Multimedia exposures to arsenic and lead for children near an inactive mine tailings and smelter site ☆

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A R T I C L E   I N F O

A B S T R A C T

Children living near contaminated mining waste areas may have high exposures to metals from the environment. This study investigates whether exposure to arsenic and lead is higher in children in a community near a legacy mine and smelter site in Arizona compared to children in other parts of the United States and the relationship of that exposure to the site. Arsenic and lead were measured in residential soil, house dust, tap water, urine, and toenail samples from 70 children in 34 households up to 7 miles from the site. Soil and house dust were sieved, digested, and analyzed via ICP-MS. Tap water and urine were analyzed without digestion, while toenails were washed, digested and analyzed. Blood lead was analyzed by an independent, certified laboratory. Spearman correlation coefficients were calculated between each environmental media and urine and toenails for arsenic and lead. Geometric mean arsenic (standard deviation) concentrations for each matrix were: 22.1 (2.59) ppm and 12.4 (2.27) ppm for soil and house dust (< 63 μm), 5.71 (6.55) ppb for tap water, 14.0 (2.01) μg/L for specific gravity-corrected total urinary arsenic, 0.543 (3.22) ppm for toenails. Soil and vacuumed dust lead concentrations were 16.9 (2.03) ppm and 21.6 (1.90) ppm. The majority of blood lead levels were below the limit of quantification. Arsenic and lead concentrations in soil and house dust decreased with distance from the site. Concentrations in soil, house dust, tap water, along with floor dust loading were significantly associated with toenail and urinary arsenic but not lead. Mixed models showed that soil and tap water best predicted urinary arsenic. In our study, despite being present in mine tailings at similar levels, internal lead exposure was not high, but arsenic exposure was of concern, particularly from soil and tap water. Naturally occurring sources may be an additional important contributor to exposures in certain legacy mining areas.

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1. Introduction

Mining and associated industries, such as smelting, generate waste materials that can contaminate the surrounding environment and be a source of exposure for nearby communities even after the facilities close. Exposure to various metal(loid)s from mining waste can occur via inhalation and ingestion of windblown soil and dust, ingestion of contaminated drinking water, and even ingestion of foods grown in personal gardens with contaminated soil.

Adverse health effects of exposure to metal(loid)s include cancer, neurodevelopmental impairment, and other systemic effects. Children are particularly susceptible to the effects of these

contaminants because their bodies are still developing (Hines et al., 2010). Lead has been associated with a decrease in IQ and various chronic diseases (Bellinger et al., 1986; Lanphear, 2005; Lanphear et al., 2005; Spanier and Lanphear, 2005). Arsenic exposure at an early age may also lead to disease later in life (Dauphine et al., 2011). Arsenic is a known carcinogen which has also been associated with decreased lung function and increased susceptibility to respiratory infections and cardiovascular effects (Ahsan et al., 2006, 2000; Bates et al., 2004; Chen et al., 1995; Dauphine et al., 2011; Navas-Acien et al., 2005; Lantz et al., 2009).

Given the potentially higher concentrations of metal(loid)s in soils and dust near mining and smelting sites, it is important to understand the various sources and pathways of exposure in order to better target exposure reduction (Gulson et al., 1994a, 1994b). In particular, children are at greater risk of exposures as they are more likely to play outdoors or on the floor and inadvertently ingest dust adhered to hands or other objects (Cohen Hubal et al., 2000). For example, in the community near a former copper smelter in Montana, Hwang et al. (1997) found a significant correlation between arsenic concentrations in residential soils and urinary arsenic in children less than 72 months old, with the highest correlation for soils in bare yards. Polissar et al. (1990) found that indoor air and dust were associated with urinary arsenic in a community nearest a former copper smelter in Tacoma, Washington. They found a stronger relationship between soil arsenic and urinary arsenic in children compared to adults, indicating that soil ingestion may be a source of exposure in children, but not adults.

In Arizona, where copper mining has a long history, the former Iron King Mine and Humboldt Smelter site (Iron King) are now listed on the National Priorities List (a.k.a., a Superfund site). The Superfund program was established by the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), which allows for the cleanup of listed sites by the United States Environmental Protection Agency (US EPA). Arsenic and lead concentrations in the mine tailings and smelter ash are well above 1000 ppm (US EPA, 2010), and arsenic and lead levels in soil near the mine could be impacted by windblown dust or rainwater runoff.

Arsenic, in particular, is known to be present in copper ores, and in Arizona, some groundwater wells are contaminated with naturally occurring arsenic as a result of the regional geology. Much of the drinking water in rural Arizona comes from private wells, providing an additional exposure source to arsenic, in addition to the soil and dust from the Iron King site. Gardenroots, a previous study looking at homegrown vegetables in the same community found arsenic in home irrigation water at levels ranging from 1.40 to 2030 ppb, and residential soil samples ranging from 3.07 to 322 ppm (Ramirez-Andreotta et al., 2013).

In response to the high levels of arsenic and lead at the Iron King site, the findings of the Gardenroots project, community interest, and the importance of early life exposures to the potential development of subsequent disease, we conducted the Metals Exposure Study in Homes (MESH) to examine the exposures of children in the community surrounding the Site. The aim of the study was to quantify the environmental levels and exposures of children and determine whether exposures were elevated compared to those of the general United States (US) population. Due to the high levels of arsenic and lead in the tailings, we hypothesized that levels of arsenic and lead in soil and house dust and exposures (as measured in urine and toenails) would be higher found in areas closer to the Iron King site than further away. We also include water ingestion as a pathway of exposure due the potential for groundwater wells in this area of Arizona to be high in arsenic (O'Rourke et al., 1999a, 1999b; Roberge et al., 2007).

2. Materials and methods

2.1. Study area and participants

We recruited households with children aged 1–11 years within a 5-mile radius of the geographic median between the Iron King Mine and Humboldt Smelter (Fig. 1). Recruitment methods included having a presence at local fairs, mailing flyers and postcards, and door-to-door canvassing from October 2011 through June 2013. A crew of local field technicians carried out the door-to-door recruitments and subsequent home visits. At least one child per household was enrolled in the study.

Upon enrollment, two home visits were scheduled at the participant's convenience, approximately one to two weeks apart. The first visit included a home walk-through and a questionnaire on the physical layout of the participant's home and property. Also during this visit, dust fall canisters were laid out, and participants were given biological sample collection materials and food and activity logs.

The parents or guardians were instructed to record food and activity/location information 4 days before the collection of a urine sample, which was to be the morning of the second visit by field staff. During the second visit, field staff collected environmental samples, and picked up the urine and toenails collected by the family and the activity and food logs.

2.2. Biological sample collection

Parents or guardians of participants were instructed to obtain urine samples the morning of the second home visit and to refrigerate them until the visit. Once transported to the field office, they were kept at $-20\,°C$ until analysis. The specific gravity of urine samples was determined using a refractometer (TS Meter Handheld Goldberg Series, Reichert Analytical Instruments). Samples were corrected for specific gravity before data analysis using the overall group mean according to Eq. (1):

$$U_{sg} = U \times (\frac{SG_{mean}-1}{SG_{measured}-1}) \tag{1}$$

where U_{sg}=specific gravity-corrected urine concentration of element (μg/L); U=uncorrected urine concentration of element (μg/L); SG_{mean}=the mean specific gravity of all individuals in the study group (1.02); and $SG_{measured}$=the specific gravity of each individual's urine sample. For summary statistics and data analyses, the specific gravity corrected urine concentrations were used.

All toenails were clipped with new nail clippers unique to each child and were collected in brown manila envelopes and kept at room temperature until processed. Toenails were sonicated in acetone for 20 min; rinsed with ultrapure water five times; and then sonicated in 1% Triton-X for an additional 20 min. They were then rinsed again with ultrapure water and dried in an oven at $60\,°C$ for 12 h before being weighed. Toenails were then placed for 12 h in 2 mL of Optima® trace metal free nitric acid and microwave digested using a CEM MARS Xpress, set at 400 W at 75% power, with a 10 min ramp up to $105\,°C$, and held at that temperature for 15 min. The sample was allowed to cool before being transferred to trace metal-free centrifuge tubes and diluted to 10 mL before laboratory analysis. A certified reference material (INSPQ/Toxicologie QMEQAS10H-02, cheveux/hair) was used for quality control. For venous blood lead testing, participants went to a local Clinical Laboratory Improvements Amendments (CLIA) certified laboratory, Labcorp, Inc. (Burlington, NC), where samples were analyzed by ICP-MS. The blood lead LOD reported was 1 μg/dL.
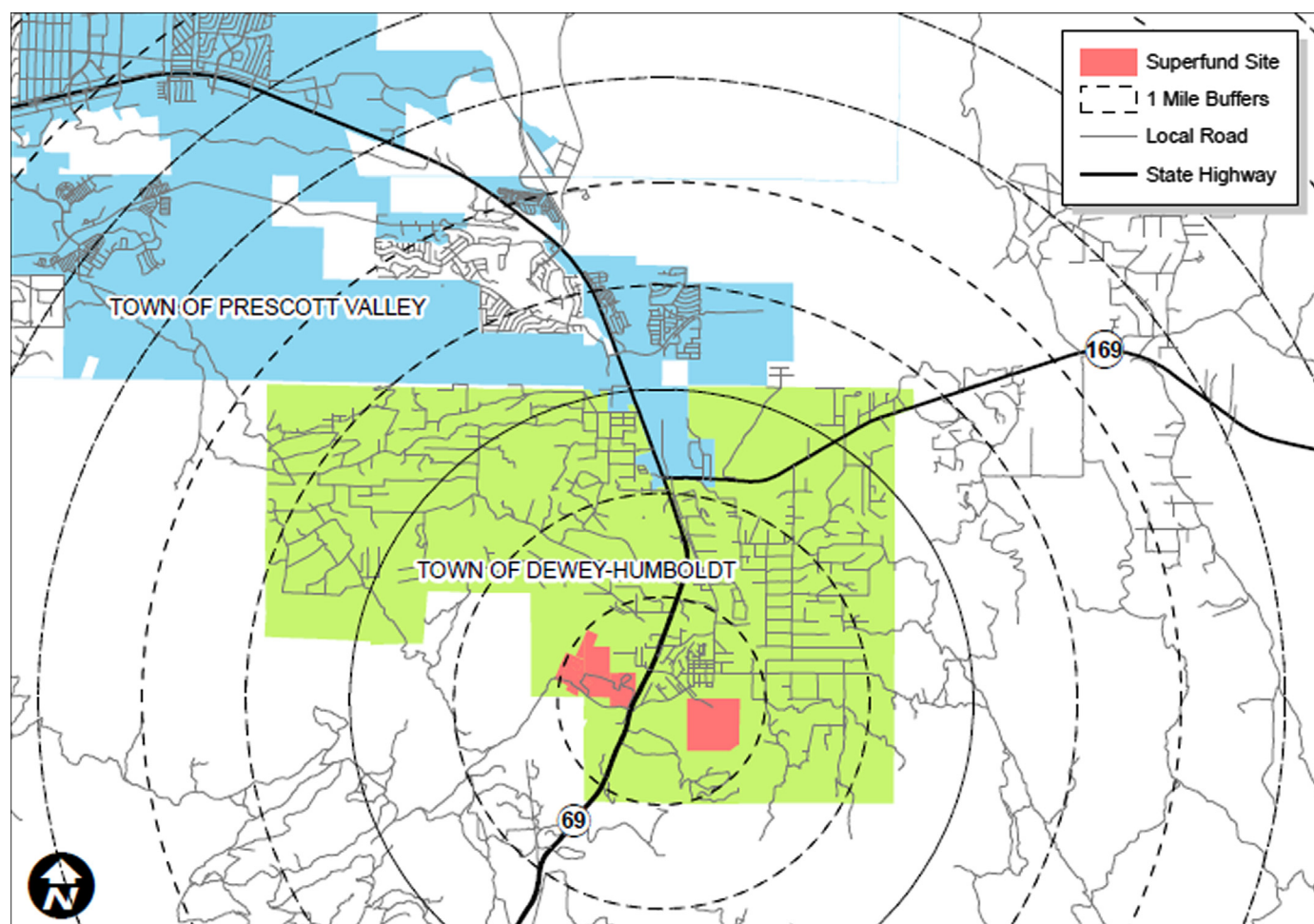
Fig. 1. Iron King Mine and Humboldt Smelter Superfund Site and surrounding area considered in MESH study.

2.3. Environmental samples

One full trowel of soil was taken from 2 points from each side of the house and composited into a single sampling bag (i.e., if the house was a rectangle, there would be a total of 8 trowels of soil collected). If the soil was too damp for collection due to precipitation, field staff returned to the property as soon as the soil was dry enough for collection. When scheduling home visits, participants were asked not to alter their usual cleaning habits in any way. Staff vacuumed a measured surface area with instructions to obtain approximately 2 g of dust using a vacuum (Hoover CH3000) with an X-Cell 100 dust collection sock (Midwestern Filtration) inserted in the crevice tool (henceforth referred to as house dust). Both soil and house dust were dried at 105–110 °C for 24 h and sieved to the following size fractions: $<63\ \mu m$, 63–150 μm, $>150\ \mu m$ to 1 mm, and >1 mm. Only the $<63\ \mu m$ sample results are reported in this paper because this fraction is more likely to adhere to hands and thus be ingested (Choate et al., 2006; Yamamoto et al., 2006). It is also a fraction that is more likely to become airborne and be inhaled. Sieved samples for soil and house dust were digested in 10 mL of Optima® trace metal-free nitric acid using a CEM Mars Xpress microwave (1600 W at 75% power, 10 min ramp to 170 °C and held for 10 min) using US EPA method 3051. Once digested, samples were centrifuged and the supernatant was pipetted out for ICP-MS analysis. Floor dust loading was calculated as the concentration of arsenic or lead in the vacuumed dust multiplied by the weight of the dust sample divided by the area vacuumed.

Dust fall was collected using four filters, 3 mixed cellulose ester (MCE) 142 mm diameter filters that were cut down to 120 mm diameter and a single 120 mm glass fiber filter (Beamer et al., 2014). They were placed in petri dishes protected by steel cans open on both ends. The concentrations of metals in the dust were determined by digesting each MCE filter in 10 mL of Optima® trace metal-free nitric acid using the same method as for soil and dust. The resulting supernatant from the filters was combined and reduced using a heat plate to 15 mL before being sent for ICP-MS analysis. Bulk dust fall rate was determined gravimetrically from the glass fiber filter using a microbalance. Dust fall rate was calculated using the equation:

$$D_{FR} = \frac{D}{SA*T}$$

where D_{FR} is the dust fall rate ($\mu g/mm^2/h$); D is the mass (μg) of dust collected on the dust fall filters; SA is the total surface area of the dust fall filters (mm^2); and T is the duration of dust fall collection (h). Dust fall concentrations for arsenic and lead were calculated as the product of the dust fall rate and the concentration of metal in dust collected on dust fall filters.

Unfiltered water samples were taken after a 2 min flush from the kitchen tap with 15 mL trace-metal free centrifuge tubes. All water samples were refrigerated for no more than 2 weeks before being preserved with Optima® trace metal-free nitric acid until pH < 2. Before the samples were sent for analysis, they were tested for turbidity. If turbidity was <1 Nephelometric Turbidity Unit (NTU), the sample was not digested prior to analysis. This criterion was met for all samples.

2.4. Laboratory analysis

Samples were sent to the Arizona Laboratory for Emerging Contaminants (ALEC) for analysis. Total metal(loid)s were measured on a Perkin Elmer ELAN DRC-II (for samples before April 2012) and on an Agilent 7700x (after April 2012). Typical operating parameters were RF power of 1400 (Elan) and 1550 (7700x) watts, plasma gas flow of 15 L/min, carrier gas flow of 1.0 L/min, with an auxiliary or makeup gas flow of 0.15 L/min. Quality control/assurance procedures for US EPA Method 6020 were followed. Calibration curves included at least 5 points, with correlation coefficients > 0.995. Creation of a satisfactory calibration curve was followed by the analysis of an Initial Calibration Blank (ICB) and Calibration Verification (ICV) solution, with a concentration in the low to mid-range of the calibration curve. A Continuing Calibration Blank (CCB) and Continuing Calibration Verification (CCV) solution were measured after every 20 samples and at the end of each batch. Each batch also included measurement of at least one quality control (QC) solution from a second source, such as the NIST 1643e Trace metals in water. Acceptable QC responses were between 90 and 110% of the certified value. A suitable internal standard (usually Rh, In, Ga or Ge) was added using on-line addition into the sample line and mixing tee. Arsenic speciation was done on an Agilent 7500 CE using an anion exchange column with ammonium carbonate gradient.

2.5. Statistical analysis

Analytical sample data were corrected by subtracting the mean of the blanks from each value. The study limit of detection (LOD) was defined as 3 times the standard deviation of the blanks for each medium and element. If a value was below the analytical limit of detection but a value was reported by the laboratory, this value was used in calculating concentrations; otherwise, values reported as non-detected (i.e. no value was reported) were replaced by $\mathrm{LOD}/\sqrt{2}$.

Data were summarized with descriptive statistics and analyzed graphically to determine the distribution of, and relationships between, biomarkers and environmental concentrations. As histograms showed non-normal distributions with a right skew, we report geometric means and standard deviations.

Various relationships between environmental media were examined using Spearman correlation coefficients. House dust/soil concentration ratios were computed to determine whether sources of metal(loids) were likely to be from indoors or outdoors. Spearman correlation coefficients were also determined between urine or toenails and each of the environmental measurements to examine the relationships between these variables.

Urine concentrations used in analyses were specific gravity-adjusted and analyzed as two groups – total arsenic species and inorganic-related arsenic species, which was distinguished as the sum of the species arsenite (AsIII), aresenate (AsV), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA). To compare the concentrations of arsenic in urine in our study to the distribution of biomarker values found in the general US population, we used data from the National Health and Nutrition Examination Survey (NHANES) 2011–2012 distributions for children aged 6–11 years. Uncorrected urine concentrations were used for this comparison because NHANES does not report specific gravity corrected values.

Since we enrolled multiple children per household, mixed-effects models with household as a random effect were run using urinary inorganic related arsenic species as an outcome variable, because this variable excludes arsenobetaine and arsenocholine, thought to come only from food. Age and gender were included in

models, regardless of significance, as these are thought to influence both non-dietary ingestion of soil and dust and metabolism of arsenic. Soil and house dust were not included in the same models; rather, models were run separately for these two predictors due to the high correlation between them. Other variables included in the analyses were floor dust loading of arsenic, dust fall concentration, and dust fall rate. A mixed-effects logistic regression was similarly run with a binary outcome variable of above or below detection limits for toenails. Continuous concentration variables in both urine and toenail analyses were log-transformed prior to analyses. All analyses were conducted in R 3.0.2 (R Foundation for Statistical Computing, Vienna, Austria).

3. Results

We recruited 70 children from 34 households, including more than one child in 22 of the households. Fifty percent of the children were male and ages ranged from 1 to 11 with a mean age of 6 years. Of those 70 children, 68 provided urine samples and 60 provided toenail samples. There was no significant difference in urine and toenail arsenic concentrations between males and females or between 1–5 year olds and 6–11 year olds, hence we compared all urine samples to the NHANES urinary values for children 6–11 years old.

3.1. Environmental samples

Summary statistics of each environmental sample medium are shown in Table 1. Eighteen homes (52%) had tap water arsenic concentrations above the US EPA Maximum Contaminant Level (MCL) of 10 ppb for arsenic. Two homes were above the US EPA lead action level of 15 ppb, which is the level at which action should be taken if 10% of samples are above this level. Twenty-seven soil samples and nineteen house dust samples were above 10 ppm, the Arizona Department of Environmental Quality Soil Remediation Level (SRL) for arsenic, which is a level at which more investigation is warranted. None of the soil or dust levels were above the lead SRL. There are guidelines for lead loading on bare floor, but no other floor dust loadings or dust fall guidelines. None of the homes exceeded the US EPA lead floor dust loading guideline of 430 μg/m² (40 μg/ft²) (US EPA, 2001). The geometric mean concentration of arsenic was greatest in soil and house dust 1–2 miles from the Iron King site, with lower concentrations both closer and further from the site (Table 2). Geometric mean concentrations of lead, on the other hand, appeared to decrease consistently with distance from the site.

3.2. Biological samples

Summary statistics of each biological matrix are shown in Table 3, and distributions of uncorrected urinary arsenic are shown in Fig. 2 compared to values for children ages 6–11 years from the 2011–2012 NHANES report (CDC, 2015) 57 of the 68 children (84%) who gave urine samples had uncorrected total urinary arsenic concentrations above the NHANES 50th percentile; of these, six (11%) children had urinary total arsenic concentrations above the 95th percentile. For urinary inorganic-related arsenic species, 57 children (84%) had urinary concentrations above the NHANES 50th percentile, and 22 children (32%) had concentrations above the 95th percentile. Uncorrected values were used for comparison because the US Centers for Disease Control (CDC) does not report specific gravity corrected-concentrations. All blood lead levels for the 46 children tested were below the CDC's action level of 5 μg/dL, with 70% below the detection limit, and 22% of urine samples had detectable lead concentrations. Only 60% of the toenail

Table 1
Summary statistics of arsenic and lead in environmental media.

Metal	N	% Detect	Units	GM	GSD	Min	Max	Above Guideline
Soil								
As	34	100%	ppm	22.1	2.59	3.13	432	79%[a]
Pb	34	100%	ppm	16.9	2.03	5.39	59	0[a]
Vacuumed Dust								
As	34	100%	ppm	12.4	2.27	1.51	103	56%[a]
Pb	34	100%	ppm	21.6	1.90	8.01	274	0[a]
Vacuum Bag								
As	32	100%	ppm	9.50	4.26	0.01	69.1	63%[a]
Pb	32	97%	ppm	16.5	4.00	0.02	90.0	0[a]
Water (tap samples)								
As	34	97%	ppb	7.46	4.46	0.03	240	53%[b]
Pb	34	56%	ppb	0.64	4.11	0.06	48	6%[c]
Dust Fall conc								
As	30	91	ppm	5.49	12.2	5.12E−05	67.3	na
Pb	30	91	ppm	35.4	11.1	6.67E−04	504	na
Dust Fall Rate								
As	30	na	µg/mm^2/h	3.19E−03	2.19E+06	1.25E−03	0.02	na
Pb	30	na	µg/mm^2/h	2.05E−02	1.69E+06	4.95E−03	0.06	na
Dust Floor Loading								
As	34	na	µg/m^2	12.4	2.27	1.51	103.34	na
Pb	34	na	µg/m^2	21.6	1.90	8.01	274.04	0

[a] Guideline is Arizona Soil Remediation Level (SRL) of 10 ppm for arsenic and 400 ppm for lead, which indicates a level where further investigation, not necessarily clean-up, is advised.
[b] Maximum Contaminant Level (MCL) of 10 ppb, which is a standard.
[c] Action level of 15 ppb.

Table 2
Geometric mean (ppm) soil and house dust concentrations of As and Pb by distance from Iron King site.

Miles from site	Element	n	Soil		Vacuum Dust	
			GM	GSD	GM	GSD
0–1	As	13	20.3	1.45	14.2	1.44
	Pb	13	22.8	1.83	26.6	1.55
1–2	As	9	48.7	2.58	19.6	1.69
	Pb	9	16.1	2.1	19.8	1.46
2–3	As	6	19.4	2.69	9.56	2.15
	Pb	6	13.8	2.41	17	1.54
3–4	As	5	10.1	3.27	5.16	1.48
	Pb	5	11.7	1.87	15.8	1.49
>4	As	1	6.41	NA	1.49	NA
	Pb	1	10.5	NA	8.03	NA

Table 3
Summary statistics of arsenic and lead biomarker levels.

Metal	N	Detected (%)	Units	GM	GSD	Min	Max
Urine (specific gravity corrected)							
As	68	100	µg/L	14	2.01	3.13	80.7
Pb	68	22	µg/L	0.339	2.72	0.016	5.05
Toenails							
As	60	60	µg/g	0.543	3.22	0.05	9.38
Pb	60	50	µg/g	5.22	14.9	0.08	3757
Blood Pb	46	30	µg/dL	1.36	1.56	<LOD	3

samples had detectable arsenic levels, and 50% of the samples had detectable lead levels. Toenail concentrations were widely more variable than urine concentrations.

3.3. Relationships between types of samples

The various relationships between concentrations of arsenic and lead in soil, house dust, tap water, floor dust loading, dust fall concentration, and dust fall rate were examined using Spearman correlation coefficients (Table 4) and dust/soil ratios (Fig. 3). The dust/soil ratios provide an indication of whether the main sources
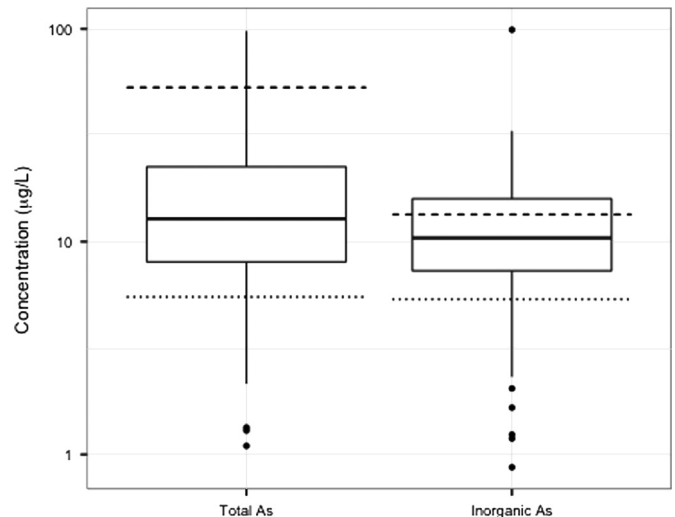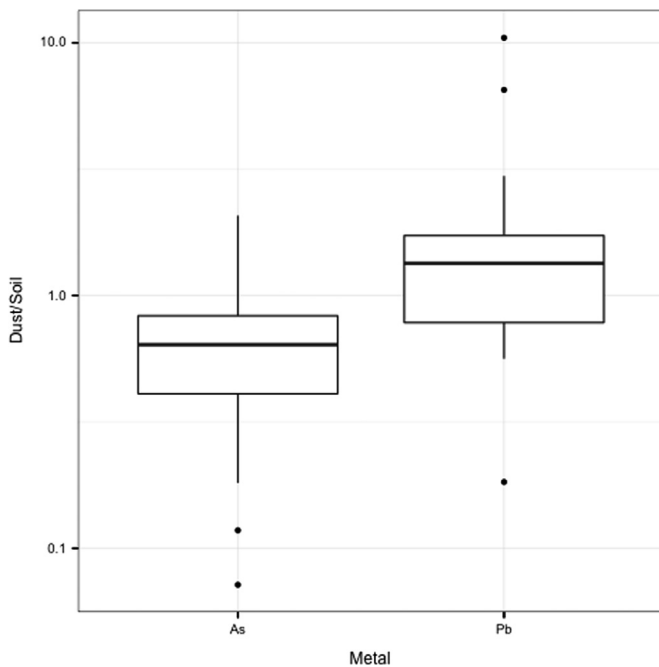

Fig. 2. Total and inorganic+metabolites concentrations in urine. Box indicates median and interquartile range (IQR), whiskers indicate $1.5 \times$ IQR and points are outliers.

of these elements in homes are likely to be indoors or outdoors, with a ratio <1 suggesting primarily outdoor sources and a ratio >1 suggesting primarily indoor sources. The highest correlations for both arsenic and lead concentrations were between house dust and soil: 0.71 ($p < 0.001$) for arsenic and 0.45 ($p=0.008$) for lead. Other significant correlations included soil arsenic levels and dust fall rate ($\rho=0.40$, $p=0.03$), house dust arsenic levels and dust fall rate ($\rho=0.47$, $p=0.01$), and between arsenic concentrations in tap water and soil ($\rho=0.35$, $p=0.003$) and house dust ($\rho=0.37$, $p=0.001$). Aside from the soil/dust correlation there were no other significant correlations for lead. Dust/soil ratios ranged from 0.07 to 2.0 for arsenic with a geometric mean of 0.56, suggesting that arsenic is primarily derived from outdoor sources. For lead, dust/soil ratios ranged from 0.18 to 10 with a geometric mean of 1.3 (Fig. 3), suggesting lead is more likely to be derived from indoor sources. There were significant moderate correlations between tap

Table 4
Spearman correlation coefficients between logged environmental variables.

	ρ	p-Value
Soil–dust		
As	0.71	< 0.001*
Pb	0.45	0.008*
Soil–dust loading		
As	0.30	0.08
Pb	0.24	0.16
Soil–dust fall concentration		
As	0.12	0.52
Pb	−0.14	0.47
Soil–dust fall rate		
As	0.40	0.03*
Pb	−0.21	0.26
Dust–dust fall concentration		
As	0.27	0.15
Pb	−0.15	0.43
Dust–dust fall rate		
As	0.47	0.01*
Pb	−0.05	0.77
Water–soil		
As	0.35	0.003*
Pb	−0.13	0.29
Water–dust		
As	0.37	0.001*
Pb	−0.19	0.13
Water–dust fall concentration		
As	−0.04	0.77
Pb	0.06	0.65
Water–dust fall rate		
As	−0.44	0.74
Pb	0.02	0.86

* Significant with $p \le 0.05$.

Fig. 3. Arsenic and lead dust:soil ratios. Box indicates median and interquartile range (IQR), whiskers indicate $1.5 \times$ IQR and points are outliers.

water concentrations and soil and dust concentrations for arsenic ($\rho=0.35$, $p=0.003$; $\rho=0.37$, $p=0.001$) but not lead.

We compared arsenic and lead in urine and toenails to determine whether these could be used interchangeably as exposure markers. Arsenic in toenails showed a significant moderate correlation with total urinary arsenic ($\rho=0.33$, $p=0.01$) and a lower

Table 5
Spearman correlation coefficients for environmental media and biomarker concentrations.

	Total As		Inorganic As	
	ρ	p-Value	ρ	p-Value
Soil				
Toenails	0.42	0.0009*		
Urine	0.32	0.008*	0.49	< 0.001*
Dust				
Toenails	0.36	0.005*		
Urine	0.39	0.001*	0.48	< 0.001*
Water				
Toenails	0.27	0.03*		
Urine	0.38	0.003*	0.40	< 0.001*
Dust fall loading				
Toenails	0.34	0.008*		
Urine	0.38	0.001*	0.51	< 0.001*
Dust fall concentration				
Toenails	0.15	0.27		
Urine	−0.1	0.46	0.01	0.9
Dust fall rate				
Toenails	0.16	0.24		
Urine	0.12	0.41	0.32	< 0.001*

* Significant with $p \le 0.05$.

correlation with urinary inorganic-related arsenic species ($\rho=0.28$, $p=0.0003$). On the other hand, there was no indication of correlation between lead in toenails and lead in urine ($\rho=-0.10$, $p=0.44$).

Table 5 shows the correlations between biological and environmental sample levels for arsenic. Correlations for these samples were low and mostly insignificant for lead. Urinary inorganic-related arsenic species had higher and more significant correlations with each environmental medium than did total urinary arsenic and toenail arsenic. Soil and house dust concentrations showed significant correlations for urinary total arsenic and inorganic-related arsenic species. The concentration of arsenic in dust fall did not show significant correlations with toenails or urine, but dust fall rate of arsenic was correlated with urine ($\rho=0.32$, $p < 0.001$). The correlation between arsenic in water and urine was similar to that for soil and dust ($\rho=0.38$, $p=0.003$ and $\rho=0.40$, $p < 0.001$ for urinary inorganic-related arsenic species). Toenail arsenic concentrations were less correlated with water ($\rho=0.27$, $p=0.03$) than soil and dust ($\rho=0.42$, $p=0.001$ for soil, and $\rho=0.36$, $p=0.005$ for dust, and $\rho=0.34$, $p=0.008$ for dust loading). Dust fall rate and dust fall concentration did not show any strong or significant correlations with urinary total arsenic. Lead was detected in less than half of the urine and toenail samples, and therefore not included in these analyses.

3.4. Mixed-effect model results

All models included age, gender, and arsenic tap water concentration with specific gravity-corrected urinary inorganic arsenic-related species as the outcome. Due to the high correlation between soil and house dust, these two variables were examined separately. Therefore, two identical sets of predictors were examined, the only difference being soil concentration in one set and house dust concentration in the other. Other variables tested included concentration in dust fall, dust fall rate, and floor dust loading (only included for the model with soil, as this variable is derived from the staff-collected vacuum dust concentration). Tap water and soil concentrations were significant predictors of arsenic in urine (Table 6), both separately and in the same model, although the AIC was lower in the former. Arsenic in house dust, floor dust loading, dust fall concentration and dust fall rate were

Table 6
Mixed models of predictors of urinary inorganic As (specific gravity corrected).

	Value	Std Error	p-Value	AIC
Model 1				131.2
(Intercept)	2.187	0.275	< 0.001	
Age	− 0.016	0.031	0.60	
Gender (male)	0.290	0.177	0.113	
Log (tap As)	0.220	0.080	0.010[*]	
Model 2				133.8
(Intercept)	1.631	0.512	0.003	
Age	− 0.016	0.031	0.621	
Gender (male)	0.293	0.181	0.117	
Log (soil)	0.323	0.149	0.038[**]	
Model 3				143.6
(Intercept)	1.308	0.487	0.012	
Age	− 0.019	0.030	0.539	
Gender (male)	0.361	0.176	0.050[**]	
Log (tap As)	0.207	0.077	0.012[**]	
Log (soil)	0.294	0.137	0.041[**]	
Model 4				116.9
Intercept	1.268	0.421	0.006	
Age	− 0.024	0.028	0.390	
Gender (male)	0.223	0.162	0.183	
Log (tap As)	0.189	0.066	0.008[**]	
Log (soil)	0.372	0.121	0.005[**]	
Log (dust fall As conc)	− 0.066	0.037	0.088[*]	
Model 5				116.9
Intercept	2.314	3.528	0.518	
Age	− 0.020	0.028	0.493	
Gender (male)	0.212	0.169	0.221	
Log (tap As)	0.198	0.076	0.016[**]	
Log (soil)	0.308	0.151	0.052[*]	
Log (As dust fall rate)	0.051	0.170	0.766	

[*] Significant with $p \leq 0.05$.
[**] Significant with $p \leq 0.10$.

not significant predictors of arsenic in urine when included with age, gender, and tap water concentration, although floor dust loading and dust fall rate had p-values of approximately 0.1. In models with soil, dust fall concentration and dust fall rate were not significant predictors (Table 6), although these models had the lowest AIC. None of the environmental concentrations were found to be significant predictors (data not shown) in the logistic analysis with toenail concentration above/below the LOD as an outcome variable.

4. Discussion

In the community around the Iron King Superfund site, exposure to both arsenic and lead were of concern, due to levels exceeding 1000 ppm in the mine and smelter waste. High lead exposures in children are especially of concern due to the range of developmental effects that can occur. However, our study found that lead exposure was low in all children, while urinary arsenic levels were higher than those found in a nationally representative sample of children aged 6–11 years, especially for urinary inorganic-related arsenic species. Soil and tap water arsenic levels for many homes were higher than guideline or regulatory standards and were significant predictors of exposure. In addition to contamination of soil with arsenic, high levels of arsenic in groundwater have been found in this area of Arizona, and private well owners are particularly vulnerable to arsenic exposure if they do not test their wells. Additionally, at the time of this study, one of the local community water providers was in violation of drinking water standards for arsenic, because of difficulty in reducing the naturally-occurring arsenic in the groundwater. Although the Arizona State Soil Remediation Level (a guideline for further investigation) for arsenic is 10 ppm, sampling by our group

and colleagues have found that even areas considered background several miles from the site can have arsenic levels higher than this. Determining whether arsenic in soil, dust, and water is due to natural or anthropogenic sources is not possible, due to the lack of a stable isotopic "fingerprint."

Arsenic in indoor house dust likely comes primarily from outdoors, while lead may have more varied sources in house dust. Average arsenic levels in the yard soil of homes were higher closer to Iron King compared to further away. Interestingly, the levels appeared to be higher 1–2 miles from the site, rather than in the mile closest to the site. There are several possible explanations for this. Depending on a home's location relative to prevailing wind patterns, deposition patterns could be a contributor (Stovern et al., 2014). However, as noted earlier, the natural geology of the area allows for areas of high arsenic concentrations in soil. Additionally, there is a possibility of some yards having fill material that came from the mine or smelter tailings, although we could not corroborate this for the homes we sampled. We did not have a large sample size, therefore we expect a higher level of spatial heterogeneity in sample concentrations, and cannot make a generalization as to arsenic and lead concentrations at various distances from the site. Arsenic concentrations in soil and dust were above guideline levels in the majority of homes. Soil concentration was shown to be a predictor of urinary arsenic concentrations. Given that arsenic in house dust was positively correlated with soil and dust fall rate, and the low dust/soil ratios, arsenic in house dust most likely comes from the outdoors. Thus, both tap water and soil may be important contributors to children's exposure near Iron King. These results show that risk assessments for metal(loid)s in legacy mining areas need to account for different pathways and routes of exposure.

Our findings that soil and house dust are related to children's arsenic exposure in the community surrounding Iron King have some similarities with findings of other studies near former metal industry Superfund sites. For example, Hwang et al. (1997) studied exposure in children less than 6 years old in the community of Anaconda, Montana, near a former smelter that is now a Superfund site. While arsenic in soil (GM 236 ppm) and vacuumed dust (GM 63 ppm) samples were higher than in our study, Hwang et al. found low, but significant correlations between arsenic levels in soil samples from different areas of the home yards and inorganic urinary arsenic, but no correlation with house dust (Hwang, et al., 1997). Similarly, in our study, while the correlation between arsenic levels in house dust and soil is relatively strong, only soil turned out to be a significant predictor of urinary arsenic in mixed models. Differences between the studies may be due to the fact that children in Montana spend less time outside due to weather conditions, as compared to the community around Iron King.

In Tacoma, Washington, Polissar et al. (1990) conducted an exposure assessment in children and adults near a copper smelter. Mean soil and dust arsenic concentrations were 353 and 375 ppm, respectively. They also conducted air and dust fall sampling. They found that children aged 0–6 years had the highest urine and hair arsenic concentrations of the sampled population, and that soil arsenic had a greater relationship with urinary arsenic in those ages 0–13 years compared to older individuals. They also found that a model including coarse indoor air particles and hand wash concentrations explained about 50% of the variability in urinary arsenic, indicating that indoor air and dust can be a large contributor to overall exposure. Drinking water arsenic concentrations were fairly low in the Tacoma population, compared to our study. This suggests that exposure via airborne dust in the home could account for a significant amount of exposure in children when arsenic levels in tap water are low, although the route of exposure may be through incidental ingestion of settled dust, rather than inhalation. In our study house dust was a less significant predictor

of children's exposures than soil; arsenic in house dust most likely comes from soil and possibly airborne dust, considering that the rate of dust fall in the home is correlated with arsenic levels in house dust samples and urine.

An analysis of data from the National Human Exposure Assessment Study (NHEXAS) in Arizona found a significant difference between mining and non-mining areas for arsenic concentrations in house dust, soil, outdoor air, beverages and water consumed, and total exposure (O'Rourke et al., 1999a). Another study in the Arizona towns of Hayden and Winkelman, which are near an active copper smelter, did not find a significant relationship between house dust and inorganic arsenic in urine (Hysong et al., 2003). This study, however, was done primarily in adults, and it is possible that children in areas with higher soil and dust arsenic levels would also have higher inorganic-related arsenic exposures, as the Polissar study found. In comparison to NHEXAS Arizona (O'Rourke et al., 1999b), MESH concentrations of lead in soil would have all been below the detection limit from that study (69.7 ppm). NHEXAS soil lead levels ranged from 118 to 350 ppm, but 85% of the values were below the detection limit. The lowest detected value was at the 90th percentile. Dust concentrations had a wider range in MESH, with the maximum value similar to that in NHEXAS, where dust sample concentrations ranged from 85 to 280 ppm. Lead in drinking water ranged from 0.1 to 28.4 ppb in NHEXAS, with the median below detection limits (0.1 ppb).

One unique outcome of our study compared to other exposure studies near Superfund mining and smelter sites is that tap water was a strong predictor of arsenic exposure, in addition to soil. Arsenic in local groundwater sources is likely naturally occurring, rather than from mine and smelter waste leaching. Interventions to reduce exposure to arsenic in this community, therefore, should be based on both reducing exposures to soil and dust and to drinking water. Reducing exposure to arsenic from tap water may necessitate sustained public outreach and education on water testing and treatment (Lothrop et al., 2015). Future work will entail identifying different structural and behavioral household factors that result in lower dust accumulating in homes.

5. Conclusion

Arsenic exposures were found to be of greater concern than lead in the community surrounding the Iron King Mine and Humboldt Smelter Superfund Site in Arizona, despite concentrations of both elements being several thousand ppm in the mine tailings and smelter ash. There was a consistent decrease of lead in soil with distance from the site but this appeared not to be a critical source of exposure. For arsenic in soil, concentrations were highest 1–2 miles away from the site, rather than 0–1 miles away, and then decreased with increasing distance from the site, possibly due to the area's geology, although our small sample size makes it difficult to generalize across the locale. Soil, house dust, and tap water arsenic concentrations were significantly correlated with both urinary arsenic, particularly inorganic-related arsenic species, and toenail arsenic, indicating that ingestion of soil, dust, and tap water are each important routes of exposure for children in a community with elevated levels of arsenic in these media. Because of factors like naturally high arsenic concentrations in groundwater, our study shows that local geological characteristics can play an important role in exposure assessment for legacy mining sites and that researchers and risk assessors need to account for multiple routes of exposure and non-site related sources that may be unique to an area.

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