Supplementary Materials to

Speciation and mobility of mercury in soils contaminated by legacy emissions from a chemical factory in the Rhône valley in canton of Valais, Switzerland

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This Supporting Information includes 10 pages, 4 tables, and 7 figures: Page

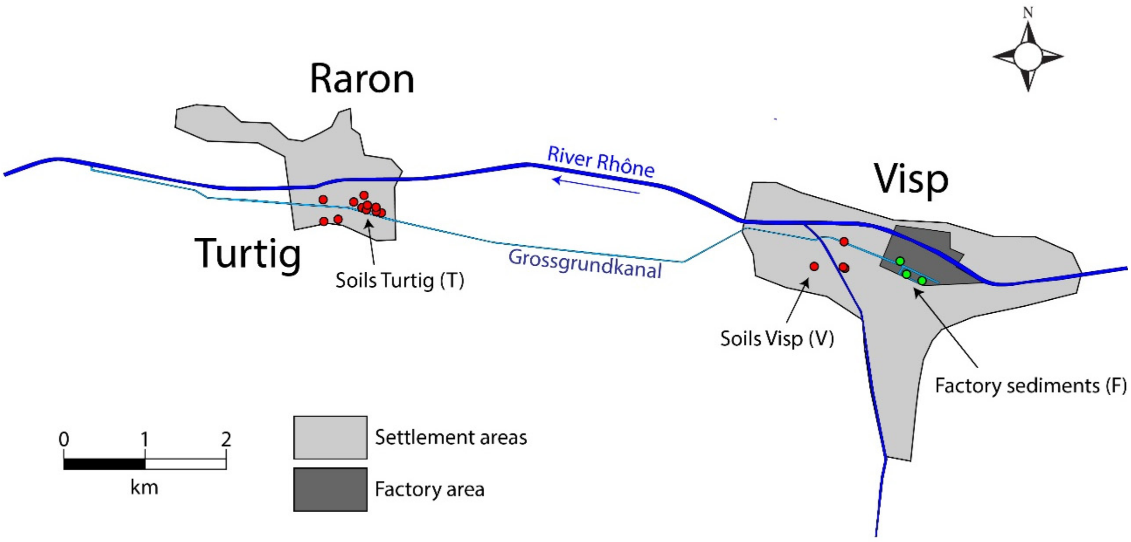

Figure S1. Schematic map of the Visp-Turtig area with respect to the regional Swiss map showing the sample locations. Red symbols represent samples from the settlement area (soils) and green symbols represent sediment samples from the chemical facility site (sediments). Direction of surface water flow in both the canal (Grossgrundkanal) and the Rhône River is from right to left. Base map is courtesy of the Swiss Federal Office of Topography (Swisstopo).

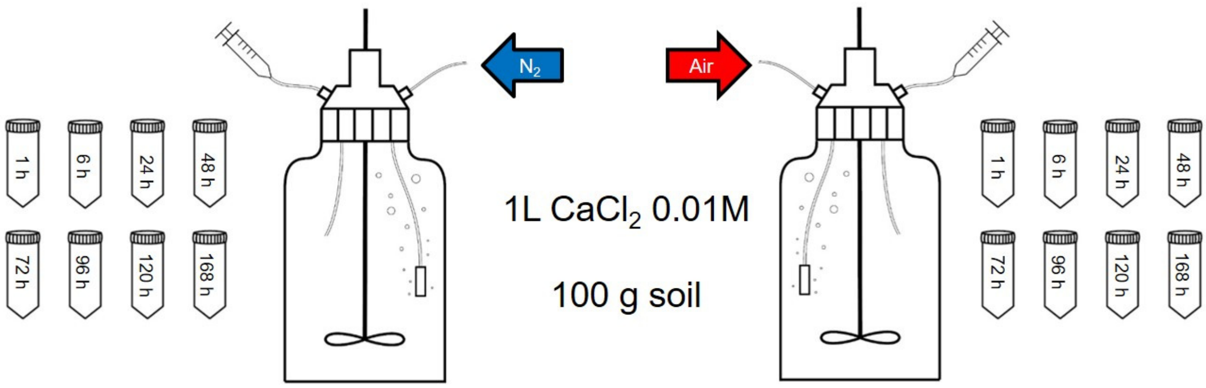

Figure S2. Schematic diagram describing the set-up of the redox reactor experiment using field sample T-S9.

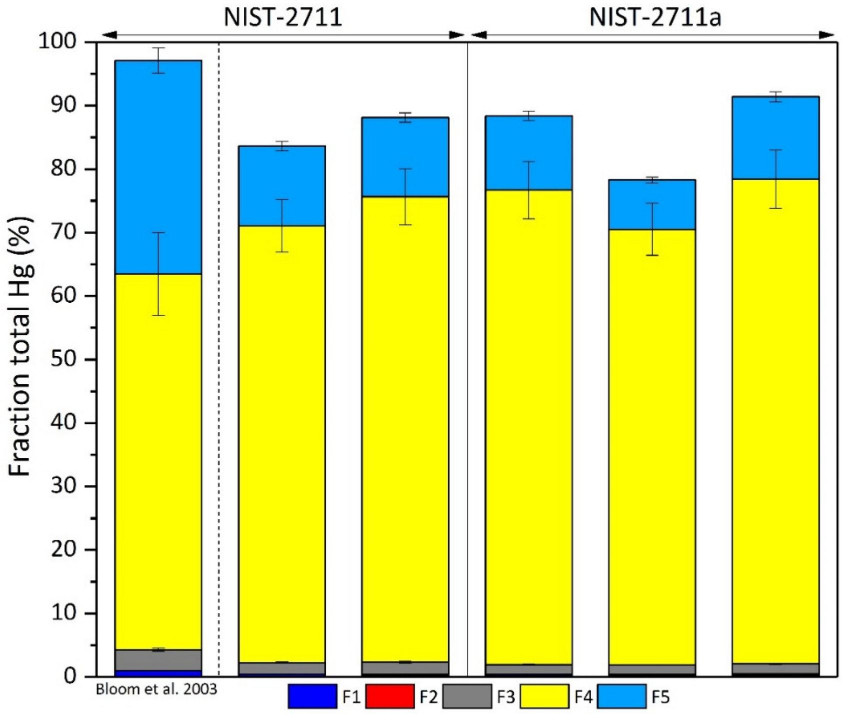

Figure S3. Sequential extraction results for standard reference materials (SRM) NIST-2711 and NIST-2711a (Montana Soil), as compared to previously published results of Bloom et al. 2003 [1], where a conservative uncertainty of 3% is assigned to the concentration measurements. Analytical uncertainty on the concentration measurement of each fraction of the two SRMs is ±6%.

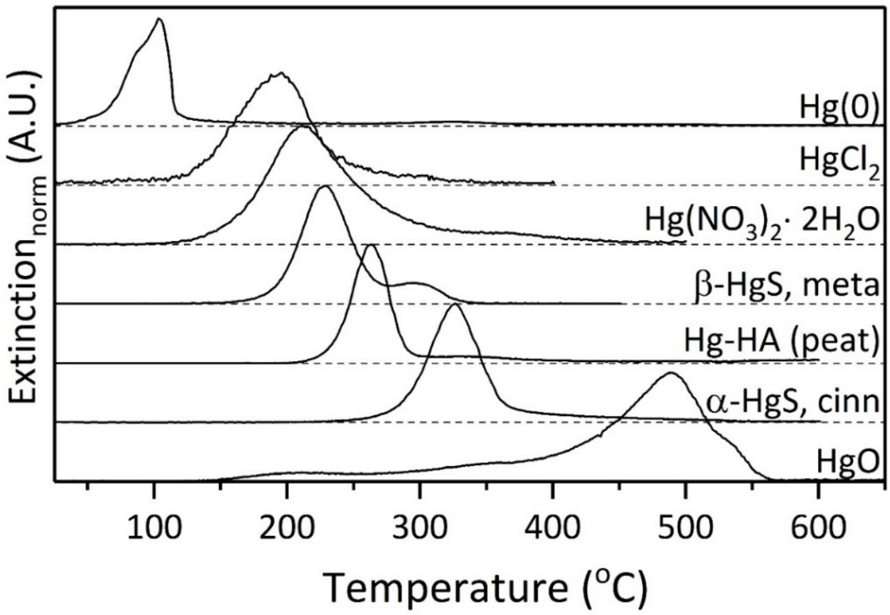

Figure S4. Thermal desorption curves of Hg from selected Hg reference compounds used for comparison with soil and sediment samples. The reference compounds used were: Elemental Hg sorbed on quartz sand (Hg(0)), mercuric chloride ($HgCl_2$), mercury nitrate ($Hg(NO_3)_2 \cdot 2H_2O$), metacinnabar (β-HgS, meta), Hg in humic acid extracted from a peat (Hg-HA (peat)), cinnabar (α-HgS, cinn), and mercuric oxide (HgO).

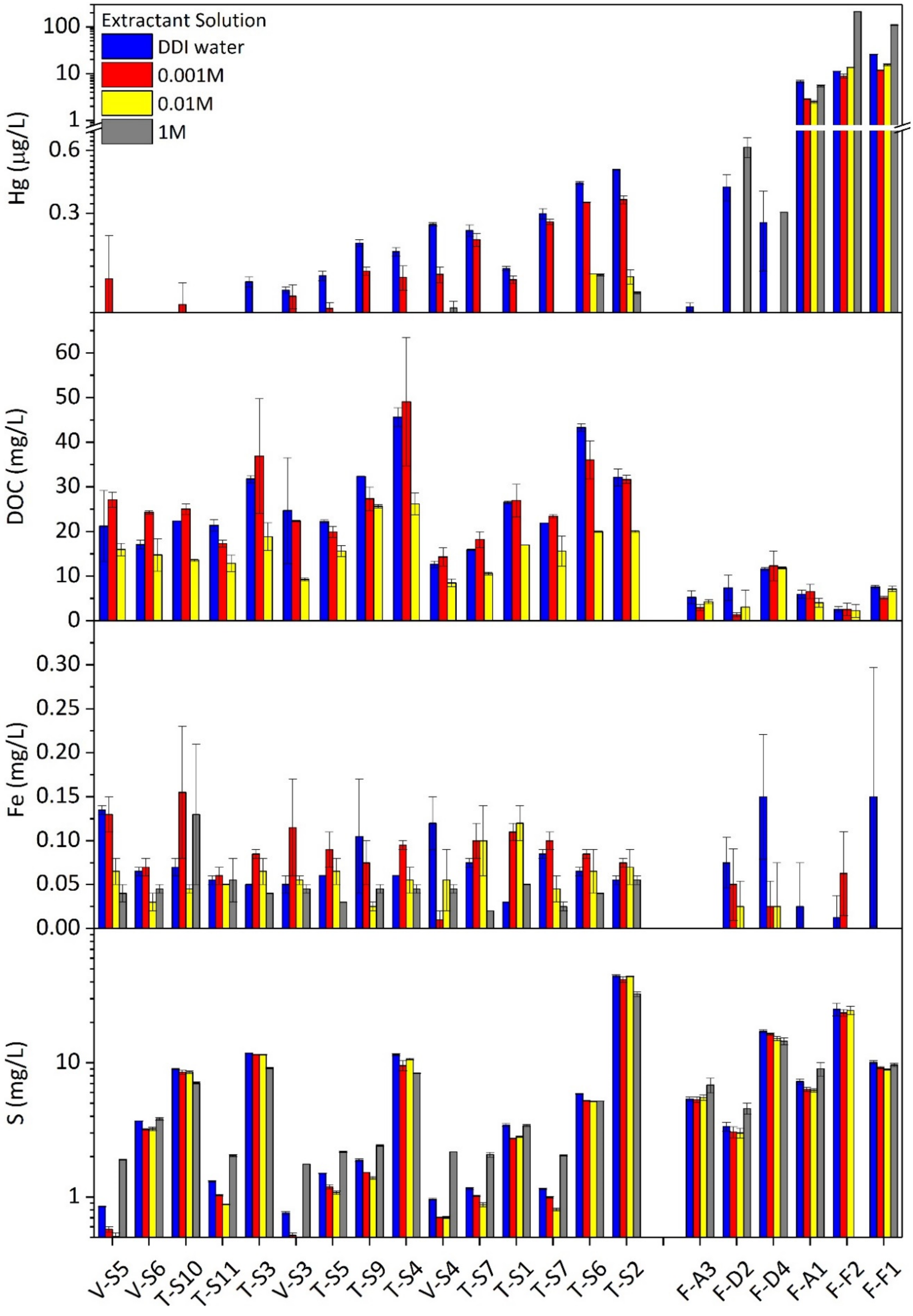

Figure S5. Hg, dissolved organic carbon (DOC), Fe and S concentrations in the various batch extractions for the field samples. Samples are grouped by soils and sediments and ordered by increasing total Hg concentration from left to right within each group. Error bars represent the range of duplicate extractions.

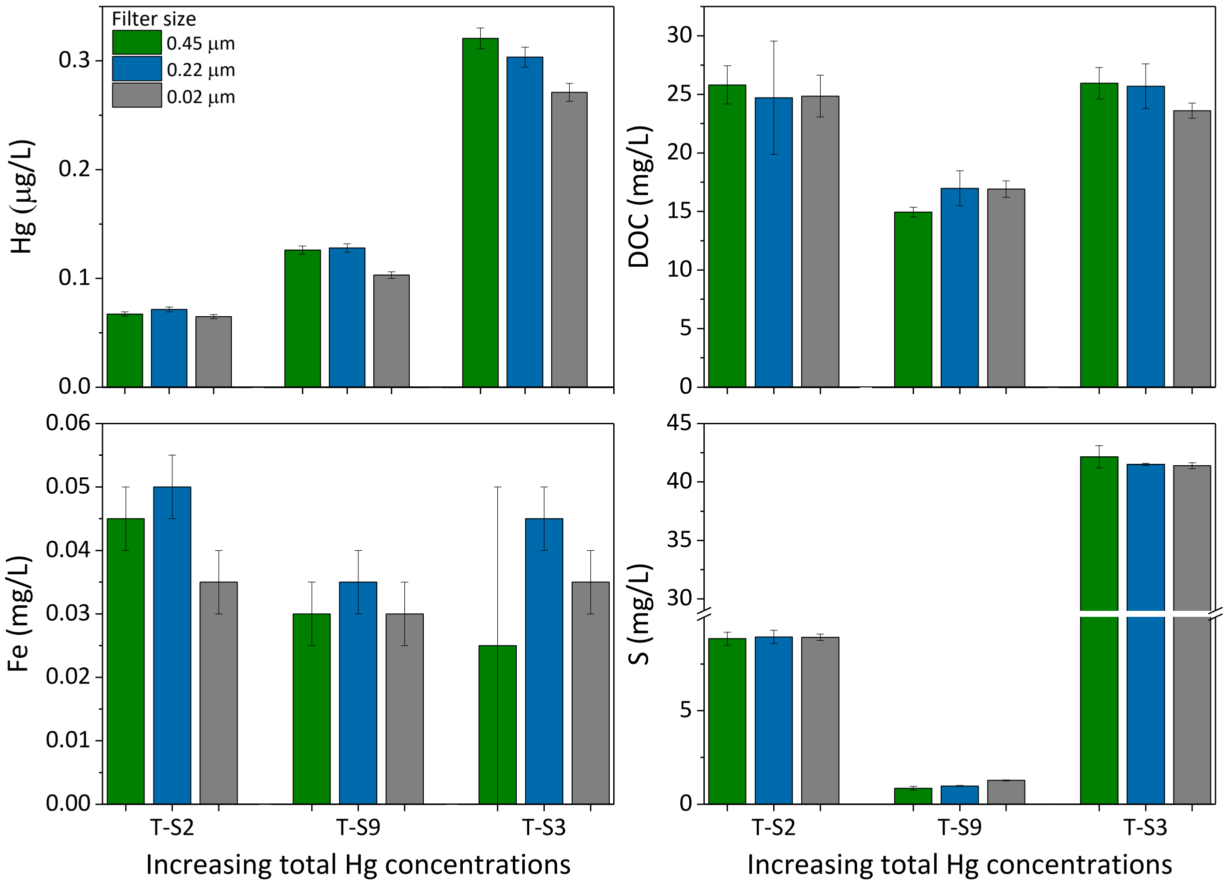

Figure S6. Results of filtration tests with batch extracts of three soils samples using 0.001 M $CaCl_2$ and a solid:solution ratio of 1:10. Total Hg concentrations in the soils increase from left to right. Error bars represent the range of duplicate extractions.

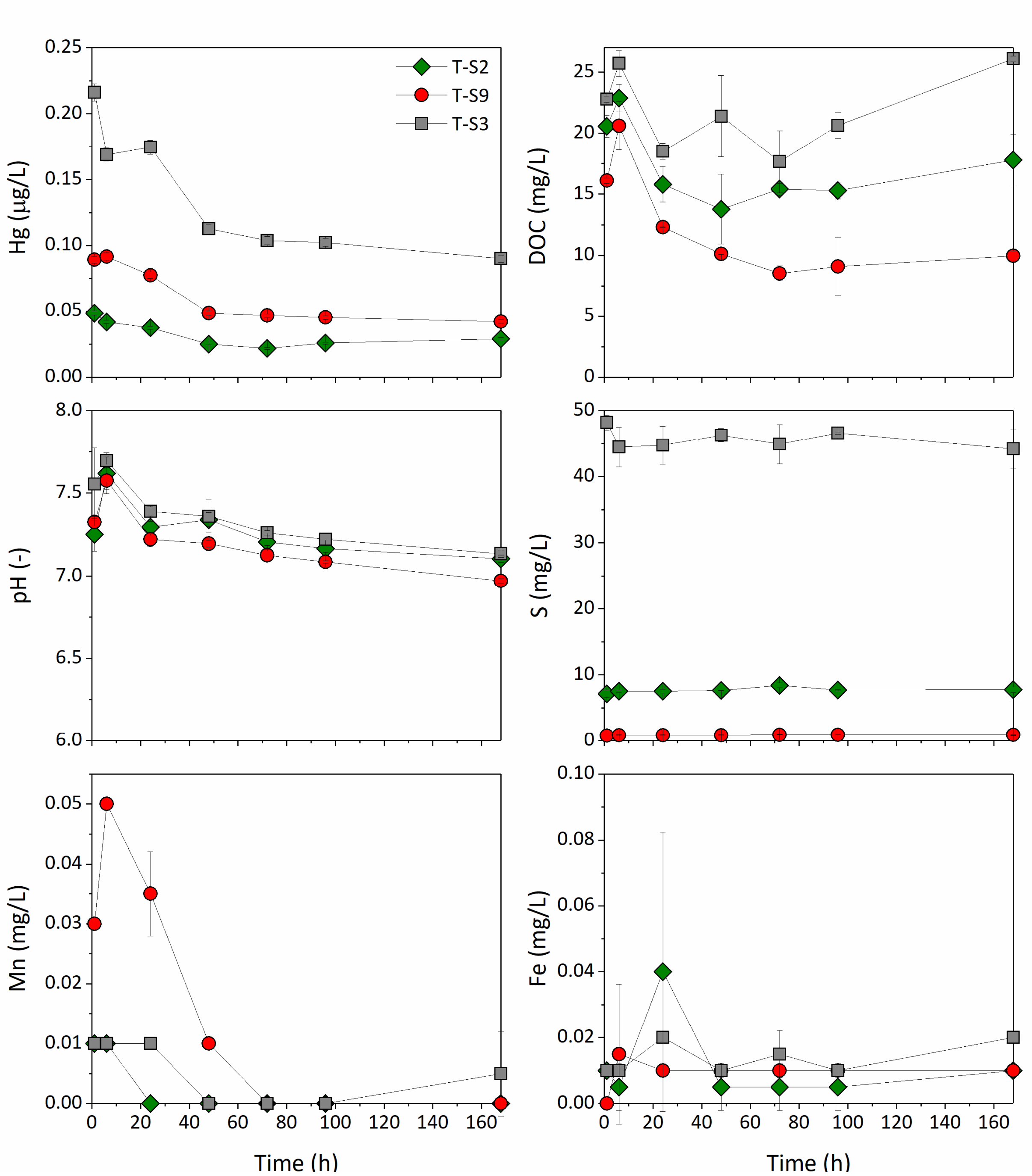

Figure S7. Results of time-dependent batch extractions of three soils. Error bars represent the range of duplicate extractions.

Table S1. Characteristics of soil (V,T) and sediment (F) samples. Within each group samples are ordered by increasing Hg concentration. Uncertainty on all Hg measurements by CV-AFS is ±6%.

		Hg content[1]			Elemental composition[2]							CaCl$_2$-extractable Hg[3]			
	Depth	Hg_{TD}	Hg_{VBBo}	pH	TIC	OC	Al	Si	S	Ca	Fe	DDI	0.001M	0.01M	1 M
	(m)	------ (mg/kg) ------			------------------------------------ (g/kg) --							------------------- (μg/kg) -------------------			
V-S3	0 - 0.2	0.49	0.46	6.2	0.1	23.9	79.3	212	0.70	16.7	38.4	0.98	1.45	0.27	0.80
V-S6	0 - 0.2	0.67	0.64	7.5	3.4	17.3	75.5	219	0.69	26.6	32.7	0.78	0.53	0.29	0.34
T-S2	0 - 0.2	1.17	1.13	7.7	9.1	19.2	71.7	197	1.00	46.4	32.1	0.93	1.09	0.35	0.41
T-S6	0 - 0.2	1.30	1.20	7.8	9.2	16.0	66.4	210	0.77	47.0	27.2	0.89	0.65	0.35	0.25
T-S4	0 - 0.2	2.84	2.85	8.1	10.1	13.2	72.3	204	0.80	47.4	33.9	1.41	0.99	0.42	0.29
V-S4	0 - 0.2	3.24	3.31	7.6	6.0	19.4	73.3	206	0.53	44.5	29.1	1.28	1.20	0.42	0.85
T-S7	0 - 0.2	4.03	4.45	7.4	8.0	18.0	74.8	212	0.73	44.7	32.3	1.50	1.05	0.51	0.48
T-S11	0 - 0.2	4.08	4.09	7.8	3.3	20.5	76.3	215	0.72	35.4	29.4	2.15	1.58	0.74	0.62
T-S5	0 - 0.2	5.48	5.85	8.1	10.9	16.6	73.5	191	0.97	49.8	35.2	1.96	1.48	0.59	0.44
V-S5	0 - 0.2	5.96	5.74	7.2	7.8	12.6	76.6	217	0.47	39.1	28.8	2.65	1.53	0.64	1.05
T-S9	0 - 0.2	6.22	7.95	7.5	2.7	20.7	73.7	222	0.59	30.0	28.8	2.48	2.24	0.80	0.69
T-S1	0 - 0.2	9.11	10.26	7.6	8.3	19.3	80.3	200	0.70	40.0	38.6	1.63	1.44	0.64	0.40
T-S10	0 - 0.2	11.31	11.09	7.2	10.1	25.4	66.4	194	1.08	52.0	27.6	2.99	2.73	0.68	0.68
T-S8	0 - 0.2	28.06	28.14	7.6	2.9	26.2	79.2	209	0.98	23.5	32.9	4.20	3.38	1.53	1.52
T-S3	0 - 0.2	28.38	26.85	7.9	7.5	20.0	77.9	199	1.62	41.3	37.4	4.87	3.49	1.49	1.25
F-A3	1.0 - 1.5	3.54	2.6	8.0	16.9	2.8	97.1	190	0.30	41.2	43.6	1.1	0.5	0.5	0.8
F-D2	0.5 - 1.0	16.41	14.6	7.9	16.4	6.5	72.8	175	0.51	48.3	36.9	4.0	0.8	0.7	6.2
F-D4	1.5 - 2.0	68.91	73.8	7.3	16.3	105.6	75.1	149	0.96	40.8	40.1	2.7	0.3	0.7	3.0
F-A1	0 - 0.5	76.74	44.4	10.5	48.5	0.8	48.1	141	1.32	121.4	21.6	67.9	29.1	25.3	55.3
F-F2	0.3 - 0.6	136.96	106.4	8.0	14.7	1.5	60.4	185	0.92	42.7	21.6	113.6	89.0	137.4	2133.4
F-F1	0 - 0.3	174.72	133.1	7.7	16.2	12.2	71.0	175	0.70	44.5	30.3	260.1	118.6	157.4	1100.7

[1] Hg contents determined after total digestion (Hg_{TD}) and VBBo extraction (Hg_{VBBo}) using CV-AFS; [2] elemental composition determined by X-ray fluorescence analysis, except for total inorganic carbon (TIC) and organic carbon (OC); [3] amounts of Hg extracted within 24 h in batch reactors with soil:solution ratio of 1:10 using doubly deionized water (DDI) or 0.001 M, 0.01 M, and 1 M $CaCl_2$ solutions, respectively.

Table S2. Results of the sequential extractions of soil (V,T) and sediment (F) samples. Within each group samples are ordered by increasing Hg concentration. “n” represents the number of replicate extractions made in parallel. Uncertainty is the standard deviation (σ) of the replicate extractions.

Sample	F1	σ	F2	σ	F3	σ	F4	σ	F5	σ	sum F1-F5	n
	(%)											
V-S3	1.57	0.27	0.42	0.11	66.41	2.06	2.74	0.53	2.50	0.27	73.64	3
V-S6	0.75	0.05	0.48	0.07	69.17	1.38	3.55	0.44	1.09	0.24	75.05	3
T-S2	0.38	0.03	0.21	0.04	58.74	2.33	18.96	0.19	1.01	0.03	79.30	3
T-S6	0.60	0.11	0.33	0.11	65.30	2.85	27.36	1.59	34.34	7.87	127.93	3
T-S4	0.17	0.01	0.03	0.02	74.24	1.23	10.40	0.37	1.94	0.17	86.78	3
V-S4	0.25	0.10	0.05	0.02	68.83	0.02	11.86	0.61	1.07	0.05	82.06	3
T-S7	0.14	0.01	0.05	0.03	25.35	0.42	53.47	3.71	10.88	0.82	89.90	3
T-S11	0.21	0.003	0.04	0.005	64.94	2.75	16.14	0.42	1.84	0.11	83.18	3
T-S5	0.13	0.005	0.02	0.01	77.35	0.60	23.02	0.65	3.91	0.69	104.42	3
V-S5	0.14	0.01	0.06	0.01	28.84	2.77	41.79	0.83	14.83	2.43	85.67	3
T-S9	0.18	0.01	0.04	0.01	44.10	1.42	48.08	10.80	15.14	9.68	107.54	3
T-S1	0.09	0.003	0.03	0.02	72.68	1.52	12.32	0.77	2.28	0.35	87.40	3
T-S10	0.11	0.02	0.05	0.01	5.53	0.36	56.51	15.07	18.68	14.26	80.90	3
T-S8	0.09	0.01	0.02	0.002	6.66	0.17	51.87	7.82	37.23	5.77	95.88	3
T-S3	0.09	0.01	0.01	0.001	3.75	0.14	12.98	0.24	30.02	1.75	46.86	3
F-A3	0.60	0.71	0.35	0.15	14.10	3.65	45.34	8.95	32.12	7.54	92.51	3
F-D2	0.11	0.02	0.04	0.00	1.12	0.06	48.01	2.68	45.41	2.02	94.69	2
F-D4	0.02	0.01	0.03	0.03	1.26	0.44	61.53	5.42	41.76	1.86	104.60	3
F-A1	0.21	0.00	1.12	0.06	1.25	0.03	13.85	1.21	80.91	1.67	97.33	3
F-F2	1.56	0.16	0.04	0.01	0.46	0.01	15.87	2.46	69.25	3.15	87.17	3
F-F1	0.45	0.04	0.04	0.02	2.72	0.23	11.17	0.06	61.95	3.64	76.32	3

Table S3. VisualMINTEQ calculations of the speciation of dissolved Hg in the presence of different $CaCl_2$ and DOC concentrations at pH 7.5. Concentrations were chosen to be similar to batch extracts of soils, except for the comparison calculation with extremely high Hg (20 mg/L).

Species (%)	0.001M $CaCl_2$ 0.35µg/L Hg(II) 32mg/L DOC 7.5 pH	0.01M $CaCl_2$ 0.35µg/L Hg(II) 32mg/L DOC 7.5 pH	0.001M $CaCl_2$ 0.35µg/L Hg(II) 0.01mg/L DOC 7.5 pH	0.001M $CaCl_2$ 0.35µg/L Hg(II) --- 7.5 pH	0.001M $CaCl_2$ 20mg/L Hg(II) 32mg/L DOC 7.5 pH
$Hg(OH)_2$	--	--	--	8.2	20.9
$HgCl_2$	--	--	--	47.0	11.4
$HgCl_3^-$	--	--	--	0.94	0.2
$HgCl_4^{-2}$	--	--	--	--	--
HgClOH	--	--	--	43.8	34.4
Hg-DOC	100	100	100	--	33.1

Table S4. VisualMINTEQ calculations of the speciation of dissolved Hg in the presence of different concentrations of $CaCl_2$ and DOC, and pH representing the measured values in batch extracts of factory sediment F-F2.

Species (%)	MQ 11.4 µg/L Hg(II) 2.6 mg/L DOC 8.7 pH	0.001M $CaCl_2$ 8.9 µg/L Hg(II) 2.6 mg/L DOC 8.5 pH	0.01M $CaCl_2$ 13.74 µg/L Hg(II) 2.3 mg/L DOC 8.1 pH	0.4 M $CaCl_2$ 213.3 µg/L Hg(II) 5.3 mg/L DOC 7.0 pH
$Hg(OH)_2$	---	---	---	---
$HgCl_2$	---	---	0.02	2.0
$HgCl_3^-$	---	---	---	16.2
$HgCl_4^{-2}$	---	---	---	69.8
HgClOH	---	---	0.025	---
Hg-DOC	100	100	99.9	12.0

References

1. Bloom, N.S.; Preus, E.; Katon, J.; Hiltner, M. Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Anal. Chim. Acta* **2003**, *479*, 233-248.