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Environmental Chemistry

Supplementary Material

Speciation and mobility of antimony and arsenic in a highly contaminated freshwater system and the influence of extreme drought conditions

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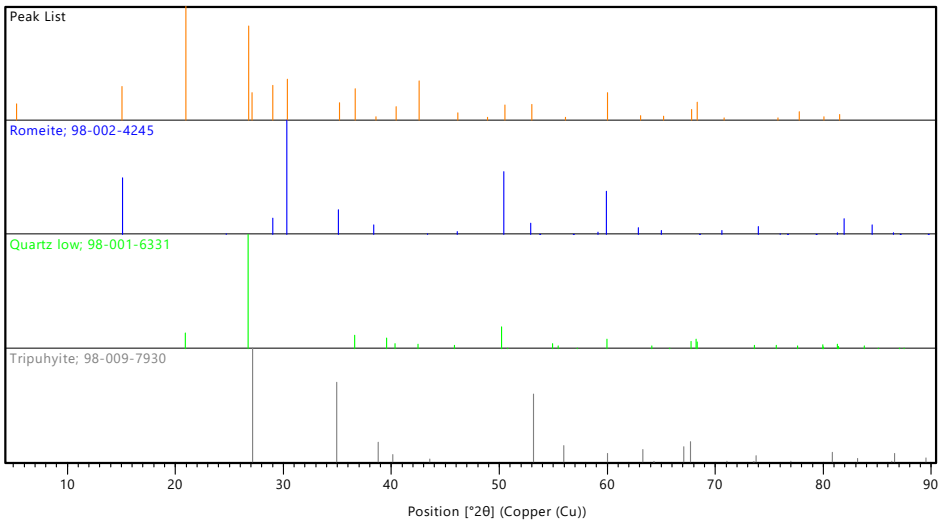

Figure S1. X-ray diffraction peaks from oxidised material used as XAS standard, removed from a Bakers Creek stibnite sample, showing match with roméite and tripuhyite.

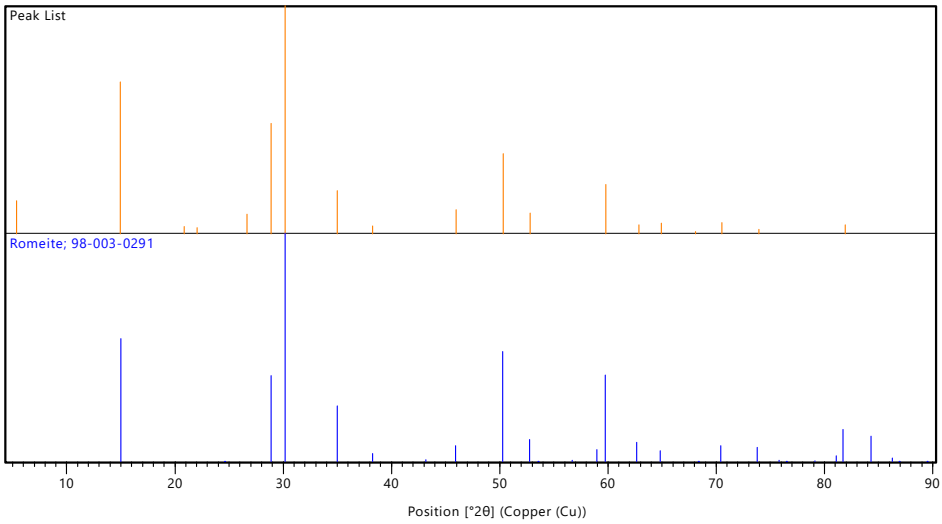

Figure S2. XRD pattern of oxidised material from Bakers Creek stibnite sample showing match to roméite.

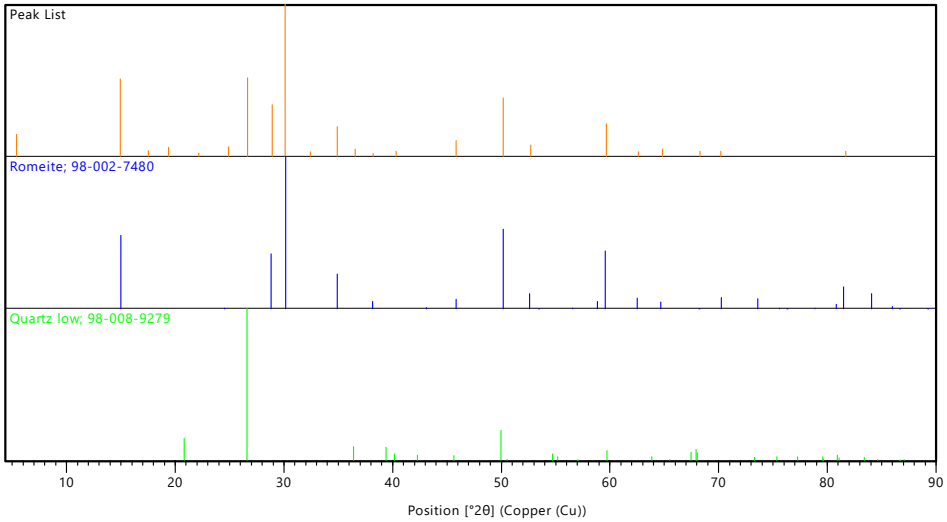

Figure S3. XRD pattern of oxidised material from Bakers Creek stibnite sample showing match to roméite and quartz.

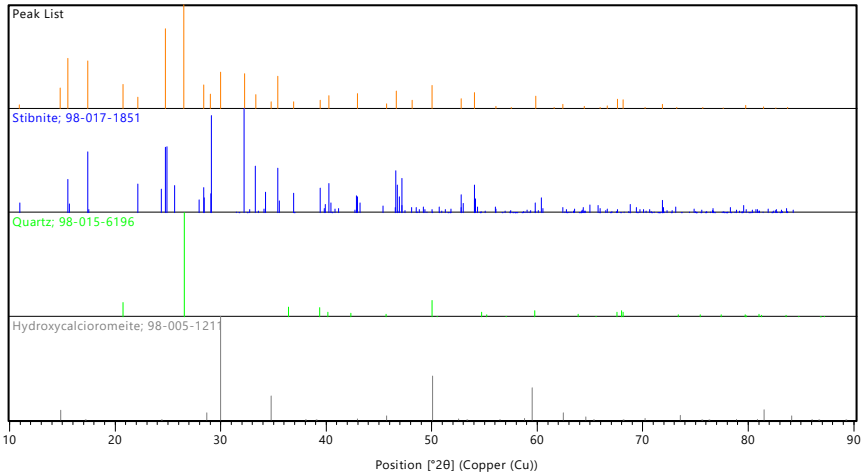

Figure S4. XRD pattern of oxidised material from Bakers Creek stibnite sample showing match to stibnite, quartz, and hydroxycalcioroméite.

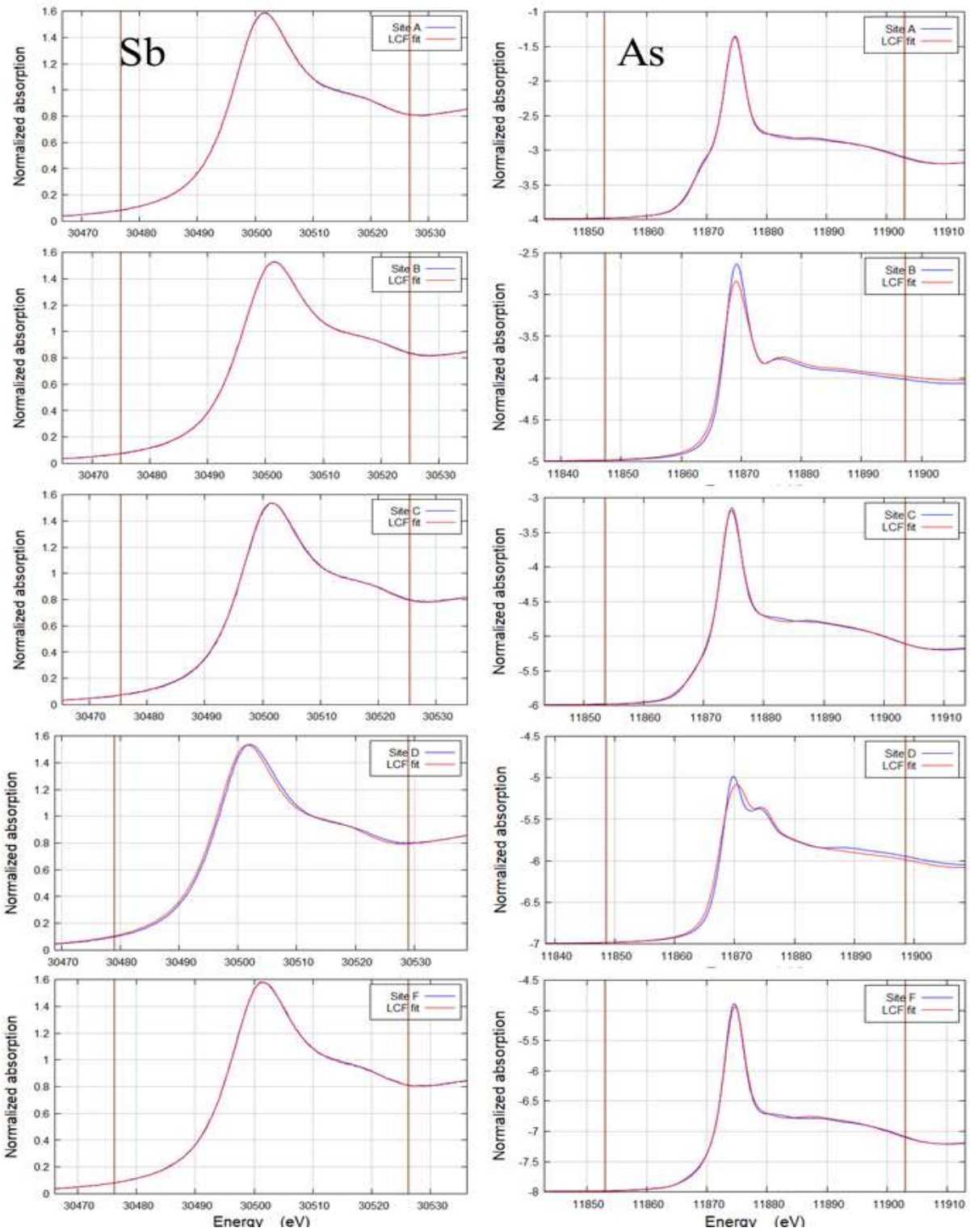

Figure S5. Linear combination fits overlaying recorded XANES spectra from Bakers Creek sediment samples.

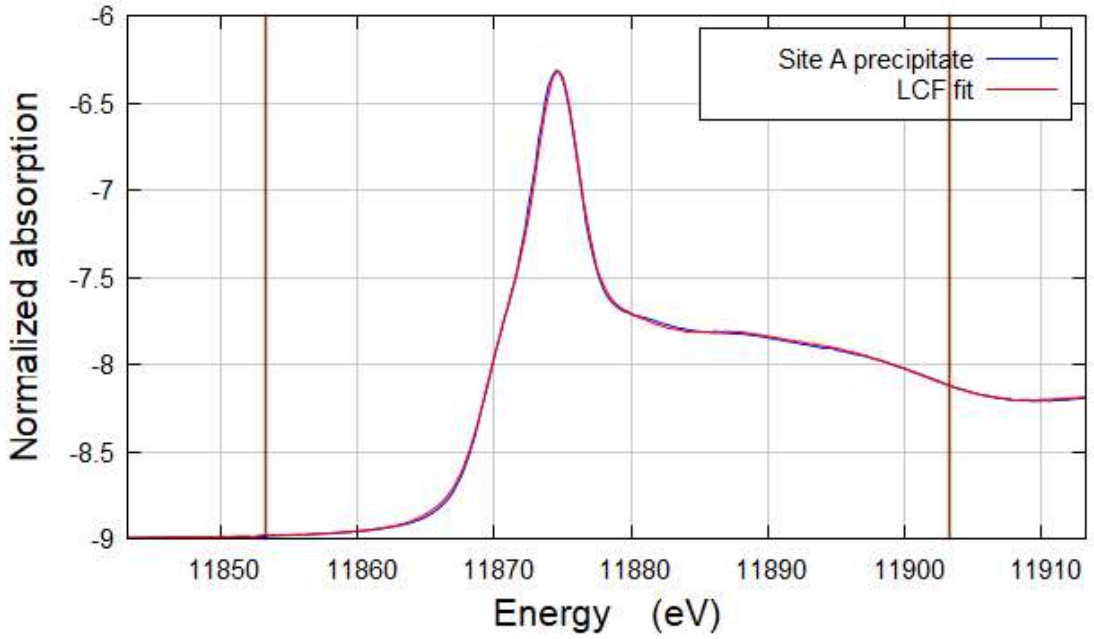

Figure S6. Linear combination fit overlaying As XANES spectra from the Fe precipitate which formed at Site A in Bakers Creek during the drought.

Table S1. GPS coordinates of sampling sites.

Site	Latitude	Longitude	Downstream distance (km)	Notes
A	393651	6616926	0	Sampling location consistent. Very low water levels in April/July, with the development of Fe-floc coating all surfaces in this time.
B (regular flow)	393716	6616584	0.4	December 2018 and February 2020 samples collected from this site.
B (drought)	394517	6572617	0.6	April and July 2019 samples collected from this deep waterhole.
C	394429	6615344	2	Site sampled only once due to access issues.
D	395278	6615318	3	Sampling location consistent. Water always available, but very low levels in April/July.
E	395707	6615119	N/A	Tributary. Site sampled only once (February 2020) due to no flowing water under regular flow conditions.
F	395782	6614871	3.7	Sampling location consistent. Water always available in the sampled pool.

Table S2. Correlations between metalloid concentrations and species in sediments and other environmental components.

Site(s)	Component 1	Component 2	r and p-values
A,B,C,D,F	Sediment Sb (mg kg^{-1})	Downstream distance (km)	$r(3) = 0.64$, $p = 0.25$
A,B,C,D,F	Sediment As (mg kg^{-1})	Downstream distance (km)	$r(3) = 0.46$, $p = 0.44$
A,B,C,D,F	Sediment Sb(V)	Downstream distance (km)	$r(3) = 0.76$, $p = 0.14$
A,B,C,D,F	Sediment Sb(V) mineral	Downstream distance (km)	$r(3) = -0.83$, $p = 0.08$
A,B,C,D,F	Sediment As(V)	Downstream distance (km)	$r(3) = -0.076$, $p = 0.90$
A,B,C,D,F	Sediment orpiment	Downstream distance (km)	$r(3) = 0.12$, $p = 0.85$
A,B,C,D,F	Sediment As(III)	Downstream distance (km)	$r(3) = -0.37$, $p = 0.54$
A,B,C,D,F	Sediment As(III)	Sediment orpiment	$r(3) = 0.51$, $p = 0.38$
A,B,C,D,F	Sediment As(V)	Sediment orpiment	$r(3) = -0.99$, $p < 0.001$
A,B,C,D,F	Sediment Sb(V)	Sediment As(V)	$r(3) = -0.67$, $p = 0.21$
A,B,C,D,F	Sediment Sb(V) mineral	Sediment orpiment	$r(3) = -0.03$, $p = 0.97$

Table S3. Hamilton test results for Sb linear combination fits optimal fit and highest ranked fit excluding oxidised stibnite. Values for degrees of freedom (a) were taken from the estimated number of measurements provided by ATHENA.

Site	Fit rank	Fit components	R-factor	Hamilton test	p-value
A	1st	Sb(V) 0.759 Oxidised stibnite 0.237	0.000099	r = 0.627 a = 2.2 b = 1	0.36
	9th	Sb(V) 0.977	0.000035		
B	1st	Sb(V) 0.701 Oxidised stibnite 0.242	0.000064	r = 0.646 a = 2.2 b = 1	0.38
	8th	Sb(V) 0.847 Sb(III) 0.143	0.000022		
C	1st	Sb(V) 0.859 Oxidised stibnite 0.105	0.00019	r = 0.950 a = 2.2 b = 0.5	0.65
	2nd	Sb(V) 0.966	0.00020		
F	1st	Sb(V) 0.835 Oxidised stibnite 0.114	0.000097	r = 0.822 a = 2.2 b = 0.5	0.38
	8th	Sb(V) 0.936 Sb(III) 0.056	0.00012		

Table S4. Speciation of dissolved metalloids, total suspended metalloids, and field measurements of water samples. Total aqueous phase concentrations are the sum of dissolved species and suspended sediment metalloid.

Site	Date	Dissolved Sb(III) (µg L^{-1})	Dissolved Sb(V) (µg L^{-1})	Suspended Sb (µg L^{-1})	Total aqueous Sb (µg L^{-1})	Dissolved As(III) (µg L^{-1})	Dissolved As(V) (µg L^{-1})	Suspended As (µg L^{-1})	Total aqueous As (µg L^{-1})	pH	Eh (mV)[1]	EC (µS)	Temp (°C)
A	Dec 18	0	67 ± 1.3	1.0 ± 0.3	68 ± 1.2	1.3 ± 0.08	7.3 ± 0.3	1.0 ± 0.05	9.6 ± 0.2	7.48	651	88	24
B	Dec 18	0	66 ± 0.8	1.2 ± 0.05	67 ± 0.8	1.3 ± 0.1	8 ± 0.5	1.1 ± 0.03	10 ± 0.5	7.33	641	80	25
C	Dec 18	0	134 ± 2.5	1.2 ± 0.08	136 ± 2.6	1.4 ± 0.07	9.2 ± 0.4	1.3 ± 0.08	12 ± 0.4	7.4	670	92	24
D	Dec 18	0	146 ± 6.0	1.5 ± 0.03	148 ± 6.0	1.5 ± 0.1	9.5 ± 0.3	1.7 ± 0.4	13 ± 0.2	7.42	641	93	22
F	Dec 18	0	125 ± 4.3	1.3 ± 0.1	126 ± 4.4	1.4 ± 0.08	5.4 ± 0.1	1.7 ± 0.02	8.6 ± 0.06	7.13	647	97	21
D	Feb 19	3.4 ± 0.7	35 ± 1.3	0.5 ± 0.03	39 ± 0.6	5 ± 0.2	270 ± 6.8	7.9 ± 0.3	284 ± 7	6.7	610	642	23
F	Feb 19	0	142 ± 1.7	1.1 ± 0.06	143 ± 1.7	0.6 ± 0.04	166 ± 1.6	2.9 ± 0.07	170 ± 1.6	7.19	601	522	23
A	April 19	0	510 ± 21.4	2.8 ± 0.6	513 ± 21	6.6 ± 1.3	4.4 ±1.8	12.8 ± 3.6	24 ± 4	6.56	458	631	19
B	April 19	0	1042 ± 21	2.9 ± 0.7	1045 ± 14	2.5 ± 0.2	63 ± 2.0	9.2 ± 2.4	74 ± 2.8	5.58	541	1194	19
D	April 19	0	150 ± 2.1	0.7 ± 0.1	151 ± 2.1	3.2 ± 0.06	168 ± 3.4	7.5 ± 0.4	178 ± 3.7	6.9	547	664	17
F	April 19	0	199 ± 0.6	0.4 ± 0.07	199 ± 0.7	4.0 ± 1.3	146 ± 7.4	2.4 ± 0.3	153 ± 7	6.82	620	486	18
A	July 19	0	92 ± 2.3	2.7 ± 1.3	95 ± 3.2	0.1 ± 0.08	7.3 ± 0.3	15 ± 1.9	22 ± 2.1	6.86	498	589	12
B	July 19	0	240 ± 5.3	14 ± 1.5	255 ± 6.6	0.2 ± 0.2	13 ± 0.5	61 ± 1.2	75 ± 1.4	7.14	506	1313	12
D	July 19	0	123 ± 1.5	1.4 ± 0.6	124 ± 1.9	1.8 ± 0.3	115 ± 0.8	15 ± 1.9	128 ± 2	6.77	623	957	12
F	July 19	0	111 ± 1.5	0.7 ± 0.1	111 ± 1.3	4.4 ± 3.2	67 ± 4.5	7.9 ± 1.0	83 ± 1.8	7.34	605	528	12
A	Feb 20	0	2.6 ± 4	n.d.[2]		0.4 ± 0.1	0.9 ± 0.5	n.d.		7.32	643	102	21
D	Feb 20	0	24 ± 0.5	n.d.		0.6 ± 0.004	9.3 ± 0.4	n.d.		7.38	633	132	23
E	Feb 20	0	115 ± 3.3	n.d.		0	17 ± 0.4	n.d.		7.12	698	96	25

[1] Eh values are relative to the standard hydrogen electrode.

[2] Suspended sediment data not available for February 2020 samples due to logistical constraints during COVID-19 shutdowns.

Table S5. Interlaboratory assessment of samples for total mass balance recovery. All concentrations in μg L^{-1}, with the sum of trivalent and pentavalent species from AFS analysis compared to total metalloid concentration to calculate recovery percentage. December 2018 total concentrations were assessed by ICP-OES, and April 2019 and February 2020 total concentrations assessed by ICP-MS. February 2020 comparisons were run in triplicate, with results displayed as means ± standard error.

Sample	As(III)	As(V)	Total As (ICP)	As recovery	Sb(III)	Sb(V)	Total Sb (ICP)	Sb recovery
Site A (Dec 18)	1.1	7.7	8.8	100 %	0	66	70	94 %
Site B (Dec 18)	1.1	7.7	8.6	102 %	0	66	66	101 %
Site C (Dec 18)	1.5	8.4	11	89 %	0	130	144	90 %
Site D (Dec 18)	1.7	9.0	12	88 %	0	153	157	98 %
Site F (Dec 18)	1.5	5.2	7.8	86 %	0	130	142	92 %
Site A (Apr 19)	7.7	2.5	29	35 %	0	471	630	75 %
Site B (Apr 19)	2.4	62	64	101 %	0	1069	1060	101 %
Site D (Apr 19)	3.3	162	156	106 %	0	148	150	99 %
Site F (Apr 19)	4.2	137	142	100 %	0	198	202	98 %
Site A (Feb 20)	0.4 ± 0.1	1.3 ± 0.3	4.3 ± 0.3	41 % ± 9	0	2.6 ± 1.3	6.3 ± 0.3	40 % ± 19
Site D (Feb 20)	0.6 ± 0.004	9.3 ± 0.3	10 ± 0.7	93 % ± 7	0	24 ± 1.5	38 ± 2.8	63 % ± 4
Site E (Feb 20)	0	18 ± 0.2	17 ± 1.5	107 % ± 8	0	115 ± 2.5	141 ± 1.2	82 % ± 1