Supplementary Information for:

Internal tree cycling and atmospheric archiving of mercury: examination with concentration and stable isotope analyses.

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S1 – Sampling images and additional information

Figure S1.1*: Images of sampling (a) Norwegian spruce (Picea abies) and (b)(c) European larch (Larix decidua, left) with an 5.15 mm diameter increment borer.*

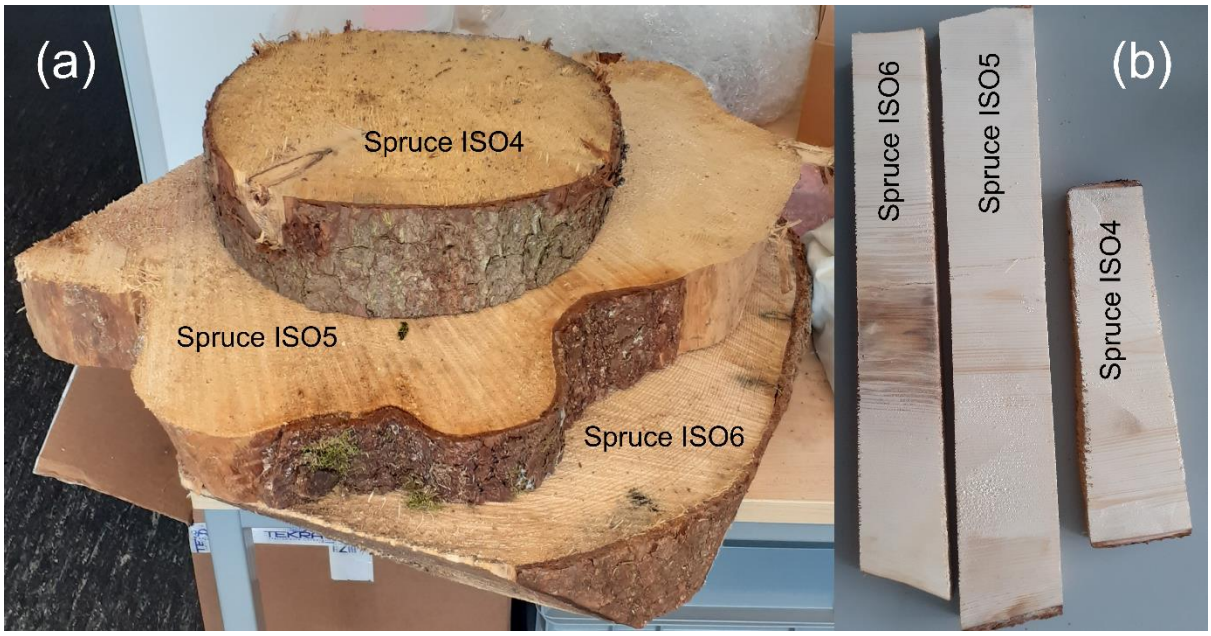

Figure S1.2*: (a) Tree "cookies" or slices from the Spruce ISO trees. These show the inhomogeneity in radial growth particularly in spruce ISO5. (b) Cuts made by the drop saw of the spruce ISO trees.*

Figure S1.3*: Breaking up of samples with chisel for final use. All exposed surfaces after drop saw cut were removed. Chisel and surface was cleaned (see below) between each sample.*

Cleaning of surfaces and equipment.

Sampling of tree cores at breast height. The borer was cleaned with Cintranox surfactant and then rinsed with Milli-Q water before transport to the field. Between uses it was rinsed with distilled water and isopropyl alcohol and wiped dry with Kimwipes. The same cleaning procedure was used for lab scalpel, chisel, and all surfaces used.

S2 – Passive air sampling method description and data

GEM concentrations were measured by *Mer*PAS® (Tekran Instruments) GEM passive air samplers (PASs). These samplers have been shown to measure GEM (Stupple et al., 2019; Szponar et al., 2020). The locations of the passive sampling sites are shown in Figure 1 of the main paper. The PASs were deployed ≈1 m above the ground from December 12th 2018 to April 1st 2019 (deployment time (DT): ≈110 days; see Table S2.1). The baseline sampling rate (SR) was adjusted for temperature (mean: 0.9°C ; Lenzkirch station; 47.8597 °N, 8.2308 °E; ≈6 km south of former industrial site; no wind speed measurements at this station) and wind speed (mean: 2.83 m s^{-1}; Freiburg im Breisgau weather station; 48.0033 °N, 7.8558 °E; ≈26 km west of industrial site) according to McLagan et al. (2017; 2018). This produced an adjusted SR of 0.125 m^3 day^{-1}. That was utilised to determine the GEM concentrations from the measured total Hg (THg) concentrations in the activated carbon of the PASs according to equation (*GEM conc. = m / [SR*DT]*; where *m* is the mass of THg on activated carbon; and *DT* is deployment time) is from McLagan et al. (2016). THg was measured in the activated carbon using a DMA80 according to methods listed in McLagan et al. (2016; 2017; 2018). These concentrations were blank corrected (McLagan et al., 2016; 2017; 2018) based on the mean THg concentration of the two field blanks (0.87 µg kg^{-1}). All data are shown in Table S2.1. SRM2685c (high sulphur content coal; NIST) was run throughout the analyses and recovery was 99 ± 6 % (*n* = 23).

Table S2.1*: Relevant data from GEM PAS deployments including final GEM concentrations.*

Sample Name	Blank adjusted Hg (ng)	THg Carbon Conc. (µg kg^{-1})	DT (days)	**GEM conc. (ng m^{-3})**	longitude	latitude
P1	36.9	66.7	109.99	**2.6**	8.187194	47.92221
P2	52.6	90.0	109.95	**3.7**	8.188121	47.92222
P3	33.8	61.4	109.96	**2.3**	8.188511	47.92257
P4	38.8	69.9	109.97	**2.7**	8.190560	47.92287
P5	46.8	92.2	109.90	**3.3**	8.191352	47.92271

S3 – Total Hg concentration of tree ring segments

***Table S3.1**: Concentration data for individual tree ring segments. For trees ISO4-6 the concentrations were measured in the traps for pre-concentration and calculated for the mass of wood combusted.*

Sample		THg [µg kg^{-1}]
Spruce 1	0-5	51.02
	5-10	27.21
	10-15	11.94
	15-20	12.39
	20-25	12.09
	25-30	6.90
	30-35	7.39
	35-40	11.17
	40-45	18.75
	45-50	27.70
	50-55	35.86
	55-60	38.02
	60-65	105.94
	65-67	286.18
	67-69	521.10
	69-71	194.53
	71-73	125.03
	73-75	95.75
	75-77	91.98
	77-79	63.82
	79-81	60.01
	81-83	52.35
	83-86	54.70
Spruce 2	0-5	21.92
	5-10	15.38
	10-15	11.51
	15-20	9.22
	20-25	12.68
	25-30	4.42
	30-35	27.18
	35-40	106.68
	40-42	72.80
	42-44	195.22
	44-46	211.95
	46-48	157.61
	48-50	118.91
	50-52	152.95
	52-54	175.13
	54-56	165.13
	56-58	92.83
Spruce 3	0-5	34.85
	5-10	5.09
	10-15	4.50
	15-20	3.27
	20-25	4.18
	25-30	4.91
	30-35	7.60
	35-40	11.19
	40-45	17.13
	45-49	16.61

Sample		THg [µg kg^{-1}]
Larch 1	0-5	36.93
	5-10	5.16
	10-15	4.56
	15-20	6.71
	20-25	7.84
	25-30	9.42
	30-35	16.19
	35-41	49.94
	40-42	63.02
Larch 2	0-5	8.13
	5-10	11.96
	10-15	2.33
	15-20	5.05
	20-25	5.67
	25-30	9.80
	30-35	11.75
	35-40	14.14
	40-45	16.21
	45-47	24.97
Larch 3	0-5	24.93
	5-10	8.14
	10-15	3.38
	15-20	6.38
	20-25	12.93
	25-28	12.29
Spruce BG	0-5	22.81
	5-10	17.51
	10-15	11.00
	15-20	3.69
	20-25	5.75
	25-30	6.45
	30-35	5.83
	35-40	7.25
	40-45	7.03
	45-50	5.95
	50-55	7.04
	55-60	14.97
	60-65	9.16
	65-70	7.30
	70-75	9.22
	75-80	7.16
	80-85	7.93
	85-90	6.99
	90-95	12.31
	95-97	9.30

"A" and "B" denote replicated combustions of same age segments from different sides of the tree cookies and "" marks replicates minor differences in age segments*

Sample		THg [µg kg^{-1}]
Spruce ISO4	Bulk Bark	71.92
	Outer Bark	155.77
	Inner Bark	57.72
	0-5 A	13.07
	0-5 B	2.59
	5-10 A	8.96
	5-10 B	3.03
	10-15 A	7.42
	10-15 B	3.41
	15-25	8.53
	25-35	10.84
	35-45	26.13
	45-55	36.85
	55-60	44.10
	60-66	41.36
	66-70	48.18
Spruce ISO5	Outer Bark	326.15
	Inner Bark	163.05
	0-5	14.87
	5-10 A	5.84
	5-10 B	4.69
	10-15 A	5.28
	10-15 B	2.51
	15-35	8.53
	35-45 A	23.30
	35-45 B	7.88
	45-55	56.33
	55-60	24.72
	60-65	20.81
	65-70	27.22
	70-75	32.07
	75-80	47.23
	80-90	37.20
	90-100	48.66
Spruce ISO6	Bulk Bark	47.08
	0-5 A	2.36
	0-5 B	7.81
	5-10 A*	1.09
	5-15 B*	1.59
	10-15	0.89
	15-25 A	0.94
	15-25 B	1.45
	25-35 A	1.16
	25-35 B	3.19
	35-45	2.93
	45-55	16.18
	55-60	25.30
	60-65	32.70
	65-70	34.64
	70-75	40.87
	75-80	47.59
	80-90	82.25
	90-100	55.89
	100-109	65.83

S4 - Mercury stable isotope data and quality control/assurance

For the measurement of traps from pre-concentration the AFS/AAS (DMA-80L, Milestone Instruments) was calibrated on a daily basis with NIST-3133 to assure the accuracy of results. Throughout all measurement sessions, a calibration standard was measured repeatedly to assess instrument drift and recoveries were 98 ± 5 %. All used chemicals were ACS or European Pharmacopoeia (Ph. Eur.) grade. Chemicals used for the preparation of BrCl solution (KBr and $KBrO_3$) were heated in a muffle furnace at 220 °C for 8h before use and the $SnCl_2$ reagent solution used to reduce Hg on the online cold vapor system was purged with N_2 to remove potential trace Hg contamination. v/v HNO_3) and subsequently rinsed with ultra-pure water before use. The limit of detection (LoD) and limit of quantification (LoQ) were determined based on the standard error (σ) and slope (S) of the calibration curve of the AFS detection cell (used for the lower concentration range). Over all sessions the LoD was 0.04 ± 0.03 ng Hg and the LoQ 0.11 ± 0.09 ng Hg. Note that the LoD and LoQ are reported in absolute amounts (ng of Hg) instead of concentrations because the sample uptake volume can be adjusted according to the sample concentration. All traps had a concentration far above the LoQ (> 10 ng ml^{-1}) in order to achieve a sufficiently high signal intensity after diluting traps to an acid strength of < 10 % (v/v) for isotope analysis on the MC-ICP-MS.

Table S4.1*: Isotope data of individual tree samples. Samples marked with "A" and "B" were pre-concentrated in separate runs from different sides of tree cookies, "*" marks replicates with minor differences in age segments. Bulk bark is sampled from the same side as replicates A, outer and inner bark from the same side as replicates B.*

Sample		**δ^{202}Hg**		**Δ^{199}Hg**		**Δ^{200}Hg**		**Δ^{201}Hg**		**Δ^{204}Hg**	
		[‰]	**2SD [‰]**	**[‰]**	**2SD [‰]**	**[‰]**	**2SD [‰]**	**[‰]**	**2SD [‰]**	**[‰]**	**2SD [‰]**
Spruce ISO4	Bulk Bark	-3.88	0.10	-0.25	0.07	-0.06	0.04	-0.21	0.11	0.07	0.12
	Outer Bark	-3.70	0.07	-0.19	0.05	0.03	0.06	-0.05	0.04	0.12	0.06
	Inner Bark	-3.62	0.07	-0.13	0.05	-0.06	0.06	-0.10	0.04	-0.03	0.06
	0-15 A	-1.75	0.07	-0.07	0.05	0.01	0.06	-0.08	0.04	-0.03	0.06
	0-15 B	-1.70	0.07	-0.15	0.05	-0.07	0.06	-0.21	0.04	0.10	0.06
	15-25	-2.84	0.04	-0.12	0.05	-0.07	0.04	-0.15	0.05	0.06	0.10
	25-35	-3.75	0.04	-0.11	0.05	-0.01	0.04	-0.13	0.05	0.01	0.10
	35-45	-3.76	0.04	-0.03	0.05	0.03	0.04	-0.08	0.05	0.00	0.10
	45-55	-4.13	0.10	-0.10	0.07	-0.03	0.04	-0.17	0.11	0.02	0.12

Sample		δ^{202}Hg		Δ^{199}Hg		Δ^{200}Hg		Δ^{201}Hg		Δ^{204}Hg	
		[‰]	2SD [‰]	[‰]	2SD [‰]	[‰]	2SD [‰]	[‰]	2SD [‰]	[‰]	2SD [‰]
	55-60	-3.72	0.04	-0.08	0.05	-0.02	0.04	-0.11	0.05	-0.06	0.10
	60-65	-4.23	0.10	-0.05	0.07	-0.05	0.04	-0.10	0.11	0.04	0.12
	65-70	-4.24	0.10	-0.04	0.07	-0.04	0.04	-0.11	0.11	0.00	0.12
Spruce ISO5	Outer Bark	-4.21	0.07	-0.12	0.05	-0.04	0.06	-0.13	0.04	-0.09	0.06
	Inner Bark	-4.19	0.07	-0.10	0.05	-0.01	0.06	-0.05	0.04	-0.11	0.06
	0-5	-3.20	0.04	-0.17	0.05	-0.02	0.04	-0.20	0.05	0.06	0.10
	5-15 A	-2.89	0.07	-0.15	0.05	-0.02	0.06	-0.10	0.04	0.06	0.06
	5-15 B	-2.68	0.07	-0.09	0.05	-0.05	0.06	-0.18	0.04	0.04	0.06
	15-35	-4.04	0.04	-0.12	0.05	-0.06	0.04	-0.11	0.05	0.06	0.10
	35-45 A	-3.70	0.04	0.00	0.05	0.05	0.04	0.04	0.05	-0.01	0.10
	35-45 B	-3.84	0.07	-0.11	0.05	-0.02	0.06	-0.01	0.04	0.04	0.06
	45-55	-4.36	0.10	-0.06	0.07	-0.05	0.04	-0.06	0.11	0.06	0.12
	55-60	-4.37	0.04	-0.05	0.05	-0.05	0.04	-0.05	0.05	-0.03	0.10
Spruce ISO5 (cont.)	60-65	-4.36	0.04	0.00	0.05	0.00	0.04	0.03	0.05	0.06	0.10
	65-70	-4.30	0.10	-0.02	0.07	-0.01	0.04	-0.04	0.11	0.01	0.12
	70-75	-4.20	0.04	0.01	0.05	0.03	0.04	0.03	0.05	0.03	0.10
	75-80	-4.13	0.04	0.03	0.05	0.00	0.04	0.03	0.05	0.01	0.10
	80-90	-4.29	0.04	0.08	0.05	0.00	0.04	0.03	0.05	0.09	0.10
	90-100	-4.60	0.10	0.01	0.07	-0.02	0.04	-0.02	0.11	0.00	0.12
Spruce ISO6	Bulk Bark	-3.81	0.10	-0.15	0.07	-0.03	0.04	-0.16	0.11	-0.44	0.12
	0-5	-3.41	0.07	-0.14	0.05	-0.02	0.06	-0.12	0.04	0.08	0.06
	0-40 A*	-3.08	0.07	-0.10	0.05	-0.01	0.06	-0.14	0.04	0.05	0.06
	0-45 B*	-3.10	0.07	-0.17	0.05	-0.03	0.06	-0.10	0.04	0.09	0.06
	45-55	-4.50	0.04	-0.11	0.05	0.00	0.04	-0.14	0.05	0.17	0.10
	55-60	-4.08	0.07	-0.04	0.05	0.02	0.06	-0.03	0.04	-0.01	0.06
	60-65	-4.30	0.07	-0.01	0.05	-0.01	0.06	-0.02	0.04	-0.02	0.06
	65-70	-4.12	0.07	0.00	0.05	-0.01	0.06	-0.04	0.04	-0.08	0.06
	70-75	-4.17	0.07	0.00	0.05	0.03	0.06	0.07	0.04	-0.11	0.06
	75-80	-4.39	0.07	-0.01	0.05	0.03	0.06	0.00	0.04	0.03	0.06
	80-90	-4.42	0.10	-0.01	0.07	-0.07	0.04	-0.07	0.11	0.00	0.12
	90-100	-4.49	0.10	0.04	0.07	0.03	0.04	0.03	0.11	-0.02	0.12
	100-107	-4.60	0.10	0.02	0.07	-0.02	0.04	0.04	0.11	-0.09	0.12

***Table S4.2**: Session averages and 2SD values of repeated measurements of secondary standard "ETH Fluka".*

Session Date	Hg conc. [µg L^{-1}]	n	$\delta^{202}Hg$		$\Delta^{199}Hg$		$\Delta^{200}Hg$		$\Delta^{201}Hg$		$\Delta^{202}Hg$	
			Average [‰]	2SD [‰]	Average [‰]	2SD [‰]	Average [‰]	2SD [‰]	Average [‰]	2SD [‰]	Average [‰]	2SD [‰]
25.02.2021	5	6	-1.49	0.10	0.08	0.07	0.02	0.04	0.00	0.11	0.02	0.12
29.04.2021	2.5	4	-1.41	0.04	0.08	0.05	0.03	0.04	0.02	0.05	-0.01	0.10
05.05.2021	2.5	5	-1.44	0.07	0.06	0.05	0.01	0.06	0.04	0.04	0.01	0.06
Overall	2.5 - 5	15	-1.45	0.10	0.07	0.06	0.02	0.04	0.02	0.08	0.01	0.10

The efficiency of the pre-enrichment setup using combustion and trapping on a DMA-80 Hg analyser has been tested using a liquid and two solid QC standards. The Hg recoveries the traps were 103 ± 12 % for BCR-482 (n =13); 95 ± 4 % for CC-141 (n = 16) and 102 ± 4 % for NIST-3133 (n = 12) as reported in McLagan et al 2022.

Mass dependent fractionation (MDF) is reported as the deviation from the isotopic composition of the standard reference NIST-3133 using delta notation and expressed in per mil (‰):

$$\delta^{xxx}Hg\ (‰) = \left(\frac{\frac{^{xxx}Hg}{^{198}Hg}\ sample}{\frac{^{xxx}Hg}{^{198}Hg}\ NIST-3133} - 1 \right)$$

Mass independent fractionation (MIF) is the deviation of the measured δ-values from the expected fractionation determined from measured $\delta^{202}Hg$ and the kinetic MDF law derived from transition state theory. MIF values are represented by capital delta notation (Blum & Bergquist, 2007):

$\Delta^{199}Hg = \delta^{199}Hg - (\delta^{202}Hg \times 0.2520)$

$\Delta^{200}Hg = \delta^{200}Hg - (\delta^{202}Hg \times 0.5024)$

$\Delta^{201}Hg = \delta^{201}Hg - (\delta^{202}Hg \times 0.7520)$

$\Delta^{204}Hg = \delta^{204}Hg - (\delta^{202}Hg \times 1.4930)$

S5 – Combining traps for tree samples with low THg concentration

For several tree samples from the background period the Hg concentration in traps was too low for isotope analysis after the combustion and trapping. Traps of these samples were pooled using a purge and trap setup. Individual traps were added to a gas washing bottle and filled to 500 ml with ultra-pure water (18.2 MΩ cm). Reduction of Hg to Hg(0) was initiated by adding 1 ml of 30 % (w/v) hydroxylamine to neutralize BrCl followed by the addition of 5 ml of 20 % (w/v) tin chloride ($SnCl_2$) dissolved in 1M HCl. The gas washing bottle was purged with nitrogen for 120 minutes to transfer all Hg(0) to a 5 ml inverse aqua regia trap with HCl replaced by BrCl.

Table S5.1*: Sample list of the individual traps that were combined for isotope analysis.*

Individual traps		Combined traps	Individual traps		Combined traps
Tree ISO4 0-5 A Tree ISO4 5-10 A Tree ISO4 10-15 A	→	Tree ISO4 0-15 A	Tree ISO4 0-5 B Tree ISO4 5-10 B Tree ISO4 10-15 B	→	Tree ISO4 0-15 B
Tree ISO5 5-10 A Tree ISO5 10-15 A	→	Tree ISO5 5-15 A	Tree ISO5 5-10 B Tree ISO5 10-15 B	→	Tree ISO5 5-15 B
Tree ISO6 0-5 A Tree ISO6 5-10 A Tree ISO6 10-15 A Tree ISO6 15-25 A Tree ISO6 25-35 A Tree ISO6 35-45 A	→	Tree ISO6 0-45	Tree ISO6 5-15 B Tree ISO4 0-5 B Tree ISO4 5-10 B Tree ISO4 10-15 B	→	Tree ISO6 5-35

For quality assurance the setup was tested using 0.25 µg L^{-1} (n=3) and 0.5 µg L^{-1} (n=2) NIST-3133 solutions and sampling in regular time intervals to determine the time required for complete removal of Hg from the gas washing bottles. The average Hg recovery in the traps was 100.9 ± 6.2 %.

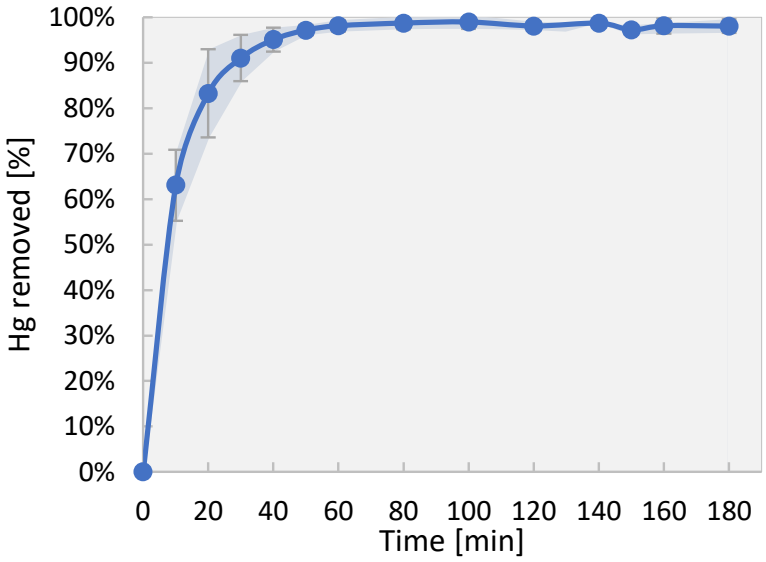

Figure S5.1*: Percentage of Hg removed from the gas washing bottle during the purge and trap method using a dilute NIST-3133 solution.*

S6 – MDF and MIF data for individual trees and relationship with THg

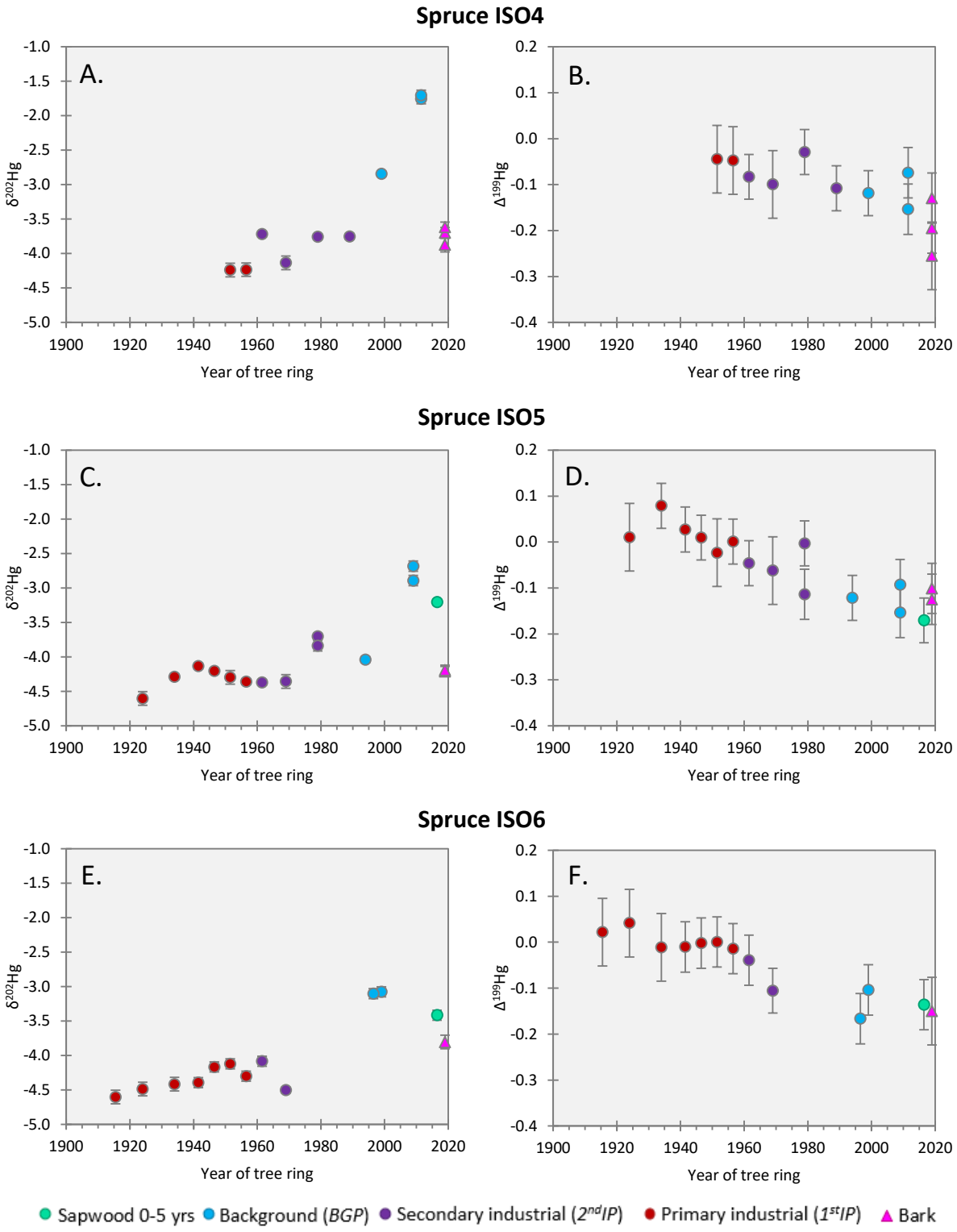

Figure S6.1: δ^{202}Hg (Panel A, C, E) and Δ^{199}Hg (Panel B, D, F) in tree rings dated by year for samples from individual spruce trees (ISO4-6).

S7 –Relationship between THg and MDF and between THg and MIF

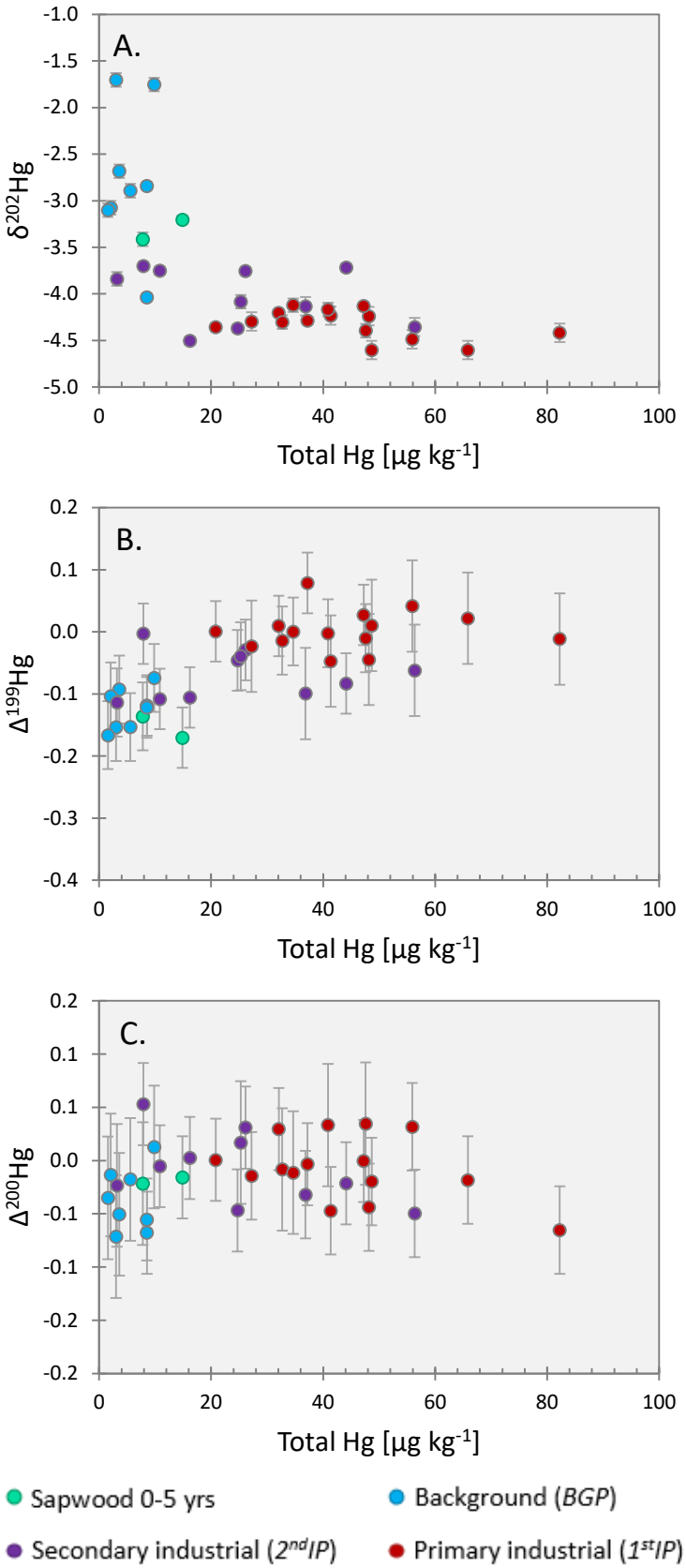

***Figure S7.1**: Relationships between THg samples and $\delta^{202}Hg$ (Panel A), $\Delta^{199}Hg$ (Panel B) and $\Delta^{200}Hg$ (Panel C).*

S8 – Odd and Even mass number MIF

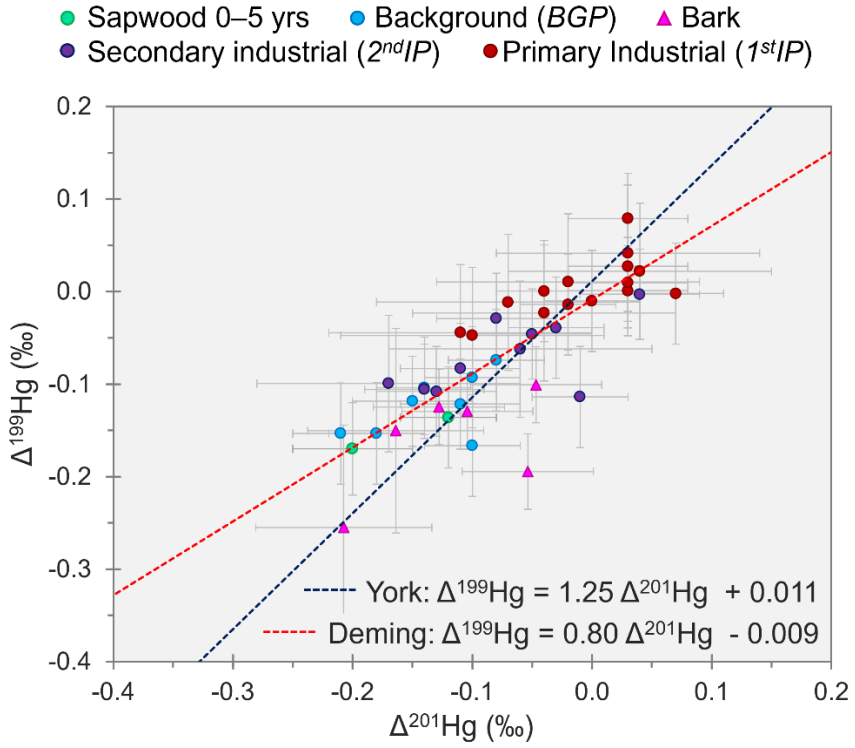

***Figure S8.1**: Relationship between $\Delta^{200}Hg$ and $\Delta^{204}Hg$ (even mass number MIF) for bole wood and bark samples from spruce ISO4-6 trees.*

There was a single $\Delta^{204}Hg$ data outlier, the bulk bark sample from spruce ISO6 (Figure S8.2 below). The analysis of this sample was scrutinised in detail, but no analytical artefacts were detected. We cannot postulate an explanation for why this single $\Delta^{204}Hg$ value so different to all other samples (bark or bole wood).

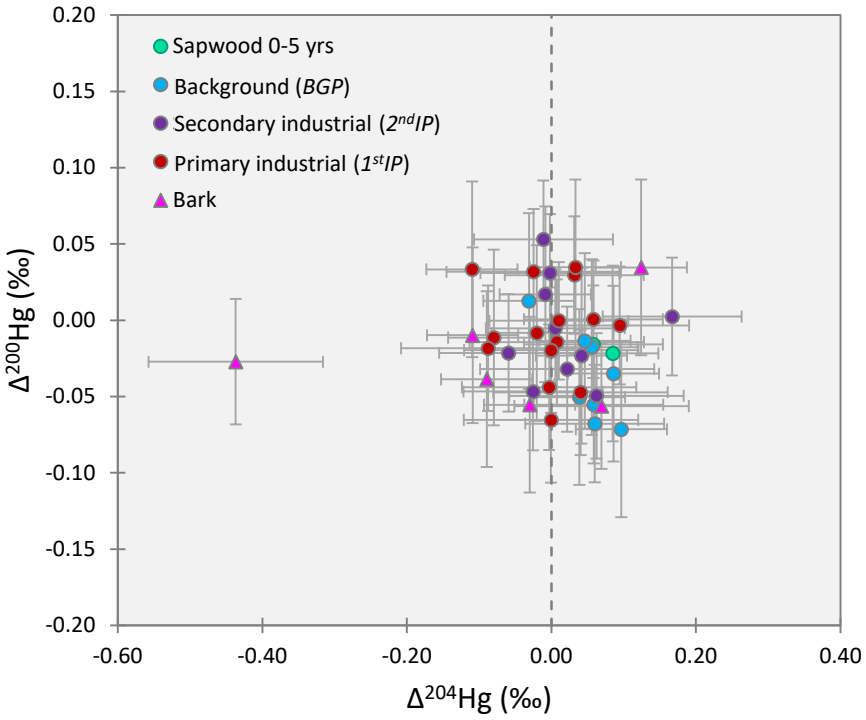

***Figure S8.2**: Relationship between Δ^{200}Hg and Δ^{204}Hg (even mass number MIF) for bole wood and bark samples from spruce ISO4-6 trees.*

References

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