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Supplementary material

Relationship of arsenic speciation and bioavailability in mine wastes for human health risk assessment

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Table S1. Soil contamination health investigation levels for arsenic in Australia (NEPC, 2013)[1]

Soil contamination Health Investigation Levels (mg kg^{-1})			
Residential A (low density with garden)	Residential B (high density with minor garden)	Residential C (open space recreational)	Residential D (commercial and industrial)
100	500	300	3000

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Table S2. Statistical data for arsenic, cadmium, copper, cobalt, iron, lead and zinc

An earlier version had *n* = 61 for BAc measurement. Following a review of this data set, 10 sample sets for PBET were removed because they were considered unreliable, giving a useable data set of *n* = 51. The set of total and metal concentrations in the original data set was considered to be reliable for 57 mine waste and environmental samples. Statistical data summary for arsenic, cadmium, copper, cobalt, iron, lead, nickel and zinc concentrations (mg kg^{-1}) (*n* = 57 for As, Cu, Pb and Zn; for Cd, there were two samples at detection limit, giving *n* = 55, and a lesser number of analyses for Co, Fe and Ni because not all samples were analysed for these three metals. MSA, measures of sampling adequacy

Statistic		Arsenic	Cadmium	Copper	Cobalt	Iron	Lead	Nickel	Zinc
MSA		57	55	57	42	47	57	52	57
Mean		1140	81.4	47 400	360	105 000	9270	72.0	14 600
s.e.		369	18.7	134 000	84.8	12 940	1950	16.3	3300
Median		282	25.0	4450	142	57 000	4270	27.5	4900
s.d.		2790	139	101 100	550	88 700	14700	117	24 900
Variance		7 770 000	19 200	10 200 000 000	302 189	7 870 000 000	217 000 000	13 800	619 000 000
Range		13 100	750	576 000	3000	280 000	68 600	679	108 000
Minimum		3	2	40	14	16 000	39	1	16
Maximum		13 100	750	576 000	3010	296 000	68 600	680	108 000
Percentiles	25	120	10.0	864	44.8	43 500	1530	16.0	1220
	50	280	25.0	4450	142	57 000	4270	27.5	4900
	75	6100	68.0	23 400	476	181 000	8250	84.00	9760
	95	10 300	360	251 000	1210	281 000	46 600	320	78 400

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Table S3. Results for NIST SRM (standard reference materials) – soil

NIST-2710a	As (mg kg^{-1})
Certified value (mg kg^{-1})	1540 ± 10 (1300–1600)
Found mean ± s.e., *n* = 2	1607 ± 29
Percentage recovery	104
NIST-2711a	
Certified value	107 ± 5 (81–112)
Found mean ± s.e., *n* = 2	113 ± 7
Percentage recovery	106

Table S4. Results for certified reference materials – blood and urine (blood-metal control certified reference material (CRM) (Seronorm, Sero As, Billingstad, Norway) and Lyphocheck Urine Metals Control Level 1)

Certified reference material	Total As concentration (mg kg^{-1})	
	Blood Seronorm Level 2	Urine Lyphocheck Level 1
Certified value	13.2 (11.9–14.5)	67 (53–80)
Measured results for present project mean ± s.e., *n* = 3	13.98 ± 0.34	71.38 ± 0.59
Percentage recovery	106	107

Table S5. Statistical data for pH and total organic carbon (TOC) and percentage bioaccessibility (BAc)

Variable	*n*	Mean	s.d.	Minimum	Maximum	Percentiles		
						25th	50th (median)	75th
pH	48	6.60	1.5	3	9	6.4	7.0	7.5
TOC	48	2.35	2.37	0.07	10.5	0.96	1.6	2.9
BAc (%)	48	13.7	14.5	0.70	79	5.2	10.1	14.9

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Table S6. Statistical data for principal component analysis of pH, TOC, BAc, arsenic, cadmium, copper, cobalt, iron, lead, nickel and zinc concentration data

Correlation matrix

		pH	TOC	BAc	Arsenic	Cadmium	Copper	Cobalt	Iron	Lead	Nickel	Zinc
Correlation	pH	1.000	0.186	–0.052	–0.259	–0.403	0.049	–0.092	–0.125	–0.498	–0.147	–0.339
	TOC	0.186	1.000	0.751	0.005	–0.214	0.495	0.547	0.207	–0.180	0.564	–0.240
	BAc	–0.052	0.751	1.000	0.305	–0.188	0.364	0.538	0.343	–0.122	0.363	–0.223
	Arsenic	–0.259	0.005	0.305	1.000	–0.052	0.471	0.395	0.478	–0.114	0.234	–0.168
	Cadmium	–0.403	–0.214	–0.188	–0.052	1.000	–0.110	–0.186	–0.179	0.715	0.041	0.380
	Copper	–0049	0.495	0.364	0.471	–0.110	1.000	0.540	0.385	–0.127	0.845	–0.238
	Cobalt	–0.092	0.547	0.538	0.395	–0.186	0.540	1.000	0.703	–0.220	0.595	–0.239
	Iron	–0.125	0.207	0.343	0.478	–0.179	0.385	0.703	1.000	–0.161	0.387	–0.022
	Lead	–0.498	–0.180	–0.122	–0.114	0.715	–0.127	–0.220	–0.161	1.000	0.162	0.605
	Nickel	–0.147	0.564	0.363	0.234	0.041	0.845	0.595	0.387	0.162	1.000	0.061
	Zinc	–0.339	–0.240	–0.223	–0.168	0.380	–0.238	–0.239	–0.022	0.605	0.061	1.000

KMO and Bartlett's Test

Kaiser–Meyer–Olkin measure of sampling adequacy		0.608
Bartlett's test of sphericity	Approximate Chi-square	260.631
	d.f.	55
	Significance	0.000

Anti-image matrices

		pH	TOC	BAc	Arsenic	Cadmium	Copper	Cobalt	Iron	Lead	Nickel	Zinc
Anti-image covariance	pH	0.509	–0.085	0.077	0.132	0.060	–0.075	0.026	–0.035	0.052	0.066	–0.006
	TOC	–0.085	0.190	–0.174	0.081	–0.017	0.006	–0.038	0.061	0.034	–0.038	0.010
	BAc	0.077	–0.174	0.269	–0.096	0.051	–0.002	–0.012	–0.041	–0.052	0.030	0.019
	Arsenic	0.132	0.081	–0.096	0.353	0.003	–0.111	–0.053	–0.061	–0.008	0.070	–0.034
	Cadmium	0.060	–0.017	0.051	0.003	0.445	–0.030	–0.041	0.038	–0.210	0.034	0.011
	Copper	–0.075	0.006	–0.002	–0.111	–0.030	0.100	0.047	–0.003	0.043	–0.081	0.080
	Cobalt	0.026	–0.038	–0.012	–0.053	–0.041	0.047	0.242	–0.177	0.058	–0.058	0.102
	Iron	–0.035	0.061	–0.041	–0.061	0.038	–0.003	–0.177	0.385	0.019	–0.002	–0.112
	Lead	0.052	0.034	–0.052	–0.008	–0.210	0.043	0.058	0.019	0.267	–0.056	–0.090
	Nickel	0.066	–0.038	0.030	0.070	0.034	–0.081	–0.058	–0.002	–0.056	0.085	–0.073
	Zinc	–0.006	0.010	0.019	–0.034	0.011	0.080	0.102	–0.112	–0.090	–0.073	0.462
Anti-image correlation	pH	0.588[A]	–0.275	0.208	0.310	0.125	–0.332	0.075	–0.080	0.141	0.318	–0.012
	TOC	–0.275	0.629[A]	–0.770	0.313	–0.058	0.040	–0.177	0.225	0.151	–0.297	0.032
	BAc	0.208	–0.770	0.626[A]	–0.312	0.148	–0.014	–0.047	–0.127	–0.193	0.200	0.053
	Arsenic	0.310	0.313	–0.312	0.499[A]	0.006	–0.588	–0.182	–0.165	–0.027	0.406	–0.085
	Cadmium	0.125	–0.058	0.148	0.006	0.669[A]	–0.141	–0.126	0.093	–0.609	0.173	0.025
	Copper	–0.332	0.040	–0.014	–0.588	–0.141	0.543[A]	0.301	–0.013	0.262	–0.879	0.372
	Cobalt	0.075	–0.177	–0.047	–0.182	–0.126	0.301	0.711[A]	–0.580	0.227	–0.406	0.305
	Iron	–0.080	0.225	–0.127	–0.165	0.093	–0.013	–0.580	0.707[A]	0.058	–0.012	–0.265
	Lead	0.141	0.151	–0.193	–0.027	–0.609	0.262	0.227	0.058	0.625[A]	–0.374	–0.257
	Nickel	0.318	–0.297	0.200	0.406	0.173	–0.879	–0.406	–0.012	–0.374	0.520[A]	–0.366
	Zinc	–0.012	0.032	0.053	–0.085	0.025	0.372	0.305	–0.265	-.257	-.366	0.631[A]

[A]Measures of sampling adequacy (MSA).

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Communalities

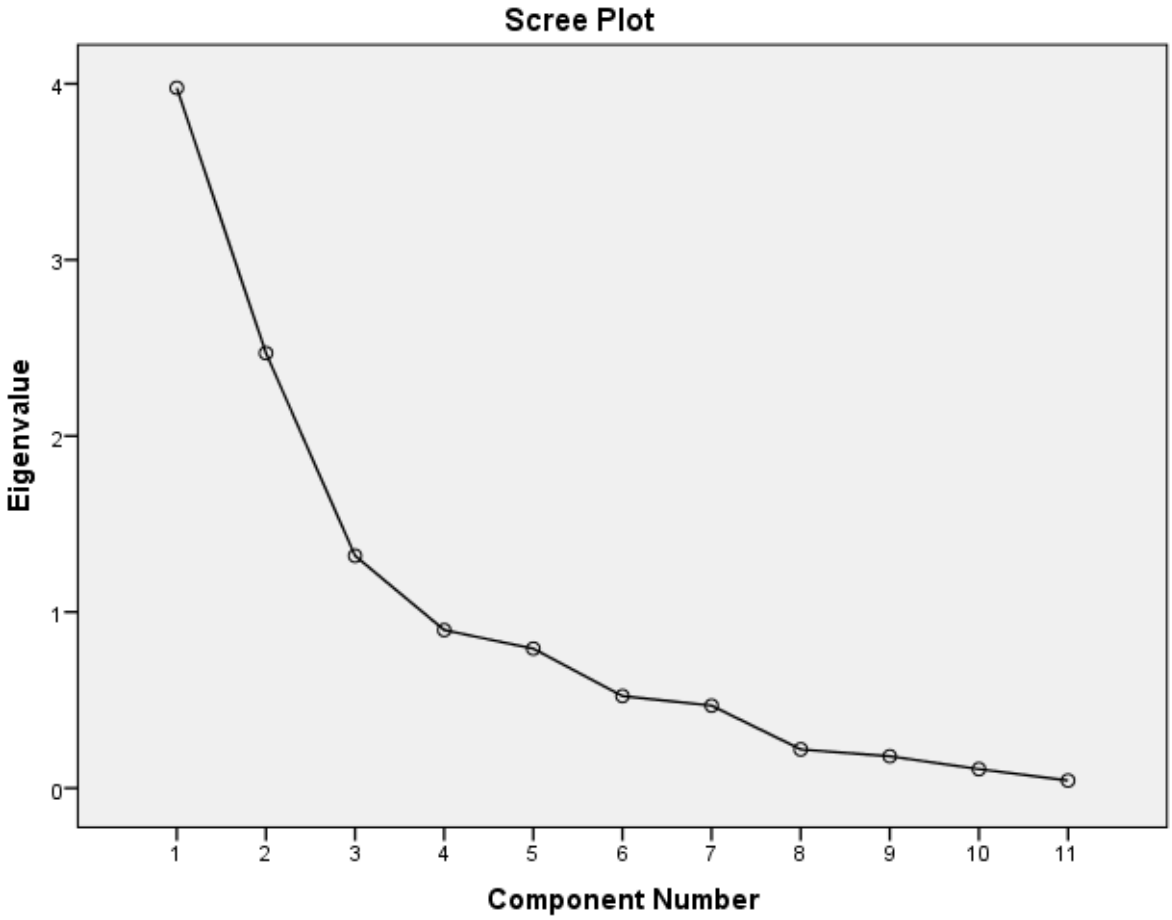
Extraction method: principal component analysis

	Initial	Extraction
pH	1.000	0.633
TOC	1.000	0.883
BAc	1.000	0.565
Arsenic	1.000	0.735
Cadmium	1.000	0.653
Copper	1.000	0.665
Cobalt	1.000	0.751
Iron	1.000	0.668
Lead	1.000	0.861
Nickel	1.000	0.799
Zinc	1.000	0.553

Total variance explained

Extraction method: principal component analysis. When components are correlated, sums of squared loadings cannot be added to obtain a total variance

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings
	Total	Percentage of variance	Cumulative percentage	Total	Percentage of variance	Cumulative percentage	Total
1	3.977	36.152	36.152	3.977	36.152	36.152	3.526
2	2.470	22.459	58.611	2.470	22.459	58.611	2.703
3	1.319	11.994	70.604	1.319	11.994	70.604	2.335
4	0.898	8.159	78.764				
5	0.792	7.201	85.965				
6	0.523	4.757	90.722				
7	0.469	4.261	94.983				
8	0.220	2.001	96.984				
9	0.181	1.644	98.628				
10	0.108	0.980	99.608				
11	0.043	0.392	100.000				



Component matrix

Extraction method: principal component analysis; three components extracted

	Component		
	1	2	3
Cobalt	0.846	0.147	–0.114
Copper	0.788	0.193	
TOC	0.730		0.590
BAc	0.712		0.232
Nickel	0.706	0.464	0.293
Iron	0.649	0.197	–0.456
Lead	–0.364	0.824	0.224
pH		–0.729	0.311
Cadmium	–0.365	0.709	0.130
Zinc	–0.390	0.625	
Arsenic	0.507	0.219	–0.656

Reproduced correlations

Extraction method: principal component analysis. Residuals are computed between observed and reproduced correlations. There are 28 (50.0 %) non-redundant residuals with absolute values greater than 0.05

		pH	TOC	BAc	Arsenic	Cadmium	Copper	Cobalt	Iron	Lead	Nickel	Zinc
Reproduced correlation	pH	0.633[A]	0.265	0.079	–0.329	–0.502	–0.060	–0.085	–0.241	–0.556	–0.199	–0.453
	TOC	0.265	0.883[A]	0.655	–0.026	–0.220	0.617	0.544	0.196	–0.169	0.668	–0.255
	BAc	0.079	0.655	0.565[A]	0.222	–0.189	0.592	0.585	0.368	–0.160	0.597	–0.220
	Arsenic	–0.329	–0.026	0.222	0.735[A]	–0.115	0.386	0.536	0.672	–0.151	0.268	–0.125
	Cadmium	–0.502	–0.220	–0.189	–0.115	0.653[A]	–0.140	–0.219	–0.156	0.746	0.110	0.598
	Copper	–0.060	0.617	0.592	0.386	–0.140	0.665[A]	0.685	0.510	–0.109	0.671	–0.179
	Cobalt	–0.085	0.544	0.585	0.536	–0.219	0.685	0.751[A]	0.630	–0.212	0.632	–0.249
	Iron	–0.241	0.196	0.368	0.672	–0.156	0.510	0.630	0.668[A]	–0.176	0.416	–0.174
	Lead	–0.556	–0.169	–0.160	–0.151	0.746	–0.109	–0.212	–0.176	0.861[A]	0.191	0.679
	Nickel	–0.199	0.668	0.597	0.268	0.110	0.671	0.632	0.416	0.191	0.799[A]	0.043
	Zinc	–0.453	–0.255	–0.220	–0.125	0.598	–0.179	–0.249	–0.174	0.679	0.043	0.553[A]
Residual	pH		–0.079	–0.131	0.070	0.099	0.109	–0.007	0.117	0.058	0.052	0.113
	TOC	–0.079		0.097	0.031	0.006	–0.123	0.003	0.011	–0.011	–0.104	0.015
	BAc	–0.131	0.097		0.083	0.001	–0.228	–0.047	–0.025	0.038	–0.234	–0.003
	Arsenic	0.070	0.031	0.083		0.062	0.085	–0.141	–0.194	0.037	–0.033	–0.044
	Cadmium	0.099	0.006	0.001	0.062		0.029	0.033	–0.023	–0.031	–0.068	–0.218
	Copper	0.109	–0.123	–0.228	0.085	0.029		–0.145	–0.126	–0.018	0.174	–0.059
	Cobalt	–0.007	0.003	–0.047	–0.141	0.033	–0.145		0.072	–0.008	–0.038	0.011
	Iron	0.117	0.011	–0.025	–0.194	–0.023	–0.126	0.072		0.015	–0.029	0.152
	Lead	0.058	–0.011	0.038	0.037	–0.031	–0.018	–0.008	0.015		–0.029	–0.074
	Nickel	0.052	–0.104	–0.234	–0.033	–0.068	0.174	–0.038	–0.029	–0.029		0.018
	Zinc	0.113	–0.015	–0.003	–0.044	–0.218	–0.059	0.011	0.152	–0.074	0.018	

[A]Reproduced communalities.

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Pattern matrix

Extraction method: principal component analysis. Rotation method: Oblimin with Kaiser normalisation. Rotation converged in seven iterations

	Component		
	1	2	3
TOC	0.952	–0.122	0.311
Nickel	0.858	0.306	
BAc	0.714		
Copper	0.704		–0.250
Cobalt	0.596	–0.120	–0.449
Lead		0.933	0.135
Cadmium		0.805	
Zinc		0.725	
pH		–0.650	0.455
Arsenic			–0.861
Iron	0.221		–0.716

Structure matrix

Extraction method: principal component analysis. Rotation method: Oblimin with Kaiser normalisation

	Component		
	1	2	3
TOC	0.881	–0.278	
Nickel	0.835	0.167	–0.344
Copper	0.780	–0.133	–0.456
Cobalt	0.747	–0.216	–0.623
BAc	0.744	–0.213	–0.258
Lead		0.917	0.103
Cadmium	–0.151	0.804	
Zinc	–0.202	0.735	
Ph		–0.664	0.434
Arsenic	0.243		–0.855
Iron	0.445	–0.122	–0.781

Component correlation matrix

Extraction method: principal component analysis. Rotation method: Oblimin with Kaiser normalisation

Component	1	2	3
1	1.000	–0.163	–0.293
2	–0.163	1.000	–0.004
3	–0.293	–0.004	1.000

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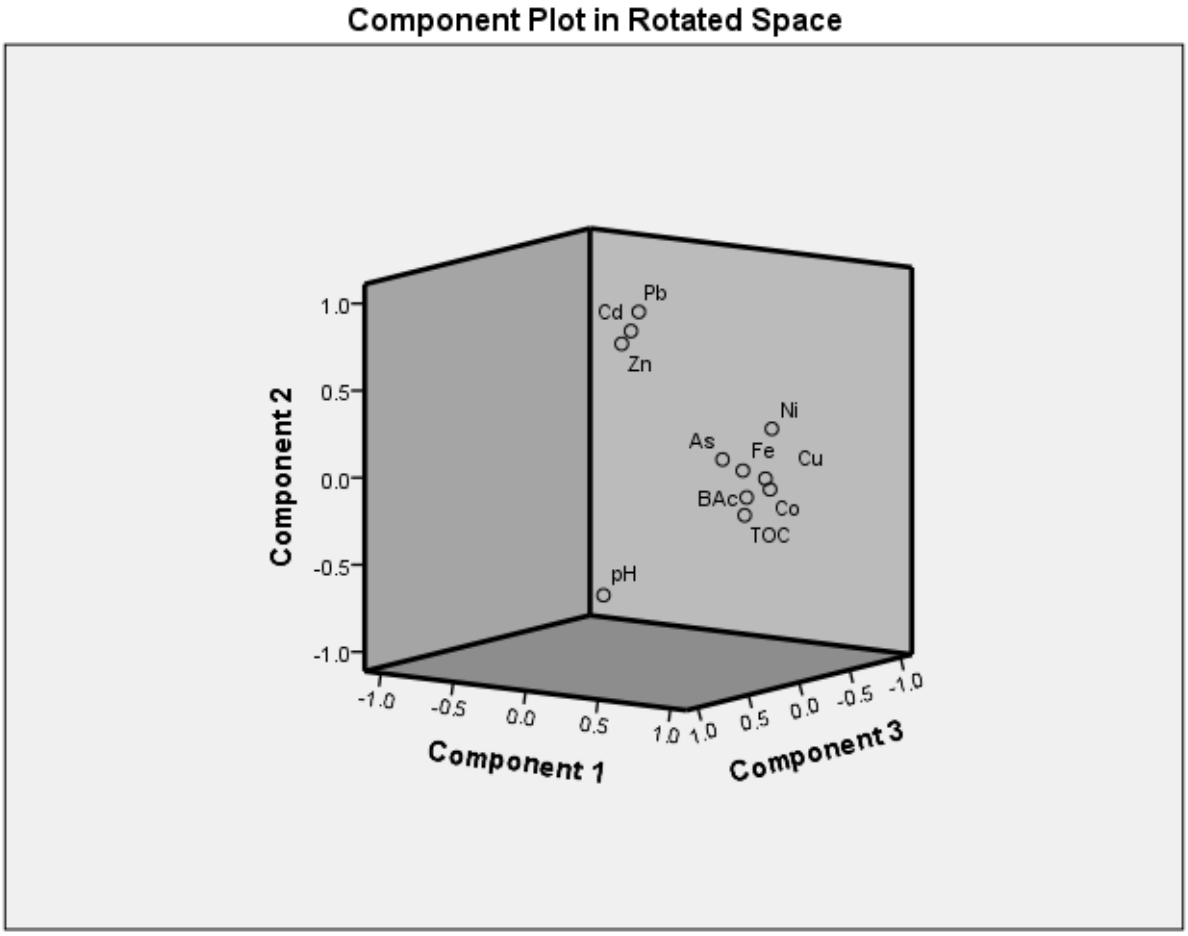

Table S7. Calculation of As bioaccessibility (%) resulting from X-ray absorption near-edge spectroscopy (XANES) fitting spectra for As speciation from mine waste samples for comparison with As bioaccessibility (%) measured using simulated gastric extraction ((As BAc/As Total) × 100)

XAS, X-ray absorption spectroscopy

		Composite carpet dustM2	Composite roof dustM2	Composite soilM2	Dispersed mineralisationM1	Processing areaM1	Waste rockM1	TailingsM1	Processing dust1M2	Concentrate dustM2	TailingsM2	Mineral outcropM2	Processing residueM2
As total (mg kg^{-1})		37.93	223	7	102	1514	16	6	341	180	222	190	3132
Standard	RBAc[A]												
Sodium arsenite	100 %												
Sodium arsenate	58 %	26 %		24 %					26 %				10 %
Arsenic tri-iodide	5 %												
Calcium arsenate	36 %		3 %	10 %					19 %				
Ferric arsenate pure material	35 %	45 %	84 %	74 %	100 %		98 %	47 %	43 %		23 %	94 %	73 %
Arsenic(V) oxide hydrate	33 %												
Calcium arsenite	28 %											7 %	
Fe : As (1 : 1)	26 %												
Fe : As (3 : 1)	19 %												
Fe : As (6 : 1)	15 %												
α-Arsenic	15 %												22 %
Arsenopyrite	05 %					85 %		37 %		20 %	25 %		
Scorodite	03 %												
Arsenic(III) sulfide	02 %	29 %						12 %	20 %	80 %	39 %		
Arsenic(III) oxide	02 %												
Realgar	01 %		14 %	9 %							13 %		
Aluminium arsenate[B]						14 %							
Percentage bioaccessible XAS		31 %	14 %	15 %	15 %	5 %	15 %	14 %	28 %	6 %	6 %	35 %	17 %
Percentage soluble As/total As measured		31 %	11 %	15 %	14 %	11 %	8 %	10 %	15 %	8 %	10 %	35 %	10 %

[A]Relative bioaccessibility (RBAc) (reference sodium arsenite = 100 %).

[B]RBAc for aluminium arsenate was not measured.

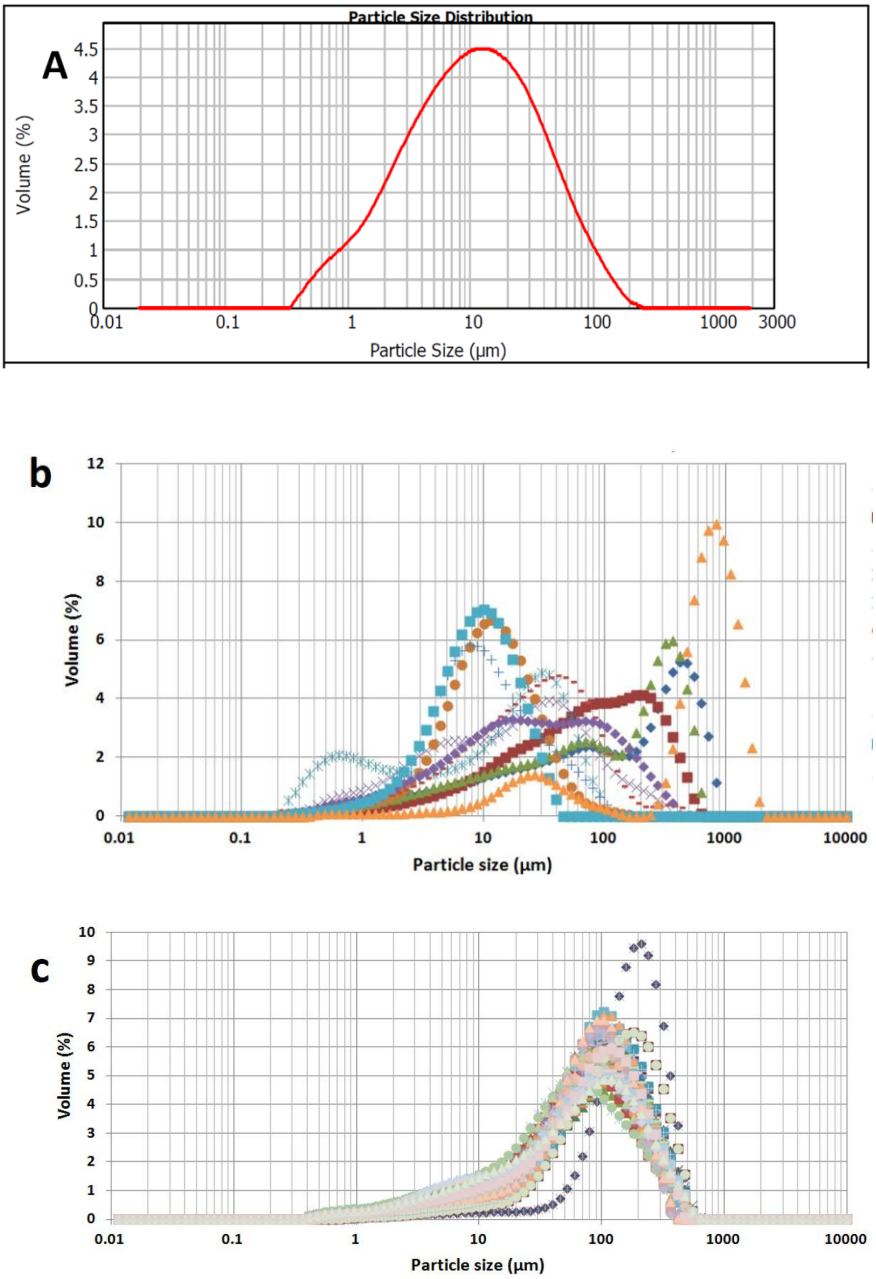

Fig. S1. Particle size distributions by volume of mine waste and soil measured by Malvern Mastersizer 2000 at the University of Queensland. (a) Example of particle size distribution for a typical mine waste material ground and then sieved to <250 µm for subsequent analysis. Mechanical grinding of all bulk mine waste rock and mineralised materials and some samples of mine waste for rat bioavailability study (see Table 1) was aimed to achieve a particle size distribution profile similar to that in (a). (b) Examples of particle size distributions for some mine waste samples (n = 11) sieved to <250 µm (note most of samples are <100–250 µm, some are similar to the ground mine waste with a median size of ~10 µm). (c) Examples of particle size distributions for some soil samples (n = 15) sieved to <250 µm (note the profile is centred at ~100 µm).

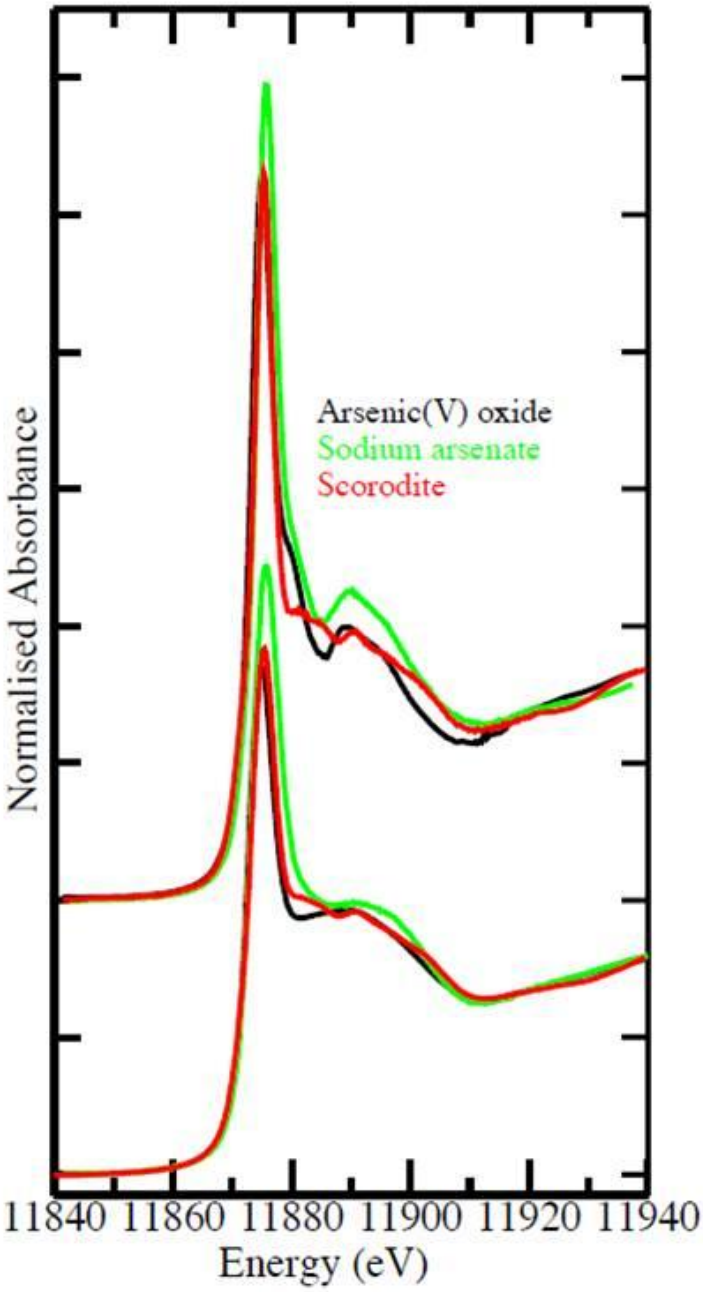

Fig. S2. Comparison of As K-edge XANES spectra for arsenic(V) oxide (black trace), sodium arsenate (green trace) and scorodite (red trace), recorded at ANBF (below – data from main text – diluted in BN to ~1000 ppm) and at the Australian Synchrotron XAS beam line (above – diluted to <100 ppm in cellulose, recorded at 5 K in fluorescence mode).

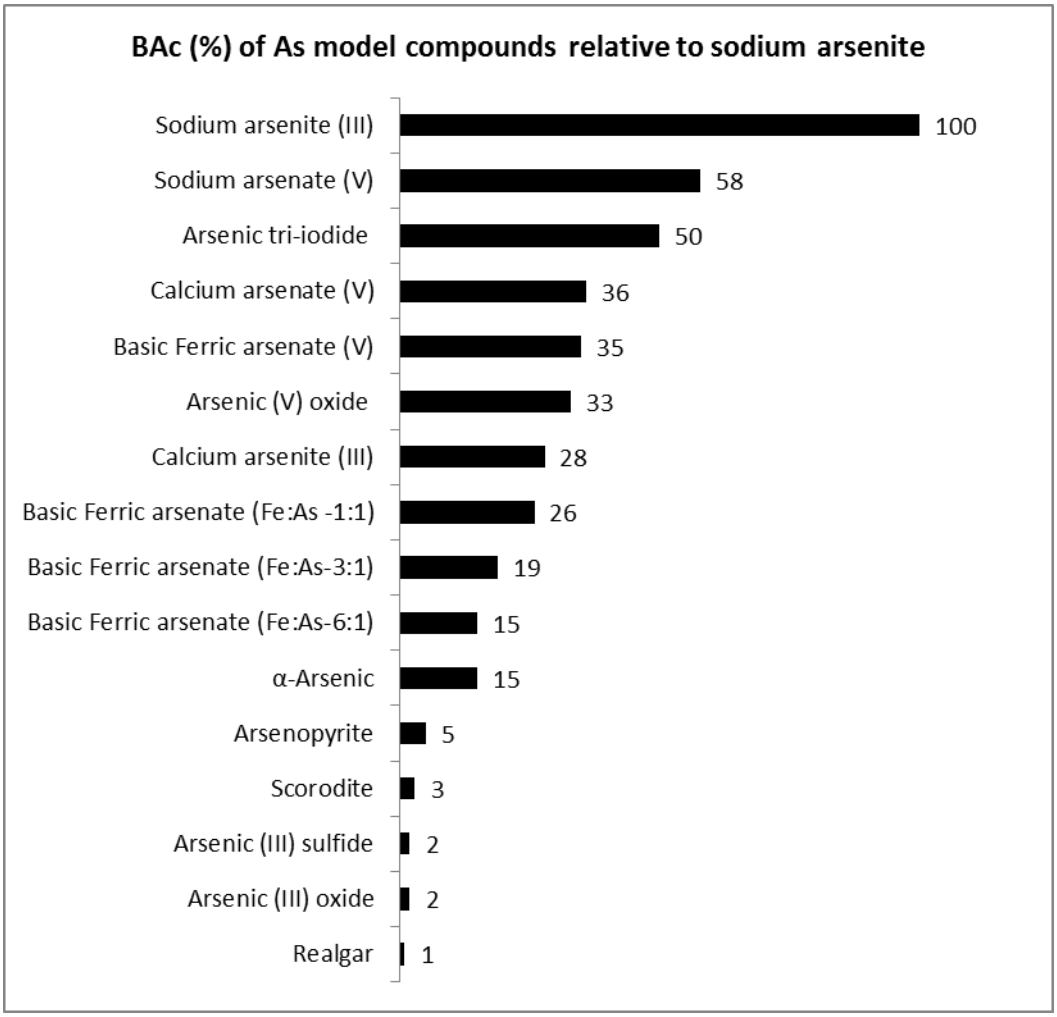

Fig. S3. Relative bioaccessibility in percentage form of arsenic reference compounds from measured PBET values normalised against the bioaccessibility of sodium arsenite and used for XANES analysis of arsenic speciation in mine site and environmental sample.

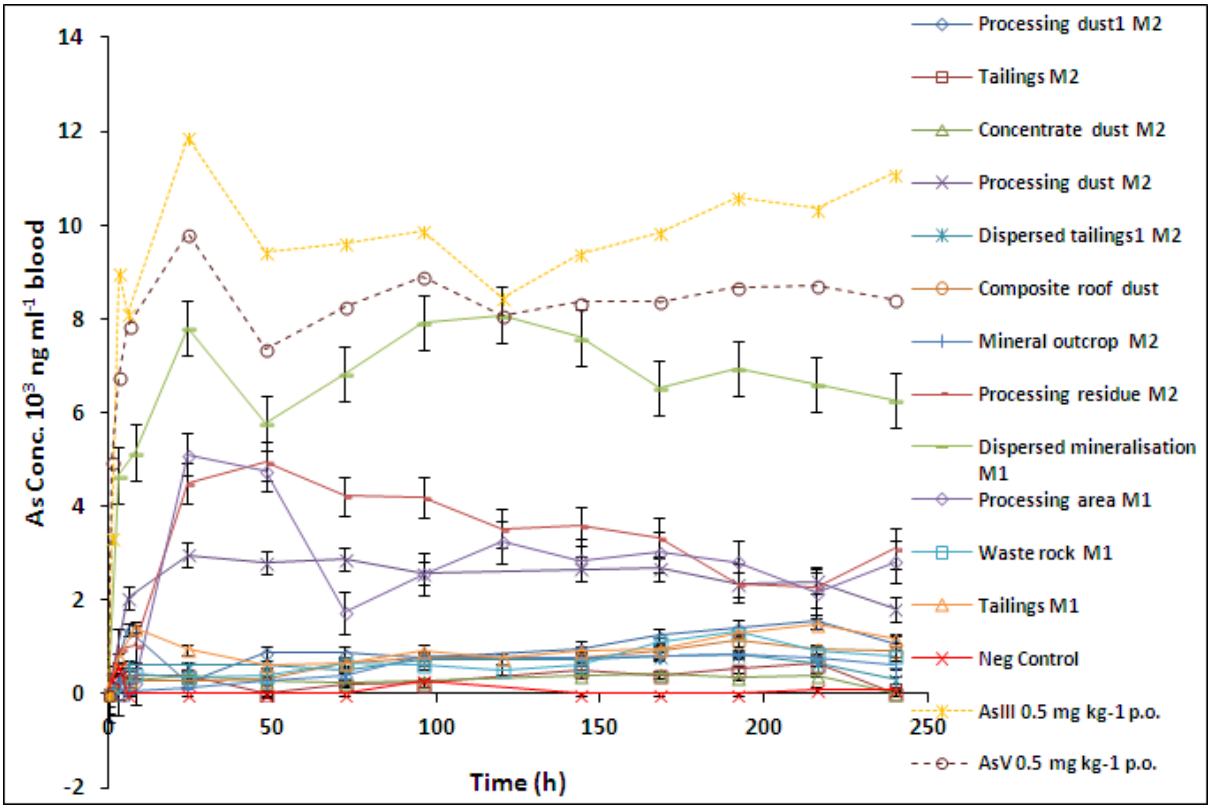

Fig. S4. Arsenic blood concentration–time curve for different mine wastes orally dosed to groups of rats, and the negative control group dosed with an equivalent volume of water and fed on normal rat feed. (Mean ± s.e., *n* = 4–5.)

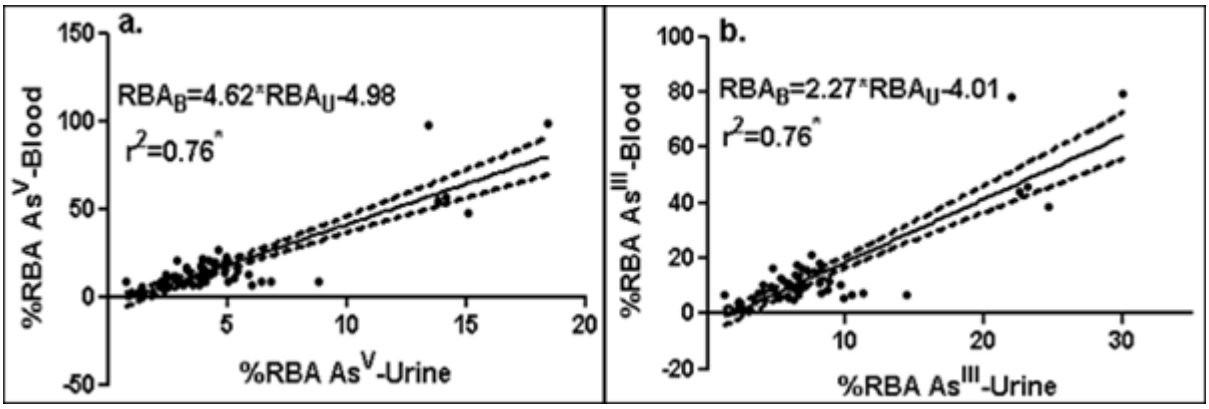

Fig. S5. Comparison between the RBA determined from As concentrations in rat blood (B) and urine (U), for (a) As^{V}; and (b) As^{III}. Line of best fit (solid line) and 95 % confidence intervals (dashed line); *, statistically significant at $P < 0.01$.

Reference

[1] Guideline on Health-based investigation levels. Schedule B7, in *National Environment Protection (Assessment of Site Contamination) Measure. – Guideline on Investigation Levels for Soil and Groundwater* **2013** (National Environmental Protection Council: Canberra) pp. 10–11. Available at http://www.scew.gov.au/nepms/assessment-of-site-contamination.html [Verified 3 November 2015].