12 and P-14) and one adult female (P-17) were obtained from hunters during the official spring hunting season. Young males (P-15 and P-16) were inadvertently caught in fishing nets during the autumn-winter period. Sampling of the seal tissues have been done in the field, followed by freezing at -18°C and transportation (frozen) to the laboratory of the Institute of Geochemistry SB RAS. In the clean laboratory, samples were weighed on the analytical balances and placed into the 1L flask (cleaned by 10% HNO_3, 10% HCl and MilliQ water) at -40°C. Frozen samples were freeze-dried at -80°C during 48h. Freeze-dried samples were weighed to estimate the loss of the moisture. Final samples were placed into double zip-lock bags and kept in a refrigerating chamber.

Quantification of Hg Species by Isotope Dilution GC-ICPMS. Hg species quantification by isotope dilution was found in good agreement with total Hg concentration measured with DMA-80 analyser (Milestone, USA) for all samples and for certified biological reference materials (tuna fish muscle ERM-CE464, dogfish liver DOLT-4 and pigmy sperm whale liver NIST QC03LH3). An enriched isotope pattern deconvolution method[2] was used to investigate species interconversion artefacts during the analytical procedures. Typical detection limits (DL) for this method are 0.7% for the demethylation and 0.3% for the methylation[3]. In general the transformation artefacts were low and occurred unpredictably in some hair and kidney samples. The use of the isotope dilution technique associated with GC-ICPMS thus represents a valuable tool for the accurate measurement of Hg species in complex biological tissues, confirming earlier results[4].

Stable Isotope Ratios Measurements.

A delta notation (‰) relative to the reference standard NIST SRM 3133 is used to express the Hg isotopic composition[5] of a sample (equations (1) to (5)).

$$\delta^{xxx}Hg = [(^{xxx}Hg\ /\ ^{198}Hg)_{sample} / (^{xxx}Hg\ /\ ^{198}Hg)_{NIST\ 3133} - 1] \times 1000 \qquad (1)$$

where xxx is 204, 202, 201, 200 or 199 are the different Hg isotopes measured and $(^{xxx}Hg/^{198}Hg)_{NIST3133}$ is the average of the two bracketing standards. The mass independent fractionation (MIF) is expressed as follows:

$$\Delta^{199}Hg = \delta^{199}Hg - 0.252 \times \delta^{202}Hg \qquad (2)$$

$$\Delta^{200}Hg = \delta^{200}Hg - 0.502 \times \delta^{202}Hg \qquad (3)$$

$$\Delta^{201}Hg = \delta^{201}Hg - 0.752 \times \delta^{202}Hg \qquad (4)$$

$$\Delta^{204}Hg = \delta^{204}Hg - 1.493 \times \delta^{202}Hg \qquad (5)$$

In both laboratories, extraction yields have been checked using CVG-MC-ICP-MS ^{202}Hg isotope signals (Volts), and sample-standard NIST 3133 were matched to within 15%. External reproducibility has been evaluated by the repeated analysis of reference materials such as whale liver (QC03LH03), dogfish liver (NRC CNRC DOLT-4), tuna fish muscle (ERM-CE464), and UM-Almadén during each session of analysis (**Table S3**).

Sample preparation for total Hg isotopic composition measurements at IPREM-LCABIE (Pau, France). Seal tissue samples were mixed with 5 mL of HNO_3 and 1.25 mL of HCl and left overnight. Then, 5 mL of deionized water was added and this mixture was heated in a digiPREP system (SCP Science, France) at 80ºC during 4 hrs (90 min of ramp and 2.5 hrs of heating time). For total conversion of all the Hg to iHg 1mL of freshly prepared BrCl was added. To remove an excess of BrCl from the solution, 0.5mL of 30% hydroxylamine was added before analysis. The final solution was diluted 5 times. A home-made Cold Vapor Generator (CVG) was used as sample introduction system in MC-ICPMS, in which a sample is mixed with a $SnCl_2$ solution ($SnCl_2$ 3%

w/v, HCl 10% v/v). A 10 µg.L^{-1}Tl solution is introduced in a dry aerosol form with a DSN100 desolvating nebulizer (Nu Instruments, Wrexham, UK) and is mixed with the sample Hg vapour in a double entry plasma torch. Hg concentrations of the analysed solutions vary from 0.5 to 2 µg.L^{-1}. Blanks solutions were measured before each standard and sample and signals were subtracted using "on peak zero" signals.

Sample preparation for total Hg isotopic composition measurements at GET (Toulouse, France). For the digestion of beluga whale samples, 5 mL of bi-distilled nitric acid (15N) was added to 0.2g of fresh frozen sample in a 50mL pyrex vessel, and closed by a Teflon cap. Complete Hg extraction was performed with a CEM Discover microwave (180°C, 225 PSI, 10 min). Tests was carried out with or without BrCl reagent addition (0.1 ml, Method EPA 1631) and no significant differences has been observed in terms of final HgT recoveries (>90%). The mixtures were finally diluted in an inverse aqua regia (3 HNO_3 : 1 HCl, 20 vol.% MilliQ water) for analysis. Final solutions contained 2.5 or 5 ppb of total Hg concentration and were introduced in a ThermoFinnigan Neptune MC-ICP-MS by using a Cold Vapor Generation system (HGX200, Cetac).

Sample preparation and analytical techniques for Hg species-specific stable isotope composition analysis (Hg-CSIC) at IPREM-LCABIE (Pau, France). About 200 mg of dried sample was digested in 5 mL of 25% Tetra Methyl Ammonium Hydroxide under soft microwave-assisted extraction (CEM discover, 75°C, 4 min). Between 1 to 5 mL of the extract was derivatized in 5 mL acetate buffer (pH=3.9) with about 0.5-1mL of sodium-tetrapropylborate ($NaBPr_4$ 1%) into 1 mL of organic phase (hexane) after 5 minutes of hand shaking. A preconcentration step under a gentle Ar flux has been applied for low concentration samples in order to reach a final concentration of 20 to 200 µg.L^{-1} of both Hg species in the organic phase. 3µL of samples was injected into a gas chromatograph (Thermo Focus, see parameters below). In order to measure Hg species-specific isotopic ratios, the gas chromatograph was hyphenated to the MC-ICP-MS under wet plasma conditions[6]. Here a 200 µg.L^{-1}Tl solution is introduced as an internal standard via a 200 µL.min^{-1}

micro-concentric nebulizer combined to a cinnabar spray chamber. A double entry plasma torch was used to mix Tl aerosol and GC flow. Isotopic ratios of both iHg and MeHg were measured with a species-specific sample-standard bracketing sequence. The Time Resolved Analysis mode (TRA) was used to acquire the transient signals. The data treatment strategy used to calculate Hg isotopic ratios is the Linear Regression Slope (LRS) method described by Epov et al.[7].

Precision and Accuracy of Hg Stable Isotope Ratios Measurements.

Measurements of total Hg isotopic composition by CVG-MC-ICPMS of external standards (UM Almadén, ERM-CE464, DOLT-4, QC03LH3) were processed within all the analytical sessions. Delta values obtained for ERM-CE464 and Um-Almadén were in good agreement with published values[8-10]within the analytical uncertainties. We used UM-Almaden (*n* = 21) and whale liver QC03LH3 (*n* = 27) long-term reproducibility to express the uncertainty (2SD) on the seals and belugas measurements, respectively, because they had higher number of measurements than ERM-CE464(*n* = 7) and DOLT-4 (*n* = 4) (**Table S3**).

For Hg CSIC measured by GC-MC-ICPMS, the considerably higher amount of sample derivatized (~5mL) compared to Hg speciation measurements by GC-ICPMS (0.02 to 0.5mL), induced a lower derivatization yield of the Hg species. This was observed comparing transient signal intensities between samples and NIST 3133, even with higher amounts of $NaBPr_4$ (1 mL) added to ensure efficient derivatization. Although one study suggested the possible occurrence of isotope fractionation artefact during the ethylation step[11], this artefact was not found to induce a significant bias within the precision of the measurements performed by GC-MC-ICP-MS. To investigate the hypothesis of isotopic fractionation artefacts during the sample preparation, we compared the isotopic signatures obtained by GC-MC-ICPMS and CVG-MC-ICPMS in all samples and standards. Hence, Hg total isotopic composition, Hg CSIC and Hg species fractions must be related by the following equation:

$$\delta^{xxx}Hg_{total} = \delta^{xxx}Hg_{iHg} * f(iHg) + \delta^{xxx}Hg_{MMHg} * f(MMHg) \qquad (6)$$

where f is the fraction of the Hg species considered (f(iHg) + f(MMHg) =1); $\delta^{xxx}Hg$ is the total Hg isotope composition measured by CVG-MC-ICPMS; $\delta^{xxx}Hg_{iHg}$ and $\delta^{xxx}Hg_{MMHg}$ are the species specific stable isotope composition of iHg and MMHg measured by GC-MC-ICPMS, respectively.

Hair Hg-CSIC. This unique sample have not been included in the manuscript Hg CSIC MIF discussion because it is not an internal tissue and may thus be exposed to external transformations in the water column(Hg adsorption, Hg absorption, Hg photoreduction). Furthermore, it is also likely that hair do no integrate the same period of Hg exposure as do internal organs[12]. While MIF of both iHg and MMHg species was not significantly different from the MIF of the total Hg in the different internal tissues of seals (i.e. liver, kidney, muscle, pancreas, diaphragm, thick intestine), we measured strong differences among Hg species anomalies ($\Delta^{201}Hg$ or $\Delta^{199}Hg$) in the hair, with higher values for MMHg than for iHg ($\Delta^{199}Hg$ = 5.94±0.14‰ and 1.05±0.21‰ (2SD on analysis triplicates), respectively). This suggests that seal hair may reflect some photochemical process occurring on the hair during the mammal lifespan, strongly indicated by the residual MMHg enriched in odd isotopes relative to iHg following photodemethylation patterns[9]. Alternatively, it could also be the result of external supply of different Hg species from the water column adsorbed onto the hair. However, the photodemethylation explanation is privileged because of the MIF of total Hg similarity between the hair and the other organs such as liver and muscle, suggesting no external Hg source. The hair ratio $\Delta^{199}Hg:\Delta^{201}Hg$ of total Hg, MMHg and iHg is 1.21, 1.20 and 1.24, respectively, indicating that both Hg species originate predominantly from MMHg photodemethylation. We thus hypothesized that the different Hg species anomalies observed in the haircome directly from MMHg photodemethylation, at the hair surface, of MMHg previously accumulated in the hair via trophic transfer. This is the best assumption to explain why Hg total

MIF is the same than in the other organs (and hence this MIF can be used to track Hg source as previously suggested[13]), and why MMHg anomaly (Δ^{201}Hg) is significantly higher(about 4‰) than iHg anomaly. Additional studies with larger number of samples are clearly needed to improve and corroborate such hypothesis.

References

1. Zeisler, R.; Harrison, S. H.; Wise, S. A., *The Pilot national environmental specimen bank : analysis of human liver specimens*. NBS SP 656: Washington, DC, 1983; p 135.
2. Rodriguez-Gonzalez, P.; Rodriguez-Cea, A.; Garcia Alonso, J. I.; Sanz-Medel, A., Species-Specific Isotope Dilution Analysis and Isotope Pattern Deconvolution for Butyltin Compounds Metabolism Investigations. *Analytical Chemistry* **2005,** 77, 7724-7734.
3. Navarro, P.; Clemens, S.; Perrot, V.; Bolliet, V.; Tabouret, H.; Guerin, T.; Monperrus, M.; Amouroux, D., Simultaneous determination of mercury and butyltin species using a multiple species-specific isotope dilution methodology on the European, *Anguilla anguilla* glass eel and yellow eel. *International Journal of Environmental Analytical Chemistry* **2013,** 93, (2), 166-182.
4. Monperrus, M.; Rodriguez-Gonzalez, P.; Amouroux, D.; Garcia Alonso, J. I.; Donard, O. F. X., Evaluating the potential and limitations of double-spiking species-specific isotope dilution analysis for the accurate quantification of mercury species in different environmental matrices. *Analytical and Bioanalytical Chemistry* **2008,** 390, (2), 655-666.
5. Blum, J. D.; Bergquist, B. A., Reporting of variations in the natural isotopic composition of mercury. *Analytical and Bioanalytical Chemistry* **2007,** 388, 353-359.
6. Epov, V. N.; Rodriguez-Gonzalez, P.; Sonke, J. E.; Tessier, E.; Amouroux, D.; Maurice-Bourgoin, L.; Donard, O. F. X., Simultaneous Determination of Species-Specific Isotopic Composition of Hg by Gas Chromatography Coupled to Multicollector ICPMS. *Analytical Chemistry* **2008,** 80, (10), 3530-3538.
7. Epov, V. N.; Berail, S.; Jimenez-Moreno, M.; Perrot, V.; Pecheyran, C.; Amouroux, D.; Donard, O. F. X., Approach to measure Isotopic Ratios in Species Using Multicollector-ICPMS Coupled with Chromatography. *Analytical Chemistry* **2010,** 82, (13), 5652-5662.
8. Perrot, V.; Epov, V. N.; Pastukhov, M. V.; Grebenshchikova, V. I.; Zouiten, C.; Sonke, J. E.; Husted, S.; Donard, O. F. X.; Amouroux, D., Tracing Sources and Bioaccumulation of Mercury in Fish of Lake Baikal-Angara River Using Hg Isotopic Composition *Environmental Science & Technology* **2010,** 44, (21), 8030-8037.
9. Bergquist, B. A.; Blum, J. D., Mass-dependant and –independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* **2007,** 318, 417-420.
10. Perrot, V.; Pastukhov, M. V.; Epov, V. N.; Husted, S.; Donard, O. F. X.; Amouroux, D., Higher mass-independent fractionation of methylmercury in the pelagic food web of Lake Baikal (Russia). *Environmental Science & Technology* **2012,** 46, (11), 5902-5911.
11. Yang, L.; Sturgeon, R. E., Isotopic fractionation of mercury induced by reduction and ethylation. *Analytical and Bioanalytical Chemistry* **2009,** 393, (1), 377-385.
12. Magos, L.; Clarkson, T. W., The assessment of the contribution of hair to methyl mercury excretion. *Toxicology Letters* **2008,** 182, 48-49.
13. Laffont, L.; Sonke, J. E.; Maurice, L.; Hintelmann, H.; Pouilly, M.; Bacarreza, Y. S.; Perez, T.; Behra, P., Anomalous Mercury Isotopic Compositions of Fish and Human Hair in the Bolivian Amazon. *Environmental Science & Technology* **2009,** 43, (23), 8985-8990.

Table S1. Total Hg concentration and Hg species concentration (ppb, dw) for beluga, seal and certified reference material samples, measured by DMA80 and ID-GC-ICPMS, respectively. Recovery of Hg species by ID-GC-ICPMS (%) is compared to total Hg concentration measured by DMA80. Total Hg and Hg speciation was in agreement with certified values for both BCR-CRM464 and NRC-CNRC DOLT-4.

	DMA 80	ID-GC-ICPMS				
	[Hg]tot	[MMHg]	SD	[Hg(II)]	SD	recovery (%)
P 17-Li	19062	1056	102	17050	1107	95
P 17-Mu	752	760	69	114	4	116
P 17-Ki	7980	634	1	7767	137	105
P 17-Tl	535	290	9	252	12	101
P 17-Ha	2538	2212	123	531	78	108
P 17-Pa	702	396	12	337	15	104
P 17-Di	1748	842	87	330	4	67
P 14-Li	791	357		494		108
P 16-Li	6463	1021	39	4445	224	85
P 16-Ki	2787	609	8	1883	76	89
B-134	4246	851	29	3395	133	100
B-125	29122	2575	109	28585	947	107
B-146	28331	929	38	24043	1999	88
B-137	11560	813	58	8498	927	81
B-420	70000	864	26	47228	819	69
B-444	52992	1849	297	27609	895	56
B-440	6919	1268	47	4761	119	87
B-455	110893	1011	55	74842	7840	68
B-055C	108111	3384	152	97128	8986	93
B-070C	11677	765	81	10180	202	94
B-058C	1315	573	26	908	15	113
CEM 464	5240 (certified)	4991	158	177	34	99
DOLT 4	2580 (certified)	1229	82	1201	46	94

Table S2. Total Hg isotopic composition measurements on different external standards with different matrix used for the long term reproducibility (2SD) on the total Hg isotope composition analysis of the biological samples.

sample	n	δ^{202}Hg (‰)	± 2SD	δ^{201}Hg (‰)	± 2SD	δ^{200}Hg (‰)	± 2SD	δ^{199}Hg (‰)	± 2SD	Δ^{201}Hg (‰)	± 2SD	Δ^{200}Hg (‰)	± 2SD	Δ^{199}Hg (‰)	± 2SD
UM-Almadén	21	**-0.59**	0.17	**-0.47**	0.12	**-0.29**	0.11	**-0.17**	0.10	**-0.02**	0.09	**-0.02**	0.06	**-0.02**	0.08
CRM 464	7	**0.82**	0.26	**2.60**	0.14	**0.49**	0.17	**2.61**	0.02	**1.95**	0.09	**0.07**	0.01	**2.40**	0.06
DOLT 4	4	**-0.35**	0.20	**0.71**	0.06	**-0.14**	0.06	**1.03**	0.07	**0.98**	0.19	**0.02**	0.03	**1.12**	0.11
Whale liver	27	**-0.79**	0.11	**0.35**	0.13	**-0.33**	0.06	**0.97**	0.11	**0.95**	0.12	**0.06**	0.04	**1.17**	0.11

Table S3. Total Hg isotopic ratio, total and Hg species concentration ($ng.g^{-1}$, dw) in seal liver and muscle samples that have not been measured for Hg species-specific isotope ratio. Error on delta values are given by the long term reproducibility (2SD) of UM-Almadén (n=21, see **table S3**). Total Hg concentration is the sum of iHg and MMHg concentration for each sample.

samples		[Hg(II)]		[MMHg]		[Hg]total									
		mean	2 SD	mean	2 SD	mean	$\delta^{204}Hg$	$\delta^{202}Hg$	$\delta^{201}Hg$	$\delta^{200}Hg$	$\delta^{199}Hg$	$\Delta^{204}Hg$	$\Delta^{201}Hg$	$\Delta^{200}Hg$	$\Delta^{199}Hg$
Livers	P- 8 Li	529		188		717	0.94	0.71	4.43	0.45	5.24	-0.12	3.89	0.09	5.06
	P- 10 Li	271		219		489	1.87	1.32	5.05	0.75	5.47	-0.10	4.06	0.09	5.14
	P- 12 Li	163		133		296	1.31	0.94	4.41	0.55	4.94	-0.10	3.70	0.08	4.70
	P- 15 Li	7907	304	1091	94	8999	-0.79	-0.46	2.43	-0.18	3.40	-0.09	2.78	0.06	3.52
Muscles	P- 8 Mu	40	5	164	7	204	3.03	2.16	5.75	1.20	5.78	-0.20	4.13	0.11	5.24
	P- 10 Mu	25	2	113	1	139	2.47	1.75	5.21	0.96	5.42	-0.14	3.89	0.08	4.98
	P- 12 Mu	33	11	164	1	197	2.64	1.87	5.20	1.05	5.30	-0.15	3.79	0.11	4.83
	P- 14 Mu	26	1	133	16	159	2.50	1.73	5.21	0.95	5.36	-0.08	3.91	0.08	4.93
	P- 15 Mu	205	24	896	98	1101	2.17	1.60	3.90	0.90	3.81	-0.22	2.69	0.10	3.41
	P- 16 Mu	135	14	648	61	783	2.05	1.44	4.65	0.79	4.89	-0.11	3.56	0.07	4.53

Table S4. Summary of the Hg species (iHg and MMHg) and total Hg concentration in the different organs and tissues of the aquatic mammals, associated with their isotopic composition. Measurements of international standard reference material of fish tissues certified for MMHg and total Hg concentration are also included. *Here are reported official sample codes for Beluga whale samples from NIST, but for better readability in the main manuscript and figures, sample codes for Beluga whale samples were abbreviated as B-xxx, with "B" being officially "MMXXL" as recommended by NIST.

Sampling site	age	δ^{15}N	tissue	sample	Hg, dw	(ng/g)	SD	f MMHg	SD	f Hg(II)	SD	δ^{202}Hg	2 SD	δ^{201}Hg	2 SD	δ^{200}Hg	2 SD	δ^{199}Hg	2 SD	Δ^{201}Hg	2 SD	Δ^{200}Hg	2 SD	Δ^{199}Hg	2 SD
East. Chukchi Stock	13	17.7	liver	MMO4L	[Hg]$_{tot}$	4246	162					-1.37	0.11	-1.07	0.13	-0.65	0.06	-0.31	0.11	-0.03	0.12	0.04	0.04	0.04	0.11
North Alaska				-134	[MMHg]	851	29	0.20	0.01	0.80	0.03	0.03	0.35	0.01	2.44	0.15	1.17	-0.18	0.70	-0.02	2.18	0.13	0.99	-0.19	0.62
Beluga whales					[iHg]	3395	133					-1.85	0.31	-1.31	0.12	-0.86	0.18	1.21	0.36	0.08	0.15	0.07	0.12	1.68	0.39
Delphinapterus	30	18.0	liver	MMO4L	[Hg]$_{tot}$	31160	1055					-1.31	0.11	-1.11	0.13	-0.65	0.06	-0.38	0.11	-0.13	0.12	0.01	0.04	-0.05	0.11
leucas				-125	[MMHg]	2575	109	0.08	0.00	0.92	0.03	-0.91	0.17	-0.64	0.85	-0.76	2.59	-0.87	0.01	0.04	0.98	-0.30	2.68	-0.64	0.06
					[iHg]	28585	947					-1.69	0.40	-1.60	0.02	-0.89	0.34	-0.61	0.02	-0.32	0.32	-0.04	0.14	-0.18	0.08
	55	17.8	liver	MMO4L	[Hg]$_{tot}$	24972	2037					-0.97	0.11	-0.96	0.13	-0.51	0.06	-0.36	0.11	-0.23	0.12	-0.02	0.04	-0.11	0.11
				-146	[MMHg]	929	38	0.04	0.00	0.96	0.08	2.55	1.19	1.18	2.14	0.99	1.84	1.26	0.36	-0.74	1.70	-0.29	1.71	0.62	0.60
					[iHg]	24043	1999					-1.60	0.21	-1.31	0.17	-0.84	0.18	-0.32	0.36	-0.11	0.06	-0.04	0.22	0.09	0.31
	13	17.4	liver	MMO4L	[Hg]$_{tot}$	9311	985					-1.41	0.11	-1.21	0.13	-0.70	0.06	-0.45	0.11	-0.15	0.12	0.01	0.04	-0.10	0.11
				-137	[MMHg]	813	58	0.09	0.01	0.91	0.10	0.37	0.29	-0.30	1.21	0.00	0.62	-0.18	0.76	-0.58	1.34	-0.18	0.69	-0.27	0.69
					[iHg]	8498	927					-1.94	0.31	-1.69	0.20	-1.00	0.08	-0.51	0.25	-0.24	0.04	-0.03	0.10	-0.02	0.17
	35	18.1	liver	MM11L	[Hg]$_{tot}$	80164	7121					-1.07	0.11	-1.03	0.13	-0.56	0.06	-0.41	0.11	-0.23	0.12	-0.02	0.04	-0.14	0.11
				-420	[MMHg]	978	181	0.01	0.00	0.99	0.09	-0.37	1.34	-0.06	0.56	-0.90	2.09	-0.84	0.94	0.21	0.45	-0.71	1.42	-0.75	0.60
					[iHg]	79187	6940					-0.93	0.37	-0.96	0.34	-0.42	0.20	-0.36	0.31	-0.26	0.11	0.04	0.03	-0.13	0.23
	34	17.6	liver	MM11L	[Hg]$_{tot}$	53666	745					-0.92	0.11	-0.85	0.13	-0.45	0.06	-0.28	0.11	-0.16	0.12	0.01	0.04	-0.05	0.11
				-444	[MMHg]	1538	102	0.03	0.00	0.97	0.01	1.50	0.34	1.51	0.85	1.09	1.04	0.54	1.47	0.38	1.10	0.34	1.21	0.16	0.38
					[iHg]	52128	643					-1.03	0.23	-0.86	0.27	-0.53	0.27	-0.32	0.03	-0.09	0.27	-0.02	0.17	-0.06	0.06
	12	17.7	liver	MM11L	[Hg]$_{tot}$	6029	166					-1.18	0.11	-0.94	0.13	-0.61	0.06	-0.22	0.11	-0.05	0.12	-0.01	0.04	0.08	0.11
				-440	[MMHg]	1268	47	0.21	0.01	0.79	0.02	0.89	0.04	0.52	0.15	0.27	0.37	0.43	0.66	-0.15	0.12	-0.17	0.35	0.21	0.67
					[iHg]	4761	119					-1.46	0.21	-1.13	0.03	-0.80	0.21	-0.18	0.08	-0.03	0.13	-0.07	0.11	0.18	0.03
	44	17.9	liver	MM11L	[Hg]$_{tot}$	92341	2247					-0.80	0.11	-0.78	0.13	-0.39	0.06	-0.24	0.11	-0.17	0.12	0.02	0.04	-0.04	0.11
				-455	[MMHg]	1279	227	0.01	0.00	0.99	0.02	-	-	-	-	-	-	-	-	-	-	-	-	-	-
					[iHg]	91062	2020					-0.49	0.12	-0.50	0.02	-0.22	0.16	-0.13	0.17	-0.14	0.11	0.02	0.22	-0.01	0.20
	-	17.7	liver	MM15L	[Hg]$_{tot}$	100512	9138					-0.99	0.11	-0.97	0.13	-0.49	0.06	-0.42	0.11	-0.23	0.12	0.00	0.04	-0.18	0.11
				-055C	[MMHg]	3384	152	0.03	0.00	0.97	0.09	1.43	0.05	0.80	0.40	1.79	2.19	0.72	0.81	-0.28	0.44	1.07	2.17	0.36	0.79
					[iHg]	97128	8986					-0.72	0.41	-0.85	0.28	-0.42	0.32	-0.53	0.23	-0.31	0.18	-0.06	0.14	-0.34	0.13
	-	18.0	liver	MM15L	[Hg]$_{tot}$	10945	283					-1.06	0.11	-0.86	0.13	-0.61	0.06	-0.31	0.11	-0.06	0.12	-0.07	0.04	-0.04	0.11
				-070C	[MMHg]	765	81	0.07	0.01	0.93	0.02	1.30	-	1.42	-	0.07	-	0.18	-	0.44	-	-0.59	-	-0.15	-
					[iHg]	10180	202					-1.26	0.07	-0.98	0.26	-0.65	0.25	-0.18	0.32	-0.03	0.21	-0.01	0.22	0.14	0.30
	-	18.2	liver	MM15L	[Hg]$_{tot}$	1481	41					-0.39	0.11	-0.07	0.13	-0.22	0.06	0.24	0.11	0.22	0.12	-0.02	0.04	0.34	0.11
				-058C	[MMHg]	573	26	0.39	0.02	0.61	0.01	1.56	0.46	1.45	0.53	0.69	0.22	0.85	0.76	0.28	0.49	-0.09	0.30	0.46	0.65
					[iHg]	908	15					-0.86	0.43	-0.38	0.70	-0.40	0.37	0.44	0.39	0.27	0.43	0.03	0.17	0.65	0.28
Lake Baikal	9	13.7	liver	P-17Li	[Hg]$_{tot}$	18106	1209					-0.65	0.17	2.03	0.12	-0.23	0.11	3.05	0.10	2.52	0.09	0.09	0.06	3.21	0.08
Russia					[MMHg]	1056	102	0.06	0.01	0.94	0.06	3.56	0.28	5.52	1.89	1.87	2.13	4.84	0.38	2.85	0.43	0.08	0.58	3.94	0.39
Seals					[iHg]	17050	1107					-0.94	0.22	2.06	0.10	-0.30	0.04	3.19	0.09	2.77	0.07	0.17	0.07	3.43	0.03
Phoca Sibirica	2	14.4	liver	P-16Li	[Hg]$_{tot}$	5465	263					-0.43	0.17	3.33	0.12	-0.16	0.11	4.55	0.10	3.66	0.09	0.05	0.06	4.66	0.08
					[MMHg]	1021	39	0.19	0.01	0.81	0.04	2.05	0.94	5.24	0.90	1.03	0.64	5.30	0.23	3.70	0.20	0.00	0.17	4.79	0.01
					[iHg]	4445	224					-0.88	0.38	3.13	0.27	-0.42	0.35	4.71	0.10	3.79	0.01	0.03	0.16	4.94	0.00
	0.1	15.7	liver	P-14Li	[Hg]$_{tot}$	852						1.10	0.17	4.69	0.12	0.63	0.11	5.18	0.10	3.86	0.09	0.08	0.06	4.91	0.08
					[MMHg]	357		0.42	0.00	0.58	0.00	2.68	0.07	5.50	0.77	1.34	0.19	5.46	0.55	3.48	0.71	0.00	0.22	4.78	0.53
					[iHg]	494						-0.21	0.13	3.84	0.08	-0.16	0.07	5.22	0.03	4.00	0.02	-0.05	0.13	5.28	0.01
	9	13.7	kidney	P-17Ki	[Hg]$_{tot}$	8400	139					-0.64	0.17	2.40	0.12	-0.23	0.11	3.48	0.10	2.88	0.09	0.09	0.06	3.64	0.08
					[MMHg]	634	1	0.08	0.00	0.92	0.02	2.19	0.64	4.91	0.59	1.12	0.47	5.06	0.02	3.27	0.11	0.02	0.15	4.51	0.14
					[iHg]	7767	137					-1.01	0.06	2.32	0.09	-0.47	0.24	3.67	0.14	3.08	0.04	0.04	0.21	3.92	0.13
	1	14.4	kidney	P-16Ki	[Hg]$_{tot}$	2492	84					-0.49	0.17	3.16	0.12	-0.17	0.11	4.35	0.10	3.53	0.09	0.07	0.06	4.47	0.08
					[MMHg]	609	8	0.24	0.00	0.76	0.03	1.79	0.47	4.47	0.46	0.85	0.35	4.72	0.38	3.12	0.11	-0.05	0.11	4.27	0.26
					[iHg]	1883	76					-1.22	0.19	2.85	0.44	-0.61	0.13	4.28	0.35	3.77	0.30	0.00	0.22	4.59	0.39
	9	13.6	muscle	P-17Mu	[Hg]$_{tot}$	874	73					2.35	0.17	4.90	0.12	1.26	0.11	4.61	0.10	3.13	0.09	0.08	0.06	4.02	0.08
					[MMHg]	760	69	0.87	0.08	0.13	0.00	2.56	0.54	5.12	0.35	1.27	0.53	4.80	0.00	3.19	0.05	-0.02	0.26	4.15	0.13
					[iHg]	114	4					-0.43	0.61	3.52	1.09	0.01	0.97	4.47	0.03	3.84	0.64	0.23	0.67	4.58	0.18
	9	12.1	pancreas	P-17Pa	[Hg]$_{tot}$	733	26					1.22	0.17	3.78	0.12	0.71	0.11	4.07	0.10	2.86	0.09	0.09	0.06	3.76	0.08
					[MMHg]	396	12	0.54	0.02	0.46	0.02	2.54	0.11	4.86	0.30	1.31	0.06	4.43	0.57	2.95	0.38	0.03	0.12	3.79	0.60
					[iHg]	337	15					-0.66	0.33	2.42	0.16	-0.28	0.28	3.71	0.19	2.91	0.09	0.05	0.11	3.87	0.27
	9	13.7	thick	P-17TI	[Hg]$_{tot}$	542	21					1.01	0.17	3.55	0.12	0.59	0.11	3.81	0.10	2.79	0.09	0.08	0.06	3.56	0.08
			intestine		[MMHg]	290	9	0.53	0.02	0.47	0.02	2.31	0.18	4.88	0.05	1.22	0.16	4.42	0.39	3.14	0.09	0.06	0.06	3.84	0.34
					[iHg]	252	12					-0.74	1.00	2.46	1.38	-0.36	0.57	3.40	0.38	3.02	0.63	0.01	0.07	3.59	0.13
	9	13.7	diaphragm	P-17Di	[Hg]$_{tot}$	1172	91					1.68	0.17	4.18	0.12	0.91	0.11	4.13	0.10	2.91	0.09	0.06	0.06	3.71	0.08
					[MMHg]	842	87	0.72	0.07	0.28	0.00	2.60	0.15	4.96	0.02	1.29	0.21	4.42	0.18	3.00	0.09	-0.01	0.14	3.77	0.14
					[iHg]	330	4					-0.83	0.17	2.13	0.19	-0.46	0.50	3.55	0.23	2.75	0.06	-0.04	0.41	3.76	0.28
	9	14.0	hair	P-17Ha	[Hg]$_{tot}$	2743	202					2.39	0.17	6.03	0.12	1.26	0.11	5.73	0.10	4.23	0.09	0.06	0.06	5.13	0.08
					[MMHg]	2212	123	0.81	0.04	0.19	0.03	2.45	0.63	6.81	0.54	1.24	0.41	6.56	0.02	4.97	0.07	0.01	0.10	5.94	0.14
					[iHg]	531	78					-0.35	0.17	0.58	0.17	-0.25	0.17	0.96	0.16	0.85	0.30	-0.07	0.08	1.05	0.21
International			liver	DOLT-4	[Hg]$_{tot}$	2685	85					-0.20	0.17	0.60	0.12	-0.07	0.11	0.84	0.10	0.76	0.09	0.03	0.06	0.90	0.08
standards				dogfish	[MMHg]	1253	44	0.47	0.02	0.53	0.02	0.18	0.38	1.02	0.22	0.08	0.18	0.91	0.12	0.88	0.07	-0.01	0.37	0.86	0.02
					[iHg]	1432	41					-0.89	0.82	-0.02	0.70	-0.54	0.50	0.72	0.32	0.65	0.09	-0.09	0.09	0.95	0.11
			muscle	CRM 464	[Hg]$_{tot}$	5321	228					0.83	0.17	2.22	0.12	0.48	0.11	2.17	0.10	1.60	0.09	0.06	0.06	1.96	0.08
				tuna fish	[MMHg]	5102	214	0.96	0.04	0.04	0.00	1.13	0.11	2.58	0.08	0.71	0.12	2.49	0.25	1.73	0.17	0.15	0.17	2.21	0.28
					[iHg]	219	15					-1.27	0.50	0.77	0.14	-0.55	0.38	1.66	0.21	1.72	0.24	0.09	0.13	1.98	0.09

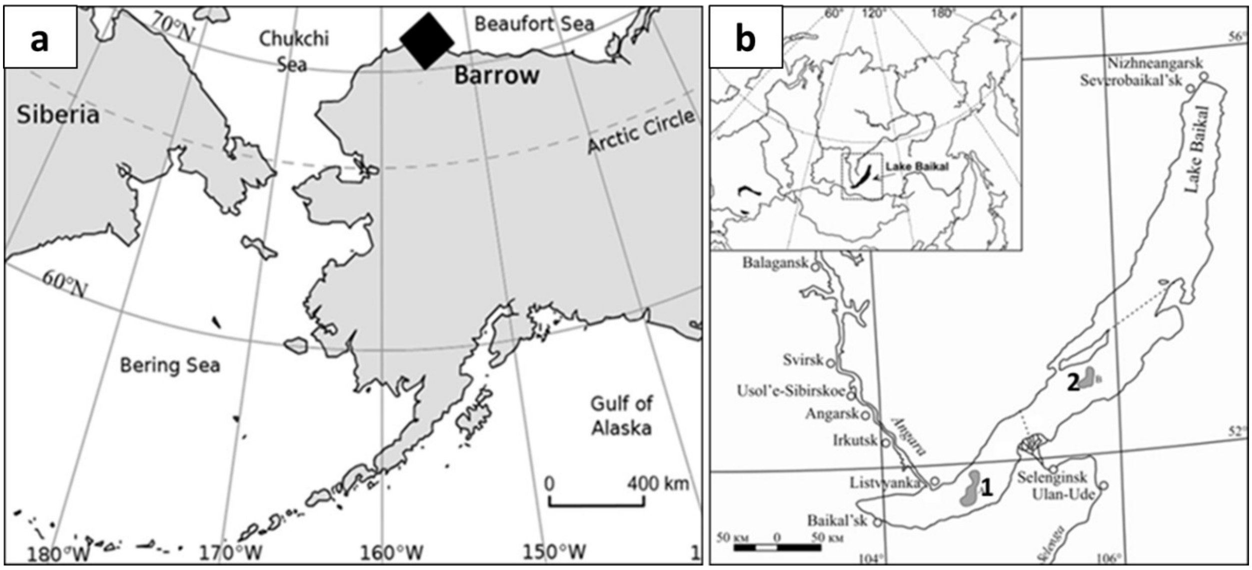

Figure S1. Localisation of the sampling sites for (a) belugas whales from Chukchi Sea and (b) seals from Lake Baikal (P-8, P-14, P-15, P-17 (sampling site 1) and P-10, P-12, P-16 (sampling site 2)).

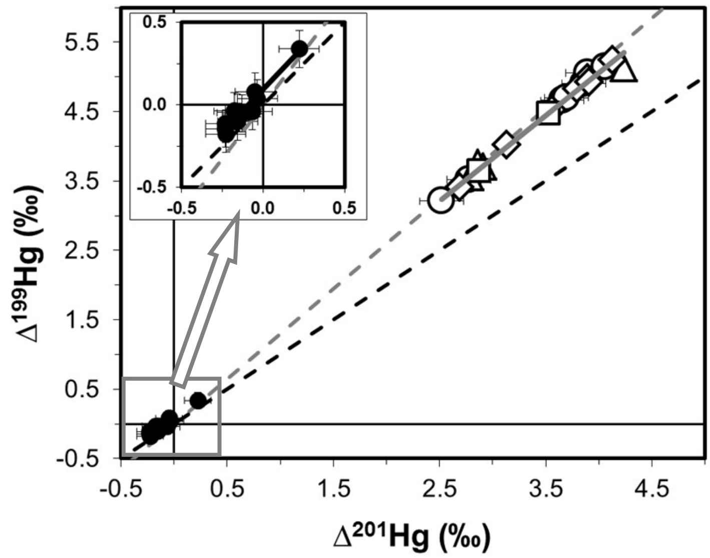

Figure S2. Δ^{199}Hg versus Δ^{201}Hg for total Hg in seal tissues (open symbols) and beluga livers (black circles). The grey dashed line represents the ratio Δ^{199}Hg:Δ^{201}Hg expected from photodemethylation of MMHg, and the black dashed line represents the ratio Δ^{199}Hg:Δ^{201}Hg expected from photoreduction of inorganic iHg[9]. All seal tissues are located on the "MMHg photodemethylation slope" (linear regression (*n*= 19, slope=1.23, R^2=0.99, p<0.0001), grey solid line). For beluga liver, the low MIF and associated uncertainties for each sample do not allow to conclude with confidence if samples lie either on the "iHg photoreduction slope" or the "MMHg photodemethylation slope".