Exponent™

Management Plan for Arsenic in Rock and Soil

Prepared for

Ketchikan Pulp Company
Ketchikan, Alaska

E^{x}ponent˙

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Prepared for

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MANAGEMENT PLAN FOR ARSENIC IN ROCK AND SOIL

Exponent has conducted a focused evaluation to assess the potential risks associated with arsenic-bearing topsoil and rock products that are planned for use at the Ketchikan Pulp Company (KPC) facility. This management plan presents the results of the evaluation and recommended guidelines for using this material. Detailed information regarding the data presented in this document is included the following attachments:

- Attachment A—*Measurement of the Relative Absorption Factor for Arsenic in KPC Samples*

- Attachment B—*Identifying the Mineral Form of the Arsenic Source*

- Attachment C—*Quality Assurance Review Summary—Chemical Analyses of Solid and Aqueous Samples*.

The purposes of this management plan are 1) to evaluate the potential risks to onsite workers and the potential for arsenic to leach from the rock products and migrate to Ward Cove; and 2) to establish practices for use of rock products that result in acceptable health protection for current and future workers at the facility.

BACKGROUND

Rock products of various size fractions (D1 gravel to shot rock) have been stockpiled at the KPC facility or will be purchased in the future for use at the KPC site. Some of this rock contains elevated arsenic concentrations. Because of the elevated arsenic concentrations, some rock planned for use in filling the access road ditch had been stockpiled pending determination of the appropriate use of this material.

In addition, South Coast, Inc. was contracted to provide topsoil to cover the Dawson Point landfill. The topsoil is a blend of decomposed hog fuel from KPC and overburden from construction projects. As of April 1998, approximately 5,000 cubic yards (CY) have been stockpiled at the KPC site and another 6,000 CY have been placed on the land-fill. South Coast, Inc. sampled some of the piles and analyzed the samples for arsenic. The result of the analysis was that arsenic concentrations ranged between 20 to 40 mg/kg.

Two filtered leachate samples collected from the KPC hog fuel pile on January 20, 1997, had soluble arsenic concentrations of 13 and 14 μg/L (CAS 1997).

APPROACH

The following tasks were completed in developing the management plan:

- Evaluate current and planned uses of topsoil and rock

- Determine leachability of arsenic from topsoil and crushed rock

- Determine bioaccessibility of arsenic from topsoil and crushed rock

- Prepare a risk assessment for crushed rock and topsoil at the facility

- Prepare draft guidelines for management of rock products.

CURRENT AND PLANNED USE OF IMPORTED SOIL AND ROCK PRODUCTS

Information about the topsoil used as landfill cover was obtained from Andy Maloy, KPC. Two contractors for KPC, Jeff Hegedus of Philip Services Corporation and Marty Gilliland of Ty-Matt, Inc. provided information about sand and rock products.

Topsoil

South Coast, Inc. fabricated topsoil from hog fuel and overburden from road building projects. This material was used as part of a landfill cap on the wood waste and ash disposal landfill. After the topsoil was spread on the landfill cap, it was planted with grass.

Sand

Very little sand has been used in the demolition project. Only one 10-CY load has been used during the past year. The sand, which was purchased from a Seattle-based company and barged to the KPC site, was used to backfill around a pipe.

Crushed Rock Containing Fines

1-in.-minus (D1) rock—One-in.-diameter and smaller material is the most common rock product used for the demolition project. D1 rock is produced at quarries by blasting the rock face, crushing the rock chunks, and passing the crushed rock through a series of shaking screens with increasingly smaller openings. All the material that passes through the 1-in.-diameter screen is considered D1 rock. D1 rock can be used for roadbeds because the finer particle sizes can be suitably compacted. D1 rock is also used for pipe ditch backfill, structural subgrade (i.e., foundations under a building), temporary surface ramps, and road resurfacing.

1.5-in.-minus rock—This material is like D1 except the largest diameter is 1.5-in. rather than 1-in. This rock can also be used for roadbeds, especially in areas of heavier or more frequent traffic.

3-in.-minus rock—This material is used for structural subgrade and for temporary surface ramps for heavy equipment. This is the least used of the three types of rock products that contain fines.

Crushed Rock without Fines

Washed rock—Screened and washed rock products are used occasionally when free water drainage is needed for certain subgrades. Small quantities of washed rock in the 1.5-, 3-, and 8-in.-diameter classes have been or may be used at the KPC facility.

Riprap—This material is 3 in. in diameter and larger (usually 3 to 12 in.). Riprap is used for heavy structural fill (e.g., bridging a soft spot in a planned road) and for stabilizing slopes.

Shot Rock

Shot rock refers to rock that is blasted from a natural face of a quarry. It is used directly without crushing or screening. The rock fragments are sharp-edged and variable in size. Fines typically sift to the bottom of the pile as the rock is handled and stockpiled. Therefore, a truckload of shot rock has very few fine particles. Shot rock is used for seawall construction, slope stabilization, and ditch drainage.

LEACHABILITY OF TOPSOIL AND CRUSHED ROCK

Twelve topsoil and rock samples were collected on April 14, 1998, and analyzed for total and leachable (i.e., extractable by synthetic precipitation leaching procedure [SPLP]) arsenic (Table 1). Composite grab samples were collected from piles of recently purchased 3-in.-minus and D1 rock (three composites of each rock type). Three composite samples were also collected from the stockpiled topsoil and from the topsoil recently placed on the landfill. Each composite consisted of five subsamples collected at a depth of 0–6 in.

For total arsenic analyses, the following sample preparation methods were followed:

- The 3-in.-minus rock was washed, crushed, and sieved to 2 mm.

- The D1 rock was crushed and sieved to 2 mm.

- The topsoil samples were sieved to 2 mm.

TABLE 1. TOTAL AND SPLP-EXTRACTABLE ARSENIC AND BIOACCESSIBILITY OF SOIL AND ROCK SAMPLES

Sample Type/Sample ID	Total Arsenic[a] (mg/kg)	SPLP-Extractable Arsenic (mg/L)	Bioaccessibility (percent)
Topsoil (mixed hog fuel and overburden)			
LS0001	13.8	0.01 *U*	5.5
LS0002	26.1	0.01 *U*	24.1
LS0003	11.1	0.01 *U*	14.2
SS0001	23.1	0.01 *U*	39.8
SS0002	46.3	0.01 *U*	30.3 [b]
SS0003	20.9	0.01 *U*	35.6
Average	23.6		24.9
Maximum	46.3		39.8
D1 Rock (1-in. minus)			
R10001	105	0.01 *U*	1.6
R10002	162	0.01 *U*	9.6
R10003	312	0.01 *U*	8.4 [c]
Average	193		6.6
Maximum	312		9.6
Rock (3-in. minus)			
R30001	152	0.01 *U*	--
R30002	172	0.01 *U*	--
R30003	65.5	0.01 *U*	--
Average	130		
Maximum	172		
Onsite Soil			
NSFS-01	1,130 [d,e]	--	5.5 [c]
NSFS-02	280 [d,f]	--	5.1
WRLD-C1	230 [d,g]	--	2.4
Average	186	--	4.3
Maximum	259	--	5.5
Rock ("red shale" type from old pile at west end of access road)			
SHTR-1[h]	7 [i]	--	7.2

Note SPLP   - simulated precipitation leaching procedure
--   - indicates no analysis performed

[a] Total arsenic concentration for the fraction that is less than 2 mm.

[b] Average bioaccessiblity of a triplicate analysis of this sample.

[c] Average bioaccessiblity of a duplicate analysis of this sample.

[d] The bulk soil was sieved to <2 mm, and this analytical result is for <2-mm fraction.

[e] 62 percent of the soil passed through the 2-mm sieve.

[f] 45 percent of the soil passed through the 2-mm sieve.

[g] 42 percent of the soil passed through the 2-mm sieve.

[h] The rock sample was crushed to <2-mm prior to analysis.

[i] The rock sample was first crushed until it passed through a 0.63-mm seive. The >0.63-mm fraction was archived and the remaining sample was passed through a 250-μm sieve. The analytical result presented here is for the 250 μm–0.63 mm fraction. The <250-μm fraction of this sample contained 6.98 mg/kg arsenic.

For SPLP analyses, the 3-in.-minus rock samples were washed to remove fines. The SPLP analyses were run on the bulk ("as is") samples of D1 rock (including fines) and topsoil.

The results of the total and SPLP analyses are shown in Table 1. Total arsenic ranged from 65 to 172 mg/kg in 3-in.-minus rock, 105 to 312 mg/kg in D1 rock, and 11 to 46 mg/kg in the topsoil samples. SPLP results were all at or below the detection limit of 0.01 mg/L, indicating that the arsenic is highly resistant to leaching.

This finding is consistent with the SPLP results of the quarry rock samples presented in the draft remedial investigation report (Exponent 1998a). Of the 28 quarry rock samples submitted for SPLP analysis, only one sample (the "red shale with quartz intrusion" sample with 4,150 mg/kg total arsenic) had detectable amounts of arsenic (1.26 mg/L) in the SPLP extract. Those quarry rock samples were crushed and the material (including fines) that passed through a 1-in.-diameter sieve was analyzed for SPLP-extractable arsenic.

The results of the SPLP analyses indicate that no significant leaching of soluble arsenic would be expected from topsoil used at the landfill or from crushed rock. Crushed rock used as road cover material will be subject to grinding and abrasion from vehicle traffic; however, the SPLP results indicate that very little soluble arsenic would be released under these conditions. The primary pathway for transport of arsenic from crushed rock would be surface water transport of fine particles containing arsenic. This form of arsenic is less susceptible to migration to groundwater or to marine waters.

BIOAVAILABILITY OF ARSENIC IN TOPSOIL AND CRUSHED ROCK

While leachability is a measure of potential transport of arsenic from soil or rock, bioavailability provides a measure of potential exposure from direct contact with arsenic in soil or rock. The degree to which arsenic is absorbed following ingestion has been found to vary depending on the mineral forms of arsenic and the characteristics of the matrix (e.g., particle size) in which the arsenic is found. Forms of arsenic with limited water solubility are generally poorly absorbed. Although little direct experimental evidence is available, dermal absorption of arsenic from solid matrices is also expected to be low when water solubility is low.

Differences in arsenic absorption from different matrices have been demonstrated in studies conducted in laboratory animals and in *in vitro* studies designed to mimic dissolution in the human gastrointestinal (GI) tract. Good agreement has been observed between the animal studies and the *in vitro* studies (Ruby et al. 1996). These studies have been used to derive relative absorption factors (RAFs) that provide a measure of the reduced bioavailability of arsenic from a solid matrix relative to the bioavailability of soluble arsenic forms dissolved in water.

Materials from the KPC facility were tested using an *in vitro* method that Exponent developed and termed the physiologically based extraction test (PBET). This method,

which has been published (Ruby et al. 1993; Ruby et al. 1996), is currently being validated by a consortium that includes representatives from government agencies, universities, and private companies. The PBET procedures were presented in SOP 312, which was included in Technical Memorandum No. 9 (Exponent 1998b).

The PBET provides a measure of the relative dissolution of arsenic in the GI tract, rather than a direct measure of relative absorption into the body. Consequently, the results of this test have been termed "relative bioaccessibility" to distinguish them from measures of relative bioavailability. Because bioavailability of an ingested compound is in large part limited by its solubility in GI tract, bioaccessibility provides a reliable estimate of relative bioavailability. Estimates of *in vitro* arsenic bioaccessibility and *in vivo* arsenic bioavailability (measured using animal models) in various solid matrices have been very similar (Ruby et al. 1996). Therefore, because the bioaccessibility estimates provide a conservative means to evaluate absorption in the GI tract and have produced similar estimates to those in animal studies, the bioaccessibility estimates are used here to derive RAFs. The RAFs are then used to assess risks from occupational exposure to arsenic in crushed rock and topsoil at the KPC facility.

The six topsoil samples and the three D1 rock samples that were analyzed for SPLP-extractable arsenic were also analyzed for bioaccessibility by the PBET. The crushed 3-in. rock samples were not tested because D1 rock has more associated fine-grained material and thus provides a protective means to evaluate D3 rock. The results of these tests (Table 1) were used in the risk assessment presented below to support guidelines for managing imported topsoil and crushed rock. Concurrent with these analyses, Exponent analyzed bioaccessibility of three onsite soil samples[1] and the "red shale" type rock that has been commonly used onsite.

As shown in Table 1, the D1 rock samples had very low bioaccessibility, ranging from 1.6 to 9.6 percent and averaging 6.6 percent. The arsenic in the rock samples is present as arsenopyrite (see Attachment B), a mineral with extremely low solubility, which is consistent with low observed bioaccessibility. The arsenic bioaccessibility of the topsoil samples ranged from 5.5 to approximately 40 percent with an average of 25 percent. On average, the topsoil values are substantially higher than bioaccessibility estimates for any other samples, including onsite soil samples. It is possible that the presence of hog fuel in the topsoil samples may either increase bioaccessibility of arsenic from added overburden or be a source of more bioaccessible arsenic forms. (As indicated previously, leachate from hog fuel had soluble arsenic concentrations ranging from 13 to 14 μg/L.) The variability in the bioaccessibility values of the topsoil samples may be related to the relative proportion of overburden and hog fuel.

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[1] These soil samples (two from the nearshore fill area, NSFS-01 and NSFS-02, and one from the wood room/log deck area, WRLD-C1) were selected because they had the highest arsenic concentrations of any RI soil samples excluding samples from areas subject to early action.

RISK ASSESSMENT OF TOPSOIL AND CRUSHED ROCK PRODUCTS

Risk assessment methods and parameters developed in Section 6.0, *Baseline Risk Assessment* of the draft remedial investigation (Exponent 1998a) were used together with the results of the *in vitro* PBET analyses to derive risk estimates associated with various uses of rock and with the use of topsoil on the landfill. These risk calculations were in accordance with risk assessment guidance provided by the U.S. Environmental Protection Agency (EPA) and the Alaska Department of Environmental Conservation (ADEC) (U.S. EPA 1989a,b, 1991, 1996, 1997a,b,c; ADEC 1997). Risk assessments typically consist of the following four steps: data evaluation and identification of chemicals of potential concern (CoPCs), exposure assessment, toxicity assessment, and risk characterization. In this evaluation, arsenic is the only CoPC. Toxicity and risk characterization methods described in the draft risk assessment (Exponent 1998a) are applied here. A site-specific exposure assessment was conducted evaluating the means by which people may be exposed to arsenic in rock products or soil. With the exception of site-specific *in vitro* analyses, exposure assessment methods and parameters were those identified in the draft risk assessment (Exponent 1998a).

Potential for Exposure to Arsenic in Rock Products and Soil

Two types of materials were identified as potentially containing arsenic above background levels: 1) topsoil fabricated from hog fuel and overburden from road building, and 2) rock products. Human receptors could potentially be exposed to arsenic in these products either by direct contact (i.e., ingestion or dermal contact) or through transport to other media (e.g., surface water transport of arsenic-enriched particles from a roadbed to sediments in a drainage ditch). Transport of <u>soluble</u> arsenic is expected to be very limited (based on the SPLP results); thus, transport to groundwater and subsequently to marine waters would not be significant.

Future KPC site use is assumed to be occupational based on consideration of development plans underway. The potential for future workers to directly contact arsenic from rock or soil during various planned uses of these products is summarized as follows:

- **Sand**—Very little sand has been used and there is no reason to believe that arsenic concentrations are elevated because the sand is typically from a source outside of Southeast Alaska.

- **1-in.-minus (D1) rock**—Use of D1 rock for road beds, temporary surface ramps, and road resurfacing (maintenance) is the most likely way that people could be exposed to fines from crushed rock. Use in pipe ditch backfill or structural subgrade (i.e., foundations under a building) could result in limited contact during construction activities.

- **1.5-in.-minus rock**—Use of 1.5-in.-minus rock for building roads and parking lots could also result in exposure to arsenic from fines.

- **3-in.-minus rock**—This material is used for structural subgrade and for temporary surface ramps for heavy equipment. Potential for contact with arsenic in products would be limited to the time frame of the construction projects.

- **Washed rock**—Use of screened and washed rock products for free water drainage in certain subgrades is unlikely to result in human exposure because of the absence of fine-grained materials that result in direct contact exposure.

- **Riprap**—Use of riprap for heavy structural fill (e.g., bridging a soft spot in a planned road) and for stabilizing slopes is also unlikely to result in human exposure for the reasons identified for washed rock.

- **Soil**—Future workers performing maintenance at the landfill and trespassers could contact the topsoil used as cover at the landfill.

Thus, in the risk assessment, exposures to arsenic in D1 rock and in soils through ingestion and dermal contact were quantitatively evaluated. These calculations were carried out using the methods and the parameter estimates described in the draft risk assessment (see Tables 6-2, 6-3, and 6-4 of Exponent 1998a). Specifically, estimates were derived assuming that future workers might contact these materials 250 days per year over a 25-year period. Although exposures would be considerably less if the materials were used in small areas, the conservative assumptions were used here to determine whether the use of these materials should be restricted based on health concerns.

Risk estimates were derived using the maximum and mean concentration values for the topsoil used for landfill cover and D1 rock. In addition, the maximum and mean RAFs derived from the *in vitro* tests were used in risk estimates.

Toxicity Assessment and Risk Characterization

The toxicity values for arsenic were those identified by EPA in the Integrated Risk Information System database, i.e., a carcinogenic slope factor of 1.5 $(mg/kg\text{-}day)^{-1}$ and a reference dose of 0.0003 mg/kg-day. The risk characterization was conducted consistent with the approach in Section 6.0, *Baseline Risk Assessment*, of the draft remedial investigation (Exponent 1998a) and findings were compared with the decision risk levels identified in the remedial investigation. Although this management plan is not part of the remedial investigation and feasibility study (RI/FS) process, the RI/FS decision risk levels are also consistent with EPA guidance as applied at many other sites nationwide and with recent proposed guidelines identified by ADEC. The decision risk levels are as follows:

- Incremental cancer risks are less than 1 in 100,000 (1×10^{-5}) and/or the hazard indices for noncancer adverse effects are less than 1—No further action will be considered.

- Incremental cancer risks are between 1 in 100,000 (1×10^{-5}) and 1 in 10,000 (1×10^{-4}) for cumulative risk and/or hazard indices for noncancer adverse effects are between 1 and 10—CoPCs in this risk range will be identified as CoCs, and development of cleanup options (i.e., inclusion in the feasibility study) will be considered but may not be required.

- Incremental cancer risks are greater than 1 in 10,000 (1×10^{-4}) for pathways or for cumulative risks and/or hazard indices for noncancer adverse effects are greater than 10—CoPCs will be identified as CoCs, and cleanup options will be developed for this area/pathway (i.e., this area will be carried into the feasibility study).

Upper-bound excess cancer risk estimates calculated for ingestion and dermal contact were summed to derive total risk estimates (Table 2). None of the estimates were greater than the upper-bound decision risk level identified in the RI/FS as requiring additional consideration in the feasibility study (i.e., 1×10^{-4} for carcinogens and a hazard index of 10). The maximum risk estimate for topsoil (9×10^{-6}) indicates that even with the conservative assumptions of occupational exposure to these soils, risks are expected to be within acceptable levels.

Only the total risk estimates for the D1 rock (e.g., 4×10^{-5} based on maximum concentration and RAF values) fall within the range of estimates that would be considered for inclusion in the feasibility study. However, as shown in Table 2, these total risk estimates for D1 rock, like the other estimates for topsoil, are significantly influenced by the inclusion of highly conservative risk estimates for the dermal contact pathway. In calculating these risk estimates, dermal absorption of arsenic from these materials was assumed to be 3 percent, a value derived from a study that applied highly soluble arsenic acid (H_3AsO_4) to soil (Wester et al. 1993). Given that the results of the PBET analyses indicate significantly reduced oral bioaccessibility of the materials from the KPC facility relative to soluble forms of arsenic, the assumption of 3 percent dermal absorption is likely to significantly overestimate dermal exposures. For D1 rock, derived exposure estimates could be 10 times too high.

Arsenic Concentrations Associated with Decision Risk Levels

Concentrations of arsenic that would lead to risk estimates at 1×10^{-4} and 1×10^{-5} decision risk levels were calculated[2] to assist in decision-making regarding future use of rock and

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[2] In calculating concentrations based on excess cancer risk, target risk levels of 1.49×10^{-5} and 1.49×10^{-4} were used. These values would result in a risk estimate of 1×10^{-4} or 1×10^{-5}, respectively, when following the standard procedure of showing risk estimates as one significant figure.

TABLE 2. RISK ESTIMATES FOR ARSENIC IN SOIL AND ROCK

Site Area	Concentration (mg/kg)	Relative Absorption Factor[a]	Upper Bound Excess Carcinogenic Risk Estimate			Upper Bound Noncancer Hazard Index		
			Soil Ingestion	Dermal Contact[b]	Total	Soil Ingestion	Dermal Contact[b]	Total
Topsoil								
Maximum	46	0.40	5×10^{-6}	4×10^{-6}	9×10^{-6}	0.03	0.03	0.06
Mean	24	0.25	2×10^{-6}	2×10^{-6}	4×10^{-6}	0.01	0.01	0.02
D1 rock (1-in.-minus)								
Maximum	312	0.10	8×10^{-6}	3×10^{-5}	4×10^{-5}	0.05	0.2	0.2
Mean	193	0.066	3×10^{-6}	2×10^{-5}	2×10^{-5}	0.02	0.1	0.1

[a] Relative absorption factor based on *in vitro* results, see text.

[b] Dermal absorption assumed to be 3.2 percent, see text.

soil products. Using the assumptions described above for occupational exposure including ingestion and dermal contact, concentrations of 125 mg/kg in D1 rock and 75 mg/kg in soil would be associated with a 1×10^{-5} risk estimate (Table 3); concentrations as high as 1,200 mg/kg in D1 rock and 750 mg/kg in soil would be associated with a 1×10^{-4} risk level (Table 4).

If dermal absorption of arsenic is assumed to be negligible, and, therefore, risks are derived based on soil ingestion alone and the maximum RAF, arsenic concentrations of approximately 5,900 mg/kg in rock or 1,400 mg/kg in soil would result in cancer risk estimate of 1×10^{-4}. Similarly, arsenic concentrations of 592 mg/kg and 142 mg/kg were derived for rock and soil, respectively, associated with the maximum RAF and a cancer risk estimate of 1×10^{-5}.

DRAFT GUIDELINES FOR USE OF IMPORTED SOIL AND ROCK PRODUCTS

Imported Soil

The topsoil as it was fabricated by the landfill contractor can be used as a landfill cover without exceeding acceptable risk levels. If additional imported topsoil is needed, and the contractor needs to use mineral fines other than their current overburden, testing for arsenic should be required. The topsoil arsenic concentration should be less than 275 mg/kg, which would result in a cancer risk estimate of 5×10^{-5}. Although, this level allows for additional risk contributions from other chemicals, there would be no other apparent sources of cancer risk from site-related CoPCs on the final landfill cover.

Rock Products

Crushed rock products that contain fines (e.g., D1, 1.5-in.-minus, and 3-in.-minus) should not be used as the final cover for ground surfaces at the KPC site if the arsenic concentration is greater than 700 mg/kg. This would be equivalent to an excess cancer risk of 8×10^{-5}. A worker exposed to this amount of arsenic in rock products for 25 years could also be exposed to other site-related carcinogens (if any) at a risk equivalent to 2×10^{-5} before the worker's cumulative risk would exceed the trigger level of 1×10^{-4} (i.e., 8×10^{-5} and 2×10^{-5} would be 1×10^{-4}).

Arsenic screening is unnecessary for rock products that are not used for driving surfaces. The long-term exposure pathway is absent, even for rock products with fines, if the material is used for a subgrade or other use without direct surface exposure.

TABLE 3. ARSENIC CONCENTRATIONS IN SOIL ASSOCIATED WITH A DECISION RISK LEVEL OF 1×10^{-4}, OR HAZARD INDEX OF 1

| | | Concentrations Based on Excess Cancer Risk | | | | Concentrations Based on Noncancer Endpoints | | | | |
| | | Soil Ingestion | | | | | Soil Ingestion | | | |
Material Type	Decision Risk Level	Relative Absorption Factor[a]	Soil Ingestion (mg/kg)	Dermal Contact[b] (mg/kg)	Combined Pathways (mg/kg)	Decision Hazard Quotient	Relative Bioaccessibility[a] (percent)	Soil Ingestion (mg/kg)	Dermal Contact[b] (mg/kg)	Combined Pathways (mg/kg)
Soil spread on the landfill										
Maximum	1×10^{-4}	0.40	1,421	1,586	750	1	0.40	1,533	1,711	809
Mean	1×10^{-4}	0.25	2,274	1,586	934	1	0.25	2,453	1,711	1,008
D1 rock (1-in.-minus)										
Maximum	1×10^{-4}	0.096	5,922	1,586	1,251	1	0.096	6,388	1,711	1,349
Mean	1×10^{-4}	0.066	8,614	1,586	1,340	1	0.066	9,291	1,711	1,445

Note Decision risk levels are rounded to one significant figure, but represent a value of 1.49×10^{-4}.

[a] Relative absorption factor based on *in vitro* results, see text.

[b] Dermal absorption assumed to be 3.2 percent, see text.

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TABLE 4. ARSENIC CONCENTRATIONS IN SOIL ASSOCIATED WITH A DECISION RISK LEVEL OF 1×10^{-5}, OR HAZARD INDEX OF 1

Material Type		Concentrations Based on Excess Cancer Risk				Concentrations Based on Noncancer Endpoints				
			Soil Ingestion					Soil Ingestion			
	Decision Risk Level	Relative Absorption Factor[a]	Soil Ingestion (mg/kg)	Dermal Contact[b] (mg/kg)	Combined Pathways (mg/kg)	Decision Hazard Quotient	Relative Bioaccessibility[a] (percent)	Soil Ingestion (mg/kg)	Dermal Contact[b] (mg/kg)	Combined Pathways (mg/kg)
Topsoil										
Maximum	1×10^{-5}	0.40	142	159	75	1	0.40	1,533	1,711	809
Mean	1×10^{-5}	0.25	227	159	93	1	0.25	2,453	1,711	1,008
D1 rock (1-in.-minus)										
Maximum	1×10^{-5}	0.096	592	159	125	1	0.096	6,388	1,711	1,349
Mean	1×10^{-5}	0.066	861	159	134	1	0.066	9,291	1,711	1,445

Note: Decision risk levels are rounded to one significant figure, but represent a value of 1.49×10^{-5}.

[a] Relative absorption factor based on *in vitro* results, see text.

[b] Dermal absorption assumed to be 3.2 percent, see text.

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Attachment A

Measurement of the
Relative Absorption Factor
for Arsenic in KPC Samples

MEASUREMENT OF THE RELATIVE ABSORPTION FACTOR FOR ARSENIC IN KPC SAMPLES

In humans, an orally administered dose of a compound is seldom completely absorbed, and the extent of absorption of orally administered compounds differs among various exposure media. For most compounds, the toxicity values derived by the U.S. Environmental Protection Agency are not adjusted to absorbed dose (i.e., the dose response evaluation is based on the administered dose). This approach can lead to overly conservative estimates of risk of exposure to a particular chemical in a medium other than the one used in the toxicity or epidemiology studies on which the toxicity values are based. For example, both the cancer slope factor and reference dose used to assess the cancer risks and other adverse health effects, respectively, that might be associated with oral exposure to arsenic (U.S. EPA 1993) were derived from an epidemiological study that characterized health effects in a population of Taiwanese who consumed drinking water containing arsenic (Tseng 1977; Tseng et al. 1968). In contrast to arsenic in drinking water (soluble arsenic), arsenic in soil generally exists as mineral phases or soil-arsenic complexes that will be incompletely solubilized and absorbed during transit through the gastrointestinal (GI) tract. The solubility of these different forms of arsenic appears to be a critical factor controlling arsenic bioavailability (ATSDR 1993; U.S. EPA 1992). Therefore, a downward adjustment to arsenic bioavailability from soil should be made to reflect the difference between arsenic in drinking water and arsenic in soil.

For the purpose of this attachment, absolute bioavailability is defined as that fraction of the ingested element that is absorbed into systemic circulation. The term "relative bioavailability" is used to describe the bioavailability of the element in soil relative to the bioavailability of the element dissolved in water. Finally, bioaccessibility is defined as the fraction of the ingested element that dissolves in the GI tract and is available for absorption.

A relative absorption factor (RAF), which represents the relative bioavailability, is used to adjust the dose or intake of arsenic from soil so that it is comparable to the arsenic doses from water used to generate the toxicity values. Thus, for assessing oral exposure to arsenic in soil:

$$RAF = \frac{\text{fraction of element absorbed from soil}}{\text{fraction of element absorbed from dissolved form}}.$$

To assess the bioavailability of arsenic in the Ketchikan Pulp Company (KPC) soil samples, an approach that relies on previous work that Exponent has performed to assess the bioavailability of inorganic elements was used. An *in vitro* test system, termed the physiologically based extraction test (PBET), which replicates human GI-tract chemistry and function (Ruby et al. 1996), was used to determine the fraction of arsenic that would

be soluble and available for absorption in the GI tract (i.e., the fraction that is bioaccessible).

Differences in arsenic absorption from various matrices have been demonstrated in *in vivo* studies using animal models and in *in vitro* studies designed to mimic dissolution in the human GI tract. *In vivo* models assume that the fraction of arsenic mass absorbed by the animal from soil (relative to a soluble arsenic source) is similar to the fraction that would be absorbed by a human ingesting this same soil. While differences between animal and human physiology may limit the accuracy of this assumption, historically, animal studies were the only tool available for assessing the RAF. Only recently have *in vitro* procedures (i.e., the PBET) been available that can be used in this manner, and significant effort has been invested in validating the *in vitro* method for this application (Ruby et al. 1996).

The use of the PBET to estimate the bioavailability of inorganic elements is supported by good agreement between *in vivo* bioavailability data and *in vitro* bioaccessibility data for a series of arsenic- and lead-bearing samples tested in both kinds of studies (Ruby et al. 1996).

METHODS

The PBET is an extraction technique that uses a simulated GI fluid to measure the solubility of arsenic from soil under conditions that are similar to those found in the human GI tract. The details of this procedure were presented in Standard Operating Procedure 312 of Technical Memorandum No. 9 (Exponent 1998). Each time a sample is subjected to the PBET procedure, four extract samples are collected: two while the extract solution is maintained at pH 1.5, which simulates the stomach environment, and two while it is at pH 7.0, which simulates the intestinal environment. At each of these four sampling points, the extract pH is measured to ensure that it has not drifted more than 0.3 pH units away from the two target pH values of 1.5 and 7.0 (because the solubility of many minerals vary greatly with pH, tests are repeated if the pH values drift beyond ±0.3). Using this procedure, arsenic bioaccessibility was measured on six fabricated soil samples and three rock-product samples.

Bioaccessibility was also measured in three samples of onsite soil from the nearshore landfill and in an onsite rock sample of the red shale. Results of bioaccessibility analyses are summarized in Table 1 of the main text; detailed results will be described in a technical memorandum entitled *Results of Bioaccessibility and Mineralogical Analyses to Support the Baseline Human Health Risk Assessment.*

To ensure the quality of the PBET data, one soil sample was analyzed in triplicate (SS0002), and one rock sample (R10003) and one soil sample (NSFS-02) were analyzed in duplicate. In addition, two standard reference materials (Sums) were analyzed: National Institute for Standards and Technology (NIST) SRAM No. 2710 (in triplicate), and a soil sample from Butte, Montana (S-13) that was expected to contain arsenic with

similar mineralogy and relative bioavailability as the KPC rock samples. Finally, two samples of PBET extract solution spiked with 0.14 mg/L and 0.45 mg/L of arsenic were subjected to the PBET (in the absence of any soil) to quantify the arsenic recovery efficiency.

The results of the quality control sample analysis (Tables A-1 through A-3) indicate that:

1. Arsenic spike recoveries were 93 and 97 percent for the two samples tested, indicating that no significant adsorption of arsenic onto the test apparatus was occurring during the PBET (Table A-1).

2. The relative standard deviations for the two triplicate arsenic soil analyses (SS0002 and SRM2710) were 20 and 5 percent, respectively (Table A-2). These data indicate acceptable reproducibility.

3. The relative standard deviations for the two triplicate PBET extract arsenic analyses (SS0002 and SRM2710) were 14 and 22 percent, respectively (Table A-2). These data indicate acceptable repro-ducibility.

4. The relative percent difference between the duplicate soil arsenic analyses performed for R10003 was 28 percent (Table A-2), indicating that the replicate results were within control limits (i.e., the soil analy-ses had a relative percent difference of less than 35 percent).

5. The relative percent difference between the duplicate arsenic analysis of PBET extract from R10003 was 37 percent (Table A-2), which is not within control limits (i.e., the aqueous analyses had a relative per-cent difference of greater than 25 percent). This large difference among the replicate analyses of sample R10003 probably is due to heterogeneity's in this sample, and the relatively low arsenic concen-tration in this substrate (average of 30 mg/kg).

6. The measured arsenic concentrations in the triplicate NITS SRAM No. 2710 sample (575, 616, and 638 mg/kg) were all within 10 percent of the certified concentration of 588 mg/kg, indicating that the accu-racy of the solids analysis were acceptable.

7. The measured arsenic concentrations in PBET extract from the NIST standard (2.06, 2.84, and 3.20 mg/L) were not significantly different (within a probability of 0.58) than the results obtained for this sample during previous studies (Table A-3), indicating that the accuracy of PBET procedure was acceptable, given the relatively small number of previous observations for this sample (n=3).

8. The bioaccessibility value obtained for the Butte soil (10 percent for SRM-S13) was similar to the value obtained previously for this sub-strate (8 percent) during the PBET validation study (Medlin 1997).

TABLE A-1. ARSENIC SPIKE RESULTS

	Time (hour)	pH (s.u.)	Concentration of Arsenic Spike (mg/L)	Concentration in Extract (mg/L)	Spike Recovery (percent)	Relative Percent Difference
Spiked stomach solution A	0.50	1.56	0.454	0.445	98	2
Spiked stomach solution A	1.00	1.55	0.454	0.445	98	2
Spiked stomach solution A	3.58	7.07	0.454	0.440	97	3
Spiked stomach solution A	5.58	6.98	0.454	0.425	94	7
Spiked stomach solution B	0.50	1.50	0.144	0.147	102	2
Spiked stomach solution B	1.00	1.48	0.144	0.149	103	3
Spiked stomach solution B	3.92	6.87	0.144	0.145	101	1
Spiked stomach solution B	5.92	7.13	0.144	0.145	101	1
Spiked intestinal solution	NA	NA	0.2	0.231	101	14

Note: NA - not applicable

TABLE A-2. ARSENIC RESULTS OF THE REPLICATE AND TRIPLICATE ANALYSIS PERFORMED DURING THE PBET PROCEDURE

	<250 μm Soil Fraction (mg/kg)	Maximum[a] PBET Extract (mg/L)
SS0002		
Replicate 1	31.0	0.120
Replicate 2	39.1	0.101
Replicate 3	46.9	0.134
Relative standard deviation[b]	20%	14%
NIST SRM 2710		
Replicate 1	575	2.06
Replicate 2	616	2.84
Replicate 3	638	3.20
Relative standard deviation[b]	5%	22%
R10003		
Replicate 1	25.7	0.032
Replicate 2	33.9	0.022
Relative percent difference[c]	28%	37%

Note: PBET - physiologically based extraction test

[a] Four extract samples were collected throughout the testing of each replicate, but only the maximum arsenic concentration observed among these four analyses is used to characterize the bioaccessibility value of this sample.

[b] Relative standard deviation = standard deviation / average

[c] Relative percent difference = |Replicate 1 - Replicate 2| / average

TABLE A-3. MAXIMUM ARSENIC CONCENTRATION IN THE PBET EXTRACTS FROM NIST SRM SOIL NO. 2710

Study Group/Sample ID	Maximum Concentration In PBET Extracts (mg/L)
Arsenic concentration in previous tests of NIST SRM No. 2710	
Site 1	2.03
Site 2	2.28
Site 3	2.99
Arsenic concentration in tests of the NIST SRM No. 2710 conducted during this study	
Replicate 1	2.06
Replicate 2	2.84
Replicate 3	3.20

Note: PBET - physiologically based extraction test

The good quality control performance achieved for the Sums (SRAM No. 2710 and SRM-S13) and the spike samples suggest that the analytical procedures were followed properly, and that the analytical data accurately characterized the arsenic content of both the soil samples and the PBET extracts (i.e., the analytical laboratory performed the analysis well).

RESULTS

The arsenic bioaccessibility values are calculated for each of the four extracts (Table A-4) by dividing the total mass of arsenic in the extract (extract concentration × extract volume) by the total mass of arsenic in the soil being extracted (soil concentration × soil mass). In general, the highest arsenic concentrations occurred in the intestinal-phase extracts. However, samples SS0002 B, LS0002, and LS0003 released more arsenic during the low pH stomach-phase extraction.

The bioaccessibility value for a given sample was conservatively assumed to be the highest bioaccessibility measured among the individual extracts from that sample (Table A-5). For example, the four extracts collected from SS0001 following 0.5, 1, 2.7, and 4.7 hours had arsenic bioaccessibilities of 18, 26, 38, and 40 percent, respectively. Therefore, the bioaccessibility value for this sample is assumed to be 40 percent (Table A-5). When replicate or triplicate PBETs were performed, the maximum bioaccessibility from each PBET was used to calculate the average among the repeated tests (Table A-5).

The arsenic bioaccessibility values observed in the rock-product samples ranged between 1.6 and 9.6 percent, averaging 6.6 percent. The arsenic bioaccessibility values observed in the fabricated topsoil samples ranged between 5.5 and 40 percent, averaging 25 percent.

On average, the topsoil values are substantially higher than bioaccessibility estimates for any other samples, including onsite soil samples. It is possible that the presence of hog fuel in the topsoil samples may either increase bioaccessibility of arsenic from added overburden or be a source of more bioaccessible arsenic forms. As indicated previously, leachate from hog fuel had soluble arsenic concentrations ranging from 13 to 14 μg/L. The variability in the bioaccessibility values may be related to the relative proportion of overburden and hog fuel. Conversely, arsenic occurs in the rock-product as arsenopyrite, which has extremely slow solubility.

TABLE A-4. PBET RESULTS FOR SOIL AND ROCK SAMPLES

Sample ID	Time (hours)	pH (s.u.)	Arsenic[a] Concentration of Substrate (mg/kg)	Mass of Soil Tested (g)	Concentration in Extract (mg/L)	Volume of Extract (L)	Calculated Mass of Arsenic in Soil (mg)	Calculated Mass of Arsenic in Extract (mg)	Arsenic Bioaccessibility (percent)
SS0001	0.50	1.41	38.1	1.5049	0.071	0.150	0.057	0.0107	18
SS0001	1.00	1.41	38.1	1.5049	0.101	0.150	0.057	0.0152	26
SS0001	2.67	7.03	38.1	1.5049	0.146	0.150	0.057	0.0219	38
SS0001	4.67	7.12	38.1	1.5049	0.152	0.150	0.057	0.0228	40
SS0002 A	0.50	1.40	31.0	1.5059	0.054	0.150	0.047	0.0081	17
SS0002 A	1.00	1.39	31.0	1.5059	0.074	0.150	0.047	0.0111	24
SS0002 A	3.42	6.94	31.0	1.5059	0.113	0.150	0.047	0.0170	36
SS0002 A	5.42	7.07	31.0	1.5059	0.120	0.150	0.047	0.0180	39
SS0002 B	0.50	1.59	39.1	1.5009	0.073	0.150	0.059	0.0110	19
SS0002 B	1.00	1.59	39.1	1.5009	0.101	0.150	0.059	0.0152	26
SS0002 B	3.42	7.11	39.1	1.5009	0.047	0.150	0.059	0.0071	12
SS0002 B	5.42	7.10	39.1	1.5009	0.050	0.139	0.059	0.0070	12
SS0002 C	0.50	1.60	46.9	1.5035	0.056	0.150	0.071	0.0084	12
SS0002 C	1.00	1.55	46.9	1.5035	0.083	0.150	0.071	0.0125	18
SS0002 C	3.58	7.12	46.9	1.5035	0.124	0.150	0.071	0.0186	26
SS0002 C	5.58	7.01	46.9	1.5035	0.134	0.130	0.071	0.0174	25
SS0003	0.50	1.50	42.8	1.5055	0.079	0.150	0.064	0.0119	18
SS0003	1.00	1.51	42.8	1.5055	0.106	0.150	0.064	0.0159	25
SS0003	3.42	6.88	42.8	1.5055	0.140	0.150	0.064	0.0210	33
SS0003	5.42	7.10	42.8	1.5055	0.153	0.150	0.064	0.0230	36
LS0001	0.50	1.43	217	1.5031	0.064	0.150	0.326	0.0096	3
LS0001	1.00	1.42	217	1.5031	0.095	0.150	0.326	0.0143	4
LS0001	2.67	6.99	217	1.5031	0.117	0.150	0.326	0.0176	5
LS0001	4.67	7.03	217	1.5031	0.120	0.150	0.326	0.0180	6
LS0002	0.50	1.57	40.2	1.5029	0.072	0.150	0.060	0.0108	18
LS0002	1.00	1.56	40.2	1.5029	0.097	0.150	0.060	0.0146	24
LS0002	3.42	7.14	40.2	1.5029	0.034	0.150	0.060	0.0051	8
LS0002	5.42	7.08	40.2	1.5029	0.034	0.126	0.060	0.0043	7
LS0003	0.50	1.53	35.2	1.5018	0.030	0.150	0.053	0.0045	9
LS0003	1.00	1.53	35.2	1.5018	0.050	0.150	0.053	0.0075	14

TABLE A-4. (cont.)

Sample ID	Time (hours)	pH (s.u.)	Arsenic[a] Concentration of Substrate (mg/kg)	Mass of Soil Tested (g)	Concentration in Extract (mg/L)	Volume of Extract (L)	Calculated Mass of Arsenic in Soil (mg)	Calculated Mass of Arsenic in Extract (mg)	Arsenic Bioaccessibility (percent)
LS0003	3.42	7.10	35.2	1.5018	0.033	0.150	0.053	0.0050	9
LS0003	5.42	7.11	35.2	1.5018	0.038	0.148	0.053	0.0056	11
R10001	0.50	1.61	237	1.5006	0.027	0.150	0.356	0.0041	1
R10001	1.00	1.57	237	1.5006	0.034	0.150	0.356	0.0051	1
R10001	3.58	7.13	237	1.5006	0.039	0.150	0.356	0.0059	2
R10001	5.58	7.20	237	1.5006	0.042	0.126	0.356	0.0053	1
R10002	0.50	1.59	38.2	1.5063	0.021	0.150	0.058	0.0032	5
R10002	1.00	1.60	38.2	1.5063	0.027	0.150	0.058	0.0041	7
R10002	3.58	6.99	38.2	1.5063	0.037	0.150	0.058	0.0056	10
R10002	5.58	7.05	38.2	1.5063	0.040	0.128	0.058	0.0051	9
R10003 A	0.50	1.59	25.7	1.5021	0.016	0.150	0.039	0.0024	6
R10003 A	1.00	1.59	25.7	1.5021	0.019	0.150	0.039	0.0029	7
R10003 A	3.42	7.00	25.7	1.5021	0.019	0.150	0.039	0.0029	7
R10003 A	5.42	7.14	25.7	1.5021	0.032	0.133	0.039	0.0043	11
R10003 B	0.50	1.55	33.9	1.5002	0.013	0.150	0.051	0.0020	4
R10003 B	1.00	1.54	33.9	1.5002	0.017	0.150	0.051	0.0026	5
R10003 B	3.42	6.93	33.9	1.5002	0.019	0.150	0.051	0.0029	6
R10003 B	5.42	7.10	33.9	1.5002	0.022	0.132	0.051	0.0029	6
SRM 2701 A[b]	0.50	1.59	575	1.5044	1.5	0.150	0.865	0.2250	26
SRM 2701 A[b]	1.00	1.56	575	1.5044	1.84	0.150	0.865	0.2760	32
SRM 2701 A[b]	3.42	6.97	575	1.5044	2.06	0.150	0.865	0.3090	36
SRM 2701 A[b]	5.42	7.15	575	1.5044	2.05	0.130	0.865	0.2665	31
SRM 2710 B[b]	0.50	1.52	616	1.5008	2.62	0.150	0.924	0.3930	43
SRM 2710 B[b]	1.00	1.52	616	1.5008	2.84	0.150	0.924	0.4260	46
SRM 2710 B[b]	3.92	6.83	616	1.5008	2.83	0.150	0.924	0.4245	46
SRM 2710 B[b]	5.92	7.07	616	1.5008	2.82	0.140	0.924	0.3948	43
SRM 2710 C[b]	0.50	1.55	638	1.5021	2.80	0.150	0.958	0.4200	44
SRM 2710 C[b]	1.00	1.55	638	1.5021	3.20	0.150	0.958	0.4800	50
SRM 2710 C[b]	3.92	6.82	638	1.5021	3.14	0.150	0.958	0.4710	49
SRM 2710 C[b]	5.92	7.12	638	1.5021	3.00	0.145	0.958	0.4350	45

TABLE A-4. (cont.)

Sample ID	Time (hours)	pH (s.u.)	Arsenic[a] Concentration of Substrate (mg/kg)	Mass of Soil Tested (g)	Concentration in Extract (mg/L)	Volume of Extract (L)	Calculated Mass of Arsenic in Soil (mg)	Calculated Mass of Arsenic in Extract (mg)	Arsenic Bioaccessibility (percent)
SRM S13[c]	0.50	1.51	215	1.5042	0.196	0.150	0.323	0.0294	9
SRM S13[c]	1.00	1.48	215	1.5042	0.213	0.150	0.323	0.0320	10
SRM S13[c]	3.42	7.04	215	1.5042	0.027	0.150	0.323	0.0041	1
SRM S13[c]	5.42	7.14	215	1.5042	0.030	0.140	0.323	0.0042	1

Note: U -   not detected; value represents detection limit
      --   -   no analysis performed

[a] Arsenic concentration of substrate sieved to 250 μm.

[b] NIST SRM No. 2170 Montana soil.

[c] Butte, Montana, soil.

TABLE A-5. SUMMARY OF PBET RESULTS

Sample Type/ Sample ID	Bioaccessibility (Percent)
Fabricated Topsoil	
LS0001	5.5
LS0002	24.1
LS0003	14.2
SS0001	39.8
SS0002	30.3 [a]
SS0003	35.6
Average	25
Maximum	39.8
Rock Product	
R10001	1.6
R10002	9.6
R10003	8.4 [b]
Average	6.6
Maximum	9.6

Note: PBET - physiologically based extraction test

[a] Average bioaccessiblity of a triplicate analysis of this sample.

[b] Average bioaccessiblity of a duplicate analysis of this sample.

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Attachment B

Identifying the Mineral
Form of the Arsenic
Source

IDENTIFYING THE MINERAL FORM OF THE ARSENIC SOURCE

ELECTRON MICROPROBE ANALYSIS

The solubility of arsenic from soil or rock is controlled to a large extent by the mineral form in which the arsenic occurs. Because the relative bioavailability of arsenic in different matrices is related to its solubility (see Attachment A), determination of the arsenic mineralogy may provide an explanation of variations in relative bioavailability estimates among samples.

The primary tool that is used to assess the arsenic mineralogy of soil and rock samples is electron microprobe analysis (EMPA). This technology is particularly useful in assessing the mineralogy of samples that contain too few arsenic-bearing minerals to be detected by x-ray diffraction techniques. EMPA uses a variety of x-ray spectroscopic tools to generate microscopic images of individual soil or rock particles, determine their composition (i.e., mineralogy), and measure their arsenic content. This information is used to determine the distribution of arsenic among the various mineral phases of a sample.

METHODS

One sample, R10003, was analyzed using EMPA.[1] This sample, which contains 30 mg/kg arsenic, is a random sample from the D1 quarried rock that is used to prepare the top soil. The sample was processed by crushing it in a stainless-steel shatter box until the entire crushed sample passed through a 250-μm sieve. The crushed sample was then used in the EMPA.

The EMPA data for sample R10003 are provided in Table B-1, including an assessment of the mineralogy of each mineral grain evaluated, and its size based on the long-axis length. These data, together with the arsenic concentration and specific gravity of each mineral phase encountered, and the methods described in Technical Memorandum No. 9 (Exponent 1998), were used to calculate the distribution of arsenic mass among the minerals within this sample (Table B-2).

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[1] Three onsite soil samples were also analyzed using EMPA. These results will be presented in Technical Memorandum No. 14, *Results of Bioaccessibility and Mineralogical Analyses to Support the Baseline Human Health Risk Assessment.*

TABLE B-1. RAW DATA FROM THE ELECTRON MICROPROBE ANALYSIS OF KPC SAMPLE R10003

Particle No.	Mineral Phase	Mode of Occurrence	Long-Axis Dimension (μm)	Particle No.	Mineral Phase	Mode of Occurrence	Long-Axis Dimension (μm)
1	Arsenopyrite	Liberated	20	39	Pyrite	Attached	15
2	Arsenopyrite	Liberated	24	40	Pyrite	Attached	15
3	Arsenopyrite	Rimming	3	41	Pyrite	Attached	15
4	Arsenopyrite	Rimming	5	42	Pyrite	Attached	15
5	Arsenopyrite	Liberated	50	43	Pyrite	Attached	15
6	Arsenopyrite	Attached	5	44	Pyrite	Attached	15
7	Arsenopyrite	Liberated	55	45	Pyrite	Attached	15
8	Arsenopyrite	Liberated	3	46	Pyrite	Attached	15
9	Arsenopyrite	Liberated	8	47	Pyrite	Attached	15
10	Arsenopyrite	Liberated	10	48	Pyrite	Attached	15
11	Arsenopyrite	Liberated	30	49	Pyrite	Attached	15
12	Arsenopyrite	Attached	10	50	Pyrite	Liberated	20
13	Arsenopyrite	Liberated	20	51	Pyrite	Liberated	20
14	Pyrite	Liberated	25	52	Pyrite	Liberated	20
15	Pyrite	Liberated	30	53	Pyrite	Liberated	20
16	Pyrite	Liberated	75	54	Pyrite	Liberated	20
17	Pyrite	Liberated	75	55	Pyrite	Liberated	20
18	Pyrite	Liberated	75	56	Pyrite	Liberated	20
19	Pyrite	Liberated	100	57	Pyrite	Liberated	20
20	Pyrite	Liberated	100	58	Pyrite	Liberated	20
21	Pyrite	Liberated	100	59	Pyrite	Liberated	20
22	Pyrite	Liberated	100	60	Pyrite	Liberated	5
23	Pyrite	Liberated	50	61	Pyrite	Liberated	5
24	Pyrite	Liberated	50	62	Pyrite	Liberated	5
25	Pyrite	Liberated	50	63	Pyrite	Liberated	5
26	Pyrite	Liberated	50	64	Pyrite	Liberated	5
27	Pyrite	Liberated	50	65	Pyrite	Liberated	55
28	Pyrite	Liberated	50	66	Pyrite	Liberated	2
29	Pyrite	Liberated	50	67	Pyrite	Liberated	2
30	Pyrite	Liberated	50	68	Pyrite	Liberated	2
31	Pyrite	Liberated	50	69	Pyrite	Liberated	2
32	Pyrite	Liberated	50	70	Pyrite	Liberated	1
33	Pyrite	Liberated	50	71	Pyrite	Liberated	1
34	Pyrite	Liberated	50	72	Pyrite	Liberated	1
35	Pyrite	Attached	15	73	Pyrite	Liberated	1
36	Pyrite	Attached	15	74	Pyrite	Liberated	1
37	Pyrite	Attached	15	75	Pyrite	Liberated	1
38	Pyrite	Attached	15	76	Pyrite	Liberated	1

TABLE B-2. ELECTRON MICROPROBE ANALYSIS RESULTS

	Frequency Percent		Arsenic Mass Distribution	
Sample Type/ID	Arsenopyrite (percent)	Pyrite (percent)	Arsenopyrite[a] (percent)	Pyrite[b] (percent)
Crushed rock, sieved to <250 μm				
R10003	0.3	99.7	96.3	3.7

[a] The mass distribution was calculated using a specific gravity of 6 and an arsenic concentration of 46 percent.

[b] The average arsenic concentration in the pyrite phase is 60 mg/kg. This concentration, together with the specific gravity for pyrite, 5, was used to calculate the mass distribution.

ELECTRON MICROPROBE ANALYSIS RESULTS

EMPA results typically are reported in two ways: the frequency with which the arsenic-bearing particles occur in a sample, and the arsenic mass distribution among the mineral phases (Table B-2). The frequency-of-occurrence values are used to calculate the arsenic mass distribution, as discussed in Technical Memorandum No. 9. The arsenic mass in sample R10003 is distributed among two similar minerals—arsenopyrite (arsenic sulfide, or FeAsS) and pyrite (iron sulfide) containing trace amounts of arsenic—with 99 percent of the arsenic mass occurring in the arsenopyrite phase. Arsenopyrite and pyrite had arsenic concentrations of 46 and 0.006 percent, respectively, and specific gravities of 6 and 5 g/cm^3, respectively. Because both of these minerals have very low solubilities under GI-tract conditions (Davis et al. 1996), they are therefore likely to have very low bioavailabilities. This observation is supported by the physiologically based extraction test (PBET) data, which indicate that the bioaccessibility of sample R10003 is 8 percent (relative absorption factor = 0.08).

Because it was thought that the mineralogy and relative bioavailability of arsenic in sample R10003 would be similar to arsenic in Butte, Montana, soils (both R10003 and the Butte, Montana, soil were originally derived from sulfide-rich mineral deposits), a sample of the Butte, Montana, soil was included in the PBET procedure. This sample was included to provide an internal quality control sample for which both mineralogy and relative bioavailability data estimates are available (Casteel et al. 1997; Drexler 1998). The Butte, Montana, soil contains iron arsenic sulfate, a weathering product of pyrite and arsenopyrite. The relative bioavailability of this sample has been estimated to be 0.10, which is very similar to the relative bioavailability estimate of 0.08 for sample R10003. As the arsenic in the crushed rock on KPC site weathers, its mineralogy may become more like that of the Butte, Montana, soil, but its relative bioavailability is likely to remain very low.

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Attachment C

Quality Assurance Review Summary—Chemical Analyses of Solid and Aqueous Samples

QUALITY ASSURANCE REVIEW SUMMARY— CHEMICAL ANALYSES OF SOLID AND AQUEOUS SAMPLES

INTRODUCTION

Exponent performed a quality assurance review of data for chemical analyses of total metals and metals extractable by synthetic precipitation leaching procedure (SPLP). The chemical analyses for total arsenic were completed on 62 aqueous samples; 2 of which were additionally analyzed for total cadmium and lead; and 26 solid samples, 12 of which were additionally analyzed for SPLP-extractable arsenic. The quality assurance review was conducted to verify that the laboratory quality assurance and quality control procedures were completed and documented as specified in the quality assurance project plan (Appendix B in PTI 1997) and that the quality of the data is sufficient to meet the project data quality objectives (DQOs) and support the use of the data for its intended purposes. The results of the quality assurance review are presented in this report.

DATA VALIDATION PROCEDURES

Data validation was completed in accordance with U.S. Environmental Protection Agency (EPA) Level 3 specifications (U.S. EPA 1994a; PSEP 1991). During the quality assurance review, 26 results were qualified as estimated; no results were rejected.

Data validation procedures were based on EPA Contract Laboratory Program national functional guidelines for inorganic data review (U.S. EPA 1994a). Data validation procedures were modified, as appropriate, to accommodate project-specific DQOs and quality control requirements that are not specifically addressed by the national functional guidelines. The following laboratory deliverables were reviewed during the data validation process:

- Chain-of-custody documentation to verify completeness of the data

- Case narratives discussing analytical problems (if any) and procedures

- Data summary sheets to verify analytical holding times

- Method blanks associated with each sample delivery group (SDG) to check for laboratory contamination

- Results for all laboratory quality control samples used to check analytical accuracy, including matrix spikes, and laboratory control samples (LCSs)

- Results for all quality control samples used to check analytical precision, including duplicate sample analyses

- Instrument and method detection limits for all target analytes.

SAMPLE SET AND ANALYTICAL METHODS

The sample set consisted of 62 solid samples and 26 aqueous samples. The samples were analyzed for total metals by EPA Method 6020 (U.S. EPA 1994b) and SPLP-extractable arsenic by EPA Method 6010A (U.S. EPA 1992).

All analyses were completed by North Creek Analytical in Portland, Oregon.

SAMPLE DELIVERY GROUPS

All soil samples were analyzed in two SDGs. The data packages for these SDGs contained all documentation and data necessary to conduct a complete quality assurance review.

DATA QUALITY ASSESSMENT

The results of the quality control procedures used during sample analysis are discussed below. The laboratory data were evaluated in terms of completeness, holding times and sample preservation, instrument performance, method blanks, accuracy, precision, and method reporting limits.

Completeness

The results reported by the laboratory were 100 percent complete.

Holding Times

Analytical holding times were met for all samples and analyses.

Instrument Performance

The performance of the analytical instruments, as documented by the laboratory, was acceptable.

Mass Spectrometer Tuning

The mass spectrometer tuning checks conducted by the laboratory prior to sample analyses were acceptable, as documented by the laboratory.

Initial and Continuing Calibrations

Initial and continuing calibrations were completed at the required frequency and met control limits for all target analytes, as documented by the laboratory.

Contract-Required Detection Limit Standards

Contract-required detection limit standards met the criteria for acceptable performance.

Initial and Continuing Calibration Blanks

The initial and continuing calibration blank (ICB and CCB) met the criteria for acceptable performance and frequency of analysis, as documented by the laboratory.

Method Blank Analyses

Method blank analyses were completed for all target analytes and met the criteria for acceptable performance and frequency of analysis.

Accuracy

The accuracy of the analytical results is evaluated in the following sections in terms of matrix spike and LCS recoveries.

Matrix Spike Recoveries

The recoveries reported by the laboratory for matrix spike analyses met the criteria for acceptable performance and frequency of analysis, with the following exceptions. The matrix spike recoveries for arsenic associated with the solids data in both SDGs exceeded the upper control limit of 125 percent. A total of 26 results for total arsenic in solids were

qualified as estimated and may exhibit a high bias. The percent recoveries for arsenic and lead in one of two matrix spike recoveries associated with the standard reference material were outside of the control limits of 75–125 percent. No data were qualified because arsenic and lead recoveries in a second matrix spike were in control and all other associated quality control sample results were acceptable.

Laboratory Control Sample Recoveries

The recoveries reported by the laboratory for all LCSs met the criteria for acceptable performance and frequency of analysis.

Precision

The results reported by the laboratory for laboratory duplicate analyses met the criteria for acceptable performance and frequency of analysis, with the following exceptions. Arsenic results in laboratory duplicates associated with solid samples exceeded the relative percent difference (RPD) control limit of 40 percent, in both SDGs. A total of 26 solid total arsenic results were qualified as estimated and may exhibit a high or low bias.

Method Reporting Limits

The method detection limits (MDLs) and method reporting limits (MRLs) provided by the laboratories met project DQOs (PTI 1997).

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