

Supporting information

Metal and Metalloid Size Fractionation Strategies in Spatial High Resolution Sediment Pore Water Profiles

Anne-Lena Fabricius, Lars Duester, Dennis Ecker and Thomas A. Ternes*

Federal Institute of Hydrology, Department G2 - Aquatic Chemistry, Am Mainzer Tor 1,
56068 Koblenz, Germany.

Number of pages: 33

Number of figures: 2

Number of tables: 23

Sediment characteristics.

The sediment used within the experiments was sampled at stream kilometer 136 at the water gate Lahnstein (Germany, 50°18'29.47"N 7°36'46.24"O). Freeze drying was conducted by means of a GAMMA 1-16 LSC (Christ Gefriertrocknungsanlagen GmbH, Germany). To determine the element contents of the sediment, a microwave assisted digestion was carried out using a MLS µPrep-A (Ethos plus, MLS, Germany). Therefore, 1 g of the sediment was mixed with 10 mL of HNO₃ (65%) and digested applying the program listed below (Table SI1). After dilution with ultrapure water to a volume of 100 mL, the element concentrations were determined by means of inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS setup 1) as described in the experimental section of the manuscript. The element contents are given in Table SI2.

Table SI1: Microwave program.

Time (min)	Energy (W)	Temperature (°C)
9:30	500	100.0
2:41	750	125.0
7:32	1,000	210.0
5:00	1,000	205.0
15:00	500	205.0

Table SI2: Element content (measured by ICP-QMS) and standard deviations of the sediment used in the experiments.

Element	Mn	Fe	Co	As	Sb
Concentration (mg/kg)	223 ± 0.03	5,949 ± 99.36	2.99 ± 0.058	3.66 ± 0.03	0.011 ± 0.001

The content of total carbon, nitrogen, sulfur (CNS) and total organic carbon (TOC, Table SI13) were determined using a Eltra Helios (Eltra GmbH, Germany). 1 ml 1M HCl was added to 150-200 mg of the freeze-dried sediment and incubated for 3-4 h at room temperature. Subsequently, the pre-digested samples were heated to 55°C for ~12 h. Calibration was undertaken by threefold analysis of calcium carbonate (12%, pro analysis, Merck, Germany) and graphite (100% C, Eltra, Germany) and validated measuring (for channel 1, low carbon content) 100 mg CaCO₃ (12%), 200 mg graphite (100%, covered with sea sand) and ~150 mg of certified standard reference materials (1941a and 1941b; organics in marine sediment, TC 4.8% and 3.3% respectively). In the case of high carbon contents (channel 2), validation was performed by measurements of 130 mg EDTA (42.1%, pro analysi, AppliChem, Germany) and 200 mg graphite (100%, covered with sea sand). Samples were analyzed in triplicates.

Table SI3: Results of CNS and TOC analyses of the sediment used within the experiments.

TC (%)	TOC (%)	N (%)	S (%)	TC/N	TC/S
5.03	4.82	0.76	0.20	6.59	25.55

Microprefiling and microsampling.

High-resolution profiling was carried out using a microprefiling and a micro sampling (filtration) system (*missy*) developed and established in the authors' laboratory. An extensive description of the development and validation of the system and the analytical methods as well as the manufacturing of the sample probes can be found in Fabricius *et al.* (2014).¹ The microprefiling system consists of a computer controlled motorized micromanipulator and two microsensors connected to a microsensor multimeter (all Unisense, Denmark). The micro sampling system is a combination of a sampling probe connected to a micro annular gear pump (mzr®-2542) controlled by a console drive module (mzr-S06, both HNP Microsystems, Germany) and a fraction collector (rotAXYS®, Cetoni, Germany). The sampling probes, developed in the authors' laboratory¹ were made of a piece of porous polyethersulfone (PES) hollow fiber (0.45 µm) that was connected to a tube and stabilized by two pipette tips. In order to perform the measurements of the sediment parameters (the O₂ concentration and the redox potential) and the sampling of the sediment pore water in parallel, the software settings of the programs of the microprefiling and micro sampling systems (SensorTrace PRO, Unisense, Denmark and QmixElements, Cetoni GmbH, Germany) were synchronized (refer to Table SI4). Per profile 26 samples were taken, each over a distance of 1.17 mm. In order to consider the shift of the sampling depth in relation to that of the measurements caused by the dead volume of the tubings, the first two samples were excluded from further analyses. The sampling parameters and distances of the 24 samples analyzed are given in Table SI4 and SI5. To obtain a sample volume sufficient for a fractionation and a direct analysis in parallel, two samples were pooled (as described in the manuscript).

Table SI4: Measurement settings of the microprofiling and the micro sampling system.

Unisense (profiling)			Cetoni (sampling)		
Unisense start	(μm)	-10,000	Sampling velocity	(μl/min)	~3,33
Unisense end	(μm)	20,000	Intended sample volume	(μL)	500
Length profile	(μm)	30,000	Samples per profile		26
			Time per sample	(sec)	9000
Wait before measure	(sec)	430.0		(h)	2.5
Measure period	(sec)	10.0	Time per profile	(h)	60
Step size μm	(μm)	65		(d)	2.5
Measurement points		490			
Averaged speed of the probe/electrodes	(μm/min)	8.2			

Table S15. Sampling distances and mean values for pore water samples. To correlate the micropore measurements (O_2 , redox potential) with the element concentrations, the mean (rounded) values of the sampling distance were determined for each single sample and the pooled ones. Negative values indicate samples from the water body above the sediment.

Sample	Start (cm)	End (cm)	Mean (cm)	Pooled (cm)	Sample	Start (cm)	End (cm)	Mean (cm)	Pooled (cm)
1	-0.95	-0.83	-0.89	-0.83	13	0.53	0.65	0.59	0.65
2	-0.83	-0.71	-0.77		14	0.66	0.78	0.72	
3	-0.70	-0.58	-0.64	-0.58	15	0.78	0.90	0.84	0.90
4	-0.58	-0.46	-0.52		16	0.90	1.02	0.96	
5	-0.45	-0.34	-0.40	-0.33	17	1.03	1.15	1.09	1.15
6	-0.33	-0.21	-0.27		18	1.15	1.27	1.21	
7	-0.21	-0.09	-0.15	-0.09	19	1.28	1.39	1.33	1.40
8	-0.08	0.03	-0.03		20	1.40	1.52	1.46	
9	0.04	0.16	0.10	0.16	21	1.52	1.64	1.58	1.64
10	0.16	0.28	0.22		22	1.65	1.76	1.70	
11	0.29	0.40	0.35	0.41	23	1.77	1.89	1.83	1.89
12	0.41	0.53	0.47		24	1.89	2.01	1.95	

ICP-QMS analyses.

The information on the ICP-QMS measurements including the isotopes analyzed, the measurement modes (no gas = standard, He = collision cell; He gas flow of 5 mL/min) and the certified values of the certified reference materials (CRM) used are given in Table SI6. At least two of three CRMs included in each measurement differed <10% from the certified values at any time of a measurement series. Limits of detection (LoD, blank + 3 sigma) and limits of quantification (LoQ, blank + 10 sigma) of the measurements of the different experiments are given together with the results in the respective tables (see below). Measurements were performed at a RF power of 1450 W. Each sample was measured in 5 replicates.

As described in the manuscript, measurements were carried out using two different setups: setup 1 was used for routine measurements of samples of volumes of \geq 3 mL, setup 2 for sample volumes of 300 μ L. In the case of the latter, the nebulizer was directly connected to the Ar-gas line. The pressure for optimal signal intensity was manually tested and set to ~3.5 bar (~50 psi = ~1 L/min). The carrier gas line of the ICP-QMS was connected to the drainless spray chamber shear gas port and set to 0.75 L/min. Similar to setup 1, the integrated sample introduction system (ISIS) of the device was used for sample introduction, equipped with a sample loop of ~100 μ L. To avoid a time consuming switching between different measurement modes and thereby reducing the measuring time per sample, all elements were measured in the collision cell gas modus (He mode). Sample introduction was performed from a 96-deep well plate. Within the wells, 270 μ L of the sample was mixed with 30 μ L of internal standard (IS; Ge, Rh, Re, each 50 μ g/L). Matrix matched calibration standards as well as certified reference materials (CRMs) were equally treated and introduced from the well plates.

Table SI6. Information ICP-QMS analyses.

	Manganese	Iron	Cobalt	Arsenic	Antimony
Isotope	^{55}Mn	^{56}Fe	^{59}Co	^{75}As	^{121}Sb
Modus setup 1	He	He	He	He	no gas
Modus setup 2	He	He	He	He	He
Reference material	Concentration ($\mu\text{g/L}$)				
SPS-SW 2 (1:10)*	5.0 ± 0.03	10.0 ± 0.1	1.00 ± 0.005	5 ± 0.03	-
TM 27.3 **	2.27 ± 0.35	10.9 ± 3.0	2.05 ± 0.18	2.15 ± 0.30	1.51 ± 0.19
SRM 1640a ***	40.39 ± 0.36	36.8 ± 1.8	20.24 ± 0.24	8.010 ± 0.07	5.105 ± 0.046

* Surface water – trace metals, LGC standards GmbH

** Certified Reference Waters for Trace Elements, Environment Canada

*** National Institute of Standards and Technology

Preliminary experiments for CPE method adjustment.

In order to test the general applicability of the CPE method, originally developed to extract and pre-concentrate Ag nanoparticles, from samples of 40 mL to small volumes of 0.5 mL, preliminary experiments were carried out prior to the profiling experiments. Therefore, ~5 g of the sediment also used for the sediment core (refer to the manuscript) was mixed with ~40 mL of deionized water in a 50 mL polypropylene centrifuge-tube (VWR International, Darmstadt, Germany) and shaken overhead for several hours (Intelli-Mixer, ELMI Ltd., Latvia) to obtain samples comparable to the sediment pore water. To separate the water from the sediment, the samples were centrifuged for 10 min at 2000 g (Sigma Laboratory Centrifuge 3K30, Sigma Laborzentrifugen GmbH, Germany). Comparable to the size cut-off of the sample probes used in the profiling experiments, the supernatant was filtered to <0.45 µm (syringe filters Minisart NML, Celluloseacetate, Sartorius, Germany). CPE was conducted sixfold as described in the manuscript. Method blanks were determined in triplicates replacing the sample by ultrapure water. The 0.45 µm filtrate as well as the ultrapure water was acidified to 1.3% HNO₃ and analyzed together with the samples by means of ICP-QMS to determine the total element concentrations. After blank correction, the concentrations determined in the CPE fractions were related to the total concentrations of the 0.45 µm filtrates set as 100%. Recoveries were calculated by relating the sum of the two fractions to the 100% of the SPW. Results of the last preliminary experiment conducted are given in Table SI7. In contrast to the profiling experiments, CPE was carried out under normal laboratory conditions and not in the glove box probably causing biases of the Fe results due to contaminations by the laboratory background (refer also to the explanations in the manuscript).

Table SI7. Percentage of element concentrations of CPE fractions (aq = aqueous phase and TRX = Triton-X114 phase) in relation to the total concentration of the SPW 0.45 µm filtrate. Results crossed out were excluded from mean value calculation after testing for outliers (Grubbs's and Dixon-Test^{2, 3}, *p*-values Fe <0.05).

	Manganese			Cobalt			Iron			Arsenic			Antimony		
LoD: LoQ:	0.28 0.78			0.02 0.06			1.05 1.75			0.02 0.06			0.27 0.84		
Phase	aq	TRX	Σ	aq	TRX	Σ	aq	TRX	Σ	aq	TRX	Σ	aq	TRX	Σ
	107%	3.8%	111%	103%	2.7%	106%	49.4%	58.6%	108%	103%	1.4%	104%	103%	2.9%	106%
	104%	3.8%	108%	105%	4.3%	110%	253%	40.4%	294%	102%	0.0%	102%	114%	5.0%	119%
	106%	3.9%	110%	103%	3.7%	107%	41.1%	33.3%	82.3%	80.1%	0.0%	80.1%	102%	2.3%	105%
	100%	5.0%	105%	99.9%	13.7%	114%	40.6%	469%	209%	108%	12.5%	120%	97.2%	16.5%	114%
	101%	5.5%	107%	96.9%	7.5%	104%	40.2%	92.5%	133%	98.8%	1.7%	100%	96.4%	4.7%	101%
	106%	4.5%	110%	102%	7.1%	109%	46.8%	270%	317%	117%	18.8%	136%	100%	23.3%	123%
Mean	108%			106%			107%			105%			107%		
	2.3%			3.3%			25.2%			19.1%			8.8%		

Calculation of the dead volume and shift of the sampling depth.

The dead volume of the *missy* was calculated on the basis of the dead volumes of the single components including the tubings and the fittings used for connection of the probe with the tubings and the pump, the PES membrane and the useable volume of the micro annular gear pump, given by the manufacturer. The volumes of the tubing as well as of the PES membrane were calculated on the basis of equation 1 (Eq. 1).

$$V = r^2 \cdot \pi \cdot l \quad \text{Eq.1}$$

In the case of the connectors, the volume was measured by filling the adapter with water using a 250 μL syringe (Hamilton, Switzerland, Gastight #1725) and reading the difference from the scale. Since 1 mm^3 equals 1 μL , the results were not further corrected.

Table SI8. Calculation of the dead volume of the sampling systems.

Component	Symbol	Setup 2		
Inner radius tubing	r_{tube}	=	0.13	mm
Length tubing	l_{tubing}	=	800	mm
Inner radius PES membrane	r_{PES}	=	1.59	mm
Length PES membrane	l_{PES}	=	2.00	mm
Volume tubing	V_{tubing}	=	40	μL
Volume PES membrane	V_{PES}	=	16	μL
Fittings	V_{Luer}	=	~5	μL
Useable volume annular gear pump	V_{AGP}	=	17	μL
Dead volume sampling system	V_{dead}	=	~77	μL

Table SI9. Calculations of the shift of the sampling depth caused by the dead volume of the sampling system in relation to the measurements of the sediment parameters.

Component	Symbol	Setup 1
Distance for one sample	d_s	= 1.17 mm
Sample volume	V_s	= 500 μL
Dead volume	V_{dead}	= 77 μL
Distance shift due to dead volume		
$d_{\text{dead}} = \frac{d_s \cdot V_{\text{dead}}}{V_s}$	d_{dead}	= 0.19 mm

Table SI10: Mean values of the oxygen concentration, the temperature and the redox potential of the water phase and the deep sediment layers (mean of the deepest 0.5 cm). (* = sensor broken)

Start of the experiment	O ₂ concentration [mg O ₂ /L]	Temperature [°C]	Redox potential [mV]	
	Water phase	Water phase	Water	Sediment
Reference				
23.09.2014	6.9	18.1	470	-30
26.09.2014	5.8	19.1	310	-50
02.10.2014	7.3	19.8	490	-50
UF				
19.10.2014	7.3	18.8	-*	-*
22.10.2014	7.1	17.6	510	-20
25.10.2014	7.3	18.0	390	-40
28.10.2014	-*	17.4	360	-20
CPE				
07.11.2014	7.8	17.7	500	-60
13.11.2014	9.2	18.1	400	50
15.11.2014	8.6	18.2	440	50
21.11.2014	10.3	17.7	370	50
24.11.2014	8.4	17.7	370	60

Concentrations of As and Sb in pore water samples.

Together with the Mn, Fe and Co, the As and Sb concentrations were analyzed in the sediment pore water samples. The results of the reference profiles and the fractionation experiments are presented in Figure SI1 and SI2, concentrations of the individual profiles are given in Tables SI11, SI16, SI17 and SI22, SI23. The discussion of the results of the oxygen concentration and the redox potential can be found in the manuscript.

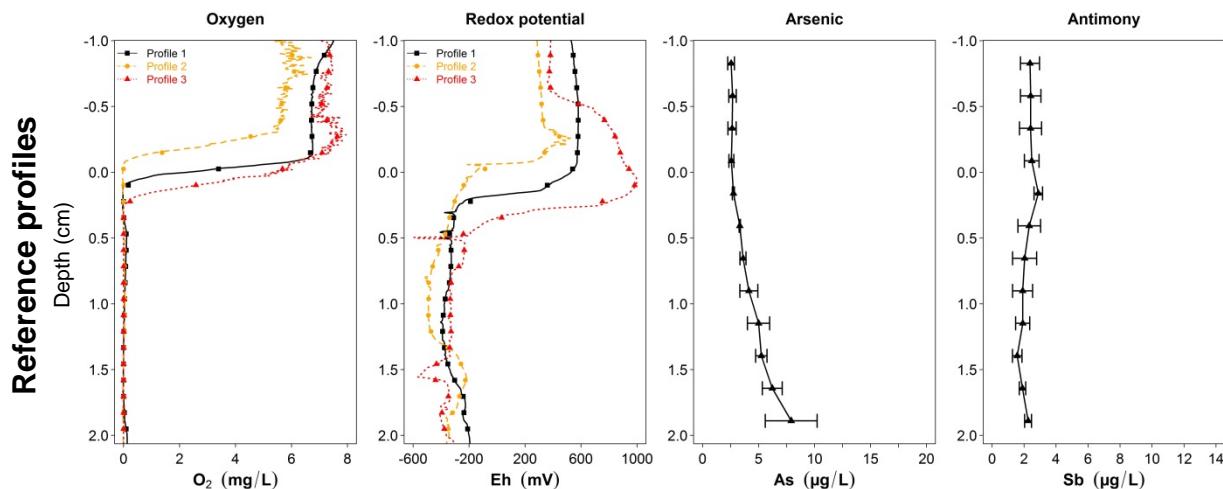


Figure SI1: Sediment depth profiles of the O_2 concentration, the redox potential as well as the As and Sb concentrations in sediment pore water samples of the three reference profiles, taken from 1 cm above to 2 cm in the sediment. Data points are plotted at the middle of the sampling distance of 2.4 mm representing in the case of the O_2 concentration and the redox potential the mean values of the sampling distance, in the case of the element concentrations the mean of the replicate profiles. Error bars represent the standard deviation of the replicate profiles including the uncertainty of the measurements as well as of the natural spatial heterogeneity

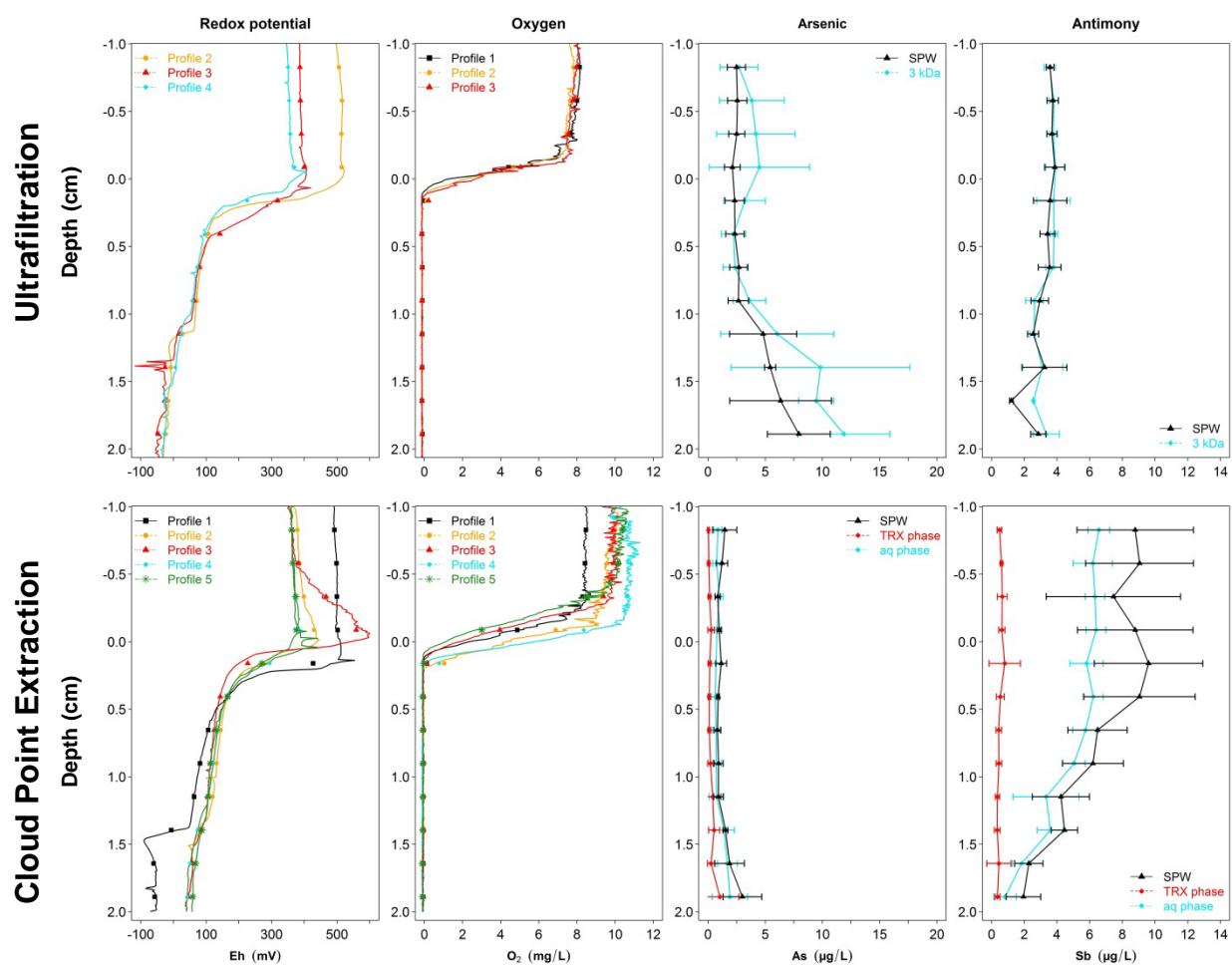


Figure 3: Sediment depth profiles of the O₂ concentration, the redox potential as well as the As and Sb concentrations in different fractions of sediment pore water samples, taken from 1 cm above to 2 cm in the sediment (SPW = sediment pore water; 3 kDa = dissolved fraction UF; TRX = surfactant rich, colloid containing CPE phase; aq phase = aqueous CPE phase containing the dissolved fraction). Data points are plotted at the middle of the sampling distance of 2.4 mm representing in the case of the O₂ concentration and the redox potential the mean values of the sampling distance, in the case of the element concentrations the mean of the replicate profiles. Error bars represent the standard deviation of the replicate profiles including the analytical uncertainty as well as the natural spatial heterogeneity of the independent profiles. For UF only three profiles for the O₂ concentration and the redox potential are given due to a broken sensor.

Regarding the total concentrations of As in the SPW samples of the different experiments, the results of the reference experiments and the UF profiles were in good agreement to each other, showing an increase of the concentration from ~2 µg/L in the overlaying water body to 8 µg/L in the SPW of the deeper sediment layers (Figures SI1 and 2 and Tables SI11, SI17). This can be explained by the reduction of Mn and Fe (oxyhydr)oxides causing a release of associated trace elements.²⁻⁴ In contrast to that, only a slight increase to ~3 µg/L of the total concentrations of the SPW was found in the samples of the CPE experiments (Figures SI1 and SI2 and Table SI22) potentially caused by less reducing conditions in the deeper areas of the sediment. However, this effect was not found for the other elements and may also be due to natural variations and/or to the low concentrations found in the SPW and related higher analytical uncertainties. Nevertheless, comparing the results of the two fractionation methods applied, As was, like Mn and Sb, nearly exclusively found in the dissolved fraction (<3 kDa of the UF and in the aqueous phase of the CPE). The concentrations determined in the surfactant rich phase of the CPE (TRX phase), containing the colloidal fraction, were below the respective quantification limit, in many cases below the detection limit (refer to Table SI22). This was equally found in other studies, even though As can be present up to ~20% in colloidal fractions of sediment pore waters.⁵⁻⁹

The results of Sb indicate a time-dependent process over the experimental period: concerning the total concentrations in the samples, the values determined in the overlaying water increased from 2 µg/L in the reference profiles (Figure SI1, Table SI11) to 3.5-4 µg/L and 8-9 µg/L in the UF and the CPE profiles, respectively (Figure SI2, SPW in Table SI17 and SI23). The concentrations in the deeper sediment layers remained constant at ~2 µg/L over the whole experimental period. This can be explained by an ongoing diffusional flux of anionic Sb ($\text{Sb}(\text{OH})_6^-$) from the sediment into the water phase under oxidizing conditions and the presence of insoluble $\text{Sb}(\text{OH})_3$ under reducing conditions,^{10, 11} leading to an inverse distribution compared to the other metal(loid)s. The finding that oxidizing conditions can

cause a flux of Sb from the sediment into the water phase was already observed in previous experiments with comparable sediment contents¹ as well as at contaminated mining sites¹⁴⁻¹⁶. These results emphasize the relevance of time-depending processes for the release of Sb and the impact of changing environmental conditions, especially with regard to contaminated urban sediments, impacted by, e.g., traffic^{12, 13} or (former) mining activities.¹⁴⁻¹⁶ Comparable to Mn and As, Sb was found in the dissolved fractions of the UF and the CPE (Tables SI17, SI23) this is in agreement to other studies showing that Sb is mainly present as dissolved anionic species in oxic surface waters and SPWs. Since for the digestion of the CPE phases a gentle procedure was applied using only HNO₃ (and no HCl which is recommended for Sb analyses), the discrepancies between the total concentration in the SPW (0.45 µm) and the two fractions might be related to certain losses of Sb due to an adsorption on vessel walls or organic material.¹⁷

Metal(loid) concentrations in SPW samples of the reference profiles.

Table SI11. Element concentrations (>LoD) and standard deviations in the sediment pore water samples (SPW, 0.45 µm filtrates) of the reference experiments and the LoDs and LoQs of the respective ICP-QMS measurements. Samples marked in grey were below the LoQ due to a required sample dilution. Results crossed out were excluded from mean value calculation after testing for outliers (Grubb's and Dixon-Test^{2,3}, *p*-values Fe <0.01, Co <0.02, testing the first 11 samples).

Depth	Manganese				Cobalt				Iron			
	Profile 1 (10/19/2014)	Profile 2 (10/22/2014)	Profile 3 (10/22/2014)		Profile 1 (10/19/2014)	Profile 2 (10/22/2014)	Profile 3 (10/22/2014)		Profile 1 (10/19/2014)	Profile 2 (10/22/2014)	Profile 3 (10/22/2014)	
LoD: LoQ:	0.15 0.34				0.01 0.03				0.29 0.74			
cm	SPW µg/L	SPW σ	SPW µg/L	SPW σ	SPW µg/L	SPW σ	SPW µg/L	SPW σ	SPW µg/L	SPW σ	SPW µg/L	SPW σ
-0.83	4.8 0.23	34.0 0.92	2.4 0.12		0.30 0.02	0.27 0.03	0.35 0.02		8.35 0.49	11.8 0.36	20.6 1.0	
-0.58	1.9 0.09	19.3 0.73	2.3 0.09		0.19 0.02	0.18 0.01	0.29 0.02		5.94 0.22	14.8 0.59	14.4 0.9	
-0.33	1.3 0.10	21.2 0.12	2.0 0.08		0.20 0.01	0.23 0.01	0.28 0.01		6.68 0.40	15.1 0.40	89.0 5.5	
-0.09	22.4 1.35	34.8 1.13	2.9 0.09		0.21 0.02	0.29 0.00	0.29 0.02		7.47 0.70	23.7 0.94	8.9 0.5	
0.16	296 8.22	199 3.55	16.0 0.52		0.56 0.56	0.45 0.03	0.32 0.01		8.22 0.72	50.4 1.03	12.7 0.3	
0.41	839 28.0	764 26.2	212 6.5		0.61 0.03	0.66 0.01	9.83 0.20		59.1 1.97	14.2 0.41	4106 99.7	
0.65	944 23.0	956 31.6	846 30.1		0.66 0.05	0.77 0.02	1.09 0.04		85.3 1.98	30.7 1.30	56.4 1.9	
0.90	992 12.2	1937 58.2	2061 89.1		0.67 0.05	1.36 0.05	2.20 0.02		116.9 1.94	133 3.99	481 20.6	
1.15	1293 52.8	2116 81.8	3108 93.2		0.90 0.05	1.53 0.05	2.77 0.17		119.8 5.46	272 10.9	503 15.0	
1.40	1983 48.9	1741 91.8	4196 191.6		1.45 0.08	1.85 0.04	3.32 0.09		117.1 4.13	302 17.6	529 24.8	
1.64	3278 76.8	1008 24.4	630 18.6		2.57 0.12	4.34 0.19	5.13 0.29		294.9 6.55	522 14.7	1001 31.8	
1.89	5589 251	2485 119	289 12		5.36 0.23	4.69 0.21	6.82 0.31		534.5 25.6	750 29.7	499 10.7	

Table SI11 continued.

Depth	Arsenic			Antimony		
	Profile 1 (09/23/2014)	Profile 2 (09/26/2014)	Profile 2 (09/29/2014)	Profile 1 (09/23/2014)	Profile 2 (09/26/2014)	Profile 2 (09/29/2014)
LoD: LoQ:	0.01 0.04			0.04 0.11		
cm	SPW			SPW		
	μg/L σ					
-0.83	2.21 0.14	1.94 0.10	2.79 0.10	2.15 0.04	1.40 0.02	3.04 0.03
-0.58	1.64 0.12	1.30 0.08	2.88 0.12	1.54 0.02	0.89 0.03	3.14 0.05
-0.33	1.49 0.15	1.99 0.06	2.78 0.27	1.42 0.05	1.30 0.04	3.19 0.06
-0.09	1.50 0.07	2.05 0.12	2.70 0.11	1.56 0.03	1.57 0.03	2.97 0.03
0.16	1.66 0.48	1.82 0.13	2.86 0.23	1.57 0.03	2.06 0.04	3.06 0.03
0.41	1.78 0.15	2.22 0.09	3.36 0.10	0.97 0.03	1.38 0.08	3.13 0.08
0.65	1.59 0.14	1.84 0.11	3.36 0.15	0.61 0.03	0.87 0.02	2.90 0.05
0.90	1.45 0.08	2.77 0.11	4.27 0.11	0.53 0.04	1.32 0.03	2.24 0.03
1.15	1.66 0.17	3.11 0.27	4.76 0.32	0.63 0.01	1.23 0.03	1.77 0.03
1.40	2.32 0.29	3.14 0.32	5.79 0.69	0.92 0.05	0.80 0.07	1.51 0.06
1.64	3.93 0.34	6.54 0.83	6.87 0.76	1.60 0.06	1.69 0.06	1.88 0.04
1.89	7.22 0.44	6.39 0.46	10.4 1.05	2.97 0.18	1.70 0.12	2.36 0.16

Metal(loid) concentrations in fractions of pore water samples after UF.

The sampling and fractionation procedure for the UF were conducted as described in the manuscript. Samples were analyzed without any further dilution by application of a newly established ICP-QMS method enabling for the measurement of sample volumes of 300 µL. The mean values of the UF graphics presented in the manuscript were calculated on the basis of the element concentrations determined in the 3 kDa fraction and the SPW for four subsequent profiles (Tables SI12 – SI16). The method blank used for background corrections was determined tenfold by filtration of ultrapure water. Equally, blank samples were measured by application of the ICP-QMS method for small sample volumes.

Table SI12. Element concentrations (>LoD) and standard deviations of the method blanks of UF (3 kDa filtrates) determined 10-fold by analyzing ultrapure water as well as the LoDs and LoQs of the respective ICP-QMS measurements. Samples <LoQ are marked in grey.

	Manganese	Iron	Cobalt	Arsenic	Antimony
LoD: LoQ:	0.46 1.28	0.60 1.18	0.10 0.25	0.13 0.49	0.22 0.61
Sample	3 kDa µg/L σ	3 kDa µg/L σ	3 kDa µg/L σ	3 kDa µg/L σ	SPW µg/L σ
1	0.46 0.09	1.15 0.05	0.29 0.06	1.12 0.27	1.11 0.04
2	<LoD	1.96 0.15	0.25 0.03	1.74 0.26	0.90 0.04
3	0.82 0.14	2.04 0.10	0.24 0.02	2.17 0.26	0.87 0.05
4	0.47 0.08	1.37 0.12	0.16 0.03	1.28 0.28	0.63 0.05
5	<LoD	2.30 0.18	0.14 0.02	1.38 0.26	0.56 0.05
6	<LoD	3.08 0.21	<LoD	1.34 0.339	0.56 0.03
7	1.05 0.08	5.12 0.54	<LoD	0.95 0.09	0.51 0.02
8	<LoD	2.51 0.17	<LoD	1.05 0.23	0.48 0.04
9	<LoD	1.84 0.21	<LoD	1.03 0.13	0.43 0.03
10	<LoD	1.00 0.17	<LoD	0.82 0.20	0.39 0.03

Table SI13. Concentrations (>LoQ) of Mn ($\mu\text{g/L}$) and standard deviations in the 3 kDa filtrates and the sediment pore water samples (SPW, 0.45 μm filtrates) of the UF experiments as well as the LoDs and LoQs of the respective ICP-QMS measurements. * = Sample lost due to errors during sampling of SPW, **= no results available due to errors during measurement.

	Profile 1 (10/19/2014)				Profile 2 (10/22/2014)				Profile 3 (10/25/2014)				Profile 4 (10/28/2014)			
LoD: LoQ:	0.44 0.23				0.60 1.61				0.37 1.01				0.77 1.89			
Depth cm	3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ		3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ		3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ		3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ	
-0.83	15.3	0.74	12.6	0.61	33.6	0.49	36.4	1.12	40.7	1.25	40.2	0.80	42.0	1.28	43.9	0.96
-0.58	14.5	0.68	13.3	0.39	25.0	1.07	25.9	0.51	26.9	0.25	26.3	0.55	32.7	1.06	34.6	0.60
-0.33	23.7	0.80	22.7	0.72	16.2	0.68	18.5	3.07	19.5	0.14	18.5	0.71	24.4	0.52	26.4	0.19
-0.09	29.2	0.52	29.1	1.51	23.2	1.73	23.0	1.02	18.4	0.30	17.3	0.44	22.8	0.40	24.6	0.85
0.16	76.0	4.77	78.2	4.08	151	3.40	108	4.06	55.7	1.45	53.1	0.70	115	1.66	103	1.48
0.41	**		512	14.0	672	28.1	485	17.8	425	8.33	428	8.31	562	5.47	595	8.31
0.65	1210	52.4	1366	79.0	1114	41.3	968	54.7	1455	31.6	1389	24.3	1234	37.7	1539	39.8
0.90	2099	83.3	2083	69.8	2084	61.8	1800	62.4	2663	53.2	3174	42.2	1962	26.4	2718	89.5
1.15	2975	172	3061	149	1457	57.3	901	48.5	4278	112	3119	43.5	2673	45.3	3119	42.1
1.40	4163	164	4365	180	2410	80.4	4953	178	2469	79.2	3836	91.9	3032	72.3	3681	81.5
1.64	50.2	1.44	247	22.2	1003	35.0	1262	44.8	3920	86.4	455	17.1	*			
1.89	29.9	1.86	**		303	3.52	558	25.3	232	9.64	8221	165	1210	19.7	1269	41.3

Table SI14. Concentrations (>LoD) of Co ($\mu\text{g/L}$) and standard deviations in the 3 kDa filtrates and the sediment pore water samples (SPW, 0.45 μm filtrates) of the UF experiments as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values <LoQ are marked in grey, samples below the respective LoD were excluded from calculations of the mean values. * = Sample lost due to errors during sampling of SPW, **= no results available due to errors during measurement.

	Profile 1 (10/19/2014)				Profile 2 (10/22/2014)				Profile 3 (10/25/2014)				Profile 4 (10/28/2014)			
LoD: LoQ:	0.12 0.93				0.10 0.26				0.15 0.28				0.17 0.45			
Depth cm	3 kDa $\mu\text{g/L}$		SPW $\mu\text{g/L}$													
-0.83	0.39	0.07	0.17	0.01	0.34	0.06	0.38	0.02	0.47	0.05	0.29	0.02	0.21	0.02	0.26	0.02
-0.58	0.35	0.02	0.17	0.02	0.32	0.04	0.29	0.01	0.66	0.16	0.31	0.01	0.17	0.01	0.27	0.01
-0.33	0.38	0.04	0.19	0.01	0.16	0.01	0.84	0.62	0.40	0.02	0.29	0.01	0.22	0.02	0.24	0.01
-0.09	0.21	0.02	0.18	0.02	0.12	0.01	<LoD		0.21	0.01	0.28	0.01	0.19	0.01	0.27	0.03
0.16	<LoD		0.19	0.02	0.17	0.02	<LoD		0.36	0.02	0.29	0.02	0.36	0.02	0.32	0.02
0.41	**		0.58	0.02	0.49	0.03	<LoD		0.47	0.02	0.60	0.03	0.74	0.02	0.90	0.05
0.65	**		1.89	0.02	1.38	0.03	1.69	0.05	1.59	0.03	2.43	0.13	1.91	0.12	2.45	0.14
0.90	2.58	0.12	<LoD		1.90	0.09	3.01	0.19	2.62	0.03	3.68	0.12	2.61	0.05	2.47	0.09
1.15	1.65	0.05	3.67	0.08	3.34	0.12	4.34	0.28	2.79	0.06	4.81	0.20	2.96	0.08	4.46	0.09
1.40	1.98	0.14	<LoD		4.37	0.19	6.17	0.25	3.64	0.26	9.57	0.13	2.08	0.12	<LoD	
1.64	<LoD		<LoD		5.85	0.32	5.87	0.45	3.65	0.05	3.52	0.10	*			
1.89	<LoD		**		3.51	0.18	6.43	0.58	4.36	0.25	10.10	0.42	3.13	0.23	6.16	0.14

Table SI15. Concentrations (>LoQ) of Fe ($\mu\text{g/L}$) and standard deviations in the 3 kDa filtrates and the sediment pore water samples (SPW, 0.45 μm filtrates) of the UF experiments as well as the LoDs and LoQs of the respective ICP-QMS measurements. * = Sample lost due to errors during sampling of SPW, **= no results available due to errors during measurement.

	Profile 1 (10/19/2014)				Profile 2 (10/22/2014)				Profile 3 (10/25/2014)				Profile 4 (10/28/2014)			
LoD: LoQ:	0.35 0.90				0.47 1.03				1.00 2.37				0.88 2.25			
Depth cm	3 kDa		SPW													
	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ												
-0.83	34.0	0.47	28.5	0.77	20.7	0.69	38.5	1.11	27.9	0.59	32.1	0.94	12.5	0.64	19.3	0.78
-0.58	22.2	0.31	16.5	0.50	12.5	0.58	28.9	0.67	30.6	0.35	32.7	0.47	10.8	0.34	17.0	0.59
-0.33	24.6	0.36	20.5	0.38	21.0	1.21	33.0	6.21	39.3	0.65	24.1	0.39	10.6	0.25	15.6	0.52
-0.09	37.1	0.72	19.9	0.37	15.5	0.75	18.0	0.68	22.8	0.57	16.0	0.56	10.4	0.11	17.4	0.86
0.16	25.1	0.57	32.8	0.85	49.8	1.14	24.6	1.19	59.3	0.36	27.3	0.47	39.3	1.91	22.0	0.90
0.41	**		45.7	0.34	35.2	1.36	39.6	2.55	14.2	0.20	11.0	0.32	15.9	0.54	26.7	0.98
0.65	101	5.61	90.1	0.65	72.1	3.81	76.0	2.42	43.9	1.14	34.9	1.59	76.8	1.58	240	12.5
0.90	378	8.03	403	14.9	29.1	0.90	214	18.1	122	1.10	628	26.9	166	6.34	1663	25.9
1.15	180	33.6	583	10.8	128	4.70	569	35.1	82.9	1.36	1417	46.9	395	19.1	2614	112
1.40	471	5.71	546	11.6	90.5	3.52	793	28.8	151	3.17	3285	63.8	504	23.9	4293	145
1.64	101	3.28	880	30.6	165	6.88	660	49.4	160	4.15	1915	72.0	*			
1.89	150	1.82	**		376	10.1	863	35.7	175	4.07	5105	102	133	5.11	4643	65.5

Table SI16. Concentrations (>LoQ) of As ($\mu\text{g/L}$) and standard deviation in the 3 kDa filtrates and the sediment pore water samples (SPW, 0.45 μm filtrates) of the UF experiments as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values <LoQ are marked in grey, samples below the respective LoD were excluded from calculations of the mean values. * = Sample lost due to errors during sampling of SPW, **= no results available due to errors during measurement.

	Profile 1 (10/19/2014)				Profile 2 (10/22/2014)				Profile 3 (10/25/2014)				Profile 4 (10/28/2014)			
LoD: LoQ:	0.89 2.29				0.48 1.29				0.22 0.57				0.20 0.49			
Depth cm	3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ		3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ		3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ		3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ	
-0.83	5.06	0.52	3.5	0.19	2.48	0.25	2.39	0.10	2.01	0.12	2.55	0.08	1.29	0.09	1.55	0.14
-0.58	8.02	0.67	3.8	0.29	2.22	0.25	2.43	0.14	3.06	0.27	2.24	0.16	2.01	0.12	1.80	0.16
-0.33	9.21	0.65	3.1	0.19	3.46	0.25	3.07	0.79	2.47	0.15	2.09	0.08	1.58	0.08	1.74	0.14
-0.09	11.0	0.43	3.1	0.12	3.30	0.09	1.82	0.27	2.26	0.18	2.13	0.21	1.47	0.15	1.48	0.10
0.16	5.78	0.74	3.3	0.27	3.12	0.11	<0.48		2.15	0.17	0.17	1.91	1.79	0.26	1.77	1.77
0.41	**		3.4	0.17	3.25	0.23	<0.48		2.30	0.20	0.20	2.04	1.15	0.10	1.54	1.54
0.65	**		3.7	0.17	3.31	0.25	2.89	0.28	2.53	0.18	2.42	0.20	1.24	0.10	1.79	0.15
0.90	5.15	0.47	<LoD		4.02	0.25	3.57	3.57	3.64	0.45	0.45	2.61	1.72	0.22	1.80	0.2
1.15	13.1	1.71	9.0	0.72	5.36	0.33	4.48	0.33	4.32	0.33	3.48	0.19	1.50	0.13	2.31	0.24
1.40	21.3	2.36	<0.89		7.20	0.42	5.09	5.09	7.33	0.89	0.89	5.78	3.56	0.13	<0.20	
1.64	11.2	1.37	155	35.2	9.01	0.74	9.48	1.32	8.21	0.64	3.19	0.58	*			
1.89	14.3	2.41	**		13.2	1.88	10.9	2.57	14.1	2.17	7.50	1.23	5.88	0.98	5.44	1.01

Table SI17. Concentrations (>LoQ) of Sb ($\mu\text{g/L}$) and standard deviation in the 3 kDa filtrates and the sediment pore water samples (SPW, 0.45 μm filtrates) of the UF experiments as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values <LoQ are marked in grey, samples below the respective LoD were excluded from calculations of the mean values. * = Sample lost due to errors during sampling of SPW, **= no results available due to errors during measurement.

	Profile 1 (10/19/2014)		Profile 2 (10/22/2014)		Profile 3 (10/25/2014)		Profile 4 (10/28/2014)	
LoD: LoQ:	0.09 0.22		0.14 0.37		0.26 0.52		0.13 0.29	
Depth cm	3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ		3 kDa $\mu\text{g/L}$ σ		SPW $\mu\text{g/L}$ σ	
-0.83	3.32	0.19	3.6	0.11	3.50	0.04	3.27	0.09
-0.58	3.71	0.07	3.7	0.20	3.48	0.13	3.28	0.09
-0.33	3.69	0.12	3.3	0.06	3.43	0.07	3.54	0.31
-0.09	3.63	0.08	3.4	0.13	3.35	0.07	3.54	0.10
0.16	2.90	0.10	3.3	0.07	3.24	0.12	2.41	0.11
0.41	**		3.2	0.13	4.02	0.06	2.9	0.19
0.65	**		2.8	0.11	3.24	0.10	3.33	0.18
0.90	1.82	0.15	<LoD		2.85	0.07	3.08	0.08
1.15	2.62	0.17	2.1	0.83	2.98	0.11	2.77	0.13
1.40	4.90	0.48	<LoD		2.59	0.11	2.29	0.19
1.64	2.59	0.16	<LoD		2.53	0.30	<LoD	
1.89	2.53	0.23	**		3.22	0.22	<LoD	
					4.33	0.15	3.19	0.36
							3.21	0.27
							2.53	
							0.04	
							*	

Metal(lod) concentrations in fractions of pore water samples after CPE

Sampling and sample preparation were carried out as described in the manuscript. After fractionation (conducted under inert argon atmosphere in a glove box) CPE phases were digested under normal laboratory conditions. Recoveries of the internal standard (100 µL Ru, 100 mg/L) added to control the digestion procedure were in a range between 90% and 110%, with the exception of 5 samples (3 x 84% - 89%, 2 x 111% - 113%). Digested samples were measured by means of ICP-QMS setup 1. SPW samples were acidified and measured directly without any further sample preparation by means of the ICP-QMS setup 2. Element concentrations of the SPW samples as well as the aqueous and the TRX phases and the blank values determined for five profiles (Tables SI18 – SI23) were used to calculate the mean value of the fractions and the SPW presented in the manuscript (Figure 2). For background correction the mean value of 10 method blanks was used, determined similarly to the samples by using ultrapure water instead of pore water samples. In cases of extremely high concentrations suggesting contaminations (Fe and Co), the results were tested for outliers (Dixon and Grubb's-test^{2,3}) and, if identified as one, excluded from mean value calculation.

Table SI18. Method blanks of CPE determined 10-fold by analyses of ultrapure water. Concentrations determined in the TRX and the aqueous phase after fractionation and microwave assisted digestion. Values <LoQ are marked in grey. Digestion-vessel specific blanks were used for background correction, resulting in negative values (<0) for some samples.

	Manganese		Iron		Cobalt		Arsenic		Antimony	
LoD: LoQ:	0.03 0.09		0.14 0.40		0.03 0.09		0.04 0.11		0.04 0.11	
	aqueous	TRX	aqueous	TRX	aqueous	TRX	aqueous	TRX	aqueous	TRX
	µg/L	σ	µg/L	σ	µg/L	σ	µg/L	σ	µg/L	σ
0.62	0.00	0.46	0.01	<0	<0	<LoD	<LoD	<LoD	<LoD	<LoD
<0		1.29	0.11	<0	85.9	2.09	<LoD	<LoD	<LoD	<LoD
0.18	0.02	1.14	0.03	<0	96.2	2.05	<LoD	<LoD	<LoD	<LoD
<0		0.15	0.01	<0	18.6	0.37	<LoD	<LoD	<LoD	<LoD
<0		<0		<0		<LoD	<LoD	<LoD	<LoD	<LoD
<0		<0		<0		<LoD	<LoD	<LoD	<LoD	<LoD
<0		<0		<0		<LoD	<LoD	<LoD	<LoD	<LoD
<0		<0		<0		<LoD	<LoD	<LoD	<LoD	<LoD
<0		<0		<0		<LoD	<LoD	<LoD	<LoD	<LoD
<0		0.78	0.04	<0	9.13	0.17	<LoD	<LoD	<LoD	<LoD

Table SI19. Concentrations (>LoQ) of Mn ($\mu\text{g/L}$) and standard deviations in the aqueous and TRX phase after CPE and in the sediment pore water samples (SPW, 0.45 μm filtrates) as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values <LoQ are marked in grey. Samples <LoD were excluded from calculation of the mean values. * = Sample lost due to errors during sampling or sample preparation procedure.

	Profile 1 (11/07/2014)				Profile 2 (11/13/2014)				Profile 3 (11/15/2014)				Profile 4 (11/21/2014)				Profile 5 (11/24/2014)			
LoD LoQ:	0.25 0.51	0.46 1.28	0.04 0.10	0.14 0.28	0.04 0.10	0.22 0.56	0.03 0.06	0.37 1.01	0.03 0.06	0.37 1.01	0.03 0.06	0.37 1.01	0.03 0.06	0.37 1.01	0.03 0.06	0.37 1.01	0.03 0.06	0.37 1.01		
Depth cm	aqueous $\mu\text{g/L}$	TRX $\mu\text{g/L}$	SPW $\mu\text{g/L}$																	
-0.83	6.35 0.64	<LoD	1.66 0.06	*			81.0 2.63	7.91 2.60	85.0 2.01	230.0 5.53	22.3 0.77	214 10.9	100 2.85	7.22 1.30	96.5 2.86					
-0.58	9.18 0.20	< LoD	3.10 0.28	*			41.0 0.97	20.1 0.48	43.6 1.23	44.4 2.58	3.90 0.11	39.9 1.26	84.9 2.43	6.79 0.25	76.7 2.58					
-0.33	5.94 0.55	< LoD	3.82 0.14	8.68 0.54	1.87 1.00	2.72 0.17	29.1 1.46	5.76 0.44	28.5 0.68	28.9 1.26	3.57 0.43	28.1 1.72	48.4 1.40	3.34 0.13	45.0 2.12					
-0.09	8.98 0.45	9.60 0.38	4.28 0.21	4.39 0.46	0.72 0.03	2.25 0.22	24.9 1.65	5.54 1.57	30.0 1.22	26.9 0.80	2.54 0.17	23.5 0.59	46.3 1.05	3.69 0.28	43.2 0.87					
0.16	42.1 2.39	1.63 0.08	36.3 2.03	4.70 0.23	1.54 0.06	9.90 0.88	69.8 1.07	5.32 0.23	73.9 2.50	51.7 1.86	7.22 0.39	46.7 1.52	71.8 1.07	5.21 0.20	67.4 3.06					
0.41	388 7.36	16.0 0.63	323.8 7.41	45.4 0.83	4.20 0.19	46.6 1.95	428 8.86	30.6 0.69	442 4.27	277 8.58	31.4 0.34	291 18.6	456 7.81	34.7 0.71	442 23.9					
0.65	1052 54.8	57.1 1.26	1267 43.0	317 10.5	19.0 0.23	279 9.07	1280 39.24	103 3.69	1551 20.6	740 13.7	93.1 2.22	614 41.3	838 16.7	57.5 1.43	906 72.3					
0.90	1734 89.1	93.7 2.97	1734 31.2	775 27.8	64.6 1.26	686 20.6	2128 54.23	173 1.64	2627 53.2	1232 35.0	178 6.19	1702 66.6	1719 39.2	122 2.37	2551 119					
1.15	2678 64.8	160 10.3	3445 147	1238 31.8	88.3 3.03	1298 50.0	2698 74.97	339 11.8	3056 44.9	1764 54.4	233 6.32	3070 95.3	0.11 0.01	215 6.96	2232 159					
1.40	3758 172	201 6.92	3903 54.7	1972 66.3	125 2.75	2321 284	3847 65.06	336 2.85	2740 63.1	2743 68.6	304 15.3	4536 227	4142 128	263 3.80	2562 111					
1.64	5278 128	223 14.9	5237 147	2187 97.7	130 4.57	2.72 0.17	4704 277	404 17.1	5871 116	3432 43.0	416 11.1	1713 56.63	4584 94.5	317 9.58	4129 226					
1.89	6105 233	315 19.1	5777 196	*			5710 309	1056 42.8	6773 107	3882 43.1	382 8.15	1891 34.84	4932 87.2	403 9.39	4305 130					

Table SI20. Concentrations (>LoQ) of Co ($\mu\text{g/L}$) and standard deviations in the aqueous and TRX phase after CPE and in the sediment pore water samples (SPW, 0.45 μm filtrates) as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values <LoQ are marked in grey. Samples <LoD and those crossed out were excluded from calculation of the mean values, the latter after testing for outliers (Dixon and Grubbs test p -value <0.01). * = Sample lost due to errors during sampling or sample preparation procedure.

	Profile 1 (11/07/2014)			Profile 2 (11/13/2014)			Profile 3 (11/15/2014)			Profile 4 (11/21/2014)			Profile 5 (11/24/2014)		
LoD: LoQ:	0.02 0.05	0.10 0.25		0.01 0.03	0.1 0.21		0.01 0.03	0.17 0.37		0.02 0.07	0.09 0.17		0.02 0.07	0.09 0.17	
Depth cm	aqueous $\mu\text{g/L}$	TRX $\mu\text{g/L}$	SPW $\mu\text{g/L}$												
-0.83	0.64 0.03	<LoD	0.26 0.02		*		0.41 0.03	<LoD	<LoD	1.28 0.07	<LoD	1.03 0.07	0.10 0.04	<LoD	0.16 0.02
-0.58	0.99 0.09	<LoD	0.41 0.05		*		0.29 0.08	<LoD	<LoD	0.41 0.04	<LoD	0.19 0.02	0.16 0.08	<LoD	0.16 0.01
-0.33	0.47 0.07	<LoD	0.29 0.02	0.21 0.04	<LoD	<LoD	0.63 0.27	<LoD	<LoD	0.23 0.02	<LoD	0.19 0.01	0.25 0.01	<LoD	0.16 0.03
-0.09	0.38 0.01	<LoD	0.36 0.04	0.26 0.13	<LoD	<LoD	0.56 0.03	0.21 0.03	<LoD	0.44 0.02	<LoD	0.20 0.00	0.93 0.03	0.11 0.01	0.15 0.01
0.16	0.90 0.89	<LoD	0.34 0.03	0.19 0.02	<LoD	<LoD	0.74 0.04	<LoD	<LoD	0.42 0.03	0.33 0.01	0.25 0.02	0.47 0.03	0.18 0.01	0.18 0.01
0.41	0.71 0.04	<LoD	0.67 0.02	0.20 0.02	<LoD	0.16 0.01	0.90 0.05	<LoD	0.50 0.03	0.69 0.03	<LoD	0.49 0.02	2.87 0.08	0.05 0.00	2.91 0.17
0.65	1.88 0.12	<LoD	1.88 0.03	0.61 0.03	<LoD	0.54 0.07	1.85 0.06	0.19 0.02	1.77 0.29	1.31 0.04	0.20 0.02	0.60 0.02	2.02 0.10	<LoD	1.71 0.05
0.90	2.88 0.18	<LoD	2.84 0.15	1.61 0.05	<LoD	1.53 0.38	3.77 0.10	0.57 0.39	2.91 0.11	2.12 0.11	0.55 0.03	1.12 0.04	2.38 0.14	<LoD	2.81 0.13
1.15	4.35 0.21	0.26 0.03	3.92 0.08	2.59 0.06	0.17 0.03	2.59 0.07	3.64 0.12	0.94 0.04	1.37 0.02	2.84 0.10	0.43 0.02	1.50 0.04		<LoD	5.00 0.26
1.40	5.29 0.32	0.40 0.02	5.46 0.10	3.91 0.09	0.22 0.03	4.54 0.61	4.72 0.11	0.64 0.04	4.44 0.09	4.34 0.17	1.06 0.08	3.49 0.18	5.71 0.24	<LoD	7.22 0.29
1.64	7.69 0.21	1.19 0.29	6.70 0.31	3.79 0.12	<LoD	0.03 0.01	5.02 0.30	0.55 0.06	5.61 0.16	4.80 0.23	0.69 0.05	1.92 0.07	5.21 0.13	<LoD	5.18 0.06
1.89	10.6 0.39	0.38 0.06	7.69 0.26		*		5.52 0.25	52.20 0.62	6.02 0.28	4.20 0.15	0.87 0.15	1.89 0.06	4.95 0.18	<LoD	5.87 0.17

Table SI21. Concentrations (>LoQ) of Fe ($\mu\text{g/L}$) and standard deviations in the aqueous and TRX phase after CPE and in the sediment pore water samples (SPW, 0.45 μm filtrates) as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values crossed out were excluded from calculation of the mean values after testing for outliers (Dixon and Grubbs test p-value <0.01). * = Sample lost due to errors during sampling or sample preparation procedure, *** = Negative values after method background correction.

	Profile 1 (11/07/2014)				Profile 2 (11/13/2014)				Profile 3 (11/15/2014)				Profile 4 (11/21/2014)				Profile 5 (11/24/2014)													
LoD LoQ:	0.48 1.49	0.44 1.18	0.26 0.45	0.88 1.62	0.26 0.45	1.06 1.71	0.18 0.26	0.75 1.07	0.18 0.26	0.75 1.07	0.18 0.26	0.75 1.07																		
Depth	aqueous	TRX	SPW	aqueous	TRX	SPW	aqueous	TRX	SPW	aqueous	TRX	SPW	aqueous	TRX	SPW															
cm	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ	$\mu\text{g/L}$	σ														
-0.83	99.9	7.75	24.2	1.73	24.6	1.85	*		18.5	0.25	***	24.8	1.45	32.2	0.75	21.2	0.54	12.5	0.11	81.6	3.13	22.9	0.55	43.7	0.93					
-0.58	122	7.15	43.4	3.89	70.3	3.15	*		16.3	0.21	30.65	0.66	11.0	0.05	42.2	1.16	33.2	1.34	13.0	0.26	38.5	2.07	31.3	0.73	29.5	0.38				
-0.33	66.6	3.58	11.7	0.92	12.9	0.77	33.0	0.48	118	0.53	14.6	0.81	15.3	0.37	79.43	0.97	6.18	0.41	4.62	0.17	0.0	0.00	10.1	0.52	22.2	0.62	17.5	0.34	11.2	0.26
-0.09	79.6	3.58	80.3	2.26	40.4	1.21	33.0	0.59	14.4	0.07	6.84	0.59	23.2	0.43	25.95	0.52	7.03	0.14	956	20.23	10.6	0.31	14.4	0.57	107	2.35	26.0	0.85	39.3	0.92
0.16	51.6	1.52	8.79	0.74	31.3	2.18	22.5	0.52	1.56	0.02	27.1	1.78	79.9	0.83	***	7.15	0.14	10.8	0.39	221	8.52	8.84	0.14	24.0	0.31	45.0	0.77	39.0	0.73	
0.41	132	2.29	5.57	0.42	34.2	1.18	25.2	0.54	22.8	0.07	8.55	0.35	0.00	0.00	53.10	0.69	6.73	0.38	26.1	0.83	22.8	0.55	8.29	0.10	238	3.99	49.6	1.07	14.4	0.35
0.65	70.9	4.85	276	7.40	48.2	2.34	141	0.76	0.00	0.00	5.86	0.44	37.9	0.50	***	14.8	0.62	50.5	1.11	30.0	0.81	10.8	0.17	105	2.15	43.5	0.73	65.0	0.88	
0.90	217	12.5	45.6	1.26	192	3.70	244	2.81	0.00	0.00	17.7	1.02	64.6	0.57	91.68	1.55	76.7	4.18	197	5.62	165	4.98	114	1.40	26.5	0.93	0.00	0.00	29.6	0.88
1.15	334	7.44	104	8.62	256	14.3	178	3.50	31.1	0.69	169	6.27	237	2.37	4285	12.7	130	3.43	639	18.89	137	3.17	319	5.35	30.0	1.00	69.4	3.18	455	10.4
1.40	377	17.8	52.3	2.74	398	9.16	496	9.57	34.1	0.57	553	30.5	1232	16.8	41.45	0.93	710	48.6	1810	46.82	805	35.6	1135	30.6	2161	63.2	137	1.20	2675	45.3
1.64	671	17.7	33.2	2.68	576	21.2	585	6.98	36.8	0.62	14.6	0.81	1830	20.7	80.66	0.63	1412	32.9	1742	27.68	289	9.50	831	12.0	3299	62.3	213	5.74	3100	62.0
1.89	588	24.8	443	30.9	507	14.2	*		1298	16.9	47266	141.6	1834	83.1	2295	27.41	4133	81.4	917	12.0	4399	78.5	464	10.7	4295	117				

Table SI22. Concentrations (>LoQ) of As ($\mu\text{g/L}$) and standard deviations in the aqueous and TRX phase after CPE and in the sediment pore water samples (SPW, 0.45 μm filtrates) as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values <LoQ are marked in grey. Samples <LoD were excluded from calculation of the mean values. * = Sample lost due to errors during sampling or sample preparation procedure.

	Profile 1 (11/07/2014)			Profile 2 (11/13/2014)			Profile 3 (11/15/2014)			Profile 4 (11/21/2014)			Profile 5 (11/24/2014)		
LoD: LoQ:	0.01 0.03	0.13 0.49		0.03 0.10	0.18 0.43		0.03 0.10	0.16 0.30		0.03 0.09	0.14 0.28		0.03 0.09	0.14 0.28	
Depth cm	aqueous $\mu\text{g/L}$	TRX $\mu\text{g/L}$	SPW $\mu\text{g/L}$												
-0.83	1.32 0.17	<LoD	3.04 0.29		*		0.50 0.19	<LoD	1.00 0.09	0.94 0.14	<LoD	0.96 0.08	0.67 0.09	<LoD	0.87 0.15
-0.58	1.19 0.21	<LoD	1.96 0.53		*		<LoD	<LoD	1.09 0.04	0.76 0.06	<LoD	0.83 0.12	0.77 0.13	<LoD	1.04 0.06
-0.33	1.44 0.09	<LoD	1.09 0.13	1.05 0.27	<LoD	0.45 0.03	0.64 0.26	<LoD	0.90 0.09	1.13 0.24	<LoD	0.89 0.11	0.60 0.03	<LoD	0.92 0.20
-0.09	1.42 0.18	0.24 0.10	1.17 0.18	0.87 0.23	<LoD	1.05 0.05	<LoD	0.75 0.05	1.05 0.07	0.90 0.10	<LoD	0.88 0.09	0.51 0.03	<LoD	0.76 0.18
0.16	1.49 0.78	<LoD	1.03 0.16	0.41 0.03	<LoD	2.00 0.25	<LoD	<LoD	0.98 0.04	0.84 0.12	<LoD	0.89 0.08	0.52 0.08	<LoD	0.85 0.06
0.41	1.11 0.20	0.10 0.04	0.92 0.06	0.41 0.16	<LoD	1.07 0.06	<LoD	<LoD	0.88 0.06	0.88 0.07	<LoD	0.81 0.07	0.55 0.04	<LoD	0.73 0.09
0.65	1.20 0.23	0.02 0.01	0.78 0.15	0.25 0.18	<LoD	0.88 0.08	0.45 0.15	<LoD	0.99 0.16	0.68 0.11	<LoD	0.32 0.05	0.92 0.05	<LoD	1.13 0.25
0.90	1.34 0.21	0.24 0.08	1.03 0.21	0.24 0.13	<LoD	0.95 0.10	<LoD	0.61 0.71	1.47 0.09	0.76 0.13	<LoD	0.35 0.03	0.93 0.08	<LoD	0.80 0.12
1.15	1.76 0.25	<LoD	1.16 0.10	0.58 0.12	<LoD	1.38 0.07	<LoD	1.67 0.22	0.55 0.02	0.91 0.11	<LoD	0.43 0.04		<LoD	1.03 0.12
1.40	2.78 0.45	0.80 0.03	1.39 0.37	0.91 0.28	<LoD	1.67 0.14	<LoD	1.21 0.12	1.49 0.24	1.89 0.25	<LoD	1.27 0.09	0.79 0.16	<LoD	1.81 0.09
1.64	2.49 0.64	0.23 0.10	2.11 0.48	1.25 0.23	<LoD	0.45 0.03	2.22 0.53	<LoD	3.54 0.24	1.48 0.32	<LoD	<LoD	0.55 0.05	<LoD	1.41 0.19
1.89	3.96 0.63	0.12 0.03	4.45 0.49		*		<LoD	3.50 0.31	4.29 0.52	2.13 0.20	<LoD	0.89 0.11	1.21 0.28	<LoD	2.39 0.32

Table SI23. Concentrations (>LoQ) of Sb (µg/L) and standard deviations in the aqueous and TRX phase after CPE and in the sediment pore water samples (SPW, 0.45 µm filtrates) as well as the LoDs and LoQs of the respective ICP-QMS measurements. Values <LoQ are marked in grey. Samples <LoD were excluded from calculation of the mean values. * = Sample lost due to errors during sampling or sample preparation procedure.

	Profile 1 (11/07/2014)				Profile 2 (11/13/2014)				Profile 3 (11/15/2014)				Profile 4 (11/21/2014)				Profile 5 (11/24/2014)			
LoD: LoQ:	0.01 0.02	0.22 0.61	0.01 0.02	0.13 0.34	0.01 0.02	0.11 0.26	0.01 0.03	0.09 0.26	0.01 0.03	0.09 0.26	0.01 0.03	0.09 0.26								
Depth cm	aqueous µg/L σ	TRX µg/L σ	SPW µg/L σ	aqueous µg/L σ	TRX µg/L σ	SPW µg/L σ	aqueous µg/L σ	TRX µg/L σ	SPW µg/L σ	aqueous µg/L σ	TRX µg/L σ	SPW µg/L σ	aqueous µg/L σ	TRX µg/L σ	SPW µg/L σ	aqueous µg/L σ	TRX µg/L σ	SPW µg/L σ		
-0.83	5.91 0.16	0.38 0.01	5.19 0.12	*			6.09 0.20	0.44 0.04	7.29 0.04	7.22 0.52	0.69 0.05	13.6 0.58	7.03 0.58	0.42 0.03	9.10 0.21					
-0.58	4.62 0.07	0.72 0.49	5.08 0.41	*			5.99 0.05	0.54 0.02	7.75 0.16	6.72 0.60	0.63 0.04	12.5 0.47	7.44 0.61	0.54 0.04	10.9 0.18					
-0.33	5.75 0.32	0.50 0.01	4.80 0.12	5.88 0.33	0.44 0.02	1.89 0.09	6.28 0.07	1.16 0.11	8.20 0.15	6.44 0.55	0.68 0.06	11.9 0.25	7.27 0.55	0.48 0.04	10.4 0.18					
-0.09	5.93 0.11	0.44 0.03	4.65 0.07	6.61 0.09	0.51 0.03	5.86 0.36	5.59 0.25	0.91 0.02	9.53 0.16	6.85 0.54	0.71 0.05	13.3 0.55	6.96 0.50	0.56 0.05	10.6 0.26					
0.16	5.20 0.14	0.23 0.01	4.44 0.16	4.42 0.06	0.49 0.02	12.55 0.73	5.90 0.13	0.36 0.02	8.26 0.30	6.88 0.46	2.51 0.20	11.9 0.34	6.64 0.48	0.44 0.04	10.8 0.27					
0.41	5.28 0.18	0.26 0.01	4.32 0.14	6.01 0.05	0.38 0.01	7.60 0.24	6.76 0.25	0.44 0.03	8.93 0.19	6.36 0.54	0.76 0.06	13.2 0.22	6.67 0.50	0.83 0.55	11.2 0.38					
0.65	4.79 0.27	0.27 0.04	4.51 0.14	5.77 0.10	0.36 0.01	6.52 0.30	5.24 0.10	0.36 0.02	6.44 0.09	6.11 0.46	0.72 0.06	5.55 0.23	6.81 0.56	0.47 0.05	9.38 0.43					
0.90	3.94 0.23	0.31 0.02	3.86 0.20	5.51 0.14	0.50 0.05	6.34 0.26	4.82 0.06	0.31 0.01	8.33 0.14	5.33 0.42	0.72 0.06	4.84 0.10	5.58 0.49	0.39 0.02	7.64 0.22					
1.15	3.12 0.21	0.30 0.05	3.64 0.10	5.03 0.21	0.35 0.05	6.04 0.25	3.75 0.12	0.24 0.00	2.0 0.04	4.76 0.37	0.58 0.04	3.53 0.07	<LoD		0.31 0.02	6.01 0.26				
1.40	2.50 0.11	0.47 0.02	3.58 0.14	4.29 0.12	0.29 0.03	5.36 0.46	3.14 0.02	0.18 0.00	3.84 0.14	4.41 0.46	0.58 0.03	4.29 0.14	3.65 0.32	0.20 0.02	5.22 0.20					
1.64	1.76 0.02	<LoD		3.36 0.09	2.37 0.13	0.05 0.01	1.89 0.09	1.07 0.06	0.25 0.23	1.94 0.11	2.38 0.14	1.54 0.12	1.32 0.06	2.13 0.17	<LoD		2.49 0.18			
1.89	<LoD		0.49 0.06	3.28 0.16	*			0.61 0.03	0.36 0.02	1.80 0.14	1.10 0.08	0.44 0.03	0.69 0.04	1.61 0.15	0.15 0.01	2.02 0.23				

REFERENCES

1. Fabricius, A. L.; Duester, L.; Ecker, D.; Ternes, T. A., New Microprofiling and Micro Sampling System for Water Saturated Environmental Boundary Layers. *Environmental Science & Technology* **2014**, *48*, (14), 8053-8061.
2. Balistrieri, L. S.; Murray, J. W.; Paul, B., The geochemical cycling of trace-elements in a biogenic meromictic lake. *Geochimica Et Cosmochimica Acta* **1994**, *58*, (19), 3993-4008.
3. Rigaud, S.; Radakovitch, O.; Couture, R. M.; Deflandre, B.; Cossa, D.; Garnier, C.; Garnier, J. M., Mobility and fluxes of trace elements and nutrients at the sediment-water interface of a lagoon under contrasting water column oxygenation conditions. *Applied Geochemistry* **2013**, *31*, 35-51.
4. Giblin, A. E., Iron and Manganese. In *Encyclopedia of Inland Waters*, Likens, G. E., Ed. Academic Press: Oxford, **2009**; pp 35-44.
5. Huerta-Diaz, M. A.; Rivera-Duarte, I.; Sanudo-Wilhelmy, S. A.; Flegal, A. R., Comparative distributions of size fractionated metals in pore waters sampled by in situ dialysis and whole-core sediment squeezing: Implications for diffusive flux calculations. *Applied Geochemistry* **2007**, *22*, (11), 2509-2525.
6. Itoh, A.; Nagasawa, T.; Zhu, Y. B.; Lee, K. H.; Fujimori, E.; Haraguchi, H., Distributions of major-to-ultratrace elements among the particulate and dissolved fractions in natural water as studied by ICP-AES and ICP-MS after sequential fractionation. *Anal. Sci.* **2004**, *20*, (1), 29-36.
7. Dabrin, A.; Roulier, J. L.; Coquery, M., Colloidal and truly dissolved metal(oid) fractionation in sediment pore waters using tangential flow filtration. *Applied Geochemistry* **2013**, *31*, 25-34.
8. Kottelat, R.; Vignati, D. A. L.; Chanudet, V.; Dominik, J., Comparison of small- and large-scale ultrafiltration systems for organic carbon and metals in freshwater at low concentration factor. *Water Air and Soil Pollution* **2008**, *187*, (1-4), 343-351.
9. Durin, B.; Bechet, B.; Legret, M.; Le Cloirec, P., Role of colloids in heavy metal transfer through a retention-infiltration basin. *Water Sci. Technol.* **2007**, *56*, (11), 91-99.
10. Filella, M.; Belzile, N.; Chen, Y. W., Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry. *Earth-Science Reviews* **2002**, *59*, (1-4), 265-285.
11. Takayanagi, K.; Cossa, D., Vertical distributions of Sb(III) and Sb(V) in Pavin Lake, France. *Water Research* **1997**, *31*, (3), 671-674.
12. Hjortenkrans, D. S. T.; Bergback, B. G.; Haggerud, A. V., Metal emissions from brake linings and tires: Case studies of Stockholm, Sweden 1995/1998 and 2005. *Environmental Science & Technology* **2007**, *41*, (15), 5224-5230.
13. Dietl, C.; Reifenhauser, W.; Peichl, L., Association of antimony with traffic - occurrence in airborne dust, deposition and accumulation in standardized grass cultures. *Science of the Total Environment* **1997**, *205*, (2-3), 235-244.
14. Okkenhaug, G.; Yong-Guan, Z.; Junwen, H.; Xi, L.; Lei, L.; Mulder, J., Antimony (Sb) and Arsenic (As) in Sb Mining Impacted Paddy Soil from Xikuangshan, China: Differences in Mechanisms Controlling Soil Sequestration and Uptake in Rice. *Environmental Science & Technology* **2012**, *46*, (6), 3155-3162.
15. Ashley, P. M.; Craw, D.; Graham, B. P.; Chappell, D. A., Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. *Journal of Geochemical Exploration* **2003**, *77*, (1), 1-14.
16. Casiot, C.; Ujevic, M.; Munoz, M.; Seidel, J. L.; Elbaz-Poulichet, F., Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France). *Applied Geochemistry* **2007**, *22*, (4), 788-798.

17. Kingston, H. M.; Haswell, S. J., *Microwave-enhanced chemistry : fundamentals, sample preparation, and applications*. Washington, DC : American Chemical Society, c1997.: **1997.**