Appendix J

Results of Mineral Speciation and Physically-Based Extraction Test (PBET)

Summary of XANES Results for Lead and Arsenic

Five lead and eleven arsenic soil samples from the site were analyzed by EPA using the X-ray absorption near edge structure (XANES) method, a type of absorption spectroscopy, to obtain information about the mineralogy and forms of lead and arsenic present in soil. Figures 1 and 2 show the lead data. Figure 1 shows the XANES spectra for the samples. It appears that lead speciation is uniform in all samples except the KS sample. Figure 2 shows the XANES patterns for the lead standards. The KS sample appears to be similar to lead carbonate (cerussite) while the other samples look like adsorbed lead to an iron oxide.

The arsenic data are presented in Figures 3 through 13. Table 1 provides a summary of the arsenic results. The HSS samples have arsenate (AsV) as the primary oxidation state. In addition, some HSS samples have scorodite. The PCON sample has a mixture of arsenate and arsenopyrite. Scorodite is the oxidation breakdown product of arsenopyrite. Scorodite further breaks down to arsenic sorbed to an iron oxide. Based on these results, the bioavailability of the PCON samples is expected to be less than the HSS samples due to oxidation processes.

Figure 1. XANES Spectra for Pb Samples

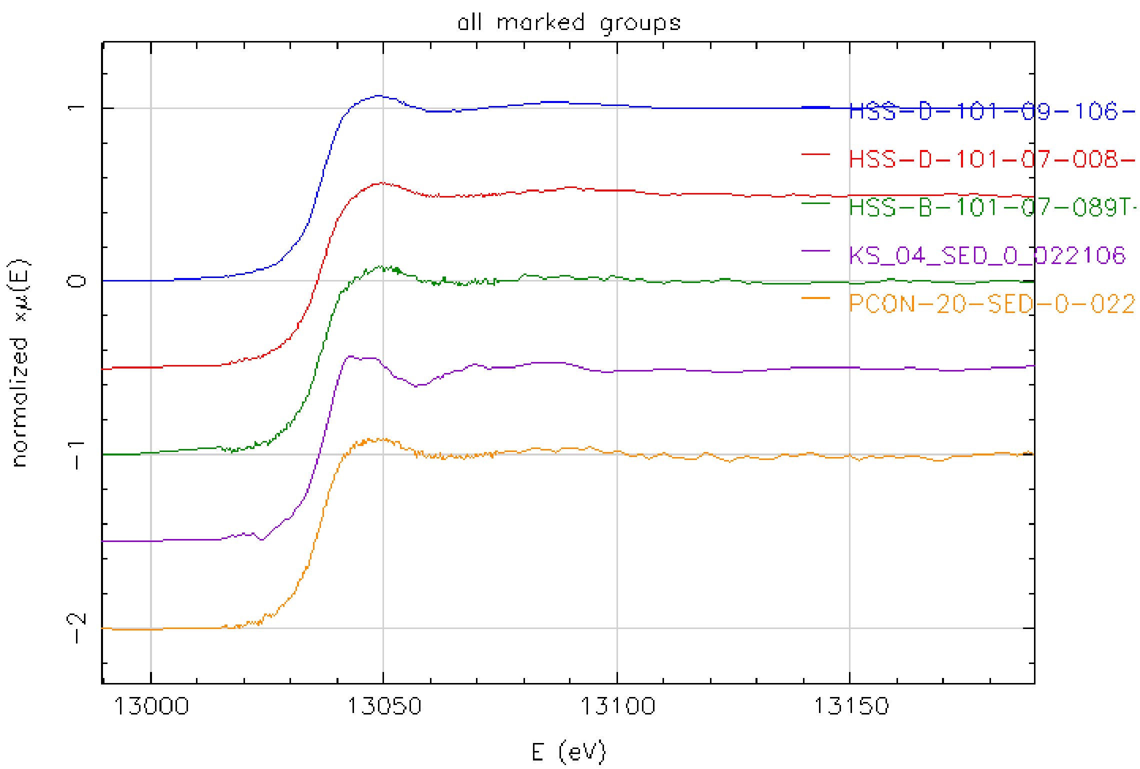


Figure 2. XANES Spectra for Pb Standards

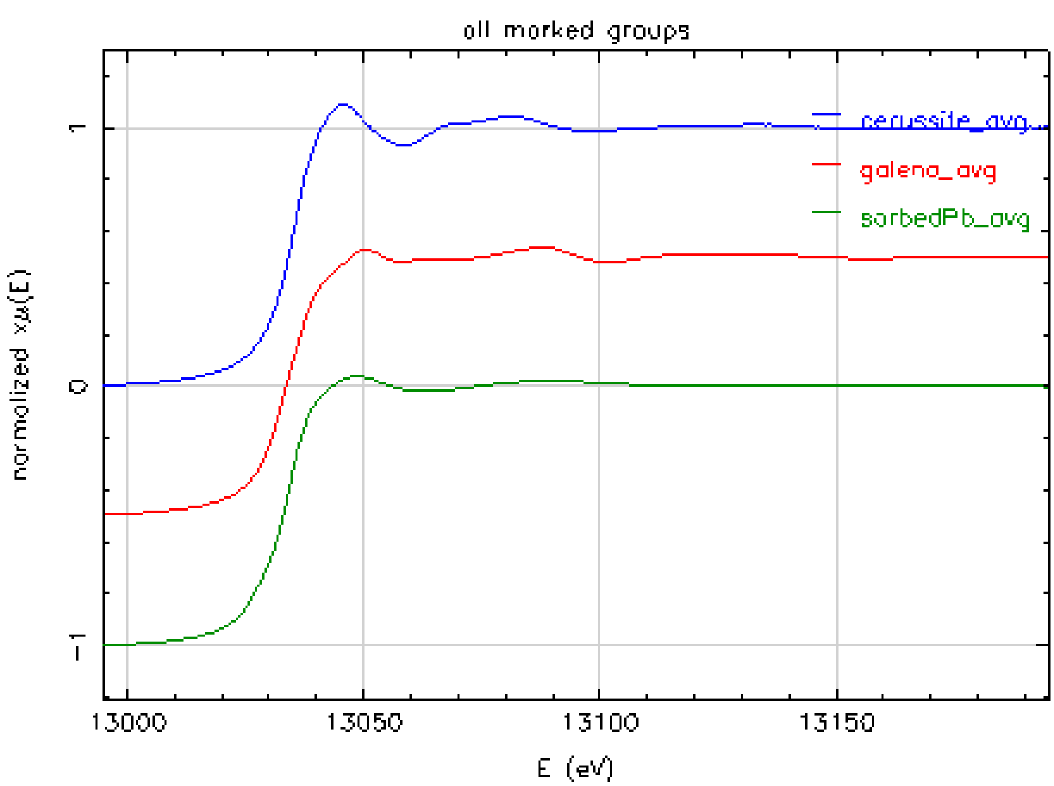
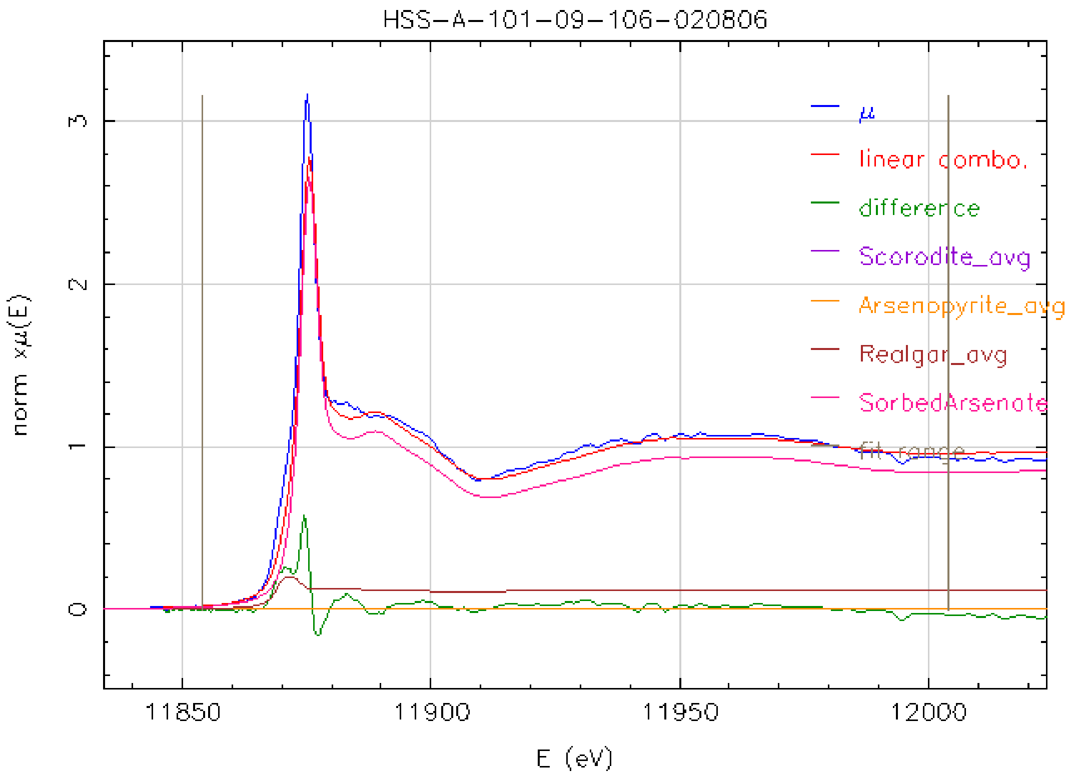


TABLE 1. **XANES Results for Arsenic**

		% Composition				
Sample #	% Error	Scorodite	Sorbed As(V)	Arsenopyrite	Realgar	Orpiment
HSS-A-101-09-106-020806	1.3		88.5		11.5	
HSS-B-101-07-089T-020706	2.0		87.1			12.9
HSS-H-101-07-008-020906	1.1		100.0			
HSS-A-101-07-089S-020706	1.1		100.0			
HSS-I-101-07-089S-020706	3.2		89.4		10.6	
HSS-I-101-07-089T-020706	2.1		96.2		3.8	
HSS-D-101-09-106-020806	1.0	35.4	59.8		4.8	
HSS-D-101-07-008-020906	2.3	1.0	86.6		12.4	
HSS-G-101-07-088-021006	3.0		65.6		34.4	
KS-04-SED-0-022106 *	48.4		100.0			
PCON-20-SED-0-02220	1.3		24.8	75.2		

* very poor data quality for this sample

Figure 3.

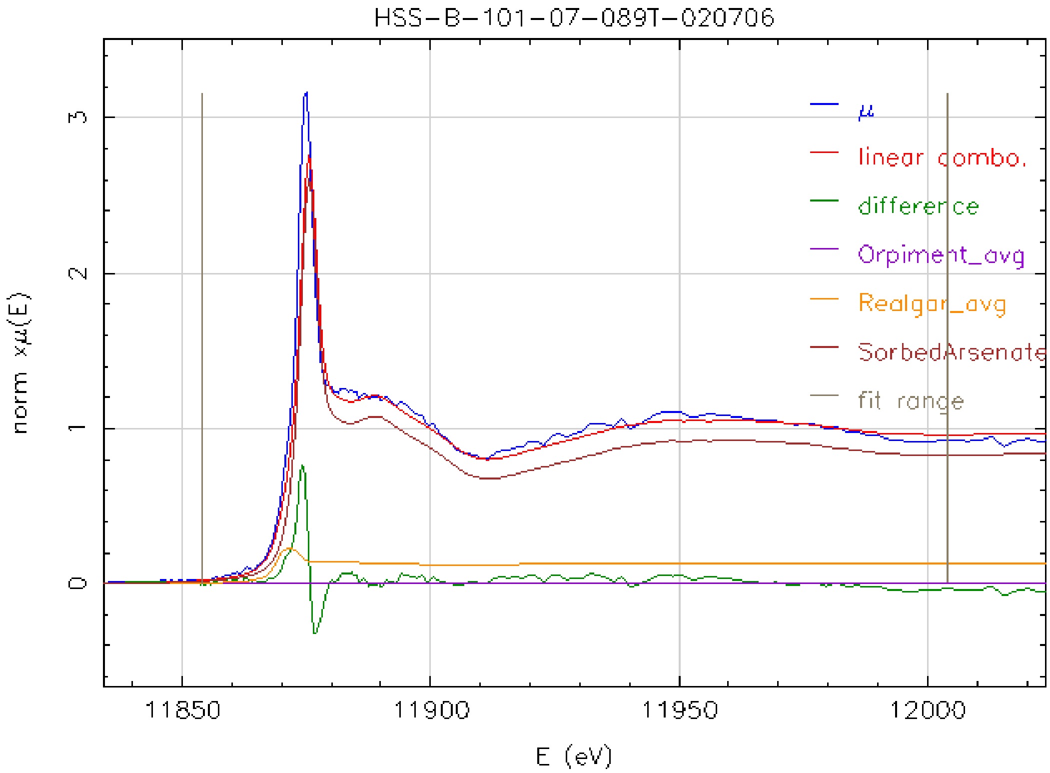


Fitting HSS-A-101-09-106-020806 as norm(E) from -20.000 to 130.000

Fit included 143 data points and 3 variables
R-factor = 0.010030
chi-square = 1.80307
reduced chi-square = 0.0127877

group	weight
19: Scorodite_avg	0.000(0.000)
20: Arsenopyrite_avg	0.000(0.000)
24: Realgar_avg	0.115(0.000)
26: SorbedArsenate	0.885(0.000)

Figure 4.

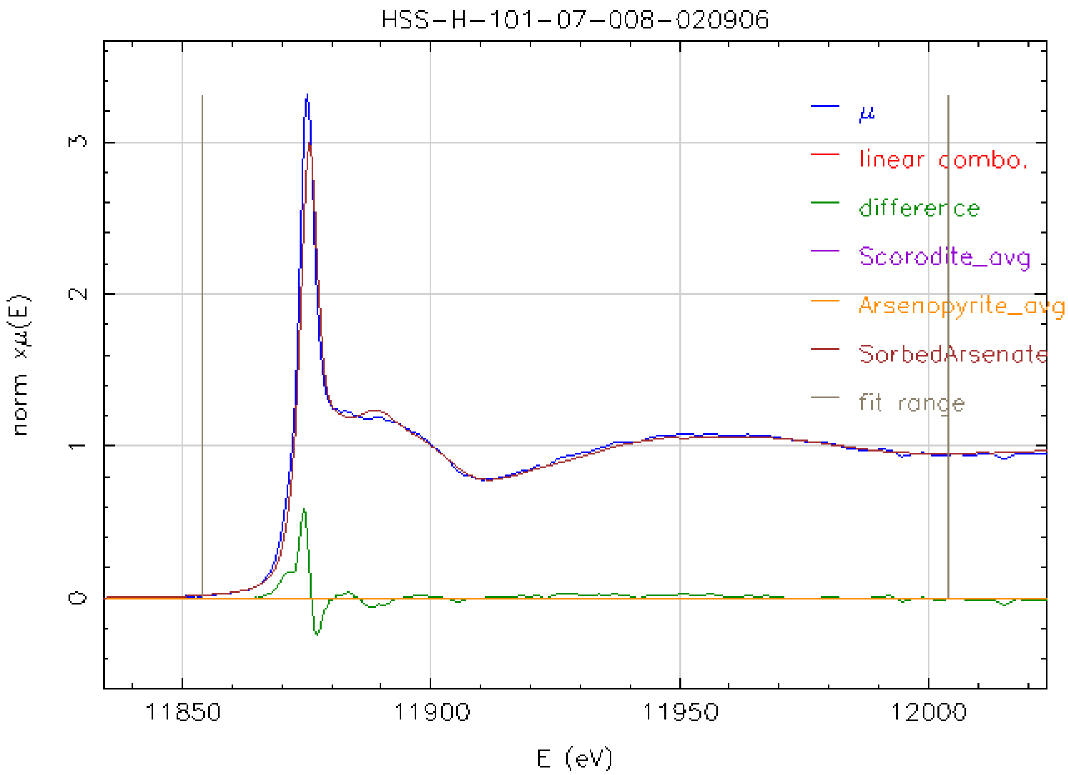


Fitting HSS-B-101-07-089T-020706 as norm(E) from -20.000 to 130.000

Fit included 143 data points and 2 variables
R-factor = 0.015881
chi-square = 2.83765
reduced chi-square = 0.0199835

group	weight
23: Orpiment_avg	0.000(0.000)
24: Realgar_avg	0.129(0.000)
26: SorbedArsenate	0.871(0.000)

Figure 5.

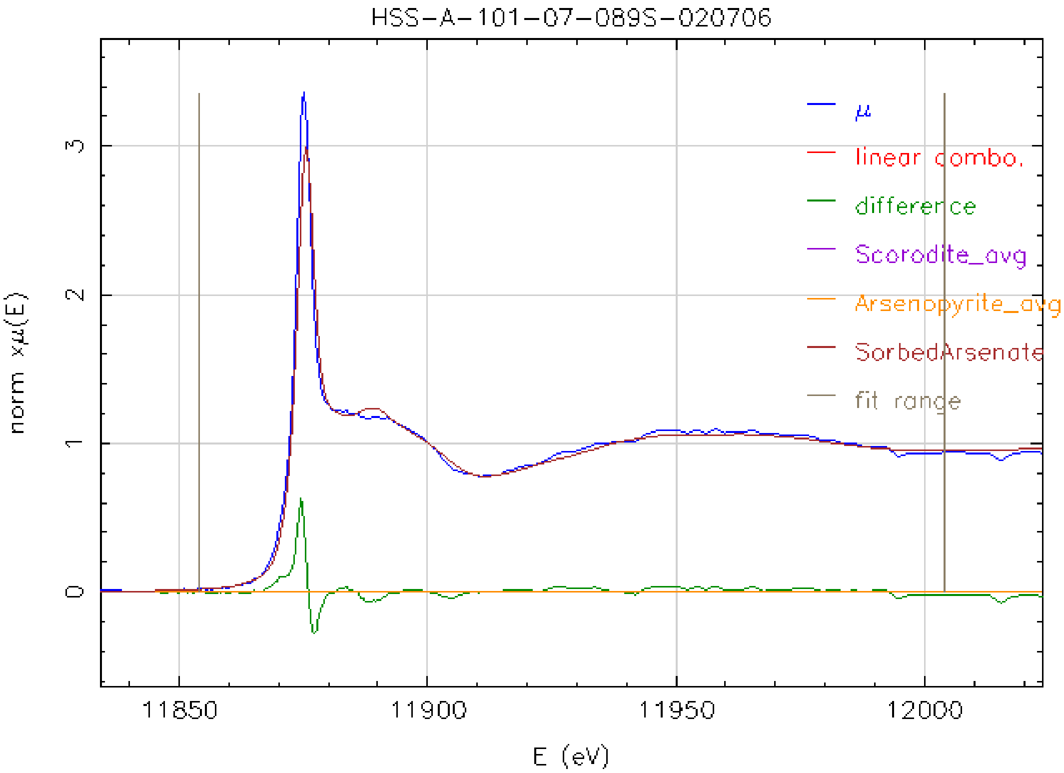


Fitting HSS-H-101-07-008-020906 as norm(E) from -20.000 to 130.000

Fit included 143 data points and 2 variables
R-factor = 0.008440
chi-square = 1.51048
reduced chi-square = 0.0106372

group	weight
19: Scorodite_avg	0.000(0.000)
20: Arsenopyrite_avg	0.000(0.000)
26: SorbedArsenate	1.000(0.000)

Figure 6.

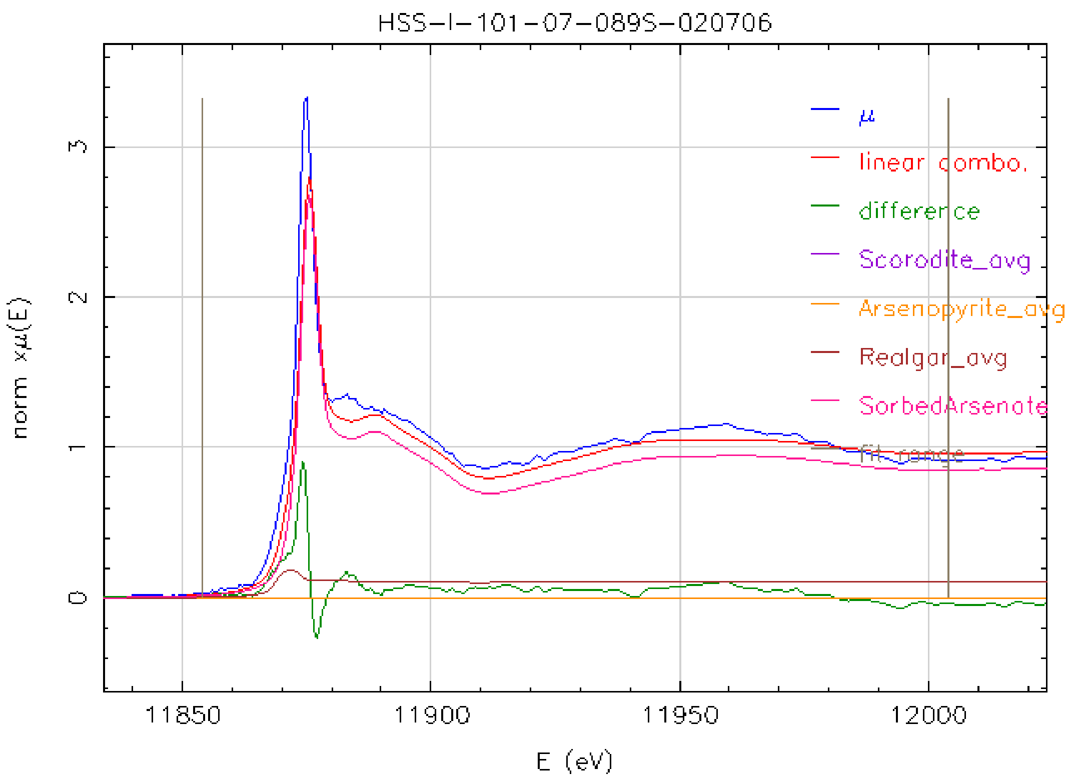


Fitting HSS-A-101-07-089S-020706 as norm(E) from -20.000 to 130.000

Fit included 143 data points and 2 variables
R-factor = 0.008537
chi-square = 1.52222
reduced chi-square = 0.0107199

group	weight
19: Scorodite_avg	0.000(0.000)
20: Arsenopyrite_avg	0.000(0.000)
26: SorbedArsenate	1.000(0.000)

Figure 7.

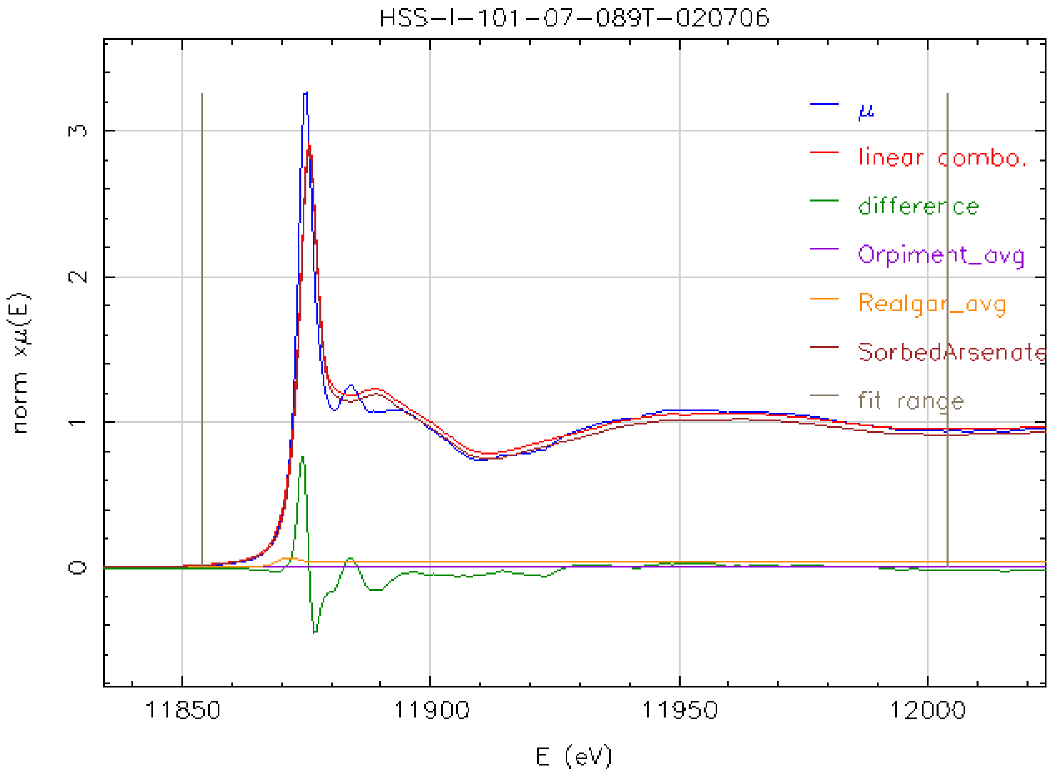


Fitting HSS-I-101-07-089S-020706 as norm(E) from -20.000 to 130.000

Fit included 136 data points and 3 variables
R-factor = 0.023288
chi-square = 4.33835
reduced chi-square = 0.0323758

group	weight
19: Scorodite_avg	0.000(0.000)
20: Arsenopyrite_avg	0.000(0.000)
24: Realgar_avg	0.106(0.000)
26: SorbedArsenate	0.894(0.000)

Figure 8.

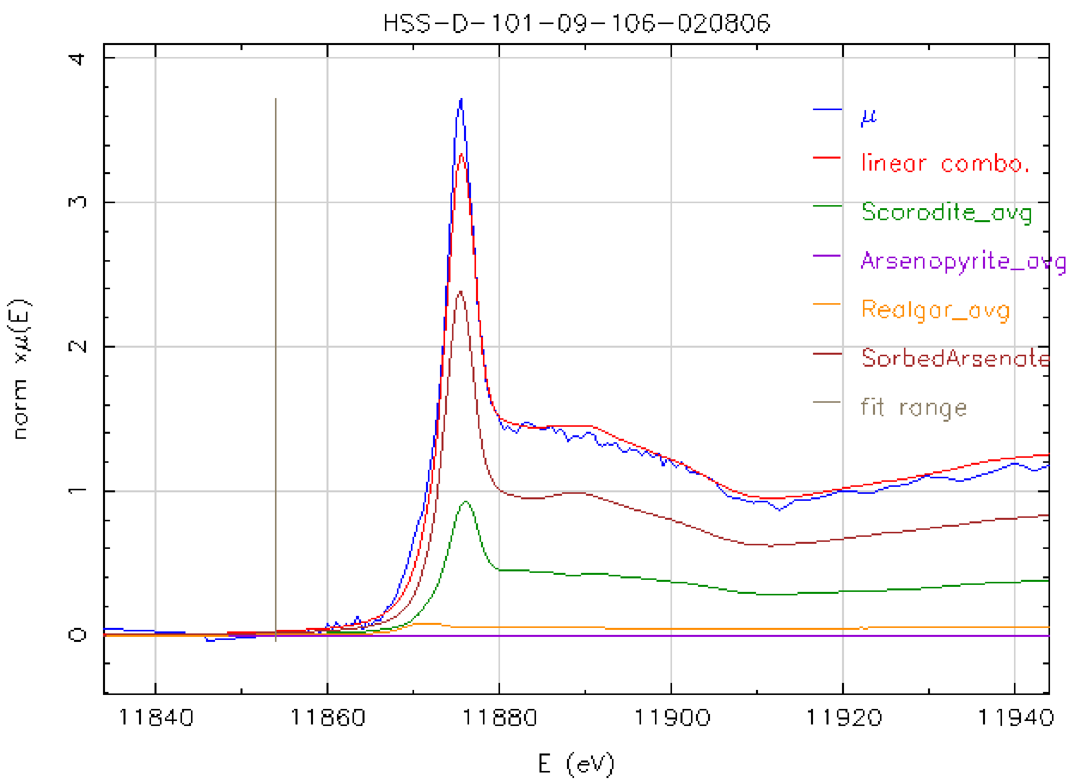


Fitting HSS-I-101-07-089T-020706 as norm(E) from -20.000 to 130.000

Fit included 143 data points and 2 variables
R-factor = 0.018143
chi-square = 3.04290
reduced chi-square = 0.0214289

group	weight
23: Orpiment_avg	0.000(0.000)
24: Realgar_avg	0.038(0.000)
26: SorbedArsenate	0.962(0.000)

Figure 9.

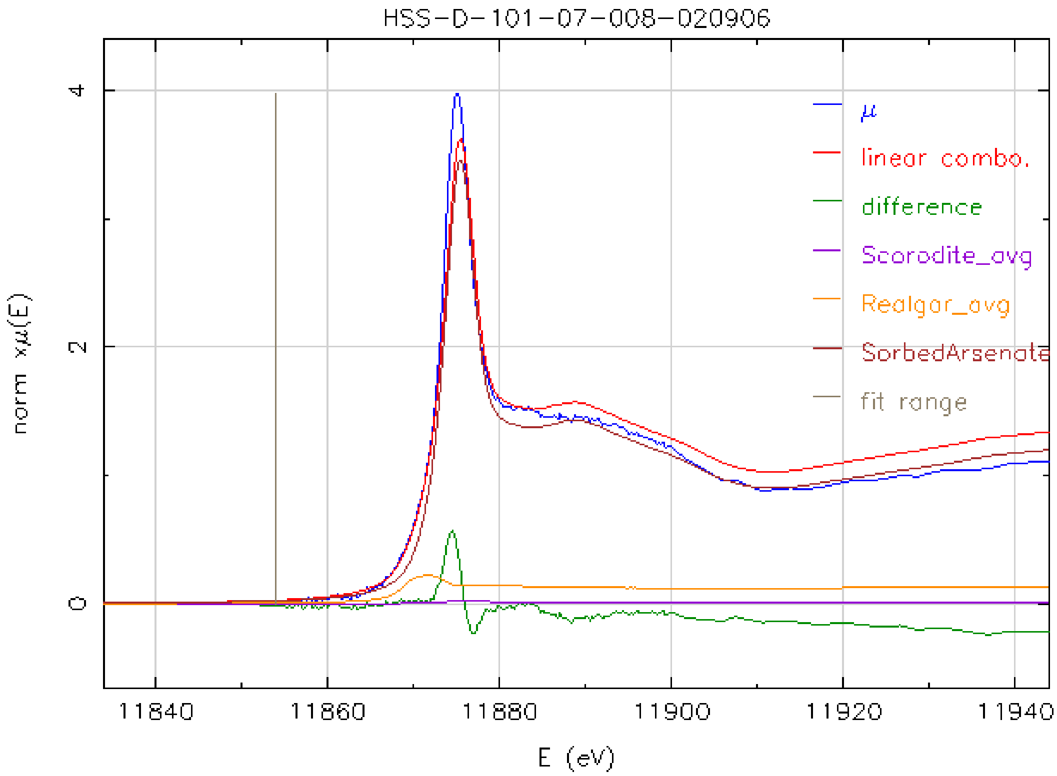


Fitting HSS-D-101-09-106-020806 as norm(E) from -20.000 to 130.000

Fit included 172 data points and 3 variables
R-factor = 0.006584
chi-square = 1.74062
reduced chi-square = 0.0102995

group	weight
19: Scorodite_avg	0.354(0.000)
20: Arsenopyrite_avg	0.000(0.000)
24: Realgar_avg	0.048(0.000)
26: SorbedArsenate	0.598(0.000)

Figure 10.

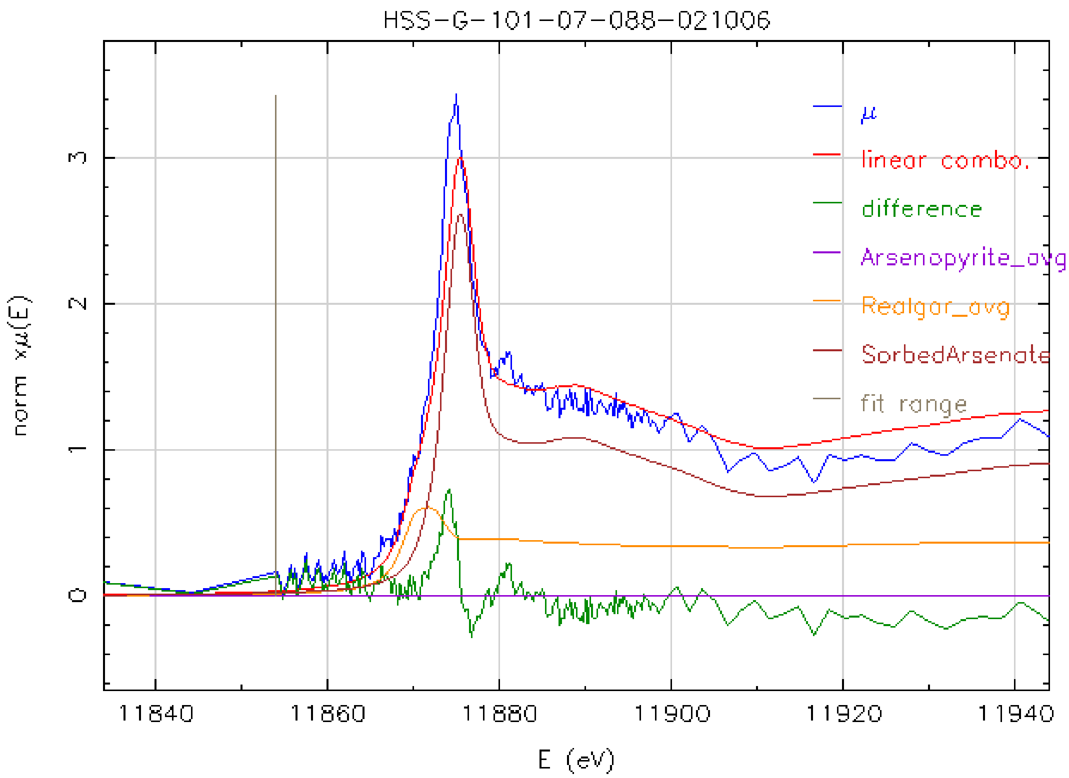


Fitting HSS-D-101-07-008-020906 as norm(E) from -20.000 to 130.000

Fit included 225 data points and 2 variables
R-factor = 0.011163
chi-square = 5.05375
reduced chi-square = 0.0225614

group	weight
19: Scorodite_avg	0.010(0.041)
24: Realgar_avg	0.124(0.024)
26: SorbedArsenate	0.866(0.047)

Figure 11.

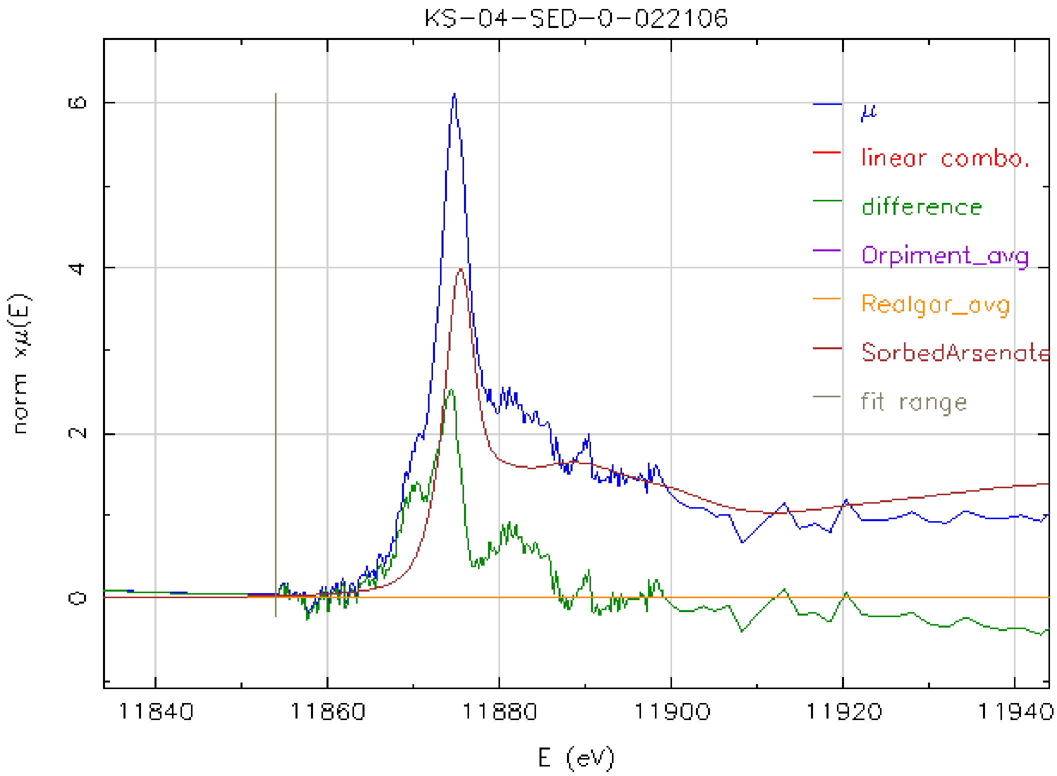


Fitting HSS-G-101-07-088-021006 as norm(E) from -20.000 to 130.000

Fit included 227 data points and 2 variables
R-factor = 0.017656
chi-square = 6.87171
reduced chi-square = 0.0304058

group	weight
20: Arsenopyrite_avg	0.000(0.000)
24: Realgar_avg	0.344(0.000)
26: SorbedArsenate	0.656(0.000)

Figure 12.

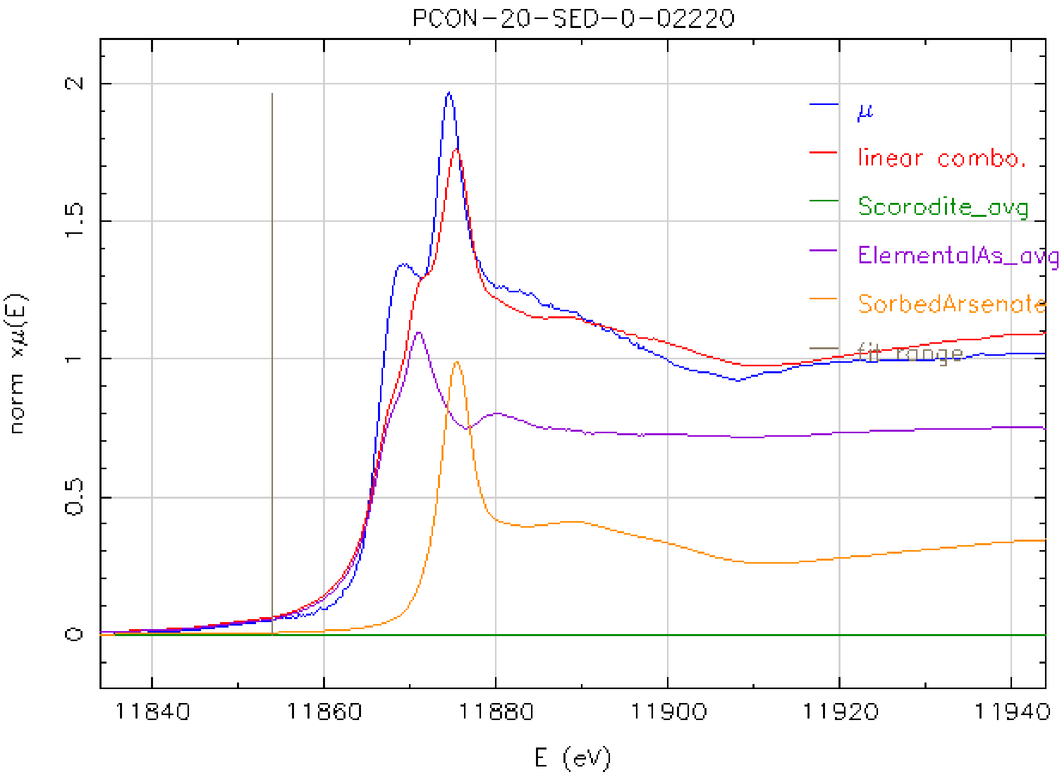


Poor data quality; not a good fit.
Fitting KS-04-SED-0-022106 as norm(E) from -20.000 to 130.000

Fit included 225 data points and 2 variables
R-factor = 0.123744
chi-square = 108.47711
reduced chi-square = 0.4842728

group	weight
23: Orpiment_avg	0.000(0.000)
24: Realgar_avg	0.000(0.000)
26: SorbedArsenate	1.000(0.000)

Figure 13.



Fitting PCON-20-SED-0-02220 as norm(E) from -20.000 to 130.000

Fit included 227 data points and 2 variables
R-factor = 0.010674
chi-square = 2.84803
reduced chi-square = 0.0126019

group	weight
19: Scorodite_avg	0.000(0.000)
21: Arsenopyrite_avg	0.752(0.000)
26: SorbedArsenate	0.248(0.000)

It is important to note, the EPA Technical Workgroup for metals does not recommend the use of the Physiological Based Extraction Tests (PBET) for arsenic.

Lead and Arsenic Availability at Asarco Site

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Available Pb and As were measured using the physiologically based extraction test (PBET) on samples sent to the University of Washington.

PBET Methods*:*

In vitro extraction was used following the procedure of Physical Based Extraction Technique developed by Ruby et al., 1999. PBET analysis were run on all soil samples in duplicate for a total of 24 samples. Blanks (glycine solution only) and a soil standard from Joplin MO were added approximately every eight samples during the PBET procedure. Samples were sieved to <250µm.

A glycine solution is required in order to act as a buffer during the extraction process. One litre of 0.4 M glycine ($C_2H_5NO_2$) solution was produced by mixing 30g of glycine powder with one litre of de-ionized water in class A glass beaker. This solution was then stirred with a magnetic bar over a low heat. Solution pH was adjusted to 2.2 during this period by addition of 12M HCl via a dropper. The pH was determined through use of a pH electrode model Ryan 410 which had been calibrated at a pH of 4 and 7. A hood was placed over the HCl due to fumes. Lastly, the glycine solution was placed into a heated water bath in order to bring the extracting solution to 37º C.

Next, soil samples were mixed with this glycine solution at a 1:100 ratio in 50 ml polypropylene centrifuge tubes. This was carried out by first measuring out approximately 0.3g sieved soil samples into the polypropylene centrifuge tubes and then adding 30 ml of the 0.4 M glycine solution. Immediately afterwards the tubes were place in a water bath pre-heated to 37° C and turned end-over-end for one hour. The solution was filtered through 0.45µm syringe filters, stored in labeled polyurethane vials and placed in a refrigerator.

The pH of the remaining solution was tested to assure that the pH did not differ from 2.2 by more than 0.5 log units.

The concentration of lead and arsenic in the extractants (mg/L and ug/L respectively) were determined on a Perkin-Elmer Atomic Absorption Spectrophotomer model AAnaylst 300. Lead was analyzed using the flame head while arsenic was analyzed using the graphite furnace. A standard curve was set for both lead and arsenic. A four point calibration curve for lead was set by use of 10, 20, 50, 100 ppm standards that resulted in a 1.0 correlation. Arsenic had a three point calibration curve set via use of 10, 20, 100 ppb standards which resulted in 0.99 correlation. Standards and blanks were also added approximately every eight samples during this section of analysis in order to ensure the quality of data output. The standard used during atomic absorption were of similar concentrations to the Pb and As concentrations in the soil samples. The blank was a dilute nitric acid solution.

Results

A table with total, percent extractable, and total available Pb and As is shown at the end of this section. For all of the samples, available As was well under 50% of total As. In fact, excluding sample # HSS-I-101-07-089T-020706, extractable As was less than 5% of total. In many cases, extractable As was below detection limits (< 1 mg kg). In addition, although total As for many of the samples was above background, it was not extremely elevated. The exception here is sample # PCON-20-SED-0-022106 where total As is extremely high. Even though extractable As for this soil is very low, the high total suggests both that additional sampling to define the extent of this extreme elevation and potentially excavation would be recommended. For all other samples, both relatively low total As as well as very low extractable As suggest that the risks posed by ingestion of As at the site are minimal.

Total Pb, as measured by US EPA, was generally low (in terms of elevation over background and regulatory limits) in comparison to total As. Exceptions were samples HSS-D-101-09-106-020806 (2990 mg kg) and HSS-B-101-09-088-021006 (92 600 mg kg). The latter sample is sufficiently contaminated in relation to other samples that it may represent an outlier in the data. It may be that this extreme contamination is highly localized. Additional sampling for total Pb in the vicinity of this sample would be recommended. Even though extractable Pb for this sample was only a fraction of total Pb, the total is sufficiently high that leaving the material in place would not be recommended. For two of the samples, the fraction of total Pb that was extractable was > 100% (HSS-G-101-09-088-021006 and HSS-B-101-07-089T-020706). The total Pb for both of these samples as measured at the University of Washington was greater (438 and 272 mg kg respectively) than the totals as measured by EPA. For these samples, it would appear that a high percentage of total Pb is extractable, suggesting that it would be bioavailable if ingested. However, totals for both are still close to national regulatory limits and so remedial actions are not called for. For all Pb samples tested where both total and extractable Pb are below regulatory limits, it is clear that these soils do not pose a hazard to human health. For others, if total Pb is only moderately elevated above standards (total Pb < 800 mg kg) and the portion of total that is extractable is sufficiently low that bioavailable Pb is below regulatory limits, it would seem that leaving the soil in place would be acceptable.

For most of the samples tested, total and available Pb and As were low in comparison to total Cu. Copper concentrations at the sites sampled may be the primary driver in remedial decision making. The exceptions to this have been detailed above.

Sample #	Total Pb mg kg	PBET Pb	Available Pb mg kg	Total As	PBET As	Available As mg kg
HSS-A-101-070895-020706	192	0.77	147	38	0.03	1
	192	0.74	143	38	0.05	2
HSS-I-101-07-0895-020706	246	0.72	178	63	0.02	1
	246	0.71	175	63	0.03	2
HSS-A-101-09-106-020806	658	0.66	435	32	0.00	0
	658	0.63	414	32	0.00	0
HSS-D-101-09-106-020806	2990	0.16	471	88	0.01	1
	2990	0.16	490	88	0.01	1
HSS-D-101-07-008-020906	388	0.80	311	113	0.04	4
	388	0.82	320	113	0.03	4
HSS-H-101-07-008-020906	248	0.70	173	70	0.02	2
	248	0.66	163	70	0.04	3
HSS-B-101-09-088-021006	92600	0.26	23684	32	0.00	0
	92600	0.29	26921	32	0.00	0
HSS-G-101-09-088-021006	296	1.71	505	20	0.00	0
	296	1.78	526	20	0.00	0
HSS-B-101-07-089T-020706	264	1.21	320	57	0.03	2
	264	1.49	393	57	0.03	2
HSS-I-101-07-089T-020706	225	0.86	194	41	0.29	12
	225	0.89	200	41	0.31	13
KS-04-SED-0-022106	325	0.04	13	60.1	0.00	0
	325	0.04	12	60.1	0.00	0
PCON-20-SED-0-022106	260	0.89	233	1720	0.00	1