









Data Summary Report Northwest Study Area Arsenic Biomonitoring Study Summer 2012

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## **Acronyms and Abbreviations**

ADEQ Arizona Department of Environmental Quality

ADHS Arizona Department of Health Services

As(III) arsenite As(V) arsenate

bgs below ground surface

CELCR cumulative excess lifetime cancer risk

CDC Centers for Disease Control and Prevention

DMA dimethylarsinic acid

ENVIRON ENVIRON International Corporation

g gram

IRB institutional review board

L liter

MMA monomethylarsonic acid

NHANES National Health and Nutrition Examination Survey

NSA Northwest Study Area

RPD relative percent difference

μg microgram

VRP Voluntary Remediation Program

WHO World Health Organization

XRF x-ray fluorescence

## 1 Introduction

BHP Copper contracted with ENVIRON International Corporation (ENVIRON) to conduct an arsenic biomonitoring study of current residents within the Northwest Study Area (NSA). In developing a plan with BHP Copper for cleanup in the NSA, the Arizona Department of Environmental Quality (ADEQ) stipulated that a two phase arsenic biomonitoring program be offered to the community as a condition to using a specific target risk goal in developing soil remediation levels for the NSA. A human health risk assessment found that arsenic levels in the study area are not expected to contribute significantly to natural background arsenic exposures from food and drinking water, nevertheless the ADEQ wishes to provide this further assurance of the minimal risk presented by the study area soils through this program. The arsenic biomonitoring program is funded by BHP Copper with oversight by the ADEQ. Participation in the program by NSA residents is voluntary.

The first sampling event occurred during the summer of 2011 (ENVIRON 2011c). The purpose of this report is to provide a data summary for ADEQ and BHP Copper of the second sampling event, which occurred in August 2012 A separate report that provides an overview of these data will also be made available to study participants.

#### 1.1 Overview of the Arsenic Biomonitoring Study

Arsenic is naturally present in most foods and in drinking water, and is widely distributed in the environment from many natural and anthropogenic sources. Studies of background exposures to arsenic in the U.S. have found that exposures are dominated by intakes from drinking water and diet, and that intakes via incidental ingestion of soil and inhalation of air contribute a negligible amount to total exposure. Fish and seafood contain the highest amounts of total arsenic, but most of the arsenic is present as nontoxic organic forms.

Biomonitoring is the measurement of a chemical or its metabolites in body tissues and fluids. Urine, blood, bone, breast milk, exhaled air, hair, nails, fat and other tissue can be used in biomonitoring studies, depending on the chemical of interest and objectives of the study. The most reliable, least invasive, and widely used screening test to measure recent arsenic exposure is measurement of arsenic in urine (ATSDR 2007). Arsenic in urine is not a measure of health effects. However, urinary arsenic levels that are within background levels expected from diet and water are helpful in confirming that recent exposures from other sources are not significant. Accordingly, urinary arsenic testing is the focus of biomonitoring offered to the community.

Most arsenic is excreted in urine within a few days of exposure; therefore, measuring arsenic in urine captures short-term exposure to arsenic. Total arsenic measurements in urine include both the more toxic forms (e.g., inorganic forms) that are typically found in soil as well as the essentially nontoxic forms (e.g., arsenobetaine) that are found in fish and shellfish. Total urinary arsenic concentrations less than 100 micrograms arsenic per liter of urine ( $\mu$ g/L) are considered normal (ATSDR 2009). ATSDR (2009) notes that levels can be significantly higher (greater than 1000  $\mu$ g/L) immediately following ingestion of seafood.

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The National Health and Nutrition Examination Survey (NHANES) conducted by the Centers for Disease Control and Prevention (CDC) measures urinary levels of metals and selected organic chemicals for the U.S. Table 1-1 presents the NHANES results for total arsenic in urine. The most recent survey, conducted in 2009 to 2010, found that the geometric mean total arsenic level was 9.28  $\mu$ g/L (CDC 2012). Half of the people tested had a total arsenic level of 8.15 micrograms per liter ( $\mu$ g/L) or less and 75% of the people had levels of 18.0  $\mu$ g/L or less. Fewer than 5% of the people had total arsenic levels greater than 85.6  $\mu$ g/L. The higher arsenic levels likely occur in people who recently consumed a seafood meal.

In Arizona, the typical urinary arsenic levels may be higher than in the U.S. as a whole. Based on experience with other arsenic biomonitoring studies within Arizona, the Arizona Department of Health Services determined that the geometric mean for Arizona residents is 18  $\mu$ g/L (ADHS 2009).

For the NSA study, total arsenic levels in urine were compared to the program reference level of  $30 \mu g/L$ . Further analysis of individual samples for speciated arsenic was indicated if the total urinary arsenic<sup>1</sup> result for that sample exceeded this reference level. The program reference level has been used previously by the Arizona Department of Health Services in biomonitoring for arsenic exposure (ADHS 2002).

Biomonitoring for soil exposure is typically conducted during seasons in which outdoor activity involving soil contact is possible. In the warm climate of the Superior area, fewer seasonal restrictions affect exposure measurement. Accordingly, the second urine sampling event was conducted during August 2012. The second sampling event for the biomonitoring study was initiated in July of 2012 with letters mailed to residents of the NSA that provided information about the biomonitoring study and how to enroll in the study.

For the second biomonitoring field event, urine samples and exposure survey information were collected from study participants on August 14<sup>th</sup> and 15<sup>th</sup>, 2012. Sample analyses included total arsenic, creatinine, specific gravity, and, in some cases, speciated arsenic.

Individual results were provided to study participants only and information that could be used to identify individual participants is excluded from this data summary report.

The first biomonitoring sampling event was conducted in June of 2011. NSA residents were invited to participate in either or both biomonitoring sampling events.

Results of both biomonitoring study events will be presented during a public meeting to be held in Superior, Arizona (anticipated in 2013).

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<sup>&</sup>lt;sup>1</sup> Where indicated, determination of reference level exceedance may be based on comparison to creatinine-corrected total urinary arsenic rather than the corresponding uncorrected total urinary arsenic result. See further discussion at section 3.2.

# 2 Summary of Summer 2012 Participant Recruitment and Sample Collection

This section provides a brief overview of the study participant recruitment, enrollment, and sample collection for the Summer 2012 biomonitoring sampling event. Additional details of the study objectives, scope, and planned procedures are documented in the "Northwest Study Area: Arsenic Biomonitoring Work Plan" (ENVIRON 2011a).

#### 2.1 Recruitment and Enrollment

Recruitment of participants occurred by mailing study announcement packets to NSA residents. The announcement packets included enrollment instructions, a biomonitoring fact sheet, and a participation consent form to be returned by residents wishing to enroll in the study. A preaddressed stamped envelope was included with each packet to facilitate return of signed consent forms for those residents choosing to complete the enrollment process.

On July 25, 2012, 102 study announcement packets were mailed to NSA residents. Recipients interested in participating in the study were requested to return their signed consent form to ENVIRON no later than August 10, 2012. A total of ten signed consent forms were received by ENVIRON, though, as described in Section 2.4, samples were collected from only eight NSA residents who had submitted consent forms. An additional pre-prepared stamped envelope was returned to ENVIRON and received sealed, but without any contents or notes that would identify which NSA resident had returned it. Two packets were returned by the postal service as undeliverable and without a known forwarding address and one packet was returned and remailed to the resident with an updated address.

#### 2.2 Sample Collection

Detailed sample collection and analysis procedures were provided to ADEQ and BHP Copper in the memorandum titled "Sample Collection, Analysis, and Quality Assurance Procedures for Northwest Study Area: Arsenic Biomonitoring Study" (ENVIRON 2011b). A summary of the procedures is provided herein.

ENVIRON provided each participant with a sample collection kit that included a pre-labeled sample collection vial, urine collection cup, re-sealable plastic bag, refrigeration pack, sample collection instructions, and a copy of the exposure survey at the beginning of the field sampling event. The kits were provided in a paper bag marked with only the participant's name. At NSA residences with more than one participant, each participant received their own sample collection kit. Participants collected their first morning void the day after receiving the sample collection kits. ENVIRON field staff retrieved the urine samples and completed exposure surveys the day of sample collection. Samples were stored in accordance with chain-of-custody procedures.

#### 2.3 Sample Analysis

ENVIRON (2011b) documents the urine sample analysis procedures. Briefly, Pacific Toxicology Laboratories, under contract with ENVIRON, analyzed each urine sample for total arsenic, specific gravity, and creatinine. A participant's urinary output and hydration can affect how dilute or concentrated the urine is, which can then affect interpretation of sample results. Creatinine

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and specific gravity measurements are conducted to allow for correction of sample results that may be needed given a participant's urinary output and/or state of hydration.

Following analysis, the remaining sample aliquots were stored at -20° C until it was determined if total urinary arsenic levels exceeded the program reference level of 30 µg/L. Per the study work plan, further analysis for speciated arsenic was required for any samples with total urinary arsenic² in excess of the program reference level. Applied Speciation and Consulting, LLC analyzed these samples for arsenite (As[III]), arsenate (As[V]), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA)³. Figure 2-1 summarizes the process used to evaluate sample results for this study.

#### 2.4 Field Sampling Event Summary

On August 13th, 2012, two ENVIRON staff members mobilized to Superior, Arizona to initiate the biomonitoring sampling event. Upon arrival, ENVIRON staff conducted a health and safety briefing according to the site-specific health and safety plan and also reviewed health and safety procedures with BHP Copper staff. A designated police officer was notified of ENVIRON's presence in the area and was on-call for all three days ENVIRON was in the field.

Initially, nine participants were enrolled in the study. One participant requested that a sample collection kit be mailed to them in advance. That participant's urine sample and completed exposure survey were retrieved on the morning of Monday, August 13<sup>th</sup> from the participant's home located within the NSA. The sample collection kits for the remaining study participants were prepared in the BHP Copper field office. A total of eight sample collection kits were constructed using sample vials pre-labeled with the confidential respondent code number (RCN) designated for each participant. ENVIRON staff then delivered five of the eight sample collection kits to the study participant homes. Two kits could not be delivered due the presence of a security dog. Also, during delivery of the sample collection kits, it was determined that one of the participants had moved from the NSA to a home outside of the NSA and was ineligible to participate in the biomonitoring study. However, the current resident of that NSA home elected to participate in the study. To accommodate the newly enrolled participant, ENVIRON staff returned later in the afternoon to provide a consent form and sample collection kit using an updated RCN. This resulted in six of the eight sample collection kits being delivered; two could not be delivered due to the presence of a security dog at the participants' home. ENVIRON staff remained at the BHP Copper field office until late afternoon to accommodate residents that may have had questions or concerns related to the study.

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<sup>&</sup>lt;sup>2</sup> Where indicated, determination of reference level exceedance may be based on comparison to creatinine-corrected total urinary arsenic rather than the corresponding uncorrected total urinary arsenic result. See further discussion in Section 3.2.

<sup>&</sup>lt;sup>3</sup> Applied Speciation and Consulting, LLC routinely includes results for a fifth arsenic species, arsenobetaine, when conducting speciated arsenic analyses. Arsenobetaine is an essentially nontoxic form of arsenic that is found in fish and seafood; therefore, it is not included in the sum of arsenic species compared to the program reference level. However, for completeness, study participants whose samples were tested for arsenic species were provided with all of their results, including arsenobetaine concentrations reported by the laboratory.

On August 14<sup>th</sup>, ENVIRON staff retrieved the participant-collected urine samples and completed exposure surveys from five of the six participants' homes; one participant elected to withdraw from the study and did not provide a sample or completed survey. The sample vials were taped to preserve the integrity of the labels and to secure the lids, and then were placed in re-sealable plastic bags. No personal identifying information was included on the samples; labels contained only the RCN and date. After sample preparation, Emily Weissinger and Meghan McKelvey delivered the remaining two sample collection kits that had been undeliverable the previous day. By close of business on August 14th, no additional NSA residents had chosen to participate in the study.

On August 15th, ENVIRON staff retrieved the remaining two participant-collected urine samples and one replicate sample, as well as the completed exposure surveys. A total of nine samples, eight investigative samples and one replicate sample, were prepared for shipment to the analytical laboratory. ENVIRON staff mailed the urine samples via FedEx with frozen gel packs and chains of custody to Pacific Toxicology Laboratories for total arsenic, creatinine, and specific gravity analyses.

## 2.5 Deviations from the Sample Collection, Analysis, and Quality Assurance Procedures

ENVIRON staff followed the procedures provided in the memorandum, "Sample Collection, Analysis, and Quality Assurance Procedures for Northwest Study Area: Arsenic Biomonitoring Study" (ENVIRON 2011b), with few exceptions. The following list summarizes deviations from procedures outlined by ENVIRON (2011b):

- Applied Speciation and Consulting, LLC routinely includes results for a fifth arsenic species, arsenobetaine, when conducting speciated arsenic analyses. Arsenobetaine is an essentially nontoxic form of arsenic that is found in fish and seafood; therefore, it is not included in the sum of arsenic species compared to the program reference level. However, for completeness, study participants whose samples were tested for arsenic species were provided with all of their results, including arsenobetaine concentrations reported by the laboratory.
- One sample result exceeded the uncorrected total arsenic reference level, but not the
  corrected reference level. Even though the procedures for this study (outlined in Figure
  2-1) state that only samples that exceed the corrected reference level will be analyzed
  for speciated arsenic, this sample was included in the speciated arsenic analysis as an
  extra precaution.

No other deviations from the Sample Collection, Analysis, and Quality Assurance Procedures (ENVIRON 2011b) are noted.

## **Exposure Survey and Analytical Results**

This section summarizes information reported by study participants on their exposure surveys for the Summer 2012 biomonitoring sampling event. Analytical laboratory results for total and speciated arsenic are also presented along with associated quality control information.

## 3.1 Exposure Survey Results

A total of eight people residing in the NSA participated in the Summer 2012 urinary arsenic biomonitoring study and completed the exposure survey (a sample survey form is included as an appendix to ENVIRON 2011a). Based on results from the surveys, participants ranged in age from about 50 to over 80 years old<sup>4</sup>, and six of the participants were female. All of the participants had lived at their current residence within the NSA for at least six months and all but one stayed overnight in their homes for the entire two weeks prior to sample collection. One participant reported being away from their residence for eight nights over the prior two week period. No participants reported eating seafood or locally-caught fish within the three days prior to sample collection, but three participants reported eating rice with three days of providing samples. This and other information obtained from the exposure surveys is presented in Table 3-1.

## 3.2 Analytical Results

Analytical results obtained during the Summer 2012 urinary arsenic biomonitoring study are summarized below.

#### 3.2.1 Total Arsenic

Table 3-2 presents the total urinary arsenic data collected in this biomonitoring study. Of the eight samples collected, arsenic was detected in six samples above the detection limit of 10 μg/L. Detected concentrations of total arsenic, uncorrected, ranged from 11.9 μg/L to 41.8 μg/L. Two of the eight sample results exceeded the uncorrected program reference level. The average total urinary arsenic concentration was 17.4 µg/L (uncorrected), assuming that all nondetect results are equal to one half of the detection limit, or 5 µg/L.

The validity of spot (untimed) urine sample measurements is indicated by review of creatinine and specific gravity results for each sample, both of which allow for corrections for varying hydration states of study subjects. Creatinine is a natural waste product of the body found in urine, which may be used to correct for variable water excretion rates (i.e., dilution) at the time of spot urine specimen collection (Barr et al. 2005). Creatinine correction assumes, on average, an individual excretes one gram of creatinine per liter of urine based on total daily mean urinary output volumes and total daily mean creatinine excretion. This is a theoretical value which may be above or below measured urinary creatinine in a given sample. Creatinine concentrations are primarily affected by the individual's hydration state, but creatinine excretion is also influenced to a lesser degree by other factors<sup>5</sup>, including gender, age, and lean body mass. Specific gravity

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<sup>&</sup>lt;sup>4</sup> This range applies to six of the eight participants, because two participants did not report their age.

<sup>&</sup>lt;sup>5</sup> The World Health Organization (WHO 1996) guideline range for urinary creatinine is 0.3 g/L to 3 g/L. Creatinine concentrations within this range are routinely used to adjust targeted analyte concentrations

represents the ratio of the density of a urine specimen to the density of water and will also vary depending on the individual's hydration state at the time of sample collection. As with creatinine, specific gravity measurements may also vary with age, gender, and health status.<sup>6</sup>

Because creatinine and specific gravity measurements are predominantly influenced by the volume of urinary output at the time of sample collection, they are used to adjust a sample for dilution effects that can influence interpretation of results for arsenic (Barr et al. 2005; Pactox 2012). For example, considering individuals of similar age, gender, and health status, a person who is dehydrated will have a more concentrated urine sample with higher specific gravity and higher levels of salts, creatinine, and arsenic than someone who is sufficiently hydrated. Conversely, someone who is very well hydrated will have a more dilute urine sample with lower specific gravity and lower levels of salts, creatinine, and arsenic. In the first case, the arsenic level in the urine may be artificially high unless adjusted for normal urine output. In the second case, the arsenic level in the urine may be artificially low without adjustment.

In this study, arsenic levels were adjusted for creatinine to correct for variable urinary output that would affect interpretation of arsenic concentrations in the samples. As discussed above, creatinine correction can also account for some of the variability in renal function and lean body mass among individuals (CDC 2009). As is typically the case, creatinine levels in this study were lower in older participants than in middle age participants. Accordingly, some of the variability in creatinine-corrected urinary arsenic results may have been due to differences in creatinine output between older and younger participants as well as other factors.

Creatinine correction was conducted according to the following equation (Pactox 2012):

$$Creatinine - Corrected\ Total\ Urinary\ Arsenic\ \left(\frac{\mu g}{g}\right) = \frac{Total\ Urinary\ Arsenic\ \left(\frac{\mu g}{L}\right)}{Creatinine\ \left(\frac{g}{L}\right)}$$

An assumed average daily urinary creatinine output of 1 g/L at normal hydration levels (Hee 1993) allows for direct comparison of creatinine-corrected results reported as " $\mu$ g/g" to uncorrected results and to a creatinine-corrected program reference level of 30  $\mu$ g/g.

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<sup>(</sup>e.g., arsenic) in spot urine samples for variability in the individual's urinary output at the time of sample collection. However, this range is not absolute. An analysis of the NHANES dataset by Barr et al. (2005) found that the WHO range may not encompass heterogeneous populations. For example, Barr et al. report 15 percent of female NHANES participants over the age of 70 had creatinine levels less than 0.3 g/L. As urinary creatinine concentrations have been shown to correlate with muscle mass, with higher urinary creatinine typically found in men than in women (Barr et al. 2005). With increasing age and coincident decreases in muscle mass, urinary creatinine concentrations decrease in both men and women (Barr et al. 2005).

<sup>&</sup>lt;sup>6</sup> The range of normal specific gravity in urine varies by laboratory, but range of 1.002 to 1.035 is generally considered acceptable for individuals with normal kidney function (Cadogan et al. 2011). Specific gravity measurements for NSA study participants ranged from 1.012 to 1.020 (Table 3-2) indicating further support for the validity of the NSA participants' urinary sample results.

Based on creatinine correction, detected sample results ranged from 21.1  $\mu$ g/g to 51.3  $\mu$ g/g (Table 3-2, Figure 3-2). Three samples exceeded the creatinine-corrected program reference level.

Specific gravity corrections were also conducted to provide an additional point of comparison for total urinary arsenic results. For specific gravity corrections, the following equation is used (Miller et al. 2004):

$$Specific \ Gravity \ Corrected \ Total \ Urinary \ Arsenic \ \left(\frac{\mu g}{L}\right) \\ = Total \ Urinary \ Arsenic \ \left(\frac{\mu g}{L}\right) \times \left[\frac{Average \ Specific \ Gravity - 1}{Sample \ Specific \ Gravity - 1}\right]$$

The specific gravity correction uses the average value for the population to normalize the arsenic concentrations based on the average dilution for the sample population. The average specific gravity for the eight samples in this study is 1.017. Detected specific gravity corrected total urinary arsenic ranged from 13.8  $\mu$ g/L to 38.3  $\mu$ g/L (Table 3-2, Figure 3-3) with one result above the program reference level. Specific gravity adjustments rely on input of a population-specific average specific gravity, thus the small number of participants and wide range of ages for participants in this study may introduce greater uncertainty in the reliability of specific gravity adjusted results versus creatinine-adjusted results for this study.

## 3.2.2 Speciated Arsenic

Three of eight samples analyzed for total arsenic in urine exceeded the creatinine-corrected program reference level of 30 µg/g and were analyzed for speciated arsenic. Speciation analysis was also conducted on one additional sample where the total urine arsenic exceeded the reference level prior to creatinine correction, but was below the reference level once corrected for creatinine. Speciated arsenic results are presented in Table 3-3 and Figure 3-4.

The toxicity of arsenic generally corresponds to its form or species. Inorganic arsenic species are the most toxic forms of arsenic and high concentrations in drinking water have been linked to increases in lung, bladder, and skin cancer in some regions of the world. Organic arsenic species are much less toxic than inorganic arsenic species and some organic forms (e.g., arsenobetaine) are thought to be essentially nontoxic. Inorganic forms of arsenic (i.e., As(III) and As(V)) and its metabolites (i.e., MMA and DMA)7, were summed for each participant with speciated results, and this sum was compared with the program reference level of 30  $\mu$ g/L (or  $\mu$ g/g creatinine). For all four participants, the sum of As(III), As(V), MMA, and DMA was less than the program reference level. Creatinine-corrected results for summed species ranged from 1.16 to 13.0  $\mu$ g/g (Table 3-3 and Figure 3-4).

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<sup>&</sup>lt;sup>7</sup> Some inorganic arsenic is converted in the human body to MMA and DMA.

## 3.3 Quality Assurance and Quality Control

All samples were collected and stored according to procedures outlined by ENVIRON (2011b).

A single replicate sample was collected. Both the investigative and replicate sample were below the detection limit of 10  $\mu$ g/L. Although the fact that both were non-detect provides some information about the agreement between the samples, it was not possible to calculate relative percent difference (RPD)<sup>8</sup> between them. However, in the Summer 2011 sampling event, the RPD between the investigative (16.9  $\mu$ g/L) and replicate (17.1  $\mu$ g/L) samples was 1.2%, falling well below the target RPD of 20%. RPD is calculated using the following equation:

$$RPD(\%) = 100 \times \frac{Result\ 1 - Result\ 2}{Average(Result\ 1, Result\ 2)}$$

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<sup>&</sup>lt;sup>8</sup> RPD is a measure of the consistency of the analytical method and provides information on the reliability of the analytical results.

## 4 Discussion and Conclusions

A limited number of NSA residents elected to participate in the second biomonitoring sampling event. Participants chose to volunteer for the study (i.e., they were not pre-selected based on any characteristic other than residence within the NSA) and may or may not be representative of NSA residents as a whole in terms of health status, activity patterns, diet, and other factors that may influence urinary arsenic concentrations.

For these eight individuals, total urinary arsenic was reported above the detection limit in six samples (75 percent detection rate). Of these six total arsenic detections, three exceeded the creatinine-corrected study reference level and were therefore analyzed for speciated arsenic. A fourth sample exceeded the uncorrected, but not the corrected, reference level. Speciated arsenic analysis was conducted for this sample as a check on the process outlined in Figure 2-1. For all four samples with speciated arsenic analysis, the sum of inorganic arsenic compounds was less than the study reference level, indicating that environmental exposure to arsenic in soil was not significant.

Urinary arsenic measurements capture recent arsenic exposures and may not be indicative of exposures occurring over a longer period of time. However, the range of total and speciated urinary arsenic concentrations reported are well within levels considered normal by ATSDR and consistent with average concentrations determined for Arizona residents based on ADHS involvement in other biomonitoring programs.

These findings are consistent with the site-specific human health risk assessment that found that arsenic levels in the study area are not expected to contribute significantly to natural background arsenic exposures from food and drinking water and provide further assurance of the minimal risk presented by the study area soils in the vicinity of NSA residents.

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## **Tables**

Table 1-1. Urinary total arsenic for the U.S. from NHANES

Survey Years	Sample Size	Geometric		Percentiles		
		Mean	50th	75th	95th	
Total Urinary A	rsenic (µg/L)					
2003 - 2004	2557	8.30	7.70	16.0	65.4	
2005 - 2006	2576	9.29	8.65	17.1	66.7	
2007 - 2008	2605	8.10	7.49	14.9	50.8	
2009 – 2010	2860	9.28	8.15	18.0	85.6	
Total Urinary A	rsenic - Creatinin	e-Corrected (µg/g	)			
2003 - 2004	2557	8.24	7.04	14.1	50.4	
2005 - 2006	2576	9.15	7.70	15.2	62.8	
2007 - 2008	2605	8.46	7.06	13.8	49.4	
2009 - 2010	2860	9.90	7.90	17.6	80.8	

Notes: NHANES: National Health and Nutrition Examination Survey conducted by the U.S. Center for Disease Control and Prevention

μg/L: microgram per liter; μg/g: microgram per gram

Table 3-1. Summary of 2012 NSA Study exposure survey results\*

Participant ID	7976	9155	8762	1927	8336	3989	1174	9862
Gender	Male	Female	Male	Female	Female	Female	Female	Female
Age Category	65+	65+	40 to 65	40 to 65	NR	65+	NR	65+
Have you lived at your residence more than 6 months?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
How many nights spent away from home in the last 2 weeks?	0	0	0	0	8	0	NR	0
Do you typically remove shoes when entering your house?	No	Yes	No	No	No	No	No	No
Is there fill material from the mines in your yard?	No	No	DK	DK	DK	DK	DK	DK
Do you have regular contact with the soil in your yard?	Yes	Yes	Yes	Yes	Yes	No	NR	Yes
Have you dug in your yard soil in the last 3 days?	Yes	No	Yes	No	Yes	No	No	Yes
Do you have any pets that spend time both inside and outside?	Yes	Yes	Yes	Yes	Yes	No	NR	No
Have you eaten locally caught fish within the last 3 days?	No	No	No	No	No	No	NR	No
Have you eaten seafood within the last 3 days?	No	No	No	No	No	No	NR	No
Have you eaten rice within the last 3 days?	No	No	Yes	Yes	No	No	Yes	No
Are you a current smoker?	No	No	No	No	No	No	No	No
Is the tap water in your house used for drinking?	Yes	Yes	Yes	Yes	Yes	Yes	No	No
In the last 3 months, have you worked with chemically treated wood?	No	No	No	No	No	No	No	No
Have you painted or done home improvement projects in the last 2	No	No	Yes	Yes	No	No	No	No

<sup>\*</sup>Questions considered to be potentially identifying (e.g., occupation) and those not relevant to any participating residents (e.g., those specific to children) are not included in this summary table.

DK = Respondent selected the "Don't Know" response to this question.

NR = A response to this question was not reported by the respondent.

Table 3-2. Total arsenic, creatinine, and specific gravity results for the 2012 NSA Study

Participant ID	Total Arsenic (μg/L)	Creatinine (g/L)	Specific Gravity (unitless)	Total Arsenic, Creatinine Corrected (µg/g Cr)	Total Arsenic, Specific Gravity Corrected (µg/L)
7976	<10	0.33	1.018	ND	ND
9155	<10	0.21	1.014	ND	ND
8762	41.8	1.22	1.018	34.3	38.3
1927	31.1	1.35	1.020	23.0	25.7
8336	14.1	0.33	1.016	42.7	14.5
3989	15.0	0.71	1.018	21.1	13.8
1174	11.9	0.50	1.012	23.8	16.4
9862	15.4	0.30	1.016	51.3	15.9

Notes: ND: not detected

<: less than

µg/L: microgram per lite g/L: gram per liter µg/g: microgram per gram

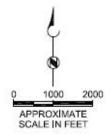
Table 3-3. Speciated arsenic results for the 2012 NSA Study

Participant ID	As(III) (μg/L)	As(V) (μg/L)	MMA (μg/L)	DMΑ (μg/L)	AsB (µg/L)	Sum of As(III), As(V), MMA, and DMA	Sum of As(III), As(V), MMA, and DMA (creatinine corrected)	Sum of As(III), As(V), MMA, and DMA (specific gravity corrected)
8762	0.93	<0.19	0.24	<0.058	3.06	1.42	1.16	1.34
1927	0.55	<0.19	1.23	10.9	5.99	12.9	9.53	10.94
8336	0.652	<0.19	0.54	0.533	<0.11	1.92	5.80	2.03
9862	1.822	<0.19	0.45	1.44	<0.11	3.90	13.0	4.15

Notes: <: less than μg/L: microgram per liter g/L: gram per liter

μg/g: microgram per gram

## **Figures**





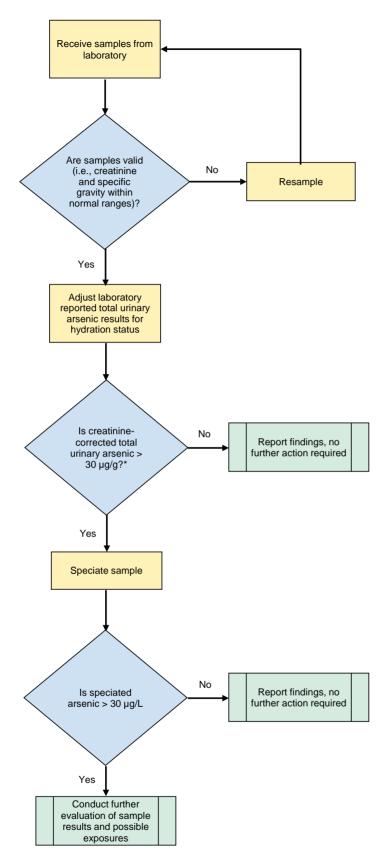
Source: Brown and Caldwell 2010



Northwest Study Area Site Location Map BHP Copper Inc. Superior, Arizona

Figure 1-1





<sup>\*</sup> Correction of total urinary arsenic for specific gravity was also performed. However, the small number of participants in the study increases uncertainty in the specific gravity corrected total urinary arsenic results. This is because the specific gravity correction method uses the average specific gravity for the sample population whereas the creatinine correction method does not rely on sample size. Consequently, for this sampling event, compliance with the program reference level was based on the creatinine-corrected results.

Figure 2-1. Sample results evaluation process

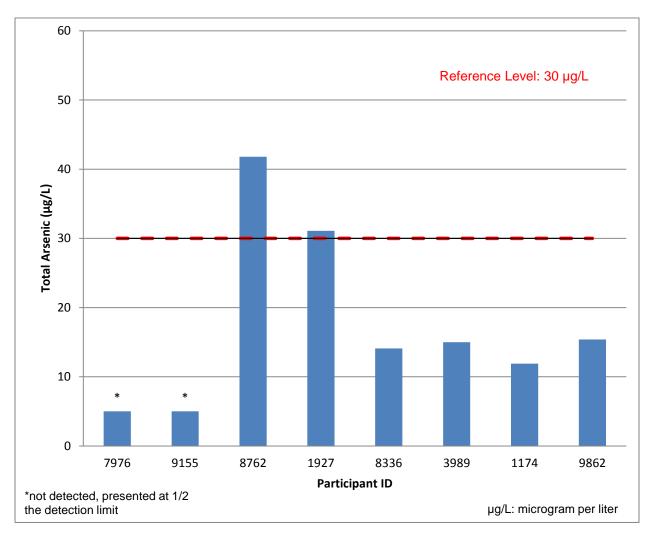


Figure 3-1. Total urinary arsenic results for the 2012 NSA Study

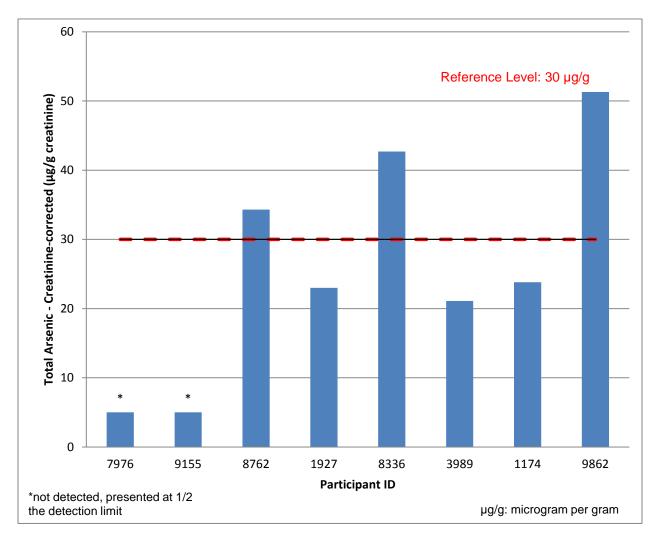


Figure 3-2. Total urinary arsenic results for the 2012 NSA Study – creatinine-corrected

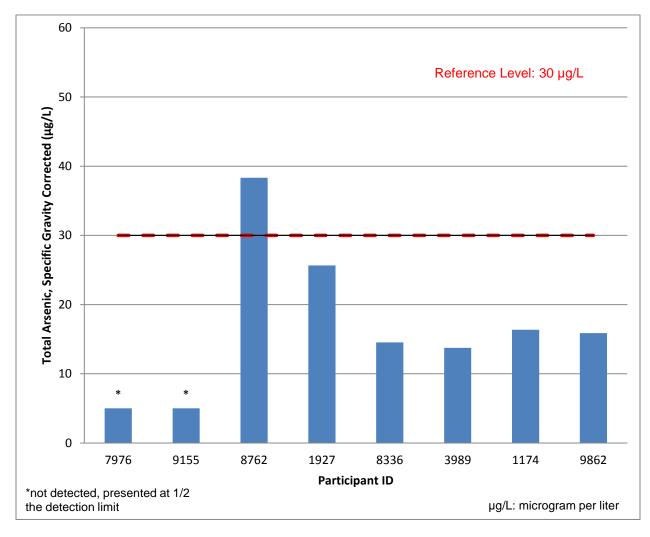


Figure 3-3. Total urinary arsenic results for the 2012 NSA Study – specific gravity corrected

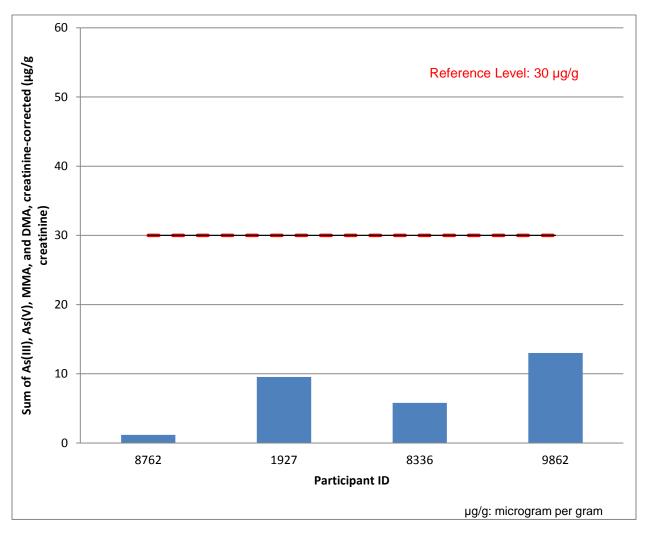


Figure 3-4. Speciated urinary arsenic results for the 2012 NSA Study - creatinine-corrected

## **Appendices**

## Appendix A: Letter to Residents Reporting Results



[Date]

[Name] [Address]

Dear [Name]:

Thank you for your participation in the Northwest Study Area Arsenic Biomonitoring Study conducted in summer 2012 by ENVIRON on behalf of BHP Copper Inc.

This letter provides a brief summary of the urine sample results associated with your participation in this study. A Fact Sheet describing the factors affecting arsenic levels in urine also is enclosed. It is normal for people to have arsenic in the urine from arsenic naturally present in food and drinking water. The purpose of this study is to find out whether your arsenic levels are higher than what normally might be expected from natural background sources. If so, we will follow up with you to evaluate whether yard soil might be a source of exposure.

ENVIRON will prepare a report for the Arizona Department of Environmental Quality (ADEQ) and BHP Copper summarizing the results of the Arsenic Biomonitoring Study. The report will be available to the public and will not include the names or addresses of study participants, which is a typical practice in studies such as this. Information about the results will also be made available at a public meeting. Individual results will not be revealed in the report or at the meeting. Your specific results will be kept confidential and are known by only you and the researchers at ENVIRON.

Dr. Schoof will be present at the public meeting and is available for private consultation via telephone if you have questions about your arsenic urinary results. If you have a question on a medical issue based on these results, your personal physician is best suited to answer that question. Your physician will consider your study results in the context of your personal health history (for example, smoking habits, occupation, etc.).

We greatly appreciate your participation. If you have any questions, please contact one of us at our toll-free number, 1-855-519-9600, or via email at ArsenicStudy@environcorp.com.

Sincerely,

Dr. Rosalind Schoof, Ph.D., D.A.B.T. Principal Investigator

Dina Johnson Project Manager Name - 2 - Date

#### **Urine Sample Results**

As part of the Northwest Study Area Biomonitoring Study, you were asked to submit a urine sample so that amounts of arsenic in your urine could be measured. The concentration of arsenic in your urine was compared to a reference level of 30  $\mu$ g/L (30  $\mu$ g/g creatinine corrected), developed by researchers from the University of Arizona for the ASARCO Hayden Smelter Site in Hayden, Arizona. If your total arsenic result was greater than this reference level of 30  $\mu$ g/L, a second test was conducted on your urine sample to measure the forms of arsenic that are most likely to be linked to arsenic exposures in the environment (i.e., not arsenic taken in from food). Total arsenic results are reported from the first test and speciated arsenic results are reported from the second test, if conducted.

The lab tested for four compounds that are likely to be associated with environmental exposures, namely arsenite (As[III]), arsenate (As[V]), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA). The concentrations reported by the lab for each of these arsenic species was added together and the sum was compared with the reference level of 30  $\mu$ g/L (30  $\mu$ g/g creatinine corrected). The lab routinely includes results for a fifth arsenic species, arsenobetaine (AsB), when conducting speciated arsenic analyses. AsB is an essentially nontoxic form of arsenic that is found in fish and seafood. It is included in the results below for your information, but it was not used to compare the arsenic in your urine to the reference level of 30  $\mu$ g/L (30  $\mu$ g/g creatinine corrected).

There are three ways in which arsenic in urine can be reported. The first, reported as micrograms of arsenic per liter of urine ( $\mu$ g/L), or parts per billion (ppb), reflects the actual measured concentration of arsenic in urine. A second value, reported as micrograms of arsenic per gram ( $\mu$ g/g) of creatinine (a protein excreted in urine in relatively constant amounts), reflects the concentration of arsenic in urine taking into account the fact that the urine may be concentrated or dilute, depending on the amount of fluids consumed. The third way of reporting arsenic includes a correction for specific gravity, which measures the relative weight of your urine to water. This test reflects the number of particles in your urine.

Please be aware that the concentrations of arsenic in your urine represent only the conditions on the day that you submitted your sample. A single urine sample cannot be used to determine whether there is or is not a health risk. In addition, a number of things (for instance, your diet on the previous 3 or 4 days) may cause the levels of arsenic in your urine to increase or decrease.

#### **Total Arsenic Results**

Parameter	Your Result	Reference Level
Arsenic (µg/L)		30
Creatinine (g/L)		0.3 - 3
Arsenic – creatinine corrected (µg/g creatinine)		30
Specific gravity (-)		1.015-1.030
Arsenic – specific gravity corrected (µg/L)		30

#### **Speciated Arsenic Results**

Parameter	Your Result	Reference Level
Sum of Inorganic Arsenic Compounds (μg/L)*		30
Inorganic Arsenic – creatinine corrected (µg/g creatinine)		30
Inorganic Arsenic – specific gravity corrected (µg/L)		30

Name - 3 - Date

\*sum of arsenite, arsenate, monomethylarsonic acid, and dimethylarsinic acid; these are the compounds most likely to be associated with environmental arsenic exposures.

## **Detailed Speciated Arsenic Results**

Parameter	As(III)	As(V)	MMA	DMA	AsB
Result (µg/L)					

As(III): arsenite As(V): arsenate

MMA: monomethylarsonic acid DMA: dimethylarsinic acid

AsB: arsenobetaine

## Appendix B: Community Summary Report

## **ADEQ & BHP Copper Inc.**

## **August 2012 Biomonitoring Results**

#### Introduction

Arizona Department of Environmental Quality (ADEQ) and BHP Copper are working together to provide Northwest Study Area (NSA) residents with information on their personal arsenic intake. Participation is voluntary. A participant's arsenic intake is evaluated by measuring the amount of arsenic in a urine sample that he or she provides. This type of study is called an "arsenic biomonitoring study."

Arsenic biomonitoring studies that use urine samples are the most reliable, least invasive, and most widely used screening test to measure recent arsenic exposure (ATSDR 2007). Arsenic is naturally present in most foods and in drinking water, and is widely distributed in the environment from many natural and man-made sources. This means that arsenic is usually present in urine. Although arsenic in urine is not a measure of health effects, when levels of arsenic measured in urine are compared to levels that would be expected from background exposures to arsenic in food and water, then arsenic biomonitoring results can help us understand whether or not a participant has likely experienced recent exposures from sources of arsenic other than food and water.

#### Results

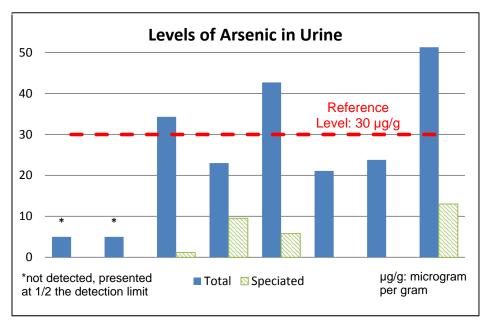
Results for total arsenic are presented for all participants. Urine was also tested for speciated arsenic when the total arsenic result was greater than the program reference level. Some forms of arsenic have very low toxicity. The speciated arsenic result presented below is the sum of the forms of arsenic with the greatest potential for toxicity at elevated levels of exposure.

Total and Speciated Arsenic Levels in Urine (µg/g, creatinine-corrected\*)

	Range	Average**	
Total Arsenic (all types of arsenic)	ND - 51.3	29.4	
Speciated Arsenic (sum of most toxic forms)	1.2 - 13.0	7.4	

Notes: ND = not detected (Detection limit for uncorrected total arsenic equal to  $10 \mu g/g$ )

<sup>\*\*</sup>Assuming uncorrected ND values are equal to 1/2 the detection limit, or 5  $\mu$ g/L



## **Conclusions**

Speciated arsenic levels in urine were all below the program reference level. These results are consistent with the site-specific human health risk assessment that found that arsenic levels in the study area are not expected to contribute significantly to natural background arsenic exposures from food and drinking water.

# Measuring Arsenic in Urine

Arsenic in urine is usually reported as the concentration of arsenic in micrograms per liter of urine (µg/L); however, the concentration of arsenic in urine is affected by how much water and other liquids a person drinks. People who drink lots of liquids will generally have lower arsenic concentrations than people who do not drink as much, even if their arsenic exposure is the same. So. arsenic in urine is also reported a second way that corrects for variation in hydration state (or how much liquid a person has drunk). The corrected result uses the level of creatinine (a protein excreted in urine in relatively constant amounts) measured in the urine to adjust the arsenic result reported by the first method. The adjusted or "corrected" result then reflects the concentration of arsenic in urine taking into account the fact that the urine may be concentrated or dilute, depending on how well hydrated the person is.

<sup>\*</sup>Corrected means that the results are adjusted for the hydration level of the participant.

# ADEQ & BHP Copper Inc. August 2012 Biomonitoring Results

## **Summary of August 2012 Event**

- Participants were recruited using recruitment letters and a telephone hotline.
- Participants' urine was collected during the week of August 13, 2012.
- Eight individuals ranging in age from about 50 to over 80\* participated.
- Total arsenic, creatinine, and specific gravity in urine were measured in all urine samples.
- Arsenic in urine was compared to the program reference value of 30 micrograms per gram (μg/g) (ADHS 2002). This value is for comparing results that have been adjusted by participants' hydration level. Creatinine is used to measure hydration level and so results have been "creatinine-corrected" to account for their level of hydration and for comparison with the reference level.
- Five of eight results were below the reference level of 30 μg/g.
- Three of eight samples analyzed for total arsenic in urine exceeded the program reference level of 30 µg/g. These samples were analyzed for speciated arsenic. Speciation was also conducted on one additional sample where the total urine arsenic exceeded the reference level prior to creatinine correction, but was below the reference level once corrected for creatinine.
- Speciated sample results were all below the program reference level of 30 μg/g (creatinine-corrected).
- \* This range applies to six of the eight participants, because two participants did not report their age.

#### What's Next?

There will be a public meeting summarizing the NSA biomonitoring program in 2013.

Questions about the NSA biomonitoring study may be directed to:

Toll-Free Phone: 1-855-519-9600 Email: arsenicstudy@environcorp.com

#### References:

ADHS. 2002. Public Health Assessment: ASARCO Hayden Smelter Site Hayden, Arizona CERCLIS #AZD008397127. Office of Environmental Health, Environmental Health Consultation Services, Arizona Department of Health Services. Prepared under a cooperative agreement with the Agency for Toxic Substances and Disease Registry.

ATSDR. 2007. Toxicological Profile for Arsenic. Revised. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. http://www.atsdr.cdc.gov/toxprofiles/tp2.pdf.











Principal Investigator for the Arsenic Biomonitoring Study