Electronic Supplementary Information (ESI)
to

Source tracing of natural organic matter bound mercury in boreal forest runoff with mercury stable isotopes

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Figure S1: Map of water sampling sites. The different water sampling locations are indicated at the lower panel. The four boreal forest catchments (reference site 1 and 2 in green and clear-cut site 1 and 2 in red) drain in the same Lillsele stream.

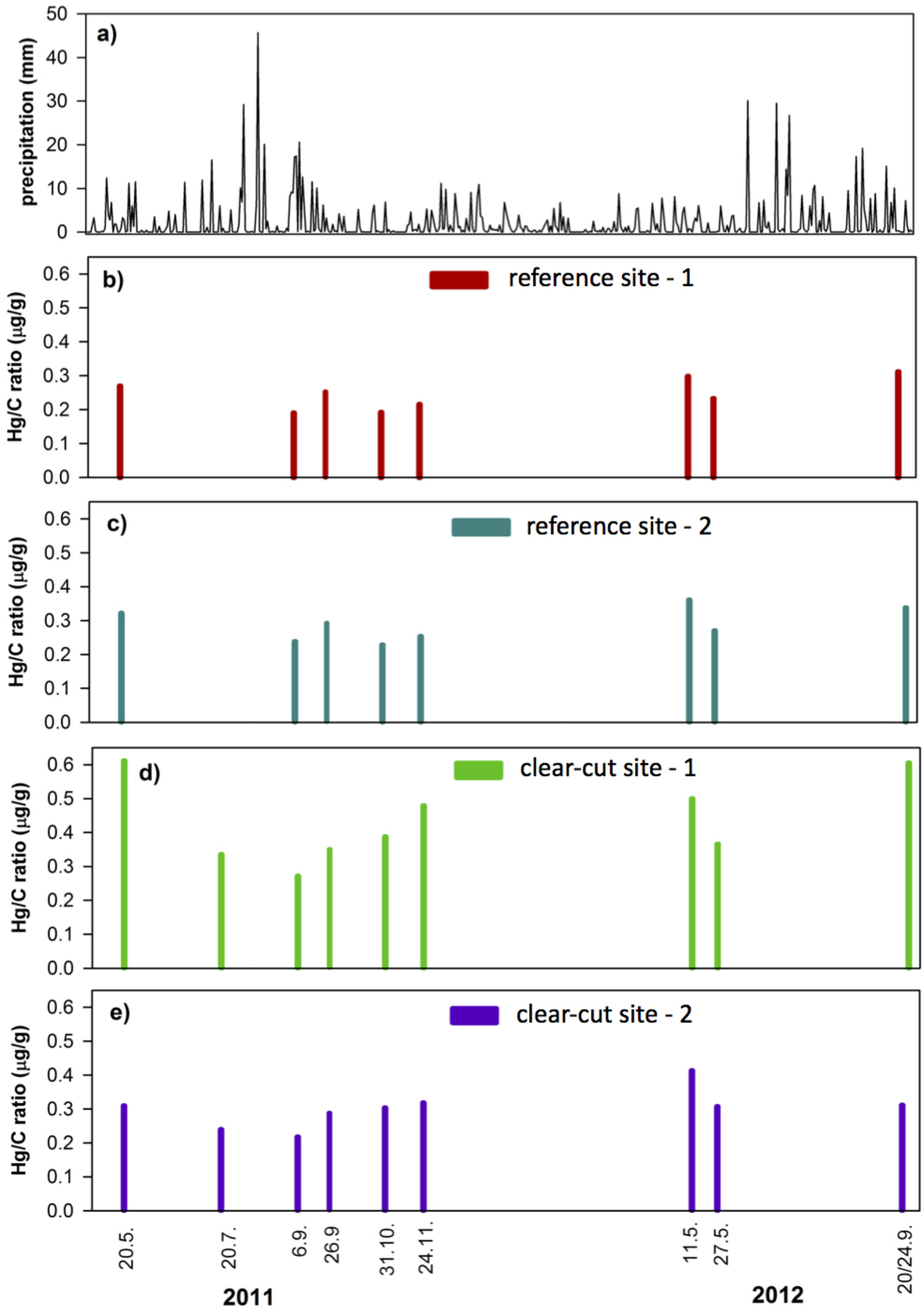

Figure S2: **a**) Precipitation at Junsele SMHI over whole sampling campaign from Mai 2011 to September 2012 (Data from Swedish Meterological Institute, SMHI). Hg/C ratios of the four sites: **b**) reference site - 1, **c**) reference site - 2, **d**) clear-cut site 1, and **d**) clear-cut site 2. (Data from Kronberg [1], [2]).

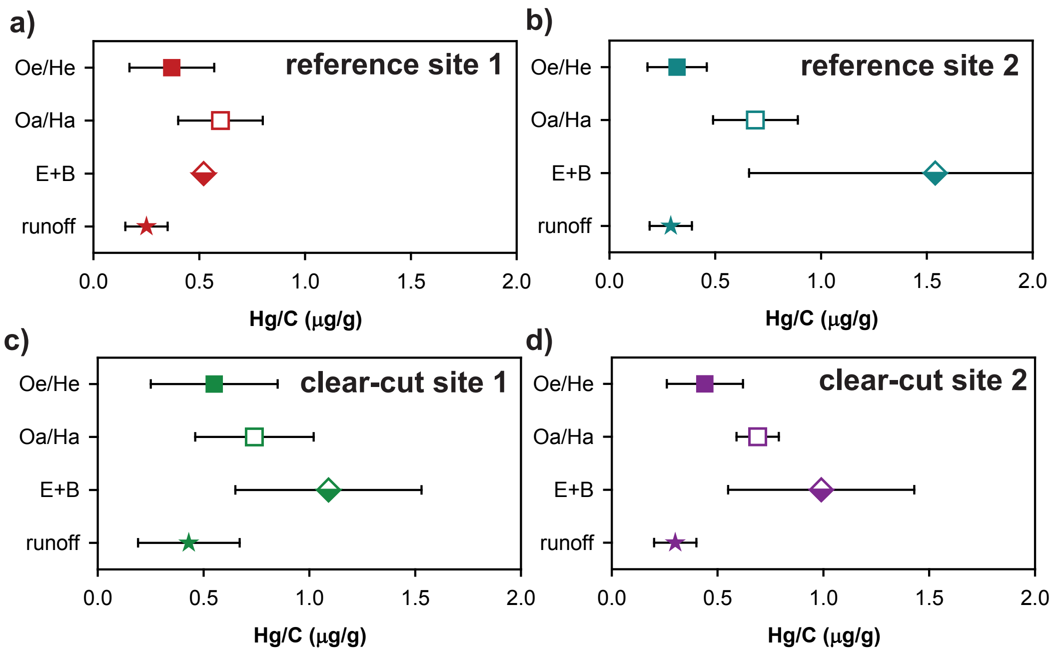

Figure S3: Hg/C ratios of boreal forest sites: The symbols represent the average and the error bars 2 standard deviation of the measured values.

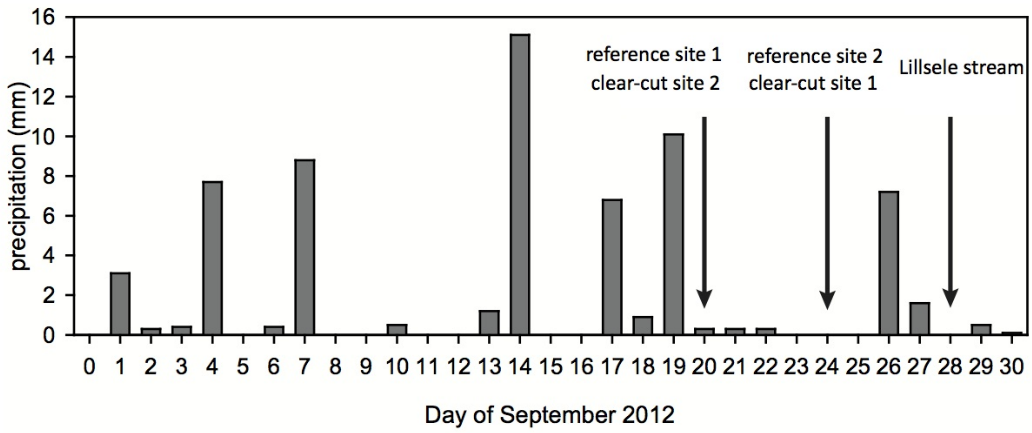

Figure S4: Precipitation at Junsele SMHI station during September 2012 (Data from Swedish Meterological Institute, SMHI). The arrows indicate the days of sampling.

Radiocarbon dating

In addition to the radiocarbon dating of the bulk soil samples we performed humic acid extractions of a selection of samples. We followed an extraction procedure for the humic acid fraction adapted from the International Humic Substances Society (IHSS)[3]. 10 g of soil sample was added to 100 ml 0.1 M HCl and shaken on a horizontal shaker for 1h. Then pH was adjusted to 7 with 1 M NaOH and 0.1 M NaOH was added to reach a solid to solution ratio of 1:10. The soil samples were shaken for 4.5 h followed by sedimentation over night under N_2 atmosphere. The samples were centrifuged at 1000 rpm for 12 min and the humic acid extract decanted. The humic acid extract was then freeze-dried for radiocarbon analysis.

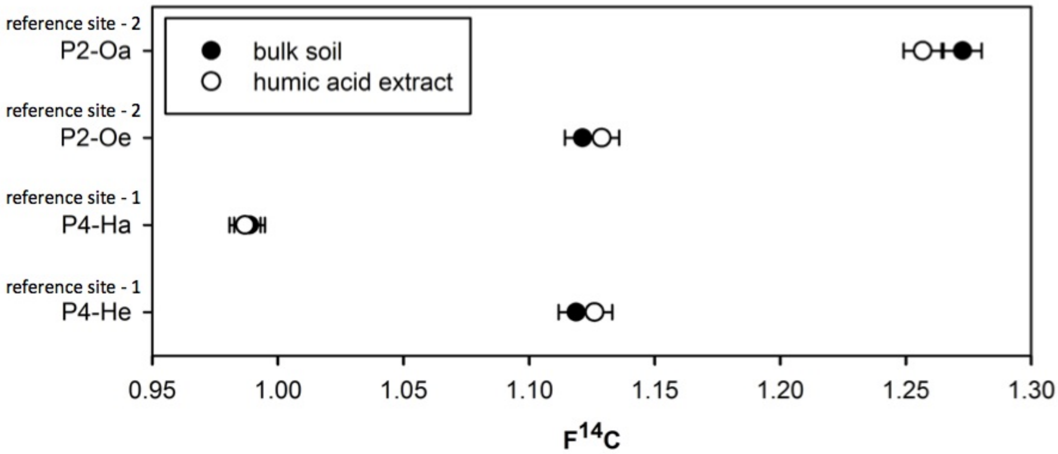

Figure S5: Comparison of radiocarbon signatures from bulk soils and humic acid extracts: The error bars represent two standard deviations of the analytical precision.

Table S1: Concentration data of soil samples from clear-cut sites: Horizon thickness, total Hg concentration (Hg tot), carbon (C) and nitrogen (N) concentration (% weight), C/N ratio, Hg/C ratio, Si concentration, distance from first-order stream (distance), and height of groundwater table (GWT) below surface during the soil sampling campaign in 2011. Distance and GWT are reproduced from Kronberg et al. [1][2].

Sample	horizon (cm)	Hg tot (ng g^{-1})	C (%)	N (%)	C/N (g g^{-1})	Hg/C (μg g^{-1})	Si (mg g^{-1})	distance (m)	GWT (cm)
clear-cut site - 1									
P1-He	4	378	39.9	1.7	26.6	0.95	24	1	0
P2-He	4	164	43.6	1.3	38.4	0.38	9	12	6
P3-Oe	8	107	43.0	0.9	56.7	0.25	6	24	34
P4-Oe	5	143	37.6	1.1	39.4	0.38	19	51	25
P5-Oe	9	312	40.3	1.3	36.0	0.77	18	72	>50
P1-Ha	23	340	32.3	1.3	28.3	1.05	48	1	0
P2-Ha	30	262	29.2	1.3	26.6	0.90	77	12	6
P3-Oa	4	216	45.7	1.1	49.4	0.47	7	24	34
P4-Oa	8	182	33.1	1.4	27.0	0.55	40	51	25
P5-E	3	18	1.9	<0.1	104.9	0.93	262	72	>50
P5-B	nd	60	4.8	0.1	51.3	1.25	178	72	>50
clear-cut site - 2									
P1-He	7	235	42.9	1.6	31.4	0.55	11	1	34
P2-He	6	246	50.1	1.5	40.1	0.49	8	6	29
P3-He	5	176	46.2	1.3	42.0	0.38	6	10	12
P4-He	7	137	43.7	1.3	39.5	0.31	5	22	10
P5-Oe	4	199	41.8	1.3	37.2	0.48	12	13	>40
P1-Ha	30	220	31.3	1.6	22.2	0.70	34	1	34
P2-Ha	25	278	40.3	1.8	25.9	0.69	19	6	29
P3-Ha	35	260	38.0	1.8	24.6	0.69	18	10	12
P4-Ha	24	213	34.2	1.8	22.5	0.62	29	22	10
P5-Oa	3	273	36.4	1.0	41.8	0.75	22	13	>40
P5-E	7	11	0.8	<0.1	nd	1.26	271	13	>40
P5-B	nd	15	2.0	<0.1	nd	0.72	211	13	>40

nd = not determined

Table S2: Concentration data of soil samples from reference sites: Horizon thickness, total Hg concentration (Hg tot), carbon (C) and nitrogen (N) concentration (% weight), C/N ratio, Hg/C ratio, Si concentration, distance from first-order stream (distance), and height of groundwater table (GWT) below surface during the soil sampling campaign in 2011. The concentration data are reproduced from Jiskra et al. [4] and distance and GWT are reproduced from Kronberg et al.[1], [2].

Sample	horizon (cm)	Hg tot (ng g^{-1})	C (%)	N (%)	C/N (g g^{-1})	Hg/C (μg g^{-1})	Si (μg g^{-1})	Distance (m)	GWT (cm)
reference site - 1									
P1-He	5	180	39	1.90	20.5	465	3428	1	80
P2-He	10	209	45	1.92	23.5	464	3861	5	38
P3-He	8	171	43	1.74	24.7	397	3335	12	38
P4-He	10	131	52	1.59	32.7	252	2639	21	12
P5-Oe	5	121	43	1.00	42.4	284	5582	29	>50
P1-Ha	68	255	44	1.92	22.9	578	26720	1	80
P2-Ha	68	307	41	1.82	22.7	744	30020	5	38
P3-Ha	40	225	43	2.21	19.4	526	14750	13	38
P4-Ha	45	240	43	2.21	19.4	561	7662	21	12
reference site - 2									
P1-Oe	10	91	40	0.53	75.9	229	4539	1	44
P2-Oe	10	160	51	1.01	51.0	311	9977	6	>40
P3-Oe	6	163	39	1.03	38.4	414	12210	14	>40
P4-Oe	4	147	45	1.01	44.1	329	11100	29	>40
P5-Oe	6	155	47	1.03	45.5	332	7340	34	>40
P1-Oa	2	188	29	0.65	44.5	646	74810	1	>40
P2-Oa	2	258	45	0.84	53.5	577	19680	6	>40
P3-Oa	2	313	38	0.91	42.3	815	16740	14	>40
P4-Oa	2	299	39	0.97	39.7	773	21020	29	>40
P5-Oa	2	247	40	0.94	42.8	616	41040	34	>40

nd = not determined

Table S3: Hg isotope data of soil samples reproduced from Jiskra et al.[4].

Samplename	name ref[4]	δ^{202}Hg (‰)	δ^{201}Hg (‰)	δ^{200}Hg (‰)	δ^{199}Hg (‰)	δ^{204}Hg (‰)	Δ^{199}Hg (‰)	Δ^{200}Hg (‰)	Δ^{201}Hg (‰)	Δ^{204}Hg (‰)	$F^{14}C$
reference site - 1											
P1-He	Histosol-He-1	-1.92	-1.84	-1.03	-0.85	-2.87	-0.37	-0.06	-0.40	-0.01	1.109
P2-He	Histosol-He-2	-2.03	-1.86	-1.07	-0.87	-3.08	-0.36	-0.05	-0.34	-0.05	1.130
P3-He	Histosol-He-3	-2.06	-1.87	-1.07	-0.86	-3.08	-0.34	-0.03	-0.32	0.00	
P4-He	Histosol-He-4	-2.04	-1.85	-1.03	-0.81	-2.97	-0.30	-0.01	-0.31	0.08	1.119
P5-Oe	Podzol-Oe-1	-2.21	-1.97	-1.08	-0.88	-3.28	-0.32	0.03	-0.31	0.01	
P1-Ha	Histosol-Ha-1	-1.55	-1.53	-0.81	-0.82	-2.23	-0.43	-0.03	-0.36	0.09	0.878
P2-Ha	Histosol-Ha-2	-1.75	-1.69	-0.93	-0.85	-2.55	-0.41	-0.05	-0.37	0.06	0.991
P3-Ha	Histosol-Ha-3	-1.64	-1.68	-0.87	-0.86	-2.41	-0.45	-0.05	-0.44	0.04	
P4-Ha	Histosol-Ha-4	-1.73	-1.68	-0.88	-0.86	-2.48	-0.43	-0.01	-0.39	0.10	0.989
P5-E	Podzol-E-1	-1.80	-1.62	-0.93	-0.70	-2.70	-0.24	-0.03	-0.26	-0.01	1.015
reference site - 2											
P1-Oe	Podzol-Oe-2	-2.56	-2.35	-1.33	-1.08	-3.79	-0.44	-0.04	-0.42	0.04	1.107
P2-Oe	Podzol-Oe-3	-2.49	-2.27	-1.24	-1.03	-3.71	-0.40	0.01	-0.40	0.01	1.121
P3-Oe	Podzol-Oe-4	-2.25	-2.08	-1.13	-0.96	-3.39	-0.39	0.00	-0.39	-0.03	1.115
P4-Oe	Podzol-Oe-5	-2.35	-2.18	-1.22	-1.02	-3.53	-0.43	-0.04	-0.41	-0.02	
P5-Oe	Podzol-Oe-6	-2.37	-2.22	-1.16	-1.98	-3.72	-0.48	-0.01	-0.43	-0.02	1.132
P1-Oa	Podzol-Oa-1	-1.93	-1.78	-0.96	-0.81	-2.93	-0.32	0.02	-0.33	-0.05	1.171
P2-Oa	Podzol-Oa-2	-2.08	-1.88	-1.05	-0.84	-3.07	-0.32	0.00	-0.31	0.04	1.273
P3-Oa	Podzol-Oa-3	-2.02	-1.88	-1.00	-0.83	-3.00	-0.32	0.02	-0.36	0.02	
P4-Oa	Podzol-Oa-4	-2.16	-1.91	-1.09	-0.86	-3.23	-0.32	-0.01	-0.29	-0.02	1.178
P5-Oa	Podzol-Oa-5	-2.01	-1.88	-1.00	-0.83	-3.03	-0.32	0.01	-0.37	-0.03	1.184
P5-E	Podzol-E-2	-2.15	-1.90	-1.11	-0.85	-3.27	-0.31	-0.03	-0.29	-0.06	1.004
P5-B	Podzol-B-1	-2.06	-1.88	-1.07	-0.87	-3.08	-0.35	-0.03	-0.33	-0.01	1.097

Mixing model

To model the endmembers of the different soil horizons we used the average and variance of the measured results. The results of the Hg isotope signatures, radiocarbon signatures and Hg/C ratios are provided in Table S4. For soil horizons with only one measurement we used the standard deviation of the analytical precision to estimate the variance on the soil horizon. For the Hg isotope mixing a two-dimensional model combining MDF (δ^{202}Hg) and MIF (Δ^{199}) signatures was used as follows:

$$\delta^{202}\mathrm{Hg}_{\mathrm{mixed}} = f_{\mathrm{Oe/He}} \times \delta^{202}\mathrm{Hg}_{\mathrm{Oe/He}} + f_{\mathrm{Oa/Ha}} \times \delta^{202}\mathrm{Hg}_{\mathrm{Oa/Ha}} + f_{\mathrm{E+B}} \times \delta^{202}\mathrm{Hg}_{\mathrm{E+B}} \tag{1}$$

$$\Delta^{199}\mathrm{Hg}_{\mathrm{mixed}} = f_{\mathrm{Oe/He}} \times \Delta^{199}\mathrm{Hg}_{\mathrm{Oe/He}} + f_{\mathrm{Oa/Ha}} \times \Delta^{199}\mathrm{Hg}_{\mathrm{Oa/Ha}} + f_{\mathrm{E+B}} \times \Delta^{199}\mathrm{Hg}_{\mathrm{E+B}} \tag{2}$$

where $f_{\mathrm{Oe/He}}$, $f_{\mathrm{Oa/Ha}}$, and $f_{\mathrm{E+B}}$ correspond to the fraction of Hg or C from the Oe/He, Oa/Ha, and E+B horizon, respectively. The fractions of the different soil horizons were simulated using the linear distributed pseudorandom number generation function and the tracer signatures were simulated using the normal distributed pseudorandom number generation function of Matlab (R2012a, MathWorks). The results from the model simulations were compared to the measured values in the runoff and the average and standard deviation (σ) of model simulations in agreement with the measured values are reported. Based on the fact that the Hg isotope signatures of the Oa/Ha horizons and the E + B horizons are statistically not significantly different, the fraction of the Oa/Ha horizons and the E + B horizons are summed up and reported in the manuscript as fraction Oa/Ha + E + B.

Table S4: Compilation of Hg isotope signatures, radiocarbon signatures and Hg/C ratios of different soil horizons and boreal forest catchment runoff. The average and standard deviation of the measured Hg isotope data were used to describe the source components in the mixing models.

Site	δ^{202}**Hg**			Δ^{199}**Hg**			**F^{14}C**			**Hg/C**		
	n	average (‰)	σ (‰)	n	average (‰)	σ (‰)	n	average	σ	n	average (μg g^{-1})	σ (μg g^{-1})
reference site - 1												
Oe/He	5	-2.05	0.10	5	-0.34	0.03	3	1.12	0.01	5	0.37	0.10
Oa/Ha	4	-1.67	0.09	4	-0.43	0.02	3	0.95	0.06	4	0.60	0.10
E	1	-1.80		1	-0.24		1	1.02		1	0.52	
runoff	1	-1.99		1	-0.33		1	1.10		8	0.25	0.05
reference site - 2												
Oe	5	-2.41	0.12	5	-0.43	0.04	4	1.12	0.01	5	0.32	0.07
Oa	5	-2.04	0.08	5	-0.32	0.00	4	1.20	0.05	5	0.69	0.10
E/B	2	-2.10	0.06	2	-0.33	0.03	2	1.05	0.07	2	1.56	0.44
runoff	1	-2.29		1	-0.38		1	1.11		8	0.29	0.05
clear-cut site - 1												
Oe/He	4	-2.04	0.28	4	-0.37	0.06				5	0.55	0.30
Oa/Ha	2	-1.81	0.17	3	-0.37	0.06				4	0.74	0.28
E/B	1	-1.76		1	-0.41					2	1.09	0.22
runoff	1	-2.05		1	-0.42					9	0.43	0.12
clear-cut site - 2												
Oe/He	4	-2.25	0.15	4	-0.41	0.06				5	0.44	0.09
Oa/Ha	4	-1.84	0.09	4	-0.41	0.07				5	0.69	0.05
E/B	0			0						2	0.99	0.22
runoff	1	-2.01		1	-0.39					9	0.30	0.05

Table S5: Hg pool size (Hg tot pool) and outflow during sampling period of September 2012 (Outflow) of boreal forest catchments. Data from Kronberg et al. [1] [2].

Site	Hg tot pool average g ha^{-1}	σ g ha^{-1}	Outflow average mg ha^{-1} month^{-1}	σ mg ha^{-1} month^{-1}
reference site - 1				
Oe/He	4.6	1.7	1.2	0.3
Oa/Ha	92.8	40.9	0.4	0.3
total	97.4		1.6	0.13
reference site - 2				
Oe	4.0	1.7	0.9	0.30
Oa	10.0	2.0	0.6	0.40
total	14.0		1.5	0.11
clear-cut site - 1				
Oe/He	8.8	4.4	2.7	1.20
Oa/Ha	18.8	6.3	2.2	0.30
total	27.6		4.9	0.35
clear-cut site - 2				
Oe/He	8.0	2.4	2.7	1.20
Oa/Ha	56.2	23.8	2.9	1.20
total	64.2		5.6	0.47

Table S6: Results of mixing models: Contributions of different soil horizons to Hg in runoff based on Hg isotopes

Site	average f (%)	σ f (%)
reference site - 1		
Oe/He	71	17
Oa/Ha	12	11
E	16	14
reference site - 2		
Oe	58	18
Oa	20	15
E/B	22	16
clear-cut site - 1		
Oe/He	55	25
Oa/Ha	25	21
B	20	16
clear-cut site - 2		
Oe/He	48	22
Oa/Ha	52	9
E/B		

Table S7: Validation of enrichment by ultrafiltration: Enrichment factor of Hg concentration in retentate relative to initial concentration, Percentage of Hg in retentate relative to total Hg in 50 L sample and yield of Hg in trap solution relative to Hg in retentate

Site	Enrichment factor	Hg in retentate (%)	yield (%)
reference site - 1	19	39	99
reference site - 2	32	50	76
clearcut site - 1	12	22	100
clearcut site - 2	15	33	70
Lillsele stream	21	44	92

Table S8: Model results of fraction of precipitation-derived Hg relative to litter-derived Hg in runoff samples (see model description in Jiskra et al., 2015 [4]).

Site	$f_{precipitation}$	SD
reference site - 1	0.15	0.05
reference site - 2	0.09	0.03
clearcut site - 1	0.13	0.04
clearcut site - 2	0.13	0.05
Lillsele stream	0.15	0.04

Table S9: Results of standards processed and measured together with the soil and water samples reported in this study and a parallel publication.[4] All measured values are in agreement with previously reported values (see references).

Standard	Name	form/matrix	n		δ^{202}Hg ‰	Δ^{199}Hg ‰	Δ^{200}Hg ‰	Δ^{201}Hg ‰	Δ^{204}Hg ‰	Reference
secondary standard	ETH-Fluka		26	average	-1.43	0.07	0.01	0.03	0.01	[5],[6]
				2σ	0.12	0.05	0.05	0.07	0.11	
procedural standard	NIST SRM 2711	Montana soil	11	average	-0.12	-0.23	0.00	-0.18	0.01	[7],[6]
				2σ	0.10	0.07	0.04	0.03	0.09	
procedural standard	Federsee-spike	Histosol[a]	2	average	-0.76	-0.01	0.00	-0.05	-0.03	
				2σ	0.09	0.08	0.04	0.12	0.04	

[a]= Histosol material has been characterized by Hoffmann et al.[8] and spiked to 2.9 μg g^{-1} with $Hg(NO_3)_2$-salt previously measured by Jiskra et al.[5].

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