Screening Level Assessment of Arsenic and Lead Concentrations in Glass Beads Used in Pavement Markings

PUBLICATION NO. FHWA-HRT-14-021

JANUARY 2014

U.S. Department of Transportation
Federal Highway Administration

Research, Development, and Technology
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FOREWORD

This report provides results of an assessment of the potential risk to human health posed by occupational and residential exposure to arsenic and lead concentrations found in glass beads used in pavement markings. The study used glass beads from samples of inventories from 15 State transportation departments to ascertain minimum screening levels based on both carcinogenic and noncarcinogenic effects, with the lower value selected as the final recommended screening level. The recommended screening levels were determined to be 220 ppm for arsenic, based on the child resident scenario, and 580 ppm for lead, based on the worker scenario. These determined screening levels are greater than the maximum content of 200 ppm for arsenic and 200 ppm for lead in glass beads prescribed in MAP-21 (the Moving Ahead for Progress in the 21st Century Act); therefore, the values specified in the existing legislation are considered protective of health based on currently available data.

The report is divided into three sections. The first section provides a detailed characterization of arsenic and lead concentrations in commercially available glass beads in current use on U.S. roadways, including the total, extractable, and bioaccessible arsenic and lead content in glass bead samples provided by State transportation departments. The second section describes the modeling methodology used to estimate the potential for adverse human health effects associated with arsenic and lead in glass beads used in pavement markings. The third section provides the human health screening levels for arsenic and lead in glass beads that are considered protective of human health. The results of the screening level assessment indicate that currently available products pose minimal health risk to humans while meeting retroreflective performance criteria.

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Director, Office of Safety
Research and Development

TECHNICAL REPORT DOCUMENTATION PAGE

1. Report No. FHWA-HRT-14-021	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Screening Level Assessment of Arsenic and Lead Concentrations in Glass Beads Used in Pavement Markings		5. Report Date January 2014 6. Performing Organization Code:
7. Author(s) Bryan Boulanger, Paul Carlson, Harry Fatkin, and Aditya Raut-Desai		8. Performing Organization Report No.
9. Performing Organization Name and Address Texas A&M Transportation Institute The Texas A&M University System College Station, Texas 77843-3135		10. Work Unit No. TRAIS 11. Contract or Grant No. DTFH68-09-E-00105
12. Sponsoring Agency Name and Address Office of Infrastructure Research & Development Federal Highway Administration 6300 Georgetown Pike McLean, VA 22101-2296		13. Type of Report and Period Covered Final Report 14. Sponsoring Agency Code

15. Supplementary Notes
Projects were performed with the cooperation and participation of the Environmental Protection Agency
Project Title: Development of Roadway Guidance Information

16. Abstract

Retroreflective glass beads used in pavement markings are a critical component of highway safety. Glass beads meeting American Association of State Highway and Transportation Officials (AASHTO) M247 specifications are the current industry standard. AASHTO M247 glass beads are fabricated using reclaimed glass cullet, offering cost effective performance while beneficially reusing sources of industrial and commercial waste glass. However, reclaimed glass cullet may contain elevated levels of arsenic and lead that can be passed through to the final product. Concern regarding the presence of arsenic and lead in retroreflective glass bead products within the U.S. marketplace resulted in recently adopted legislation that sets a 200 part-per-million (ppm = 10^6 x $\text{mass}_{\text{metal}}/\text{mass}_{\text{beads}}$) limit for both arsenic and lead for beads used on U.S. roadways. While the scientific justification for the 200 ppm limit is not immediately clear, the proposed legislation is regarded as a good-faith attempt to limit the risk associated with the presence of arsenic and lead in the beads.

This research developed a preliminary understanding of the risk associated with the presence of arsenic and lead in glass beads used in pavement marking systems to support decisionmaking. Researchers tested 15 samples of commercially available glass beads in current use on U.S. roadways from State transportation department stockpiles. The mean total concentration observed in the sampled beads across replicates was 71 ppm arsenic and 54 ppm lead. Extractable and bioaccessible arsenic levels in the beads were below instrument detection limits, and extractable and bioaccessible levels of lead in the beads were present at less than 3.6 ppm as a maximum mean value. Based on laboratory-generated characterization data, field investigations, available literature data, and the developed model, reasonably conservative screening levels for arsenic and lead in glass beads were determined to be 220 ppm and 580 ppm, respectively. Lead and arsenic levels observed in glass bead samples provided by State transportation departments were within the determined screening limits, indicating that currently available products pose minimal health risk while meeting retroreflective performance criteria.

17. Key Words Pavement markings, glass beads, health, human health, environment, risk assessment, arsenic, lead, retroreflectivity, extractable, bioaccessible	18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22161.

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 92	22. Price

Form DOT F 1700.7 (8-72) **Reproduction of completed page authorized**

SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
		NOTE: volumes greater than 1000 L shall be shown in m^3		
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact degrees)		
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact degrees)		
°C	Celsius	1.8C+32	Fahrenheit	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AASHTO	American Association of State Highway and Transportation Officials
ACS	American Chemical Society
AGBMA	American Glass Bead Manufacturing Association
ALM	Adult Lead Model
ATSDR	Agency for Toxic Substances and Disease Registry
ATV	All-Terrain Vehicle
BDL	Below the Detection Limit
BQL	Below the Quantitation Limit
CFR	Code of Federal Regulations
CSEM	Conceptual Site Exposure Model
CSL	Cancer Screening Level
DAF	Dilution-Attenuation Factor
DI	Deionized
EPA	Environmental Protection Agency
FDOT	Florida Department of Transportation
FHWA	Federal Highway Association
FP-XRF	Field-Portable XRF
GW SL	Groundwater Screening Level
HI	Hazard Index
HPLC	High Performance Liquid Chromatography
HQ	Hazard Quotient
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
IEUBK	Integrated Exposure Uptake Biokinetic Model
ILCR	Incremental Lifetime Cancer Risk
KOH	Potassium Hydroxide
MAP-21	Moving Ahead for Progress in the 21st Century Act
MDL	Method Detection Limit
NCSL	Non-Carcinogenic Screening Level
NIST	National Institute of Standards and Technology
NJIT/RU	New Jersey Institute of Technology/Rowan University
NRMRL	National Risk Management Research Laboratory
PEF	Particulate Emission Factor
PNNL	Pacific Northwest National Laboratory
PQL	Practical Quantitation Limit
QA/QC	Quality Assurance/Quality Control
RSL	Regional Screening Level
SRM	Standard Reference Material
TAMU	Texas A&M University
TFHRC	Turner-Fairbanks Highway Research Center
TTI	Texas A&M Transportation Institute
UCL95%	95-Percent Upper Confidence Limit
XRF	X-Ray Fluorescence

EXECUTIVE SUMMARY

Retroreflective pavement markings are a critical component of highway safety. Although many types of retroreflective elements can be added to pavement-marking systems, glass beads meeting the American Association of State Highway and Transportation Officials (AASHTO) M247 specification are the industry standard for providing cost effective retroreflectivity performance. Currently, AASHTO M247 glass beads are created from reclaimed glass cullet consisting of recycled glass from industrial and commercial sources. This reclaimed glass cullet feed may contain heavy metals, such as arsenic and lead, which can be passed through to the glass bead products used throughout the transportation industry. Based on the potential risk associated with the presence of arsenic and lead in the beads, MAP-21—the Moving Ahead for Progress in the 21st Century Act (Public Law 112-141) signed into law on July 6, 2012—adopted a 200 part-per-million (ppm = 10^6 x $\text{mass}_{\text{metal}}/\text{mass}_{\text{beads}}$) limit of both arsenic and lead in commercially available beads used on domestic roadways.

This research developed a preliminary understanding of the risk associated with the presence of arsenic and lead in glass beads used in pavement-marking systems to support decisionmaking. To meet the project goal, two aims were established. The first was to characterize arsenic and lead concentrations in commercially available glass beads in current use on U.S. roadways. This aim was achieved by 1) evaluating the total, extractable, and bioaccessible arsenic and lead content in glass bead samples provided by State transportation departments; 2) determining the speciation of arsenic within leachate from beads; and 3) evaluating the relationship between total arsenic content in glass beads and the retroreflective performance of the beads.

The second aim was to perform a screening level risk assessment to assess the impacts of occupational and residential exposure to arsenic and lead within glass beads. This aim was achieved by 1) developing a conceptual site exposure model (CSEM) for occupational and residential exposures to arsenic and lead in glass beads; 2) analyzing arsenic and lead concentrations in mixed glass bead/soil samples taken from a glass bead storage and transfer facility; and 3) estimating the arsenic and lead screening levels resulting in minimum risk from residential and occupational exposures to the beads.

The principal findings of this research are summarized by aim within this executive summary. Details of the methods, results, and outcomes of each aim's research evaluations are provided in the individual sections of this report. The sections include the following:

- Section 1: Characterization of arsenic and lead concentrations with commercially available glass beads in current use on U.S. roadways (Aim 1 Research).
- Section 2: Proposed model for the assessment of human health risks associated with glass beads used for pavement marking (Aim 2 Research).
- Section 3: Model-derived human health screening levels for arsenic and lead in glass beads (Aim 2 Research).

Section 3 of the report concludes with recommended guidance to support decisionmaking and recommendations for safe storage, handling, application, and removal of glass beads used in pavement markings. These recommendations are also presented in this executive summary.

AIM 1: CHARACTERIZATION OF ARSENIC AND LEAD CONCENTRATIONS IN COMMERCIALLY AVAILABLE GLASS BEADS IN CURRENT USE ON U.S. ROADWAYS

Assessment of Arsenic and Lead Content in Commercially Available Glass Beads

Methods

Samples of AASHTO M247 glass beads were requested from State transportation department inventories in current use in pavement-marking operations. These samples of glass beads (see figure 1) were shipped directly to Texas A&M University Transportation Institute (TTI) in quart- to gallon-size resealable plastic bags packaged in boxes. After all the glass beads were received and cataloged, 15 of the received Type I samples were randomly selected for analysis. Subsamples weighing 100 g of each sample were collected into new resealable, zipper bags and renamed by a technician to blind the laboratory staff running the sample extractions and analysis from the identity and location of the provided samples.

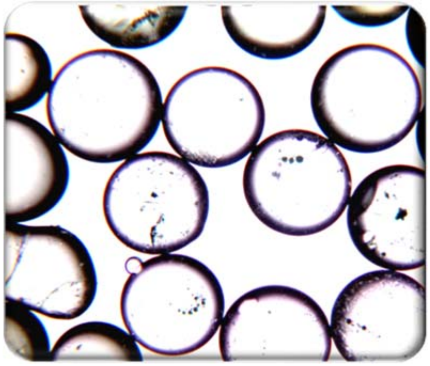


Figure 1. Photo. Magnified light table image of AASHTO M247 Type I bead sample included in this study.

Three subsamples from each of the 15 randomly selected bead samples were used to determine the total, extractable, and bioaccessible fractions of arsenic and lead in the beads. The total metals digestion was performed following the Pacific Northwest National Laboratory (PNNL) Potassium Hydroxide (KOH) Fusion digestion method, extractable metals extraction was performed following Environmental Protection Agency (EPA) Method 3050B, and the bioaccessible extraction was performed according to the in-vitro oral bioaccessibilty method.(1) The resulting digestion and extraction solutions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) according to EPA Method 6020A.

Additional studies were performed to determine the comparability of four methods used to assess total arsenic and lead contents in the glass beads. These four methods were: 1) the PNNL KOH fusion digestion followed by ICP-MS analysis, 2) EPA Method 3052 (microwave assisted hydrofluoric acid digestion) followed by ICP or atomic absorption spectroscopy (AAS) analysis to evaluate metals in siliceous solids, 3) bench-top XRF (X-ray fluorescence), and 4) Field-Portable XRF (FP-XRF).(2, 3) A National Institute of Standards and Technology (NIST) standard for metals in glass, Standard Reference Material (SRM) 612, was also analyzed for total metals using KOH fusion and EPA Method 3052.

Findings

Table 1 provides the mean total, extractable, and bioaccessible arsenic and lead content measured in the 15 samples of glass beads. Lead and arsenic were measured in all 15 samples of glass beads following total digestion of the beads at a mean concentration of 71 and 54 ppm, respectively. The mean arsenic and lead content observed in the beads were below the currently proposed limit of 200 ppm. However, large variability in total arsenic and lead content was observed between replicates of the same bead sample. Repeat analysis of both the replicates and of additional subsamples within the batch reproduced the variability. Analysis of NIST SRM 612, however, resulted in mean measured concentrations of arsenic and lead at 94 percent and 86 percent of the expected value with minimal variability between replicates. Therefore, the observed variability of arsenic and lead in the beads was determined to be caused by actual variability of metals content within the supplied samples.

Table 1. Mean ± standard deviation of arsenic and lead content (ppm) in glass beads provided by State transportation department participants.

	Total (ppm)		Extractable (ppm)		Bioaccessible (ppm)	
Bead	**Arsenic**	**Lead**	**Arsenic**	**Lead**	**Arsenic**	**Lead**
AA	75 ± 27	79 ± 50	BDL	0.38 ± 0.1	BDL	BQL
AC	11 ± 8	22 ± 19	BDL	0.74 ± 0.5	BDL	3.6 ± 5.4
BD	65 ± 36	67 ± 58	BDL	0.21 ± 0.1	BDL	BQL
BE	55 ± 24	89 ± 62	BDL	0.70 ± 0.3	BDL	BQL
BI	53 ± 25	100 ± 71	BDL	3.29 ± 1.0	BDL	1.7 ± 2.4
DA	62 ± 31	176 ± 154	BDL	$0.25 \pm 2 \times 10^{-3}$	BDL	BQL
DB	70 ± 40	161 ± 186	BDL	BDL	BDL	BDL
DC	82 ± 65	199 ± 246	BDL	BQL	BDL	BQL
DD	61 ± 27	3 ± 7	BDL	BDL	BDL	BDL
EA	51 ± 30	13 ± 13	BDL	BDL	BDL	BDL
FH	50 ± 20	72 ± 36	BDL	0.31 ± 0.1	BDL	0.19±0.01
GA	49 ± 34	10 ± 9	BDL	BDL	BDL	BDL
GB	52 ± 22	38 ± 33	BDL	BDL	BDL	BDL
GC	45 ± 15	15 ± 6	BDL	BDL	BDL	BDL
GD	35 ± 37	28 ± 26	BDL	BDL	BDL	BDL

ppm = parts per million
BDL = below detection limit (< 0.07 µg/g for arsenic, < 0.004 µg/g for lead)
BQL = below quantification limit (< 0.1 µg/g for arsenic and lead)

The extractable and bioaccessible arsenic and lead contents were significantly lower than the total arsenic and lead content of the beads. Reportable levels of arsenic were not observed in either the extractable metal or bioaccessible metal extraction solutions in any of the samples. When observed, mean concentrations of 0.8 ppm for extractable lead and 1.8 ppm for bioaccessible lead were measured. However, lead was only present in 7 of the 15 extractable metal solutions and in 3 of the bioaccessible metal solutions. The results of the arsenic and lead analysis indicate that while both metals are present in the glass matrix within the sampled beads (total metal digestions), the levels of arsenic and lead that leave the matrix under environmental (extractable metals by Method 3050B) or intestinal (oral bioaccessibility method) exposures are significantly lower.

The mean arsenic and lead content returned by each of the four evaluated methods across the 15 bead samples are shown in table 2. Although results of the intra-method comparison for analysis of total arsenic and lead in the glass bead samples were not in agreement for the samples, agreement was achieved between the results of KOH fusion and EPA Method 3052 for the NIST SRM 612 standard. While a systematic approach was used to evaluate the cause of the observed difference in the samples but not in the control, method or instrumental errors that could explain the observed difference were not identified. Therefore, because KOH fusion gave the overall most conservative (highest) estimate of arsenic and lead content observed in the beads, the authors report KOH fusion results in this technical report to represent a conservative (upper value) estimate of the total arsenic and lead content in the bead samples.

Table 2. Intra-method comparison for total arsenic and lead in the 15 glass bead samples.

	Arsenic		**Lead**	
Method	**No. of Samples with Measurable Arsenic**	**Mean Content When Present (ppm)**	**No. of Samples with Measurable Arsenic**	**Mean Content When Present (ppm)**
Portable XRF	2 of 15	8.5	3 of 15	15
Bench-top XRF	6 of 15	1.0	10 of 15	15
EPA Method	15 of 15	1.3	15 of 15	8.2
KOH Fusion	15 of 15	51	15 of 15	68

XRF = X-ray fluorescence
EPA = Environmental Protection Agency
KOH = potassium hydroxide

Arsenic Speciation

Speciation of arsenic in water has a significant impact on the toxicity of arsenic in aqueous systems. Because the beads are used and stored in locations where they could come into contact with rainfall, there was interest in determining the resulting speciation of arsenic within bead leachate for future risk assessments.

Methods

Subsamples of three glass bead samples (AA, DC, and EA) were placed in an up-flow cartridge reactor, and laboratory-prepared water (pH of 7) was passed through the cartridges at a flow rate of 30 mL/h. Cartridge effluents were sampled after 1 h, preserved with 1 percent hydrochloric acid, and refrigerated until they were analyzed. Speciation was achieved using a high-performance chromatograph with a reversed phase column operating within a binary mobile phase coupled to an ICP-MS. A complete description of the analytical method for speciation can be found in Section 1 of this report.

Findings

The speciation analysis of arsenic revealed the presence of both arsenite (As^{3+}) and arsenate (As^{5+}) as the two predominant species of arsenic in solution. Table 3 presents the results for the analysis. While total arsenic levels (As^{3+} + As^{5+}) in the pure leachate exceeded the 10 μg/L drinking water maximum contaminant level for arsenic, under environmental conditions, the impact of leachate on existing groundwater or surface water reserves would be minimal for these samples because of dilution.

Table 3. Arsenic speciation in leachate water in contact with beads.

Sample	As^{3+} (μg/L)	As^{5+} (μg/L)
AA	3.02	8.92
DC	ND	14.7
EA	1.42	10.6

ND = Non-detectable

Relationship Between Retroreflectivity and Total Arsenic Content

The relationship between arsenic content and retroreflective performance was evaluated because of historical use of arsenic within glass production as a high-temperature oxidant for removing imperfections in glass. The researchers were curious to evaluate whether higher arsenic levels would correlate to higher retroreflectivity measurements.

Methods

Retroreflective performance measurements were conducted by creating pavement markings containing glass beads on metal sheets. Immediately following paint application, glass beads were applied on the surface using a bead dispenser for even, but random and dispersed, application on the paint. After curing, a Delta LTL-X retroreflectometer was used to measure the retroreflectivity of the pavement-marking samples. Pearson's product moment correlation coefficient (r) was determined to assess the direction and the strength of the correlation between the arsenic content of the beads and their retroreflective performance.

Findings

Figure 2 shows the relationship between retroreflectivity and total mean arsenic content within the glass beads for all 15 samples. The correlation r for the dataset was determined to be 0.564, suggesting a positive moderate correlation may exist between the arsenic content and retroreflective performance. However, additional samples should be analyzed to determine whether a correlation actually exists. In this study, the range of mean arsenic contents was limited to between 15 and 88 ppm. The retroreflectivity data, however, demonstrate that suitable performance can be achieved at low arsenic levels within the beads.

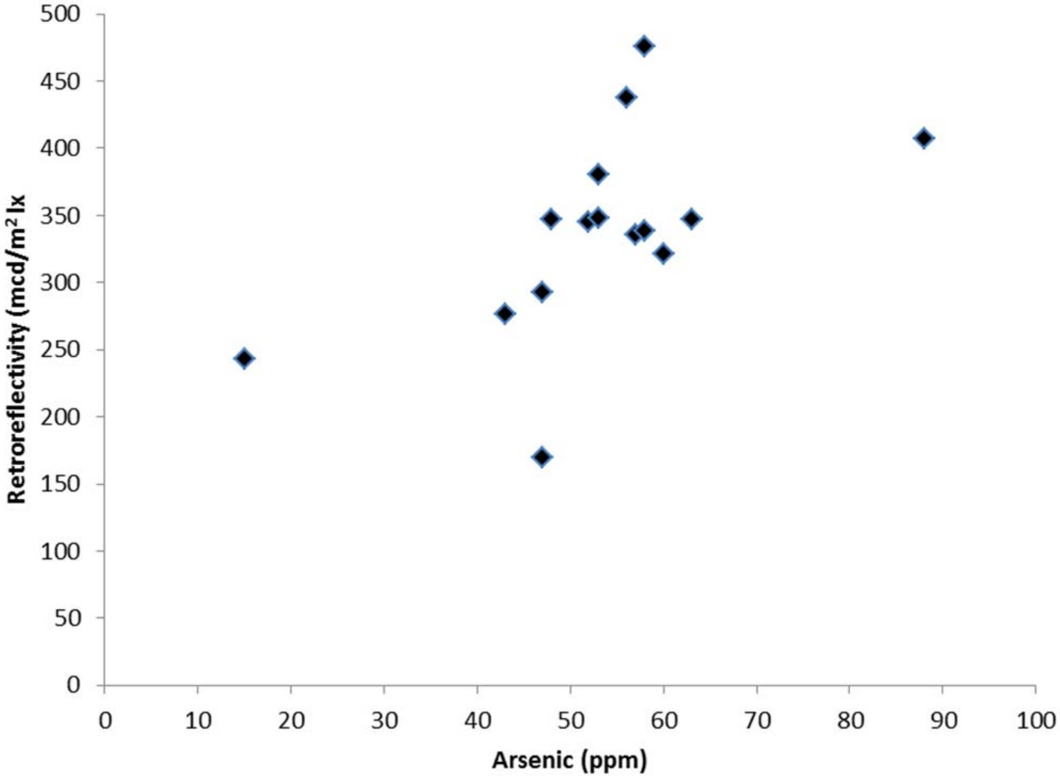


Figure 2. Graph. Relationship between mean arsenic content and mean retroreflectivity of each sample of glass beads evaluated within this research.

AIM 2: SCREENING LEVEL RISK ASSESSMENT TO ASSESS THE IMPACTS OF OCCUPATIONAL AND RESIDENTIAL EXPOSURE TO ARSENIC AND LEAD WITHIN GLASS BEADS

CSEM Development for Arsenic and Lead Glass Bead Occupational and Residential Exposures

The conceptual site exposure model was developed to assess the workflow of beads within their product lifecycle, perform a human health exposure assessment based on bead workflow, develop exposure assessment models to evaluate screening level concentrations in glass beads that are protective of human health, and identify existing sources of data for use within the developed modeling. CSEM development was based on field observation of human interactions with the glass beads during manufacturing, transportation, storage, application, and disposal of old marking residues. All field observations were conducted in an arid environment during warm, dry, and low wind conditions (< 15 mi/h). Although observations were made in an arid environment, this assessment considers a range of environmental conditions. Additional information used in this assessment was obtained through interviews with individuals involved in the glass manufacturing and highway marking industries.

Based on the completed exposure assessment, the proposed risk assessment model focused on three specific exposure scenarios:

- **Scenario 1**—Worker: roadway marking crew employee exposed through incidental ingestion, dermal contact, and inhalation of fugitive dust emissions.
- **Scenario 2**—Adult Resident: resident living in close proximity to an active bead storage yard or on top of a former storage yard exposed through ingestion of contaminated drinking water, incidental ingestion, dermal contact, and inhalation of fugitive dust emissions.
- **Scenario 3**—Child Resident: resident living in close proximity to an active bead storage yard or on top of a former storage yard exposed through ingestion of contaminated drinking water, incidental ingestion, dermal contact, and inhalation of fugitive dust emissions.

The proposed modeling framework focuses on developing quantitative measures to evaluate the screening level concentrations of arsenic and lead in glass beads that result in an increased risk. The quantitative assessment requires calculation of two components: 1) the level of metal uptake or air concentration as a function of each individual exposure route, and 2) the permissible level of exposure (screening level) due to either cancerous or non-cancerous end points considering the combined intake from the multiple routes of exposure affecting a single receptor. All calculations are based on EPA guidance documents addressing human exposure to soil, water, air, and food.(4) The contaminant exposures calculated for each receptor, environmental medium, and pathway combination are the basis for estimating the potential risk or hazard to exposed individuals.

The full list of equations used to determine the intake of metals applicable to every exposure scenario and the calculations used to evaluate the cancer and non-cancerous human health screening levels for direct contact, inhalation, and ingestion of bead-impacted groundwater are found in section 2. The proposed model (presented in section 2) was externally peer-reviewed prior to use of the model to predict screening level concentrations of arsenic and lead found in section 3.

Arsenic and Lead Concentrations in Mixed Glass Bead/Soil Samples Taken From a Glass Bead Storage and Transfer Facility

During the CSEM model development, the mass percentage of beads in soil at a storage facility and the resulting arsenic and lead content within mixed glass bead/soil samples was determined to be an important parameter. Initial assumptions used in the model included the assumption that all of the soil in a bead storage facility was composed of spilled beads with a concentration equivalent to the highest measured arsenic and lead content. To arrive at a more realistic conservative assessment, five samples of soil from a bead storage facility where beads had been stored and transferred for more than 20 years were collected and analyzed for bead mass content. The resulting arsenic and lead concentration in the mixed sample were determined. A control soil sample selected from a nearby vacant lot was used for comparison.

Method

Surface soil samples were collected, weighed, and then sieved on U.S. Sieve #30, #40, #50, and #80. The fraction of soil retained on each sieve was weighed and kept separately. An inclined plane made of a strip of Plexi-Glass® and a light table was used to manually separate glass beads, based on roundness, color, and translucence, from a representative portion of each fraction of soil. The beads separated from each fraction were then weighed. A portion of the original, non-sieved sample was digested following the PNNL KOH method followed by ICP-MS analysis of the digested solutions according to EPA Method 6020A.

Findings

Table 4 lists the average glass bead content in site soil samples collected from a bead storage and transfer facility (along with a nearby vacant field). The difference in the content of glass beads is owing to different sampling locations within the facility. The glass bead soil content varied from 19 percent to a maximum of 78 percent, with an average bead to soil content of 42 percent. Reportable levels of arsenic were observed in only two of the five site samples. However, lead was observed in all samples and in the control at concentrations ranging from 11 ppm to 120 ppm. The concentrations observed in the mixed bead samples are in excess of the background concentration by 33 percent to 400 percent. While it may be reasonable to assume that elevated arsenic and lead content in the storage facility samples are associated with the presence of glass beads, the glass bead content in field site soil sample does not correlate with the metal content in site soil samples. Based on the historical use at this site, the initial assumption that site soils would have higher concentrations of both arsenic and lead does not appear to be valid.

Table 4. Mean glass bead content (by weight) and mean ± standard deviation total arsenic and lead (ppm) in site soil samples.

Sample ID	Glass Bead Content in Soil (Weight Percent)	Total Arsenic (ppm)	Total Lead (ppm)
Sample 1	25	2.9 ± —	120 ± 160
Sample 2	20	BDL	40 ± 19
Sample 3	48	7.6 ± 0.5	35 ± 2.1
Sample 4	41	BDL	14 ± 11
Sample 5	78	BDL	12 ± 5.1
Control	0	BDL	24 ± 12

ppm = parts per million
BDL = below detection limit (< 0.07 µg/g for arsenic, < 0.001 µg/g for lead)
— indicates only one viable data point

Arsenic and Lead Screening Levels Resulting in Minimum Risk From Residential and Occupational Exposures to the Beads

Reasonably conservative screening levels for protection of human health risk from glass bead exposures were determined for each evaluated exposure scenario identified during field investigations of bead workflow. Exposure pathways included in the model were incidental ingestion of beads, incidental inhalation of beads, and ingestion of bead contaminated groundwater. The potential for leaching of arsenic to groundwater was evaluated using laboratory-generated characterization data. Lead and arsenic toxicity data used in the risk evaluation are from the Risk Assessment Information System maintained by the Oak Ridge National Laboratory.

The developed model indicates that while the majority of risk is associated with the ingestion pathway, current concentrations in the beads are within EPA's acceptable risk range of E-6 to E-4. Therefore, there is a low likelihood of adverse human health effects due to exposure to beads released to the environment. Table 5 presents the bead screening levels for arsenic and lead based on the evaluated exposure scenarios for all combined pathways. The presented results assume a source that is 42-percent beads diluted with soil (based on field-analyzed samples at a bead storage facility). Screening levels are generated based on both carcinogenic and non-carcinogenic effects, with the lower value selected as the final screening level. The recommended screening levels were determine to be 220 ppm for arsenic based on the child resident scenario and 580 ppm for lead based on the worker scenario.

Table 5. Screening levels for arsenic and lead from each scenario.

Scenario	Screening Level (ppm) Arsenic	 Lead
Adult Resident		
Carcinogenic	620	NA
Non-cancer	12,000	580
Child Resident		
Carcinogenic	**220**	NA
Non-cancer	1,700	1,050
Worker		
Carcinogenic	1,000	NA
Non-cancer	17,000	**580**

ppm = parts per million
NA = not applicable
Note: Bolded values represent the most conservative screening levels and are the recommended screening levels for arsenic and lead in glass beads.

Guidance to Support Decisionmaking

The determined screening levels for arsenic and lead are above the current maximum content of 200 ppm arsenic and 200 ppm lead adopted in legislation. Therefore, the existing legislation is determined to be protective of human health when all currently available data are considered. In addition, based on laboratory and field sample characterization completed in this study, the mean arsenic and lead concentrations observed in the beads were below the 200 ppm limit currently adopted in legislation. Therefore, the proposed limit should not present a hurdle to using existing beads already in the commercial markets for pavement-marking purposes.

Although current risk levels are minimal, field observations of bead workflow processes did identify easy-to-implement practices that would further reduce exposure. In the occupational setting, employees were observed handling the beads without gloves or masks. Concern was raised during the visits and during the model peer-review process that employees might be exposed to high levels of silica from bead dust that could lead to silicosis. Wearing gloves and respirators to protect against potential silica exposures would have the added benefit of reducing exposure to arsenic and lead.

The model also predicted potential concern regarding the impact of bead storage facilities on residential groundwater due to leaching of arsenic and lead from the beads that may occur within some climates. Current practices of bead storage prevent rainfall from leaching arsenic and lead from stored beads to groundwater. Efforts to reduce bead spillage during transfer would also reduce the likelihood that bead-contaminated media could affect groundwater. Existing locations with long-term histories of bead (and or cullet) storage and transfer may present a challenge to groundwater where shallow groundwater tables are present.

Although application of the beads does result in bead loss to the surrounding environment, long line applications in which bead loss may reach up to 30 percent under poor application practices or conditions does not appear to present a risk to human health or the environment. During long line applications (roadway center and edge line markings), bead loss occurs over a long distance and the beads quickly scatter. Long line application is also performed using bead drop equipment in a manner that does not expose employees to the lost beads. Short line applications (cross walks and intersections), however, do result in greater worker exposure and higher concentrations of spilled beads accessible to the general public. Efforts should be made to reduce excess bead loss during short line applications. Employees putting down beads should wear gloves to reduce exposure, and beads should be dropped so that the majority land on the binder (paint, thermoplastic, or epoxy). In particular, efforts should be made to reduce excess bead loss in short line applications in locations with curbs and gutters because of the potential slipping hazard.

Line removal presents a separate set of potential risks. To minimize exposure to arsenic and lead from glass beads during marking removals, employees should wear gloves, eye protection, and respirators if they are performing removal techniques that generate dust. Grinding, sand-blasting, or water blasting systems used to remove the lines should be equipped with vacuum recovery systems to reduce dust removal. Additional investigations into dust exposures during marking removal are advised.

As a final comment, arsenic and lead in glass beads may be a minor concern for environmental health and safety compared with other components in pavement-marking systems. A thorough review of the risk posed by residential and occupational exposures to components in other marking systems is advised to alleviate potential concerns for environmental and worker safety.

SECTION 1. CHARACTERIZATION OF ARSENIC AND LEAD CONCENTRATIONS WITHIN COMMERCIALLY AVAILABLE GLASS BEADS IN CURRENT USE ON U.S. ROADWAYS

INTRODUCTION

Improving the visibility of pavement markings can significantly contribute to reducing highway mortality owing to lane departures. For pavement markings to be visible to the drivers under limited visibility conditions, they must be retroreflective. Retroreflective pavement markings reflect the incoming light from vehicle headlamps back toward the vehicle. Pavement markings, which would otherwise scatter light from vehicles, are made retroreflective by embedding retroreflective elements in the marking material. Currently, glass beads complying with AASHTO M247 regulations are the industry standard for providing cost effective retroreflective performance.

The most common feed material used in the production of AASHTO M247 glass beads is reclaimed glass cullet. Reclaimed glass cullet commonly consists of glass from residential glassware, such as cathode-ray tubes from televisions, windowpanes, stained glass, incandescent bulbs, and other industrial and commercial sources. This reclaimed glass cullet feed may contain heavy metals, such as lead and arsenic, that can be passed through to the final recycled glass bead products used throughout the transportation industry. Arsenic and lead are naturally occurring metals present in mineral-based materials used to make glass and were also added to glass to achieve specific industrial purposes such as improved clarity or performance.

Two existing studies have previously reported on the composition and leachability of heavy metals found in glass beads. The New Jersey Department of Transportation/Federal Highway Association (FHWA) sponsored leaching study carried out by New Jersey Institute of Technology/Rowan University (NJIT/RU) and the American Glass Bead Manufacturing Association (AGBMA) funded study carried out at Texas A&M University (TAMU)/TTI each examined heavy metal contents present in glass beads.(5, 6) Both studies confirmed the presence of heavy metals within glass bead samples and quantified the total metal content and leached amount of metal by conducting leaching studies. While the two previous studies report the composition and leachability of heavy metals in glass beads, the representativeness of the sample sets examined within each study in comparison with the metals content of samples actually in use within commerce was unknown. Therefore, this research aimed to determine the arsenic and lead composition of beads currently in use on roadways with the United States.

The confirmed presence of metals in glass beads has raised concern regarding the potential risk of heavy metals in glass beads on human health and the environment. Particular concern focuses on the occupational safety of workers who are subject to exposure to glass beads during manufacturing, transport, and application of glass beads to pavement markings. Based on the potential risk associated with the presence of arsenic and lead in the beads, MAP-21: the Moving Ahead for Progress in the 21st Century Act (Public Law 112-141) signed into law on July 6, 2012, adopted 200 ppm arsenic and 200 ppm lead as the maximum permissible levels allowable in glass bead formulations used within the industry. Additional legislation is also proposed within several states to limit maximum amounts of arsenic and lead in glass beads.

This study was conceived and carried out to begin a formalized, but preliminary, assessment of risk associated with occupational and residential exposures to arsenic and lead in glass beads used to provide retroreflectivity to pavement markings. This goal of this research component was to characterize arsenic and lead concentrations of commercially available glass beads in current use on U.S. roadways. To meet the goal, four objectives were explored:

- **Objective 1—**Evaluate the total, extractable, and bioaccessible arsenic and lead content in glass bead samples provided by State transportation departments.
- **Objective 2—**Evaluate the relationship between total arsenic content in glass beads and the retroreflective performance of the beads.
- **Objective 3—**Determine the speciation of arsenic within leachate from beads.
- **Objective 4—**Analyze arsenic and lead concentrations of mixed glass bead/soil samples taken from a glass bead storage and transfer facility.

The team conducting the research consisted of Bryan Boulanger, formerly of TAMU's Department of Civil Engineering, and Paul Carlson from TTI. Dr. Boulanger was the lead for Objectives 1, 3, and 4, and served as the overall project coordinator and point of contact. Dr. Carlson was the lead for Objective 2. Project formulation also included contributions from Dr. Tolyamat from the EPA's National Risk Management Research Laboratory (NRMRL), Dr. Taylor from EPA's Office of Solid Waste, and Mr. Andersen of FHWA's Turner-Fairbank Highway Research Center (TFHRC). This research was carried out in Dr. Boulanger's laboratories at TAMU and in Dr. Carlson's laboratories at TTI. An intra-method comparison for total metals analysis among TAMU, EPA, and FHWA research laboratories was also conducted as part of Objective 1. The three laboratories involved included Dr. Boulanger's laboratories at TAMU, Dr. Tolyamat's Laboratories at NRMRL's Center Hill Facility, and Mr. Arnold's Laboratories at FHWA's TFHRC. The research covered in this report was conducted between April 1, 2010, and June 30, 2012.

EXPERIMENTAL METHODS

Sampling

A total of 15 samples of AASHTO M247 Type I beads acquired from State transportation departments were evaluated as part of this study. The sample size used in this study was calculated at the 95 percent confidence interval based on the sample size determination formula provided in figure 3, where n is the sample size, σ is the underlying standard deviation of metals concentrations in the beads based on past analysis, and B is the specified error of estimation.

$$n = \left[\frac{1.96\sigma}{B}\right]^2$$

Figure 3. Equation. Formula for determining sample size.

The underlying standard deviation of metals concentrations for this estimation was taken from previous analysis of arsenic content in glass beads during the TAMU/TTI AGBMA funded study. The mean ± standard deviation arsenic contents from Batch 1 and Batch 3 beads in this previous study were 83.3 ± 1.42 ppm and 393 ± 6.93 ppm, respectively. Based on an allowable margin of error of 1 percent, the corresponding sample sizes were determined to be 11.2 and 12, respectively. A final selected sample size of 15 satisfied the statistical criteria based on 95 percent confidence interval and 1 percent allowable error.

Based on the final selected sample size, Dr. Carlson made the request for samples from his contacts within State transportation departments. All samples from the transportation departments were shipped directly to Dr. Carlson in quart- to gallon-size resealable zipper bags packaged in boxes. Each of the samples received were cataloged upon receipt. Once all the samples had arrived, a team member collected the samples, took out 100 g subsamples of each bulk supplied material, and renamed the samples to blind the laboratory staff running the sample extractions and analysis from the identity and location of origin of the provided samples.

Three subsamples from each of the 15 bead samples were used to determine the total, extractable, and bioaccessible contents of arsenic and lead in the beads. KOH fusion digestion was carried out to assess the total arsenic and lead content, EPA Method 3050B was carried out to assess the extractable arsenic and lead content, and the in-vitro oral bioaccessibility method was used to assess the bioaccessible arsenic and lead content in the beads. The resulting solutions from each of these methods were analyzed by ICP-MS. Because the ICP-MS analytical method is common throughout, it is detailed first below, followed by the three processing methods.

Reagents and Standards

Deionized (DI) water was produced in the laboratory using a Barnstead Nanopure™ DI water system. DI water was used for preparing reagents, generating standards, and conducting experiments. Specpure® analytical standards for arsenic and lead were purchased from Alfa Aesar. Nitric acid (American Chemical Society (ACS) grade), hydrochloric acid (ACS grade), potassium nitrate (ACS grade), potassium hydroxide (ACS grade), and sodium hydroxide (ACS grade) were purchased through Fisher Scientific. Oxalic acid (ACS grade) was purchased from VWR International. Glycine (98.5–101.5 percent) and hydrogen peroxide (ACS grade, high purity) were purchased from JT Baker. SRM 612—Trace Elements in a Glass Matrix, was purchased from NIST.

ICP-MS Analysis

Analysis was carried out as described in EPA Method 6020A: ICP-MS. An ELAN® DRC II ICP-MS system housed within TAMU's Center for Chemical Characterization was used to quantify the concentration of arsenic and lead in solutions produced from the total metal, extractable metal, and orally bioaccessible metal extractions. All samples were preserved in 1 percent (volume/volume) nitric acid and kept at 4 °C while in storage. Samples were allowed to come to room temperature before analysis.

The Method Detection Limit (MDL) for each of the eight heavy metals using ICP-MS was determined according to 40 Code of Federal Regulations (CFR) Appendix B to Part 136, “Definition and Procedure for the Determination of the Method Detection Limit.” The MDL is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. The practical quantitation limit (PQL) was then set based on the greater of the MDL or the lowest analyzed calibration standard. A four-point calibration was used to quantitate analytes in a range from 1 to 100 μg/L. Samples in which the analytes were present at concentrations above the highest calibration standard were diluted to within the calibration range and reanalyzed.

Method for Determining Total Arsenic and Lead in Glass Bead Samples

The KOH fusion process (procedure number APSL-03) developed by the PNNL was used to dissolve a portion of the subsampled beads for total bulk bead metals content analysis.(2) In this procedure, recycled glass beads from each batch were crushed using a porcelain mortar and pestle and passed through a #140 U.S. mesh sieve (< 100 μm). Researchers weighed 0.25 ± 0.075 g of the crushed beads and transferred them into a 7 mL carbon crucible. Approximately 1.8 ± 0.4 g of potassium hydroxide and 0.2 ± 0.1 g of potassium nitrate were added to the crushed beads, and the contents were mixed by swirling. The crucible and its contents were heated using a Bunsen burner until the mixture melted and all visible effervescence subsided. Allowing all the effervescence to subside was a minor modification to the original method that allowed for reproduction of the arsenic and lead concentrations in the SRM.(2) The digestate was then allowed to cool to room temperature.

Approximately 5 mL of DI water was added to dissolve the cake-like crystalline melt, and the resulting solution was transferred to a 1,000 mL volumetric flask. Additional 5-mL aliquots of DI water were repeatedly added to the crucible until all of the melt was dissolved. The solution in the flask was diluted to approximately 500 mL total volume using DI water and acidified using 25 ± 5 mL of concentrated nitric acid to dissolve any precipitate. Researchers added 0.3 ± 0.1 g of oxalic acid crystals to dissolve any additional observed precipitate that was not dissolved with the nitric acid addition. The flask contents were then filled to 1,000 mL mark with DI water. A 15-mL aliquot of the sample was extracted from the flask, labeled appropriately, and stored at 4 °C until ICP-MS analysis.

The total metals content of glass beads was calculated from the measured concentrations using the formula in figure 4:

$$\text{Total Metal}\left(\frac{\mu g_{\text{metal}}}{g_{\text{bead}}}\right)=\frac{C\times\forall}{M}$$

Figure 4. Equation. Formula to calculate total metals content.

Where:
C = concentration of metal in fusion solution, μg/L.
∀ = volume of solvent, L.
M = mass of beads, g.

Method for Determining Extractable Arsenic and Lead in Glass Bead Samples

The extractable metals content of the glass beads was analyzed by EPA method 3050B.(7) High purity ACS grade nitric acid and high purity ACS grade hydrogen peroxide were used for this test. Refluxing columns were used as vapor recovery devices, and a water bath capable of heating up to 100 °C was used as the heat source. ICP-MS was used for analysis of samples. Researchers measured 1.0 ±0.01 g of each glass bead sample and placed them in a circular flask/digestion vessel into which a 1:1 (volume:volume) mix of nitric acid was added. The sample was heated to 95 °C in a water bath and then refluxed for 15 min.

After cooling, an additional 5 mL of concentrated nitric acid was added, and the sample was heated to 95 °C in the water bath and refluxed for 30 min. Because fumes were not observed, additional nitric acid addition and refluxing was not performed, and the sample was heated for 2 h without boiling at 95 °C and then cooled. Researchers added 2 mL of DI water and 3 mL of 30-percent hydrogen peroxide solution to the flask, and this was heated to 95 °C until effervescence was minimal. Upon cooling, the 30-percent hydrogen peroxide solution was added in 1-mL aliquots, and the above procedure repeated until effervescence was not observed. No more than 10 mL of hydrogen peroxide solution was added to the samples. The sample was heated at 95 °C without boiling for 2 h. The sample was then cooled and filtered using Whatman filter paper no. 41 and diluted to 100 mL. A 15-mL aliquot of the sample was extracted, labeled appropriately, and stored at 4 °C until analysis was conducted by ICP-MS.

The extractable metals content of glass beads was calculated from the measured concentrations using the formula in figure 5:

$$\text{Extractable Metal}\left(\frac{\mu g_{\text{metal}}}{g_{\text{bead}}}\right)=\frac{C\times\forall}{M}$$

Figure 5. Equation. Formula to calculate extractable metals content of glass beads.

Where:
C = concentration of metal in extraction solution, μg/L.
$\forall$ = volume of solvent, L.
M = mass of beads, g.

Method for Determining Bioaccessible Arsenic and Lead in Glass Bead Samples

The in-vitro oral bioaccessibility method developed by Kelly et al. was used to determine the bioaccessibility of arsenic and lead in the glass bead samples.(1) This method was found to directly correlate results from in-vivo bioavailability testing protocols for heavy metals. The Kelley et al. method was selected for use in evaluation of the accessibility of metals for biouptake because the in-vitro test is faster and eliminates in-vivo testing.

The in-vitro oral bioaccessibility method was run in a 0.4 M glycine solution with a pH adjusted to 1.5 ± 0.05 with hydrochloric acid. Researchers weighed 0.1 g of each bead and placed them in a high-density polyethylene bottle containing 100 mL of the pH-adjusted glycine solution. The reactors were tied using zip-ties to rotators (Barnstead Thermolyne LABQUAKE®) and placed in an environmentally controlled, orbital shaker chamber (LabLine Orbit Environ-Shaker, Model # 3948, Lab-Line Instruments Inc., Melrose Park, IL). The rotators were operated at their maximum rotation speed of 8 rpm (which was a modification of the original 30 rpm used in the Kelly et al. method), and the chamber temperature was maintained at 37 ± 5 °C for an hour. After 1 h, the rotators were turned off, and the samples were allowed to settle for 5 min. A 15-mL aliquot of the solid free supernatant was extracted from each bottle, labeled appropriately, and stored at 4 °C before ICP-MS analysis.

The oral bioaccessible content of arsenic and lead in the glass bead samples was calculated from the measured concentrations using the formula in figure 6:

$$\text{Bioaccessible Metal}\left(\frac{\mu g_{\text{metal}}}{g_{\text{bead}}}\right)=\frac{C\times\forall}{M}$$

Figure 6. Equation. Formula to calculate the oral bioaccessible content of arsenic and lead in glass bead samples.

Where:
C = concentration of metal in glycine solution, μg/L.
$\forall$ = volume of solvent, L.
M = mass of beads, g.

Method Comparison for Analysis of Total Arsenic and Lead Analysis in Glass Beads

Four methods were compared for their ability to evaluate arsenic and lead contents in glass beads used in pavement markings: 1) the KOH fusion method followed by ICP-MS, 2) EPA Method 3052 (microwave assisted hydrofluoric acid digestion) followed by ICP or AAS performed at EPA to evaluate metals in siliceous solids, 3) bench-top XRF performed at FHWA, and 4) FP-XRF performed at Florida Department of Transportation (FDOT). Subsamples from glass beads (with the exception of sample AA) received at TAMU were sent to each agency for testing. SRM 612 was also analyzed for total arsenic and lead by EPA and TAMU.(2, 3)

Retroreflectivity Measurements

The retroreflective performance measurements were conducted by creating pavement marking samples containing glass beads on metal sheets. The metal sheets were painted using a shoe to put down the paint. The shoe was dragged along the metal sheet to spread the paint with a uniform thickness of 15 mils over the entire length of each pavement marking sample.

Immediately following application of the paint, glass beads were applied on the surface using a bead dispenser for even, but random and dispersed, application on the paint. Three replicate markings were used to assess the retroreflectivity of each glass bead sample. After curing, the markings for 24 h, a Delta LTL-X retroreflectometer was used to measure the retroreflectivity of the pavement-marking samples in units of millicandela per square meter per lux (mcd/m^2 lx). The retroreflectivity was measured in two directions: in the direction of the paint application and the opposite direction. The retroreflectometer was used to take five independent measurements from each direction, which were summed to determine the final retroreflectivity value for each sample.

Arsenic Speciation Determination

Researchers placed 80-g subsamples of glass bead samples AA, DC, and EA in an up-flow cartridge reactor. The cartridges, previously described by Boulanger, were 25 mm in diameter and 265 mm in length.(5) pH-adjusted DI water at a pH of 7 was passed through the cartridges at a flow rate of 30 mL/h. Researchers sampled 10 mL subsamples of the cartridge effluents after 1 h. Samples were preserved with 1 percent hydrochloric acid and refrigerated at 4 °C until they were placed in a cooler and shipped to EPA's NRMRL overnight. Received samples were transferred to a refrigerator at EPA prior to analysis using a coupled high-performance chromatography (HPLC) ICP-MS system. All samples were analyzed within 2 weeks of their receipt.

Arsenic speciation was completed in the EPA's NRMRL under the guidance of Dr. Mallik Nadagouda. An Agilent 1100 series high-performance chromatograph was used to chromatographically resolve arsenic species on a ZORBAX Eclipse® XDB-C18 (5 mm by 4.6 mm (inside diameter) by 250 mm) column using a binary eluent system. The binary mobile phase consisted of DI water with either 5 mM tetrabutylammonium hydroxide (eluent A) or 2.5 mM ammonium phosphate (eluent B) that is adjusted to a pH of 6.0. pH adjustment was accomplished for eluent A using phosphoric acid and eluent B using ammonium hydroxide. A 100 μL injection introduced the sample to the front of the column, and a linear elution gradient with a flow rate of 1 mL/min was used. The linear gradient program used included 0 percent B from 0 to 1.5 min, ramped to 50 percent B at 4 min, held at 50 percent until 6 min, ramped to 100 percent B at 8 min, and returned to 0 percent B at 12 min.

The HPLC's effluent was sent to an Agilent 7500cc ICP-MS using 0.25 mm inner diameter polyetheretherketone tubing. The ICP-MS was operated in standard resolution mode for arsenic (m/z 75). Eluent flow was introduced into the ICP-MS through a micro-concentric nebulizer cell. Full operation parameters of the ICP-MS used in this method can be found in the Almassalkhi reference.(8) A seven-point external calibration curve ranging from 1 to 150 μg/L (As^{3+}/As^{5+}) was used to quantify the analytes.

Estimation of Glass Bead Mass in Site Soil Samples

Approximately 50 g of each site soil sample was subsampled and weighed. A particle size distribution using a series of U.S. Sieve #30, #40, #50, and #80 was performed, and the fraction of soil retained on each sieve was weighed and kept separately. An inclined plane made of a strip of Plexi-Glass® and a light table was used to manually separate glass beads, based on roundness, color, and translucence, from a representative portion of each fraction of soil. The glass beads from each fraction were weighed and collected. The total glass bead mass in 50 g of soil sample was calculated using the equation in figure 7.

$$\text{Total Glass Beads} = \sum (\text{Glass beads in representative portion}) \cdot \frac{\text{Weight of fraction of soil}}{\text{Weight of representative portion}}$$

Figure 7. Equation. Formula to calculate total mass of glass beads in a representative sample.

The glass bead content in the site soil samples were calculated using the equation in figure 8:

$$\%\ \text{Glass beads (by weight)} = \frac{\text{Weight of total glass beads}}{\text{Weight of soil sample } (\sim 50\text{ g})}$$

Figure 8. Equation. Formula to calculate the percentage of glass beads within a site soil sample.

Analysis of Total Metals in Respirable Fraction of Soil Samples

The respirable fraction (< 10 μm size) of soil samples and blank samples was obtained by modifying the wet sieving process, which is a common procedure to extract dust from soil samples.(9, 10, 11) Approximately 50 g of site soil sample was wet sieved using a U.S. Sieve #10, #50, #230, and #800 using DI water. Water and soil particles passing through U.S. Sieve #800 were collected and stored in a glass beaker. Water from each sample was allowed to evaporate, leaving behind flakes of soil particles. The soil was scraped out with a spatula and stored in polypropylene tubes, and analyzed for total arsenic using KOH fusion digestion and ICP-MS analysis.

Quality Assurance/Quality Control (QA/QC)

QA/QC efforts focused on several areas, including prevention of cross contamination, ensuring a representative subsampling from the initially provided samples, experimental controls and replicates, and QA/QC related to instrumental analysis. Cross contamination prevention included controls on sample handling that involved marking the subsamples. Any materials coming into contact with the glass beads during the experiment were also pre-screened for the likelihood of cross contaminating the glass beads. The DI water used in all laboratory experiments, the 1 percent nitric acid solution used for diluting samples, and the glycine solution used in the bioaccessible extraction were also evaluated for their background arsenic and lead content.

Experiments were carried out in triplicate to produce data between environmental factors that could be compared using statistical approaches. For every extraction procedure, a method blank, which consisted of analysis without using any sample, was generated. DI blanks and method blanks were also generated for all experimental procedures. The total content of arsenic and lead in the SRM 612 (glass wafer) was determined using the KOH fusion process.

Instrumental QA/QC followed the guidelines outlined in EPA Method 6060A, and the MDL was determined as described in 40 CFR Appendix B to Part 136. Interferences were not observed for arsenic and lead, and the instrument limit of detection and resulting MDLs were able to observe quantifiable concentrations of these two components within the experimentally derived samples.

RESULTS AND DISCUSSION

QA/QC

Table 6 reports the MDL in terms of the mass of metal per mass of glass bead (ppm) for the analysis of total, extractable, and bioaccessible metals in glass beads. Because the MDLs were lower than the lowest calibration standard (1 μg/L), the lowest calibration standard became the PQL. Analytes with a concentration between the PQL and the MDL are reported as below the quantitation limit (BQL). Analytes detected in the sample that were below the MDL but still had a measured value are reported as below the detection limit (BDL). Analytes with a no observable measured response are reported as non-detectable. Interferences were not observed for arsenic and lead within the experimentally derived samples.

For the total metal extraction, 0.25 g of glass beads was used in the KOH fusion method, and the final samples of extract were made up in 1 L of solution. For the extractable and bioaccessible extractions, 1 g of glass beads was used, and the final extract volume was 100 mL. Therefore, the MDLs for arsenic and lead in the glass beads for the extractable metal and bioaccessible metal extractions are different than the total metal extractions.

Table 6. MDL and PQL for arsenic and lead for total, extractable and bioaccessible metals.

Metal	Limit	Total (ppm)	Extractable (ppm)	Bioaccessible (ppm)
Arsenic	MDL	3	0.07	0.07
	PQL	4	0.1	0.1
Lead	MDL	0.16	0.004	0.004
	PQL	4	0.1	0.1

ppm = parts per million
MDL = method detection limit
PQL = practical quantitation limit

Total Arsenic and Lead

The total arsenic and lead contents in the glass beads measured using the KOH fusion method are presented in table 7 and figure 9. Arsenic content in all the glass beads examined was less than 100 ppm, while lead content was less than 200 ppm. NIST reports a nominal arsenic content of 50 ppm and a certified lead content of 38.57 ± 0.2 ppm in the SRM 612 wafers. The arsenic and lead content obtained by the KOH fusion method for the SRM are shown in table 8. The results for total metal analysis in glass beads show large standard deviations for both arsenic and lead, indicating a high degree of variability within the replicates of each bead sample. However, less than 6-percent variability was observed between three SRM replicates for both arsenic and lead over six analyses of the material.

Because all QA/QC checks were met with the instrument, and acceptable results were obtained for the SRM, variability associated with instrument and methodology was ruled out. The variability in glass beads could be associated with varying sources of glass and varying amounts of heavy metals in the recycled glass and glass cullet used for manufacturing glass beads. The inconsistency of the reclaimed product used to make the glass beads could result in a very high concentration of heavy metals in some glass beads. This variability in different samples and subsamples of glass beads used in pavement markings has also been observed in a previous study by NJIT/RU and TTI.(5, 6) In the future, extraction methods may need to be modified to process a larger subsample to reduce the chance of selecting a high metal content glass bead randomly.

Table 7. Total arsenic and lead content (ppm) in glass beads provided by State transportation department participants.

Bead	Arsenic (ppm)	Lead (ppm)
AA	75 ± 27	79 ± 50
AC	11 ± 8	22 ± 19
BD	65 ± 36	67 ± 58
BE	55 ± 24	89 ± 62
BI	53 ± 25	100 ± 71
DA	62 ± 31	176 ± 154
DB	70 ± 40	161 ± 186
DC	82 ± 65	199 ± 246
DD	61 ± 27	3 ± 7
EA	51 ± 30	13 ± 13
FH	50 ± 20	72 ± 36
GA	49 ± 34	10 ± 9
GB	52 ± 22	38 ± 33
GC	45 ± 15	15 ± 6
GD	35 ± 37	28 ± 26

ppm = parts per million

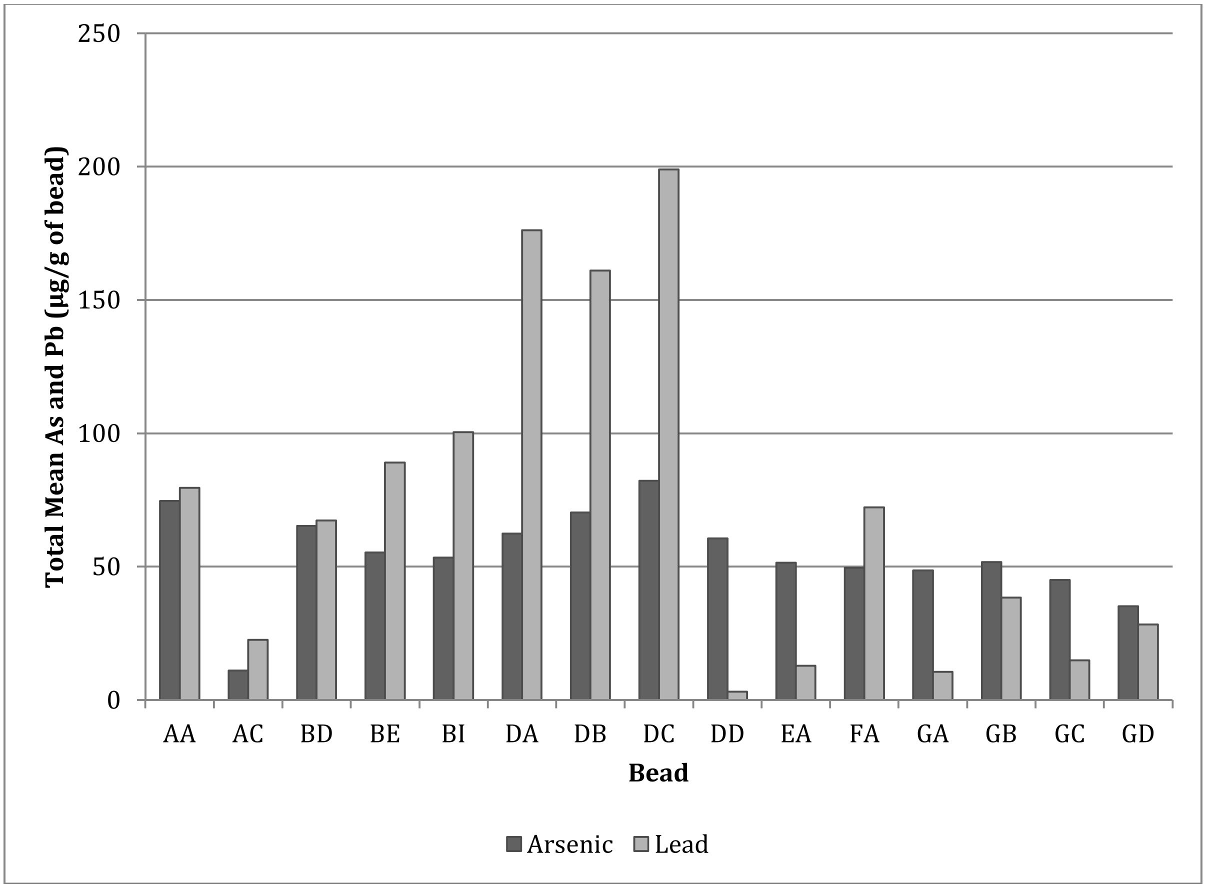


Figure 9. Graph. Total mean arsenic and lead (ppm) content in the glass beads supplied by the State transportation department participants.

Table 8. Total arsenic and lead content (ppm) in SRM.

	Arsenic (ppm)		**Lead (ppm)**	
	Measured	**Expected**	**Measured**	**Expected**
SRM 612	47 ± 5	50[a]	33 ± 6	38.57 ± 0.2[b]

ppm = parts per million
[a] Nominal arsenic concentration in glass matrix
[b] Certified lead concentration in glass matrix

Extractable Arsenic and Lead

The extractable arsenic and lead in the glass beads measured using EPA method 3050B is presented in table 9. The concentrations of arsenic were below the MDL (0.07 ppm) for all the glass beads. For lead, one sample was measured between the MDL (0.004 ppm) and PQL (0.1 ppm) and was reported as BQL. Using the PQL as a lower limit of calibration, lead was observed within the extractable metals extracts in 7 of the 15 samples at reportable concentrations. When observed, the levels of lead ranged from 0.21 ± 0.002 to 3.29 ± 1.00 µg extractable lead per gram of bead. Therefore, when present, lead within the extractable metals extracts was up to 2.5 percent of the total observed lead in the beads.

Table 9. Extractable and bioaccessible arsenic and lead content (ppm) in glass beads provided by State transportation participants.

Bead	Extractable (ppm)		Bioaccessible (ppm)	
	Arsenic	Lead	Arsenic	Lead
AA	BDL	0.38 ± 0.1	BDL	BQL
AC	BDL	0.74 ± 0.5	BDL	3.6 ± 5.4
BD	BDL	0.21 ± 0.1	BDL	BQL
BE	BDL	0.70 ± 0.3	BDL	BQL
BI	BDL	3.29 ± 1.0	BDL	1.7 ± 2.4
DA	BDL	$0.25 \pm 2\times10^{-3}$	BDL	BQL
DB	BDL	BDL	BDL	BDL
DC	BDL	BQL	BDL	BQL
DD	BDL	BDL	BDL	BDL
EA	BDL	BDL	BDL	BDL
FH	BDL	0.31 ± 0.1	BDL	0.19±0.01
GA	BDL	BDL	BDL	BDL
GB	BDL	BDL	BDL	BDL
GC	BDL	BDL	BDL	BDL
GD	BDL	BDL	BDL	BDL

ppm = parts per million
BQL = below quantification limits (<0.1 µg/g for arsenic and lead)
BDL = below detection limits (< 0.07 µg/g for arsenic, < 0.004 µg/g for lead)

Bioaccessible Arsenic and Lead

The bioaccessible arsenic and lead content in the glass beads measured is also presented in table 9. Bioaccessible arsenic concentrations were not in the reportable range for all the glass beads because the observed value was below the MDL (0.07 ppm). For lead, several of the measured values fell between the MDL (0.004 ppm) and PQL (0.1 ppm). Using the PQL as a lower limit, lead in the bioaccessible extracts was less than 0.7 percent of the lowest observed total lead concentration.

Comparison of Total Metal Content in Glass Beads Evaluated from Different Methods

The intra-method comparison for the analysis of total arsenic and lead in the glass beads included the following methods: 1) KOH fusion digestion followed by ICP-MS analysis, 2) EPA Method 3052 (microwave assisted hydrofluoric acid digestion) followed by ICP or AAS analysis to evaluate metals in siliceous solids, 3) bench-top XRF, and 4) FP-XRF. NIST SRM 612 was also analyzed for total arsenic and lead using KOH fusion and EPA Method 3052.(2, 3) KOH fusion digestions and ICP-MS analysis were completed at TAMU, EPA Method 3052 and ICP or AAS analysis was completed at the EPA's NRMRL, bench-top analysis XRF was completed on a Panalytical system at FHWA’s TFHRC, and portable XRF analysis was completed within FDOT’s laboratories.

Table 10 and table 11 provide a summary of the mean total arsenic and lead content (respectively) for each of the analyzed samples using the four methods. Results of the intra-method comparison were not in agreement for the samples, although agreement was achieved between the KOH fusion method and EPA Method 3052 for the NIST SRM 612 standard. One possible explanation for the observed difference was a difference in glass bead preparation specified within the methods. KOH fusion digestion required that all glass beads and SRM samples be crushed and sieved prior to analysis. The EPA Method 3052 digestions included whole beads that were not crushed or sieved; however, because the SRM was received as a disk, crushing the SRM was required before digestion. The portable XRF samples were not altered, but the bench-top XRF samples were fused prior to analysis. Because the methods did not agree, but did meet their respective QA/QC specifications, additional work was carried out to determine the cause of the difference between KOH fusion (an alkaline digestion) and EPA Method 3052 (an acidic digestion). However, crushing the beads did not result in a substantial change in measured arsenic or lead content when digested according to EPA Method 3052.

Sieving the crushed beads was ruled out as a source of error (due to potential metal contamination from the sieve or due to size selectivity of crushed glass beads). However, processing the SRM samples by crushing and sieving them prior to KOH fusion digestion did not indicate an issue because the SRM recovery was acceptable. Further analysis of beads and SRM to evaluate the effects of crushing and sieving did not result in any explanation of the difference in measured concentrations between the two methods when the methods were followed as described. (However, running KOH fusion on whole beads greatly reduced both arsenic and lead content measured in the samples.)

Table 10. Comparison of arsenic content (ppm) in glass beads from intra-method evaluation.

Sample ID	Total Arsenic Content (ppm)			
	Portable XRF	**EPA 3052**	**KOH Fusion**	**Bench-top XRF**
AC	ND	0.9	15	1.2
BD	ND	5.5	48	1.6
BE	ND	1.1	56	ND
BI	ND	1.0	60	ND
DA	7	1.0	47	ND
DB	ND	0.9	57	0.7
DC	ND	1.3	68	ND
DD	10	0.5	47	1.1
EA	ND	1.3	43	ND
FH	ND	2.6	58	1.0
GA	ND	0.3	53	ND
GB	ND	0.4	58	0.4
GC	ND	1.2	52	ND
GD	ND	0.5	53	ND
SRM	—	43	48	—

ppm = parts per million
XRF = X-ray fluorescence
EPA = Environmental Protection Agency
KOH = potassium hydroxide
ND = not detected
— indicates not analyzed

Table 11. Comparison of lead content (ppm) in glass beads from intra-method evaluation.

Sample ID	Total Lead Content (ppm) Portable XRF	EPA 3052	KOH Fusion	Bench-top XRF
AC	ND	4.1	30	12
BD	19	6.0	84	15
BE	ND	10	120	11
BI	15	8.6	130	22
DA	ND	2.2	230	ND
DB	ND	2.4	93	19
DC	ND	2.2	100	ND
DD	ND	3.8	4.2	9.2
EA	ND	2.7	17	ND
FH	12	5.6	55	18
GA	ND	33	14	ND
GB	ND	7.1	45	14
GC	ND	23	17	14
GD	ND	3.2	16	ND
SRM	—	42	36	—

ppm = parts per million
XRF = X-ray fluorescence
EPA = Environmental Protection Agency
KOH = potassium hydroxide
ND = not detected
— indicates not analyzed

Instrumental errors were also ruled out by analyzing extracts on more than one analytical platform. The cross-over analysis between platforms (which was also conducted in different laboratories) reproduced the extract concentrations for the digestions. Therefore, after ruling out sources of method and instrumental error, the observed difference is considered to be caused by either intra-replicate variability of arsenic and lead in the glass beads or a matrix interference/ enhancement present in the glass beads but absent in the SRM.

Despite using a systematic approach to evaluate the cause of the differences in total metals content measured using the four methods, no method or instrument errors arose that explained the observed difference. Overall, KOH fusion provided the result closest to the nominal arsenic and certified lead content of the SRM for glass. In addition, several literature reports indicated better digestion of metals from glass through alkali fusion methods compared with acid digestion.(12, 13) However, the metals considered in these studies were trace metals such as rhenium, zirconium, hafnium, thallium, and uranium. Finally, because KOH fusion gave the overall most conservative (highest) estimate of arsenic and lead content observed in the beads while meeting QA/QC limits, the authors felt most comfortable performing subsequent digestions using this method.

Relationship Between Total Arsenic Content in Glass Beads and the Retroreflective Performance of the Beads

The relationship between arsenic and retroreflective performance was evaluated because of the historical use of arsenic within glass production as a high temperature oxidant to remove imperfections in glass. The researchers were curious to evaluate whether higher arsenic levels would also correlate to higher retroreflectivity measurements, which would have implications for the performance of the beads placed on the roadway surface. The retroreflective performance of the bead samples was determined by creating pavement-marking samples on metal slabs and measuring the resulting marking retroreflectivity using a retroreflectometer. The Pearson's product moment correlation coefficient was determined and used to assess the direction and the strength of the correlation between the arsenic content of the beads and their retroreflective performance.

The total arsenic levels found through KOH fusion digestion followed by ICP-MS analysis were used to assess the relationship between arsenic content and the measured retroreflectivity of the beads applied within a pavement marking. Table 12 and figure 10 show the relationship between retroreflectivity and total mean arsenic content within the glass beads for all 15 samples.

Table 12. Mean ± standard deviation retroreflectivity and total arsenic content for each bead sample evaluated in this research.

Sample ID	Retroreflectivity (mcd/m$^{2}\cdot$lx)	Arsenic (ppm)
AA	347 ± 10	63 ± 18
AC	243 ± 8.7	15 ± 2.6
BD	347 ± 36	48 ± 13
BE	438 ± 52	56 ± 29
BI	321 ± 6.8	60 ± 25
DA	170 ± 39	47 ± 7.0
DB	336 ± 52	57 ± 38
DC	407 ± 65	88 ± 48
DD	293 ± 18	47 ± 3.1
EA	276 ± 14	43 ± 30
FH	476 ± 34	58 ± 12
GA	348 ± 19	53 ± 40
GB	338 ± 26	58 ± 23
GC	345 ± 11	52 ± 5.3
GD	380 ± 28	53 ± 47

ppm = parts per million

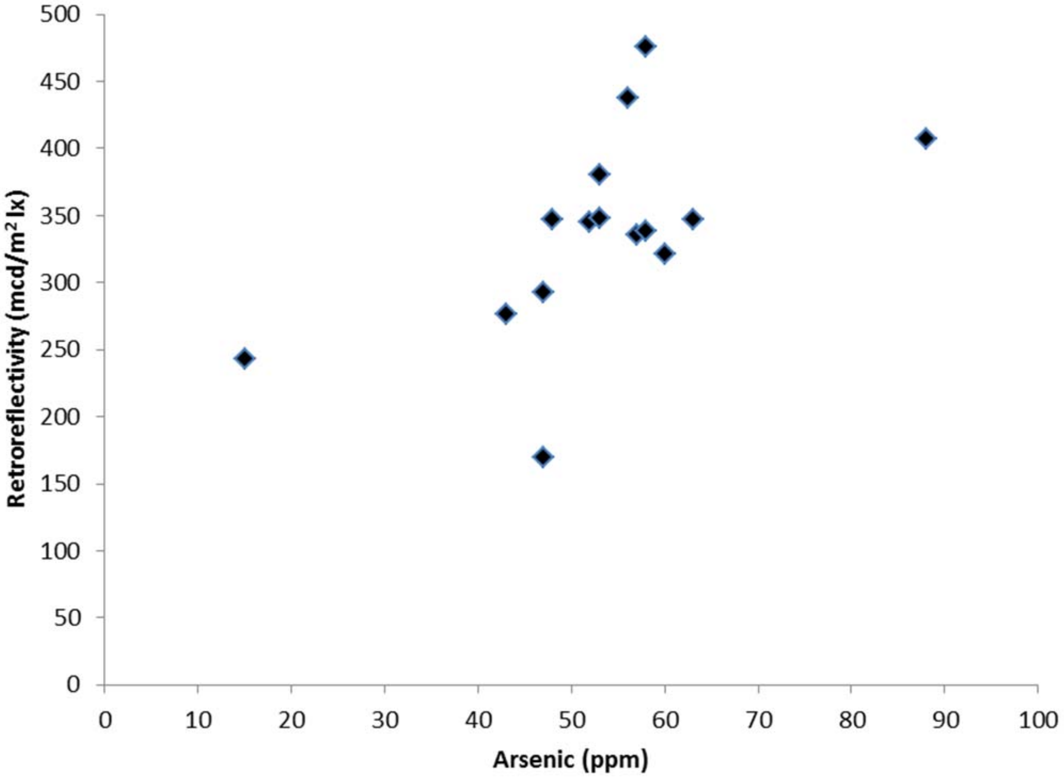


Figure 10. Graph. Relationship between mean arsenic content and mean retroreflectivity of each sample of glass beads evaluated within this research.

The calculated Pearson's product moment correlation coefficient for all 15 samples shown in figure 10 is 0.564. The coefficient indicates a positive moderate correlation between the two factors, suggesting that a correlation may exist between the arsenic content and retroreflective performance. However, additional samples should be analyzed to determine whether a correlation actually exists. In this study, the range of observed arsenic contents was limited to between 15 and 88 ppm. Arsenic contents of previously analyzed beads were an order of magnitude greater than the beads analyzed from State transportation department samples, and these high arsenic beads and beads with lower arsenic content (below 15 ppm) should be included in additional studies that explore this correlation. The retroreflectivity data, however, also demonstrate that suitable retroreflectivity performance can be achieved at low levels of arsenic.

Speciation of Metals in Leachate From Glass Beads

Arsenic speciation in water plays an important role in determining its potential toxicity to exposed organisms. Because glass beads were determined to leach arsenic, understanding the speciation of arsenic within the leachate solutions became of interest. The speciation analysis of arsenic revealed the presence of both arsenite (As^{3+}) and arsenate (As^{5+}) as the two predominant species of arsenic in solution. Table 13 presents the results for the analysis. While total arsenic levels ($As^{3+} + As^{5+}$) in the pure leachate exceeded the 10 μg/L drinking water maximum containment level for arsenic, under environmental conditions, the impact of leachate on existing groundwater or surface water reserves would be minimal for these samples owing to dilution. However, speciation data are considered during the human health risk assessment.

Table 13. Arsenic speciation observed in samples of bead leachate generated from an up-flow cartridge system.

Sample	As^{3+} (μg/L)	As^{5+} (μg/L)
AA	3.0	8.9
DC	ND	15
EA	1.4	11

ND = not detected

Characterization of Arsenic and Lead Content in Mixed Glass Bead and Soil Samples Taken From a Bead Storage and Transfer Facility

Five soil samples were collected from a glass bead storage and transfer facility of a pavement-marking company to study the contribution of glass beads to the total metal content within bead-impacted media samples. The bead storage facility has been storing beads on site for more than 20 years. Because beads were evident upon visual examination, the site samples served as a real-world exposure scenario for bead-impacted environmental media. The MDL for the field sample analysis was determined separately because a new ICP-MS was installed in the later stages of this study, and a new matrix was used. The field site MDLs are given in table 14. Because the MDLs were lower than the lowest calibration standard (1 μg/L), the lowest calibration standard became the PQL.

Table 14. MDL and PQL for arsenic and lead for total, extractable, and bioaccessible metals for storage yard soil samples.

Metal	Limit	Total (ppm)	Extractable (ppm)	Bioaccessible (ppm)
Arsenic	MDL	2.8	0.07	0.07
	PQL	4	0.1	0.1
Lead	MDL	0.44	0.011	0.011
	PQL	4	0.1	0.1

ppm = parts per million
MDL = method detection limit
PQL = practical quantitation limit

Table 15 lists the average glass bead content in site soil samples collected from a bead storage and transfer facility. The difference in the content of glass beads is owing to different sampling locations in the vicinity of the facility, including the storage zone and the transfer zone. The glass beads' content varied from 19 percent to a maximum of 78 percent. Because most of the workers at the glass beads manufacturing facility do not wear protective equipment other than a hard hat, they are likely exposed to a high volume of glass beads through various routes of exposure, including direct contact and inhalation.

Table 15 presents the total metal content of site soil samples containing glass beads. While total arsenic was only reportable in sample locations 1 and 3, the concentrations of lead in the storage facility soil samples ranged between 11 and 122 ppm. The elevated arsenic and lead content in the soil samples over the control may be associated with the presence of glass beads. However, the glass bead content in field site soil sample does not correlate with the metal content in site soil samples. A detailed study, with more samples from a variety of facilities, is needed to assess the contribution of glass beads to the total metal content of the soil.

Table 15 presents the total arsenic content in the respirable portion (< 10 μm in size). The concentrations of total arsenic were below the MDL (0.70 μg/L in aqueous phase) for all samples and are reported as BDL. These preliminary findings indicate that studies involving more samples from multiple facilities are required to evaluate the contribution of glass beads to total arsenic content in the respirable fraction of the soil.

Table 15. Glass bead content (by weight), total arsenic and lead (ppm) in site soil samples, and total arsenic (ppm) in respirable fraction of site soil samples.

Sample ID	Weight Percentage of Glass Beads in Soil	Arsenic (ppm)	Lead (ppm)	Arsenic in Respirable Fraction (ppm)
Sample 1	24.5	2.9 ± —[1]	120 ± 160	BDL
Sample 2	19.8	BDL	40 ± 19	BDL
Sample 3	48.0	7.6 ± 0.5	35 ± 2.1	BDL
Sample 4	41.2	BDL	14 ± 11	BDL
Sample 5	78.3	BDL	12 ± 5.1	BDL
Control	0	BDL	24 ± 12	BDL
SRM	—	BDL	22 ± 4.6	BDL

[1] Only one reportable data point out of three replicates
ppm = parts per million
SRM = standard reference material
— indicates not applicable
BDL = below detection limit (< 2.8 μg/g for arsenic, < 0.44 μg/g for lead)

CONCLUSIONS

Table 16 summarizes the overall number of samples and number of replicates per sample examined in this research. It also provides the mean total, extractable, and bioaccessible arsenic and lead contents measured in the entire sample set of glass beads analyzed in this study. While an intra-method comparison for total arsenic and lead content in the beads did not result in agreement among the four methods evaluated, KOH fusion digestion coupled to ICP-MS analysis reproduced the SRM content of both analytes to within 94 percent of the target value for six samples of SRM analyzed in triplicate. In addition, spiked addition controls demonstrated 106 ± 12 percent recovery of the known addition for both lead and arsenic in all spiked samples when KOH fusion was used. Therefore, the researchers have confidence that KOH fusion followed by ICP-MS analysis is a suitable method for measuring arsenic and lead content in the glass beads.

Arsenic speciation was observed in laboratory-generated samples of leachate under neutral pH conditions. Arsenate (As^{5+}) ranged from 8.9 and 15 µg/L in the leachate solution; whereas arsenite (As^{3+}) was present below 3.0 µg/L in the leachate. Arsenic and lead were also present in bead-impacted soil samples collected from a facility used for more than 20 years to store and transfer beads on site. When present, arsenic had a mean content in the site soils of less than 5.5 ppm. Lead was detected in all of the samples at contents ranging 12 to 120 ppm. (Control site lead content was 24 ppm.) Overall glass content within collected samples from the site ranged from 20 to 78 percent by weight, with an average content of 42 percent by weight.

Based on laboratory and field sample characterization completed in this study, the mean concentrations observed in the beads were below the 200 ppm arsenic and lead limit adopted in the recently approved MAP-21 legislation. Therefore, the proposed limit should not present a hurdle to using existing beads already in the commercial markets for pavement marking purposes.

Table 16. Summary of total, extractable, and bioaccessible arsenic and lead in all of the samples analyzed in this study.

			Arsenic		Lead	
Method	**No. of Samples**	**No. of Replicates Per Sample**	**Frequency of Reportable Detection (percent)**	**Mean Content When Present (ppm)**	**Frequency of Reportable Detection (percent)**	**Mean Content When Present (ppm)**
Total	15	9	100	54	100	71
Extractable	15	3	0	—	47	0.8
Bioaccessible	15	3	0	—	20	1.8

ppm = parts per million
— indicates not detected in any sample

SECTION 2. PROPOSED MODEL FOR THE ASSESSMENT OF HUMAN HEALTH RISKS ASSOCIATED WITH GLASS BEADS USED FOR PAVEMENT MARKING

INTRODUCTION

The use of glass beads in pavement markings presents the potential for contaminant release to the environment and subsequent human exposure. This section presents the proposed modeling methodology used to estimate the potential for adverse human health effects associated with arsenic and lead in glass beads used for pavement marking.

Specifically, this section presents the development of the human health risk model, including the following:

- An assessment of the workflow of pavement-marking beads within their product lifecycle.
- Identification of the potential for human exposures based on the bead workflow.
- Evaluation of the migration of contaminants from beads to human exposure points.
- Methodology and equations used to determine exposures.
- Methodology and equations used to determine a screening level concentration of arsenic and lead within the glass bead products that is protective of human health.

The risk evaluation methodology is based on observation of human interaction with the workflow of glass beads in the environment. The workflow includes interactions during manufacturing, transportation, storage, application, and disposal of old marking residues. The exposure assessment considered human exposures over a range of potential scenarios that could lead to contact with beads. The scenarios that captured the most likely and reasonably conservative exposures based on field observations were included in the exposure model development. The process of developing the model identified a number of important parameters. The required parameters were assembled from literature or laboratory measurement of glass beads where applicable. For some parameters, however, literature was either not available or demonstrated significant variability among the available sources of data. Parameters that were considered key to the development of the risk model and which indicated significant variability in parameter values are specifically highlighted in the text.

The field observations of glass bead production, storage, application, and removal were conducted in an arid environment during warm, dry, and low wind conditions. Roadway marking operations are generally conducted during periods of low winds (< 15 mi/h) to minimize bead and paint loss. Although observations were made in an arid environment, this assessment considers a range of environmental conditions. Additional information used in this assessment was obtained through interviews with individuals involved in the glass manufacturing and highway marking industries.

The laboratory investigations presented in section 1 were used to establish the total, extractable, and bioaccessible arsenic and lead content used in the model. Because of uncertainty regarding the source of the beads used in the metals analysis in experiments prior to the September 2012 TTI/TAMU report, the risk evaluation presented in this report focuses on arsenic and lead using the most recently available bead analysis.

The bead workflow assessment was conducted using English units because those are most commonly used in the United States for the applicable processes. The remaining portions of the document use SI units because English units are not used for the chemical analyses that support development of the risk-assessment models.

Background of Bead Workflow

Table 17 identifies the different stages and potential points of release of arsenic and lead within glass bead workflow. Use of glass beads as a reflective material in roadway line markings is decades old. Glass beads used in pavement markings are applied to the roadway on top of a base material that is a paint, epoxy, or thermoplastic. The beads are dropped either by a painting machine (specially designed truck or hand-cart) or by hand spreading. The bead sizes range from a fine table salt crystal up to a small ball bearing. Bead application rates, which are on the order of 192 lb/mi for a single 6-inch-wide line, result in a significant amount of beads that are not bound to the base material and are released to the environment. Additional releases of beads from markings may occur through wear due to traffic abrasion and weather, as well as during removal of the markings, such as when preparing a roadway for re-marking.

Portions of the workflow associated with the glass beads are presented in table 17, which describes each of the steps where beads are used and potentially released to the environment. The basic elements of the bead workflow include the following:

- Manufacturing.
- Transportation.
- Storage/transfer.
- Application.
- Wear/abrasion.
- Removal/disposal.

Beads are typically manufactured by melting crushed recycled glass cullet (large glass blocks) in an up-flow furnace to form the spherical glass particles. The formed particles are then passed through sieves of various sizes to isolate beads of desired size fractions that are mixed in the product formulation. Once sieved, the glass beads may be coated for various purposes (e.g., to prevent moisture accumulation, to achieve better paint adherence). The beads are then packed in large super-sacks (2,000-lb bags), smaller 50-lb bags, or in customer-specified packaging.

Table 17. Bead workflow elements and release potential.

Bead Workflow Element	Description of Release	Release Potential	Quantity Released
1. Beads arrive palletized and packaged to prevent moisture contamination	Rupture of a 2,000-lb bag possible. Majority of contents would be recovered.	Low (localized to storage yard)	< 10 lb/day
a. Where moisture contamination has occurred, workers may use hands/tools to break apart the clumps of beads resulting in direct contact.	Minimal loss while receiving/recovering/ transferring beads	Low (localized to storage yard)	< 10 lb/day
2. Bead bags are opened and used in one of two ways:			
a. Vacuum beads into painting vehicle storage containers. Worker exposure to beads may occur while manipulating the vacuum nozzle or opening/resealing the bead bags. Where vacuum transfer is not functional, bead bags may be cut and contents dumped into vehicle storage bins, resulting in potential worker contact with beads. Beads may also be spilled into the yard, increasing the potential for exposure.	Where a vacuum transfer is used, potential for release is limited to the opening and closing of bead bags. Dumping of beads from bags has greater potential for release than does vacuum transfer.	Moderate (localized to storage yard)	< 25 lb/day
b. Pour beads into a bucket for hand application. Beads may be contacted during transfer and may be spilled, requiring handling during pickup.	Minimal loss while recovering/transferring beads	Low (localized to storage yard)	< 10 lb/day
3. Vehicle application of beads may require workers to manipulate nozzles, resulting in bead contact. Excess beads (up to 15 percent) are released to the environment.	Excess beads applied to lines are released to the environment. For an application requiring six lines, a rate of 192 lb applied per 6-inch-wide line per mile results in a total of 1,150 lb/mi. For a loss rate of 15 percent of applied material, a total of 175 lb are released per mile of roadway, and assumed to be distributed 6 ft on either side of the roadway. In general, roads are re-marked every 2 to 5 years.	Moderate (large quantity, widely dispersed), most significant where roadside curbs have the potential to concentrate beads	Up to 175 lb/mi

Bead Workflow Element	Description of Release	Release Potential	Quantity Released
4. Application of beads by hand (without gloves) results in direct contact with beads. Excess beads are released to the environment.	Loss rate is greater than machine application (up to 25 percent), with a bead usage of approximately 210 lb/mi. Typical applications require 300 ft of marking in a small residential neighborhood (perhaps near a school zone with many crosswalks) per year.	Moderate (small quantity, potentially localized), most significant where curbing concentrates beads	< 0.01 lb/ft
5. Worker inspecting applied lines may contact the surface and dislodge beads.	Worker contact with the lines may result in minimal bead loss.	Small (very small amount, widely dispersed)	< 1 lb/day
6. Line abrasive wear and weathering	During lifetime of line, beads are slowly released from the line as a result of abrasive wear and weathering. Assume that 85 percent of the original load (1,150 lb/mi for six 6-inch lines) adhered to the line. Further assume that 25 percent of the adhered beads are released each year due to traffic wear and weathering.	Moderate (large quantity, widely dispersed, long duration release), most significant where curbing concentrates beads	Up to 250 lb/mi per year
7. Line removal of beads and substrate may include use of hand tools or vehicle-mounted equipment. When vacuum is not used to remove material, workers may contact beads. When vacuum is used, bead contact in the field is limited; however, it may occur when removing material from storage tank. Removal methods include mechanical grinding, hydraulics, etc.	Assume that lines are repainted when remaining retroreflectivity is 25 percent of original value, equivalent to retention of 25 percent of adhered beads, which is approximated as 250 lb/mi for a roadway section with six 6-inch lines. Releases may occur when vacuum removal of debris is not used, or when removed material is incorrectly stored in the marking company storage yard.	Moderate (Potential is moderate in the field because vacuum trucks capture nearly all debris. Vacuumed material may be released in the storage yard. Mitigation measures are highly variable in practice.)	Up to 250 lb/mi

The packed beads are shipped by truck, air, rail, and train to the end users who are the pavement-marking agencies (either public entities or private corporations). Beads are completely covered during transport to prevent contamination of the beads by moisture. Although the beads may be shipped a significant distance, there are few recorded incidents of spills due to crashes.

The pavement-marking agency, either a state/local entity or a private company, receives the beads and may store the packed beads in any number of ways. The storage areas may be covered with tarps or open air (with paved or bare ground). The storage yards may or may not include catch-basins to collect any material runoff. The beads are well protected from the elements by the shipment packaging because they tend to form clumps in the presence of moisture, leading to problems when used in the pavement-marking vehicles.

The packaged beads are taken from storage and opened for use in pavement-marking applications. Beads in super-sacks are transferred to specially designed vehicles with internal bead holding tanks that are isolated from the environment. Their transfer is generally accomplished with a vacuum attachment incorporated into the pavement-marking vehicle, but occasionally the super-sacks are hoisted above the vehicle and gravity fed into the storage tank. The super-sacks may also be transported from the storage yard into the field and staged for later use. Smaller bead bags are opened and poured into buckets for jobs requiring hand application of beads.

In the field, beads are applied to the pavement markings either by vehicle or by hand. Pavement-marking vehicles apply paint, thermoplastic, or epoxy substrate from one set of nozzles, followed by a stream of beads through other sets of nozzles. The nozzles are designed to result in beads that are buried halfway in the substrate for the best combination of adhesion and retroreflectivity, a measure of the line visibility at night. To achieve uniform bead coverage on the substrate, excess beads are applied, resulting in some bead loss along the edges of the marking. For smaller applications (e.g., small intersections, crosswalks), beads may be thrown onto the substrate by hand or, in some cases, using small fertilizer spreaders.

A portion of the beads that adhere to the substrate are slowly dislodged over a period of time owing to traffic wear and weathering until a fraction of the original number of beads are left and re-marking is required. For highways, re-marking occurs every 2 to 5 years on average, whereas the frequency is approximately 3 years for urban areas. The markings are generally re-applied when 25 percent of the original retroreflectivity remains on the roadway. When re-marking is needed, the old marking material is either covered by new markings or is removed from the roadway before laying the new markings.

Removing the remnants of old roadway markings generally involves mechanical, hydraulic, or chemical methods. Specially designed vehicles use an attachment that includes a hydraulic jet and vacuum system to remove the marking material and collect the waste. The slurry is contained within a holding tank on the vehicle for disposal, and very little material is lost to the environment. Where systems are used without vacuum recovery, the old marking material is generally left along the roadside.

Each of these steps in the bead workflow and the potential for exposure are discussed in greater detail in the following subsections.

Bead Manufacturing

The bead manufacturing process is a multistep process. The process starts when recycled glass cullet is received by the manufacturer. The cullet arrives via truck or rail and is stored in piles on the property (often exposed to the ambient conditions) until the cullet is turned into beads. The cullet is moved from the storage pile to large hoppers using a pay loader. The cullet is then passed through a series of grinders that breaks the cullet down into pea-size pellets. During the grinding portion of the process, dust suppression controls are typically used.

In the primary manufacturing process used in industry today, the ground pellets are then introduced into an up-flow furnace. The pellets are melted in the lower portion of the furnace, and the molten glass rises due to temperature-driven convection and advective air flow. The flow rate through the furnace, combined with the temperature within the furnace, creates the spherical beads as the molten glass rises, cools, and re-solidifies within the furnace. The process to create the beads results in formation of beads across several particle size fractions. The formed beads are then passed to additional hoppers and are immediately sieved to isolate beads of the desired particle size, which are then stored in bins until formulated into products.

Products are formulated by combining beads of different particle sizes together to achieve the final blend. Beads from different bins are fed by gravity through a chute, and the resulting mix of various bead sizes are packaged into super-sacks, 50-lb bags, or other customer-defined packaging.

Worker exposure to the beads occurs at three main points:

1. During formulation of the product as the blended beads are fed into their final packaging.
2. During QA/QC testing.
3. As a result of spilled beads.

During product formulation, workers aid in the process by manually aligning the chute to the packaging for the super-sacks. For the 50-lb bags, the workers hold the bags while they are filled. Samples of each formulated product are tested to ensure the correct particle size distribution and spherical shape. Workers within the quality control laboratory come into incidental contact with the beads during testing. Workers may also come into contact with the beads that are spilled during the process. However, once the beads are packaged, worker exposure to the beads is minimal. The packaged beads are transported in sealed packaging around the manufacturing floor using a palate and forklift. The beads are stored within the facility until they are loaded via forklift for transport to the consumer. Workers may also be exposed to heavy metals through contact with the glass cullet in addition to exposure to metals in the formulated bead products.

Bead Blending

At some locations within the United States, both domestic beads and foreign beads are blended into final products without onsite bead manufacturing. Worker exposure to the beads at these operations is similar to worker exposure to beads occurring during bead formulation described in the preceding subsection.

Bead Transport

The potential for bead release during transport from the manufacturer to the pavement-marking agency is minimal. Because the products are individually packaged in sacks and covered with a water-protective barrier, such as a tarp, during transport, the loss of beads and exposure to the driver are low. The beads are delivered to the consumer and off loaded into storage using a forklift.

Bead Storage and Transfer

The end user of the beads is either a public entity or a private contractor that marks roadways. The agency receives the palletized beads in either a super-sack or a 50-lb sack. The large sacks are either opened in the storage yard, where beads are transferred into the specially designed marking vehicles, or taken unopened into the field where they are staged for later use. The smaller bags are used where the markings are limited in size and/or where hand application of beads is the most practical approach.

Beads may be spilled during receipt and storage, but localized releases mainly occur during transfer of beads to equipment in the storage yard. The extent to which released beads migrate outside of the yard is a function of a number of factors, the two most important being yard construction (e.g., protective coverings, land slope, design features such as sumps) and climate (arid/dust, wet/leaching). Materials released within the storage yard are of particular interest because they may accumulate over time. Considering the durability of the beads and the low associated rate of break-down, a storage yard used over many years could accumulate a significant concentration of beads. The transfer of beads to equipment outside of the yard will also potentially result in releases to the environment; however, the beads would be distributed over a wide area reducing the likelihood of accumulation.

Bead Application

The potential exists for a significant amount of beads to be released into the environment while being applied to the base marking material. To ensure good coverage, excess beads are often applied and a level of overspill is accepted as industry practice. Methods to curtail bead loss are in limited use (e.g., vertical drops, zero relative velocity nozzles, bead sheaths). The low cost of the beads makes more precise application or the use of recovery devices relatively uneconomical.

The degree to which beads become mobilized is based on many factors (including weather, physical characteristics of the roadway, and street sweeping frequency), as well as the type of markings being applied. The general classes of roadway line markings are short (lines for intersections, traffic signals, and crosswalks) and long lines (lines applied over distance using specially designed vehicles). The application of beads to short lines is generally accomplished with small, single operator equipment or by hand spreading. The amount of bead loss is not quantified; however, an amount similar to that for long lines was observed in the field for an urban area with gutters (which tends to accumulate beads) along the roadside.

For long lines, bead application is accomplished through automated bead drop delivery systems that place beads onto the marking material in a continuous process figure 11 and figure 12). In general, beads are fed by gravity from a holding vessel to the bead drop nozzles. The amount of beads deposited and the direction of bead release is governed by manual adjustment of the nozzle aperture. In some cases, multiple nozzles may be used to provide additional bead loading for wide lines or to allow higher vehicle speeds.

Road Marking Wear and Degradation

A portion of the beads that were successfully applied to the base coat of marking material will be abrasively removed as a result of traffic wear and weathering. The majority of the detached beads will be intact, and little chipping/crushing of beads is expected to occur. The fraction of beads removed can be expressed relative to the loss of reflectivity of the lines. Where lines have lost 25 percent of the reflectivity, it can be inferred that 25 percent of the adhered bead load (assumed to be 85 percent of the applied bead load) has been removed by wear. At the point that re-marking is required, an additional layer of beads and base material is applied on top of the remaining line, or the remaining line/base material is removed. Application of several layers of lines prior to removal and re-application is typical.

Figure 11. Photo. Application of glass beads to long line markings.

Figure 12. Photo. Close-up of glass bead application to long lines.

Bead Removal/Disposal

The final disposition of the beads and base material used in roadway markings, owing to reaching the maximum feasible number of layers or to demolition and removal of the road itself, may result in release of beads to the environment. The line remnants are removed by a number of methods (including abrasives, water jets, and chemical removal), and the resulting material is either collected using a vacuum or released to the environment. When vacuum attachments are used, very little material is lost to the environment and releases are dependent on ultimate disposition of the vacuumed material in a landfill or at the equipment storage yard. In the case of mechanical removal without vacuum, the majority of remnant material (including beads or pulverized bead fractions) is likely to be lost to the environment, and a portion may become airborne. In addition, the beads would be concentrated because the remaining beads are held together in the base material that would also be removed. Because some base materials (such as epoxy and thermoplastic) would retain the beads in one area and prevent them from dispersing, the concentrations associated with removed marking material may be increased.

Human Exposures Associated With the Bead Workflow

Human exposure to glass beads using in pavement markings may occur at any phase in the workflow lifecycle of the beads. Field observations of manufacturing environments, storage facilities, product applications, and product removal were carried out to determine the individuals who are most likely to experience significant exposure to beads released to the environment. The results of the field observations are reported in the next section.

EXPOSURE ASSESSMENT

The exposure assessment presented in this section outlines the individuals and pathways by which humans come in contact with contaminants associated with glass beads during the product lifecycle. In the exposure assessment, information regarding the characteristics of bead contamination is combined with assumptions regarding the source of contamination and presence of potential receptor populations, to elucidate the nature of human health exposures. The exposure assessment includes discussions concerning exposure scenarios, pathways of exposure, and migration pathways (used to establish the environmental fate of the beads).

Potential Exposure Scenarios

Populations that could potentially be exposed to glass beads include workers, residents, recreational users, and consumers of agricultural goods. Although some exposures are more plausible than others, all of the potential exposure scenarios listed below were considered for further evaluation. When the field observations indicated a particular scenario was insignificant relative to other scenarios for the same media, that scenario was no longer considered viable and was eliminated from the exposure pathway assessment.

Occupational Exposure Scenarios

The occupational exposure scenario is based on individuals who work on a roadway marking crew or manufacturing workers. The two occupational scenarios are similar, with the primary difference being that manufacturing workers will be exposed to beads only. Roadway marking crews may be exposed to both beads and soil that has been affected by the beads.

Marking crew employees include two distinct populations of workers who experience exposures related to the handling of beads: those who apply markings and those who remove markings. However, the same person or persons may work on all tasks required by a marking crew. Manufacturing workers may also be exposed during the direct handling of the product (either during packaging or transferring of beads).

Field observations indicated that worker exposure during transportation of bead products is minimal because of the handling practices employed to keep the beads free of residual moisture. Therefore, worker exposure during transport is not considered further. However, other exposures associated with the bead lifecycle are further evaluated in this assessment for the marking crew worker and manufacturing worker scenarios.

Residential Exposure Scenarios

The residential scenario is based on an individual property affected as a result of proximity to either a roadside where beads have been applied to markings or a bead storage yard. Field observations indicate that exposures associated with roadway marking application would be less significant than residential exposures due to concentration of beads released to the bead storage yard. Therefore, the residential scenario focused on exposures associated with the bead storage yard of a pavement-marking agency and not on application of the beads along a property line.

Individuals (either adults or children) living on the affected property may be exposed both indoors and outdoors to contaminated soil, water, food, and air originating from a bead storage yard. The resident may be exposed to contamination migrating from a storage yard that is on property adjacent to the residence, or in the most conservative approach, the residence may have been built directly on top of a former bead storage yard.

Where a former storage yard is now a residential area, individuals may contact contaminated soil during daily outdoor activities. A resident may also track contamination indoors, resulting in continued exposure. If beads were left exposed to precipitation in the storage yard, the potential exists for heavy metals to leach to groundwater, which may result in additional exposure pathways (through drinking affected groundwater or irrigating a home garden). In the case of a residence adjacent to a bead storage facility, the possibility exists for metals to migrate into offsite residential soil, particularly in arid climates where wind-generated dust is prevalent. Also associated with the offsite resident is the potential for juvenile trespassing into the adjacent bead storage facility.

For both the resident onsite and offsite scenarios, there is a potential for exposure via ingestion of fish from a contaminated surface water body, consumption of home-grown vegetables (gardening), or consumption of home-raised livestock products (chickens or chicken eggs, for example). Additional residential exposure may occur to individuals near schools where numerous crosswalks are frequently re-marked and, particularly, where streets are curbed allowing beads to accumulate. The sparkling appearance of the beads may draw attention and be attractive to school children, increasing their likelihood of exposure. However, exposures mentioned within this paragraph are considered speculative, and if they occur, they will be infrequent and short in duration. Therefore, to address the most significant and likely scenarios, the residential exposures included in the development of this methodology are those associated with residents living in close proximity or on top of a bead storage yard and the trespasser accessing the storage pile from an offsite residence.

Recreational Exposure Scenarios

The recreational scenario is based on an individual who rides all-terrain vehicles (ATV) along roadways or who fishes from water bodies affected by beads. Where a sufficient amount of beads has accumulated, dust may be inhaled by the ATV rider or taken up by aquatic organisms, resulting in potentially significant exposure. The level of exposure is highly dependent on climate and the fate of beads in the environment.

Because of the expected low concentration of beads estimated and observed for roadside soils, roadside recreational activities are unlikely to result in significant exposures. In arid climates where dust generation is more prevalent, a rider is also more likely to wear a face mask filter to reduce dust inhalation. For areas with higher precipitation, the mass of beads is likely to be insufficient to significantly affect aquatic biota. In the absence of evidence of elevated roadside bead concentrations, the recreational scenario is not evaluated further.

Agricultural Exposure Scenarios

The agricultural scenario is based on a farm situated beside a roadway where beads have been applied. Beads accumulating in farmland may result in uptake into crops or livestock and subsequent human exposure. Although this scenario is possible, the area affected by beads would likely be limited, resulting in contamination of only a fraction of any total farmland. Coupled with the low frequency of bead application (perhaps every 5 years in rural areas), the agricultural scenario is unlikely to result in significant exposures and is not considered further in this assessment.

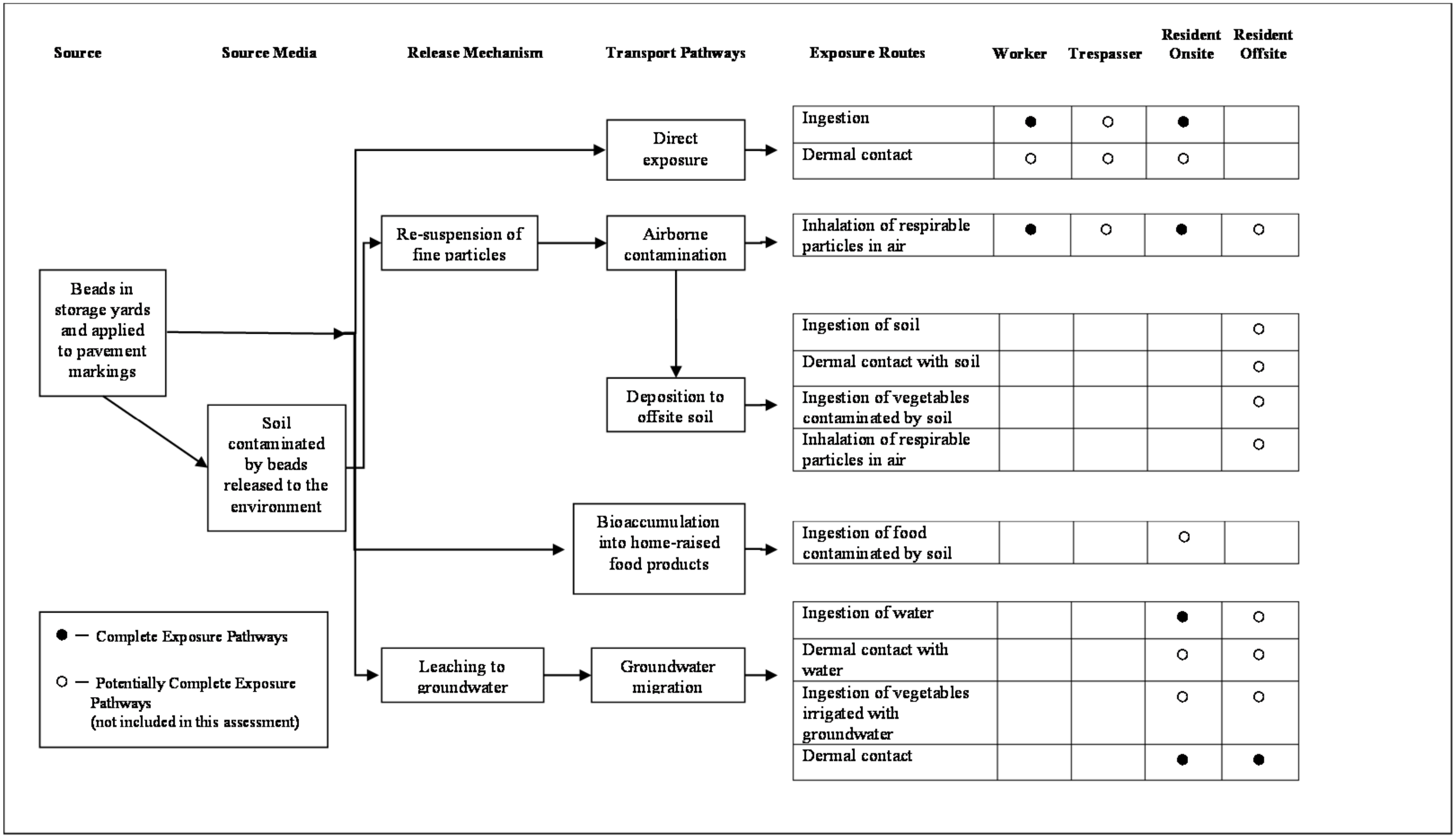
EXPOSURE PATHWAYS

Evaluation of exposure pathways allows the risk assessment to focus on the pathways with the most significant potential to contribute to adverse human health effects. Exposure pathways are considered complete when four elements are present: 1) a contaminant source, 2) a transport mechanism to a receptor location, 3) a receptor present at the location, and 4) an exposure pathway to the receptor. Incomplete exposure pathways are eliminated from further consideration. Pathways are categorized as either direct (where the point of exposure is the source of contamination) or indirect (where a transport medium is needed to connect the source to the receptor). Potential exposure pathways are evaluated for each of the exposure scenarios (see figure 13).

The manufacturing worker is exposed to beads daily in the course of production and packaging. The marking crew worker is exposed to the beads daily in the course of product handling, application, and removal. The marking crew worker is exposed in the field during line application; however, based on field observations, the majority of their exposure is likely to be in the storage yard where beads are stored and prepared for use or during line removal without a vacuum. While worker exposure during roadway marking removal is possible, some states require that the removed waste marking material be collected with a vacuum, essentially eliminating exposures in the field. Therefore, the focus of the evaluation of exposure pathways is the bead storage yard for the marking crew worker and the production/blending process for the manufacturing worker.

The residents are assumed to either live adjacent to an active bead storage yard, or under the most conservative scenario, a residential area may also be built on top of a former bead storage area. The residential soil is assumed to be contaminated by past bead releases or from airborne transport of beads from an adjacent bead yard. The residential trespasser is assumed to live adjacent to an active storage yard.

Figure 13. Diagram. Conceptual site exposure model for pavement-marking beads.



Transport Pathways	Exposure Routes	Worker	Trespasser	Resident Onsite	Resident Offsite
Direct exposure	Ingestion	●	○	●	
	Dermal contact	○	○	○	
Airborne contamination	Inhalation of respirable particles in air	●	○	●	○
Deposition to offsite soil	Ingestion of soil				○
	Dermal contact with soil				○
	Ingestion of vegetables contaminated by soil				○
	Inhalation of respirable particles in air				○
Bioaccumulation into home-raised food products	Ingestion of food contaminated by soil			○	
Groundwater migration	Ingestion of water			●	○
	Dermal contact with water			○	○
	Ingestion of vegetables irrigated with groundwater			○	○
	Dermal contact			●	●

Although the inhalation pathway provides the potential for exposure, it is unlikely to be significant. The arsenic and lead are atomically bound to the beads and are not likely to volatilize under ambient conditions. While the beads may be crushed, they are unlikely to be reduced to particles small enough to be entrained in air due to wind scour. Therefore, only the portions of the intact beads that are small enough to be inhaled are used as the inhalation source.

There is a low potential for leaching of metals from beads and subsequent sorption to soil particles that may then be inhaled. The extractable portion of metals from glass beads was shown to be low, and the fraction of leached metals sorbed to soil particles small enough to be inhaled would be minimal. However, the inhalation pathway is included in this assessment to estimate the potential for toxic effects due to silicon exposure.

For dermal pathways, beads are assumed to adhere to skin, similar to soil, resulting in an absorbed dose. Because metals typically result in low dermal exposures relative to the ingestion pathway, the dermal pathway was not quantified in the risk evaluation. Food-related pathways (home-grown vegetables/livestock) are also possible, but are not currently considered a significant source of exposure and were not included in the assessment.

In all cases, exposures are considered to occur from contact with beads and from metals lost from beads into the surrounding media. Laboratory data indicate that arsenic and lead may be leached out of the beads to soil and to groundwater; however, the potential is limited. The ingestion exposure pathway assumed that bead contaminants are absorbed through the gastro-intestinal tract and into the blood stream.

Worker Exposure Pathways

The worker exposure is assumed to occur throughout the work day. The worker is exposed to both direct (ingestion) and indirect (inhalation) pathways. Potential pathways of exposure included in the risk evaluation were as follows:

- Incidental ingestion of beads.
- Inhalation of fugitive bead particulates (if no controls are used).

As indicated previously, the dermal pathway was not included because of the low absorption of metals and uncertainty in the availability of bead contamination for dermal absorption. In addition, the potential for contamination of soil due to migration of contamination from beads is low. Therefore, only direct bead ingestion (and not soil ingestion) is included in the risk evaluation.

These pathways have the potential to be complete exposure pathways based on the four components of exposure outlined previously. Exposure via ingestion assumes that the source of contamination is the beads, the receptor is the worker handling the beads, and the worker may incidentally ingest the contamination if not wearing protective equipment. The inhalation exposure pathway assumes that the source is the spilled beads, the migration pathway is re-suspension of fugitive dust, the receptor is the worker, and the worker may inhale respirable particles if not wearing protective equipment.

Residential Exposures

Adult and child residential exposures occur throughout the day both inside a residence and outdoors. The resident would be exposed by direct pathways (ingestion) and indirect pathways (air, water, food). Direct pathways are applicable if the residence is built on top of a former storage yard, otherwise all residential exposures are indirect because a mechanism is required to transport contamination from the adjacent storage yard.

Potential indoor and outdoor exposures included in the risk evaluation were as follows:

- Incidental ingestion of beads.
- Ingestion of groundwater contaminated by bead leachate.
- Inhalation of fugitive particulates.

As indicated previously, the dermal pathway was not included because of the low absorption of metals and uncertainty in the availability of bead contamination for dermal absorption.

The food ingestion pathways were not included in the evaluation because of the low leaching potential identified in laboratory studies. Similarly, the potential for contamination of soil because of migration of contamination from beads is low and soil ingestion is not included in the risk evaluation.

Outdoor exposures occur while residents are playing or working in the bead-bearing soil and are assumed to be limited to ingestion of beads, inhalation of particulates due to wind scour, and ingestion of groundwater contaminated by bead leachate.

MIGRATION PATHWAYS

The exposure scenarios associated with the identified receptors include both direct and indirect pathways. The estimation of exposure via the indirect pathways requires modeling of bead contamination through environmental media. The general modeling methods proposed for use in the bead assessment are based on EPA guidance documents for the development of human health based soil screening levels, as described below.

The two potential migration pathways identified for heavy metals in glass beads used in pavement markings were as follows:

- Airborne suspension of respirable particulate matter affected by beads and subsequent inhalation by a receptor.

- Leaching of heavy metals from beads into infiltrating water, migration to a groundwater aquifer, withdrawal of potable water through a residential well, and subsequent ingestion by a receptor.

Developed equations and parameter values for each of these pathways are presented in the following subsections.

Air Pathway

The inhalation exposure pathway is based on suspension of particulate matter that a human could inhale into the bronchial passages of the lungs. Therefore, the assessment of the inhalation exposure requires an estimate of both the amount of material suspended in the air and the fraction of that material that could be taken into the lungs. In general, the inhalation pathway for metals is of less concern than the ingestion pathway; however, details of the inhalation pathway are presented for completeness.(14)

The suspension of soil into the air could be due to human activity in the area of contamination (e.g., vehicle traffic) or environmental causes (e.g., wind scour). The exposure scenario under consideration is based on the pavement-marking company storage yard as the source of contamination, which is subject to vehicle traffic. However, the vehicle speeds are likely to be low, and traffic would be infrequent, although this variable is difficult to quantify. Therefore, suspension of bead material due to wind scour is likely to be a more consistent and frequent source of airborne contamination and is used as the basis for further model development.

General equations for human health exposure to airborne contamination are based on the air concentration of respirable particles. The size of particles that are considered respirable is based on the deposition velocity of particulates in air and filtering ability of the human respiratory tract.

Calculation of air exposure concentrations for the modeling methods will be based on the amount of respirable material suspended into the air due to wind scour from the soil matrix containing the beads. Models describing the wind scour of soil are based on the concept of a threshold wind speed that can entrain particulates in the air.(15) A particle size of 75 μm is considered the limit for wind suspension. For the bead model, it is assumed that the distribution of contamination in the bulk beads is similar to the distribution of contamination in the smaller size fractions. The "unlimited reservoir" wind suspension model assumes that 60 percent of the erodible material would pass a 1-mm screen, which is consistent with standards for Type I and II beads, requiring that > 90 percent be less than 0.85 mm in diameter.(15, 16)

To provide a conservative value for the amount of respirable particulates in the air, the source area is assumed to have no vegetation and no surrounding buildings or trees that might significantly reduce the wind speed at the ground surface. Although only a small portion of the beads (< 5 percent for AASHTO type II beads) are in the respirable range, it is assumed that the distribution of bead sizes approximates the distribution of particle sizes in soil used to develop the wind scour model.(16)

Groundwater Pathway

The potential for migration of contaminants out of the glass beads and into groundwater is significant in the evaluation of human health risks. Groundwater ingestion pathways include two elements: 1) the leaching of contaminants out of glass beads and into infiltrating water, and 2) the migration of leachate to the groundwater and subsequent extraction from a residential well, resulting in human exposure by ingestion. The leaching of contaminants depends on the partitioning between the bead matrix and surrounding pore water, and an important parameter in the evaluation of leaching from the solid matrix is the partition coefficient (i.e., the distribution coefficient). The partition coefficient is defined as the ratio of the total metals content in a solid matrix to the metals content in the liquid matrix. Higher partition coefficients indicate that the metal is more likely to be retained in the solid matrix. The partition coefficient can be used to estimate the concentration of contamination in liquid that is in equilibrium with contaminants in soil, which can then be used to determine the impact on groundwater.

The migration of leachate to groundwater and subsequent ingestion through a residential well is highly dependent on site-specific factors related to weather conditions, soil properties, and characteristics of the groundwater aquifer. The relationship between the concentration of a contaminant in leachate and the concentration in groundwater can be expressed as a dilution-attenuation factor (DAF). In general, a high infiltration rate and low groundwater velocity leads to a low DAF, indicative of groundwater concentrations that are more significantly affected by the leachate.

A reasonably limiting DAF is approximately 10 for a low-flow aquifer with a significant infiltration rate. Although a lower groundwater velocity leading to a DAF < 10 is possible, aquifers with a DAF < 10 are less likely to be used for potable water because the capacity for the aquifer to provide a consistent volume of potable water to a household would be reduced. In addition, at very low groundwater velocities, the transport time of contaminants leaching from beads and traveling to a well would approach the exposure duration for a resident of 30 years. The use of a DAF of 10 is considered conservative because DAF values of approximately 4,000 are reasonable for high-flow aquifers with minimal infiltration.

The use of a DAF provides a simplified approach for a screening level assessment and is based on a number of modeling assumptions, including the following:

- Contamination is uniformly distributed within the source area.
- The contaminant source is in contact with the surface of the aquifer (no unsaturated zone).
- Water is withdrawn from the aquifer at the down-gradient edge of the contaminated area from a well screened within the contaminant mixing zone.

The edge of the contaminated area is used as the point of exposure because it represents a location that is significantly affected and feasible for exposure. Groundwater accessed in this area is assumed to mix with leachate to a depth that might be feasible for access to drinking water, yet the dilution is less than at locations further down-gradient from the contaminant source that might also be used for household purposes.

These assumptions are consistent with EPA recommendations for calculation of screening levels protective of residential groundwater use.(14) For calculation of a site-specific DAF, the generic evaluation may be refined based on additional data collection or interpretation.

MODELING METHODS

Based on the completed exposure assessment, the risk evaluation modeling methods focused on the following three particular exposure scenarios:

- **Scenario 1—Worker**: roadway marking crew employee exposed through incidental ingestion and inhalation of fugitive dust emissions. (Inhalation scenario assumes no protective masks are worn.)
- **Scenario 2—Adult Resident**: adult living in close proximity to an active bead storage yard or on top of a former storage yard exposed through ingestion of contaminated drinking water, incidental ingestion of beads, and inhalation of fugitive dust emissions.
- **Scenario 3—Child Resident**: child living in close proximity to an active bead storage yard or on top of a former storage yard exposed through ingestion of contaminated drinking water, incidental ingestion of beads, and inhalation of fugitive dust emissions.

A trespassing juvenile exposure scenario was considered but not evaluated because the resident exposure was considered to be more limiting. An occupational exposure scenario for the manufacturing worker was also considered but not included in the risk evaluation. It was assumed that occupational exposures would be controlled through the use of dust suppression methods and/or use of personal protective equipment where necessary.

The proposed modeling framework focuses on developing quantitative measures to evaluate potential risk and develop screening level concentrations of metals in the glass beads that are protective of human health. The quantitative assessment requires calculation of the following two components:

- The level of metal uptake or air concentration as a function of each individual exposure route.
- The permissible level of exposure (screening level) due to either cancerous or non-cancerous end points, considering the combined intake from the multiple routes of exposure affecting a single receptor.

The calculations are based on EPA guidance documents addressing human exposure to soil, water, air, and food.(4) The contaminant exposures calculated for each receptor, environmental medium, and pathway combination are the basis for estimating the potential risk or hazard to exposed individuals.

Equations Used to Calculate Exposure to Heavy Metals for Each Receptor Modeled in the Exposure Scenarios

Exposure equations are specific to each environmental medium (soil, water, and air) and pathway of exposure. The calculations of intake for each receptor due to ingestion of beads or bead-impacted soil, inhalation of particulate matter associated with beads or bead-impacted soils, and ingestion of bead-impacted groundwater are presented within this subsection. The developed equations apply to each scenario, and all direct solid matrix exposures are assumed to occur from the top 150-mm layer of soil or from the glass bead product itself. The quantified exposures are then compared with the toxicity values to determine the potential for adverse health effects.

Lead does not have established toxicity data for the evaluation of risk; instead, the exposures are related to blood lead levels to determine the potential for adverse health effects. The risk evaluation for beads used the U.S. EPA models, Adult Lead Model (ALM), and the Integrated Exposure Uptake Biokinetic Model (IEUBK) for children to estimate human health risks from lead exposure.

Because this risk evaluation focuses on arsenic and lead, the equations used are based on metals exposures for the exposure pathways described below. Because lead is evaluated with specific EPA models, the following equations are applied to exposures to arsenic.

Intake Due to the Incidental Ingestion of Beads or Bead-Impacted Soil

Figure 14 presents the equation to estimate the intake of metals from beads or bead-impacted soil due to incidental ingestion.

$$Intake \left(mg_{metal} / kg - day\right) = \frac{C_s \times IR_s \times EF \times ED \times FI}{BW \times AT}$$

Figure 14. Equation. Formula to calculate intake of metals due to incidental ingestion.

Where:
C_s = exposure concentration in solid matrix (mg_{metal}/kg_{matrix}).
IR_s = ingestion rate of solid matrix (kg_{matrix}/day).
EF = exposure frequency (days/year).
ED = exposure duration (years).
FI = bioavailable fraction (unitless).
BW = body weight (kg).
AT = averaging time (days) for carcinogens or non-carcinogens.

Exposure Concentrations Associated with Inhalation of Beads or Bead-Impacted Soils

The inhalation pathway is based on an air concentration representing an average over the exposure duration. Figure 15 presents the equation used to calculate exposure concentrations for inhalation of metals from small beads, bead dust, or from bead-impacted soils.

$$Exposure\ \ Concentration\ (mg_{metal}/m^3) = \frac{C_s \times EF \times ED \times (VF^{-1} + PEF^{-1})}{AT}$$

Figure 15. Equation. Formula to calculate exposure concentrations for inhalation of metals.

Where:
C_s = exposure concentration in solid matrix (mg_{metal}/kg_{matrix}).
EF = exposure frequency (days/year).
ED = exposure duration (years).
VF = chemical-specific volatilization factor (m^3/kg_{metal}).
PEF = particulate emission factor (m^3/kg).
AT = averaging time (days) for carcinogens or non-carcinogens.

Note that chemical-specific VF is only applicable for soil contaminants that volatilize significantly. Because metals do not generally volatilize, the VF^{-1} term in figure 15 is 0.

Intake Due to Ingestion of Bead-Impacted Groundwater

Figure 16 presents the equation used to estimate the intake of metals from groundwater used as a drinking water source.

$$Intake\,(mg/kg-day)=\frac{C_w \times IR_w \times EF \times ED}{BW \times AT}$$

Figure 16. Equation. Formula to calculate intake of metals due to ingestion of bead-impacted groundwater.

Where:
C_w = exposure concentration in water (mg_{metal}/L).
IR_w = ingestion rate of water (L/day).
EF = exposure frequency (days/year).
ED = exposure duration (years).
BW = body weight (kg).
AT = averaging (days) for carcinogens or non-carcinogens.

Risk Evaluation and Calculation of Permissible Levels of Exposure (Cancerous and Non-Cancerous Human Health Screening Levels)

The final step in the risk evaluation combines the exposure assessment and toxicity data to estimate human health risks and generate screening levels. Potential human health effects are characterized as either carcinogenic or non-carcinogenic when calculating the screening levels for each constituent via each exposure pathway.

The probability of cancer effects is assumed to be linearly related to the exposure level of a human receptor to a contaminant in an environmental matrix. An increased probability of cancer effects is assumed to occur with any increased exposure, regardless of magnitude. In other words, there is no threshold for cancer effects and some impact, however small, is expected at any level of exposure. In contrast, non-cancer effects are based on the concept of a threshold of exposure. Below the threshold, no adverse effects are expected; however, exposures exceeding the threshold only indicate an increased likelihood of the occurrence of the adverse health effects.

For this evaluation, carcinogenic effects are defined as an increased probability of cancer incidence, or an Incremental Lifetime Cancer Risk (ILCR). An acceptable ILCR of 1 additional cancer per 100,000 exposed individuals (also expressed as 0.00001 or 1E-05) is proposed as the target risk level for determining screening levels of individual metals in glass beads associated with carcinogenic effects.

Non-carcinogenic effects may be manifested in any number of health impacts (including skin lesions, reproductive effects, and kidney damage) and are represented by a Hazard Quotient (HQ). An HQ is a ratio of the intake of contaminants (or exposure concentration for inhalation) to a reference value. The reference concentration is considered a threshold level below which there is a low probability of adverse health effects. For this evaluation, an HQ of 1.0 is proposed as the target level for determining the screening levels of individual metals in glass beads associated with non-cancer effects.

The target ILCR and HQ are selected considering the acceptable target risk range established by the EPA.(17) The upper end of the risk range is an ILCR of 1 in 10,000 or 1E-04, with a lower threshold of 1 in 1,000,000 or 1E-06. For non-carcinogenic effects, a Hazard Index (HI) of 1 is the point of departure for considering mitigation of exposures. The HI is the sum of HQs for individual metals over all pathways.

The screening levels established for bead exposure must account for the multiple contaminants present in the beads and multiple pathways of exposure. An individual would experience an increased risk from each constituent and protective screening levels account for the exposure from the combination of contaminants.

Calculating Direct-Contact Cancer Screening Levels

Figure 17 presents the equation for calculating the ILCR for direct contact with beads or bead-impacted soils through the ingestion exposure pathways.

$$\text{Calculated ILCR} = \text{Intake } (mg_{metal}/kg\text{-}d) \times \text{Cancer Slope Factor (risk per } mg_{metal}/kg\text{-}d)$$

Figure 17. Equation. Formula to calculate ILCR for direct contact through ingestion.

The equation in figure 18 is used to calculate the ILCR for inhalation exposures.

$$\text{Calculated ILCR} = \text{Exposure Concentration } (mg_{metal}/m^3) \times \text{Inhalation Unit Risk (risk per } mg_{metal}/m^3)$$

Figure 18. Equation. Formula to calculate ILCR for inhalation exposures.

ILCRs are calculated specific to a particular contaminant, exposure pathway, and receptor. The slope factor relates the intake level to the probability of increased cancer. The cancer slope factors are determined from animal experiments and data from accidental human exposures where available

The overall ILCR for an individual constituent is then calculated as the sum of the ILCRs for the exposure pathways (ingestion, inhalation). The ILCRs for the constituents are then summed to provide an overall ILCR for the exposure scenario.

If the ILCRs are calculated for a unit concentration in the exposure media (e.g., 1 mg/kg), the ILCR can be used to calculate the cancer screening level (CSL) for protection of human health with the equation in figure 19.

$$CSL\ (mg_{metal}/kg_{matrix}) = \frac{\text{Media Concentration } (1\ mg_{metal}/kg_{matrix}) \times \text{Target ILCR } (1\times10^{-6})}{\text{Calculated ILCR}}$$

Figure 19. Equation. Formula to calculate CSL for protection of human health.

The resulting screening level is protective of human health for cancer effects from the exposure pathways included in the assessment. The equation in figure 19 can also be used to generate screening levels representative of a single exposure pathway (such as ingestion, inhalation) by substituting the calculated ILCR for the individual pathway for the calculated ILCR for all pathways.

Calculating Direct Non-Cancerous Screening Level

Figure 20 presents the equation for calculating the HQ for direct contact with beads or bead-impacted soils through the ingestion exposure pathways.

$$HQ = \frac{\text{Intake } (mg_{metal} / kg - d)}{\text{Reference Dose } (mg_{metal} / kg - d)}$$

Figure 20. Equation. Formula to calculate HQ for direct contact.

Figure 21 presents the equation for calculating the HQ for inhalation.

$$HQ = \frac{\text{Exposure Concentration } (mg/m^3)}{\text{Reference Concentration } (mg/m^3)}$$

Figure 21. Equation. Formula to calculate HQ for inhalation.

As indicated, the equation and parameters are specific to the pathway under consideration. The reference dose is generally expressed in mg_{metal}/kg-d and the reference concentration in mg_{metal}/m^3. These reference values are based on animal experiments or exposure to humans.

The overall HQ for an individual constituent is then calculated as the sum of the HQs for ingestion and inhalation exposure. The sum of the HQs for all constituents considered in the exposure is the HI and reflects the overall potential for toxic effects from bead exposure.

If individual HQs are calculated assuming a 1 mg/kg media concentration, then the results can be used readily to determine the non-carcinogenic screening level (NCSL) using the equation in figure 22.

$$NCSL\ (mg_{metal}/kg) = \frac{\text{Media Concentration } (1\ mg_{metal}/kg) \times \text{Target HQ}}{\text{Calculated HQ}}$$

Figure 22. Equation. Formula to calculate NCSL.

The resulting screening level is protective of human health for non-cancer effects via the pathways considered in the assessment. The above equation can also be used to generate screening levels that are representative of a single exposure pathway (such as ingestion or inhalation) by substituting the calculated HQ for the individual pathway for the calculated HQ for all pathways.

Calculating Indirect Contact Screening Levels: Ingestion of Bead-Impacted Groundwater

The development of the screening level for consumption of bead-impacted groundwater is based on permissible levels of metals in groundwater for residential use, in this case the EPA Regional Screening Levels (RSL). The screening levels for protection of groundwater are based on an ILCR of 1E-06 or an HQ of 1 used for individual contaminants.

The concentration of contaminants in beads is then related to the acceptable groundwater concentration based on the assumed leach rate of metals from beads and dilution of contaminants leaching into the affected aquifer (which is the DAF). Figure 23 presents the equation used to calculate the bead groundwater screening level (GW SL).

$$GW\ SL\ (\mu g_{metal}/g_{bead}) = \frac{Target\ GW\ Conc.\ (\mu g_{metal}/L)\ x\ DAF\ x\ Measured\ Bead\ Metals\ Conc\ (\mu g_{metal}/g_{bead})\ x\ Fraction\ of\ Beads\ in\ Source\ Area}{Estimated\ Leachate\ Metals\ Conc.\ (\mu g_{metal}/L)}$$

Figure 23. Equation. Formula to calculate GW SL.

Final Bead Screening Level

The overall screening level for any medium from direct and indirect exposures is determined by comparing the screening levels based on carcinogenic effects with those for non-carcinogenic effects. The lowest value for each medium is selected as the final screening level for protection of human health within a given scenario. By evaluating each medium independently, combined exposures to soil and water are not represented in the screening levels. Because of the conservative assumptions incorporated in the evaluation, a combined exposure using the current model would lead to a highly conservative screening level. Where combined exposures to soil and groundwater are considered feasible, refinements to the modeling assumptions could provide more representative screening levels.

The calculated screening levels for each of the scenarios evaluated will include:

- **Scenario 1—Worker:** roadway marking crew employee exposed through incidental ingestion and inhalation of fugitive dust emissions.

  The overall soil screening level for individual constituents is the lowest value of:

  - CSL (ingestion, inhalation pathways combined).
  - NCSL (ingestion, inhalation pathways combined).

- **Scenario 2**—**Adult Resident:** living in close proximity to an active bead storage yard or on top of a former storage yard exposed through ingestion of contaminated drinking water, incidental ingestion, and inhalation of fugitive dust emissions.

  The overall soil screening level for individual constituents is the lowest value of:

  - CSL (ingestion, inhalation pathways combined).
  - NCSL (ingestion, inhalation pathways combined).

  The overall groundwater screening level for individual constituents is the lowest value of:

  - CSL (ingestion pathway).
  - NCSL (ingestion pathway).

- **Scenario 3—Child Resident:** living in close proximity to an active bead storage yard or on top of a former storage yard exposed through ingestion of contaminated drinking water, incidental ingestion, and inhalation of fugitive dust emissions.

  The overall soil screening level for individual constituents is the lowest value of:

  - CSL (ingestion, inhalation pathways combined).
  - NCSL (ingestion, inhalation pathways combined).

  The overall groundwater screening level for individual constituents is the lowest value of:

  - CSL (ingestion pathway).
  - NCSL (ingestion pathway).

The equations used to determine the screening level concentrations for each route of exposure within each scenario are the same; however, the parameters used for each scenario are different based on how the receptor interacts with the beads (or bead-impacted media) within each exposure pathway. Section 3 details available data included in the exposure assessment and reports modeling effort results used to set the screening levels for arsenic and lead in glass beads.

SECTION 3. MODEL-DERIVED HUMAN HEALTH SCREENING LEVELS FOR ARSENIC AND LEAD IN GLASS BEADS

INTRODUCTION

Parameter Data Available for Development of the Modeling Method

The calculations outlined in section 2 are the basis for development of the human health screening levels. Each of the calculations contains parameters that must be defined before using the developed model. This section assigns a representative value to parameters used to determine intake or exposure concentrations and, in some cases, discusses the range of parameter values considered. The screening levels are then recommended based on the developed model run with the identified parameters. The developed CSEM is used to determine the arsenic screening level, and the ALM and IEUBK models are used to determine the screening level for lead based on each evaluated exposure scenario.

It is important to acknowledge the risk associated with the uncertainty inherent in the risk assessment and to explicitly state that any preliminary calculation of human exposures to metals in glass beads released to the environment will necessarily be based on numerous assumptions and generalizations. The use of generic input parameter values provides results that might be applicable across a range of possible site locations with region-specific considerations (e.g., weather, geology). In addition, available data derived from laboratory investigations are also the source of variability in the estimated screening levels. Where applicable, key uncertainties requiring additional sources of data (or further refinement) prior to using the presented modeling methodology are discussed. Parameters specific to individual receptors, contaminants, or the beads are also presented in the following subsections.

Receptor-Specific Exposure Parameters

Each receptor has particular metabolic or behavioral parameters that must reflect the activities associated with each scenario, and these parameter values are specific to each receptor under evaluation. The population of individuals representing the receptor group is incorporated into the values selected for these parameters to provide a conservative but reasonable estimate of exposure. General parameter values available from EPA’s risk assessment guidance documents that are used to determine arsenic screening levels are summarized in table 18.

Table 18. Exposure parameters for glass bead assessment due to direct exposures.

Parameter	**Units**	**Adult Resident**	**Child Resident**	**Worker**
Ingestion Exposure				
Soil ingestion rate	mg/day	50	200	50
Bioavailable fraction	unitless	0.1	0.1	0.1
Exposure frequency	days/year	350	350	250
Exposure duration	years	30	12	25
Body weight	kg	80	45	80
Carcinogen averaging time	days	25,550	25,550	25,550
Non-carcinogen averaging time	days	10,950	4,380	9,125
Conversion Factor—Chemicals	kg/mg	0.000001	0.000001	0.000001
Inhalation Exposure				
Particulate emission factor	m^3/kg	5.39E+08	5.39E+08	5.39E+08
Volatilization factor	m^3/kg	chemical specific	chemical specific	chemical specific
Exposure frequency	days/year	350	350	250
Exposure duration	years	30	12	25
Body weight	kg	80	45	80
Carcinogen averaging time	days	25,550	25,550	25,550
Non-carcinogen averaging time	days	10,950	4,380	9,125

Notes: Exposure parameters are consistent with EPA guidance document for ingestion and inhalation exposures.

Bioavailable fraction of 10 percent is a conservative estimate based on bead measurements (see table 9).

The worker exposure is assumed to represent light industrial activities, which excludes any heavy excavation or similar work, but does include contact with the bead/soils. The residential exposure is based on an adult and child who spend time both indoors and outdoors. While outdoors, the child/juvenile is assumed to play in the soil and beads. The adult is assumed to work in the beads and soil doing landscaping or similar activities. The following subsections describe receptor-specific parameters used in the assessment, including body weight, exposure duration, exposure frequency, ingestion rates, skin surface area, and soil/bead adherence factors.

Body Weight

The body weight used in the analysis for the worker is based on a conservative estimate for adults of 80 kg.(18) Similarly, the adult resident is based on an average adult of 80 kg. The body weight of the child is assumed to be 45 kg, which is an average of both sexes from ages 6 to 18 years old.(19) The juvenile trespasser is assumed to be exposed from age 8 to 18 years, so a body weight of 45 kg is also representative of this receptor.

Exposure Duration

The exposure duration for the worker of 25 years is based on a conservative estimate of the length of employment for an adult.(20) Although it is likely that the occupational exposure duration would be significantly shorter, the conservative value is assumed to reduce the potential for underestimates of risk in the assessment.

The residential adult exposure duration is based on a conservative estimate of the length of time spend in one residence of 30 years.(4) The residential child is assumed to live in one household from ages 6 to 18, an exposure duration of 12 years. The trespasser exposure occurs for a period of 10 years, assuming that older teenagers are less likely to continue trespassing into the storage yard. Similar to the worker exposure, the conservative values are proposed for the resident to provide protective results.

Exposure Frequency

The frequency of exposure for a marking crew worker is based on a typical schedule of 5 days per week for a total of 250 days in a year (assuming 2 weeks of vacation). However, the application of roadway markings is a weather -dependent job, and work is only conducted on days with low wind and no precipitation. In some areas of the country, weather conditions may prevent work on all but approximately 120 days each year. On days that are not suitable for applying markings, workers may be employed with the removal of old markings. Therefore, marking crew workers would be on the job for 250 days each year; however, the balance between the time spent applying lines and removing old lines would differ regionally.

A resident is typically assumed to be at home for all but 2 weeks each year, or a total of 350 days annually. Although it is likely that the exposure frequency would be significantly shorter, the conservative value is proposed. The trespasser is assumed to access the bead storage yard five times each week, for a reasonably conservative exposure frequency of 250 days each year.

Ingestion Rate

The ingestion rates of soil and water are specific to each receptor. The soil pathway applies to both marking crew worker and residential exposures, but not to the manufacturing worker. The water ingestion pathway is only applied to the residents who drink contaminated well water (assuming workers drink from municipal water systems).

Soil/Bead Ingestion: The soil/bead ingestion rate is based on the amount of soil/beads adhered to the hands, which is subsequently ingested throughout the day. It is assumed that beads behave similarly to soil, and that the concentration of contaminants in soil/beads that are ingested are consistent with the relative concentrations in soil (i.e., no preferential ingestion of highly contaminated particles).

For workers and adult residents, the average ingestion rate is assumed to be 50 mg/day.(18) It is assumed that the worker is engaged in light industrial activities and does not do any excavation work that might increase contact with soil and thereby increase the ingestion rate. Residents contact soil/beads while engaged in landscaping or other similar activities.

The average child ingestion rate of 200 mg/day is used in the assessment.(19) A resident child may exhibit pica, which is a condition that results in excessive soil ingestion (approximately 2,000 mg/day). However, the pica receptor is highly unlikely and, therefore, is not used as the basis for child soil ingestion.

Water Ingestion: The water ingestion rate applies only to residents who use potable water from a well that extracts groundwater that has been affected by a bead storage yard. The resident adult is assumed to ingest groundwater at a rate of 2.7 L/day on average.(18) Similarly, it is assumed that the child ingests water at the same rate as an adult.(19)

Contaminant and Site-Specific Exposure Parameters

Parameters that are metal specific are used to quantify exposure mechanisms that are dependent on the properties of the contaminant under evaluation. The exposure equations reflect the particular rates of uptake into humans and/or food products, based on the magnitude to which constituents may move through the human body or migrate from soil to other media. Site-specific parameters represent hydrogeology or climate conditions that affect the calculation of screening levels.

The following subsections describe contaminant-specific and site-specific parameters used in the assessment, including the gastrointestinal absorption factor, particulate emission factor (PEF), groundwater transport factors, bioavailability factors, environmental half-life, and toxicity factors.

Gastrointestinal Absorption Factor

The gastrointestinal absorption factor describes the absorption rate of contaminants that are ingested in beads through the gastrointestinal system. The bioaccessible fraction of arsenic and lead in glass beads reflects a wide range of values and is a source of uncertainty in the proposed modeling methodology. In the presented model, a gastrointestinal adsorption factor of 0.003 is used.(21)

Particulate Emission Factor

The PEF is used to determine the dust load in the air and the resulting air concentration for the exposed receptors. The dust load is dependent on soil, weather, and activity factors. The equations used in the PEF calculation are presented in figure 24 and figure 25.

$$PEF\ (m^3/kg) = \frac{Q/C \times 3600\ (seconds/hour)}{0.036 \times (1-V) \times (U_m/U_t)^3 \times F(x)}$$

Figure 24. Equation. Formula to calculate PEF.

Where:
Q/C = inverse of mean concentration at center of source (g/m^2-s per kg/m^3).
V = fraction of vegetative cover (unitless).
U_m = mean annual wind speed (m/s).
U_t = equivalent threshold value of wind speed at 7m height (m/s).
F(x) = experimentally derived function dependent on Um/Ut (unitless).

Figure 25 presents the formula for deriving the value of Q/C.

$$Q/C = A \times \exp\frac{[\ln(A_{site})-B]^2}{C}$$

Figure 25. Equation. Formula for deriving the inverse of the mean concentration at the center of the source (Q/C).

Where:
A, B, C = experimentally derived constants based on air dispersion modeling for specific climate zones.
A_{site} = area of contamination (acres).

Table 19 presents the results of the PEF calculation, which describe the emission rate of particles that have a diameter of 10 μm or less. (18)

Groundwater Transport Factors

The groundwater transport parameters are used to describe the lateral migration of contaminants that have been leached to groundwater. In general, it is assumed that the concentration of contaminants in the leachate is the concentration that reaches the groundwater. This assumption results in conservative groundwater concentrations because some contaminants will likely not reach groundwater but will remain sorbed to particles in the vadose zone. Once they reach the groundwater, contaminant transport may be retarded relative to groundwater flow within the aquifer or may disperse significantly relative to the advective motion of the aquifer. Both of these mechanisms would tend to reduce the contaminant concentration in groundwater. Groundwater transport factors also have a site-specific component related to the site hydrogeology and weather conditions.

To be conservative, a DAF of 10 is used to evaluate contaminant migration through groundwater. Calculated DAFs that range over several orders of magnitude are likely for sites throughout the United States. The DAF is linearly related to the screening level for ingestion of groundwater in the residential exposure scenarios, and a tenfold increase in DAF would increase the screening level by an order of magnitude. Therefore, the DAF is a source of a significant and key uncertainty that needs to be carefully considered for each specific site when using the current modeling methodology. In addition, if a residential groundwater well was screened across both a contaminated and uncontaminated zone in a bead-impacted aquifer, further dilution of groundwater contaminants would occur within the well.

Table 19. Calculation of particulate emission factor.

Scenario	Parameters for Dispersion Factor Calculation			Q/C Dispersion Factor (g/m^2-s per kg/m^3)	Measured Average Wind Speed at Elevation of 7 m (Um) (m/s)	Threshold Friction Velocity (m/s)	Equivalent Value of Threshold Wind Speed at 7 m (Ut) (m/s)	Parameter for Determination of Equation Describing f(x) (unitless)	Function f(x) Derived from Um/Ut (unitless)	Particulate Emission Factor (m^3/kg)
	A	B	C							
Nationwide	16	19	216	82.9	4.69	0.21	11.36	2.10	0.22	5.39E+08
Northeast (Hartford, CT)	13	19	215	65.4	3.80	0.17	9.20	2.10	0.22	4.25E+08
Southeast (Atlanta, GA)	15	18	204	71.6	4.10	0.19	9.93	2.10	0.22	4.65E+08
Central (Minneapolis, MN)	16	19	216	82.9	4.70	0.21	11.38	2.10	0.22	5.39E+08
Northwest (Boise, ID)	11	20	225	63.0	3.90	0.18	9.45	2.10	0.19	4.61E+08
Southwest (Phoenix, AZ)	10	19	212	53.5	2.80	0.13	6.78	2.10	0.19	3.92E+08

Notes**:** Calculation based on equations presented in the EPA Soil Screening Guidance and supporting sources.(14, 15)

Values for Minneapolis, MN, were found to represent the 90th percentile of results derived from air dispersion modeling for 29 cities in the United States.

Variables for site area, fraction of vegetative cover, sand percentage in soil, and measured annual average wind speed are user-entered values. All other parameters are calculated as described in EPA.(14) Parameters A, B, and C for the Dispersion Factor Calculation were generated by EPA from atmospheric modeling simulations for sites across the country and best fit regression analysis of the results.

Table assumes a 1-acre source area with no ground cover and a roughness height of 0.1 cm (open ground).

Bioavailability Factors

The bioavailability, biotransfer, and bioaccumulation factors are used to describe the contaminants' availability to biological organisms and the potential for concentration into food items such as vegetables, livestock, or fish. Recent laboratory analysis of the bioaccessibility of arsenic and lead in glass beads, as presented in table 9, indicate an average for bioaccessible lead of 1.8 ppm compared with a total lead average of 71 ppm, or an average bioaccessible fraction of approximately 2.5 percent. Table 20 presents the calculated bioaccessible fraction, which ranged from 0.06 to 16 percent, indicating significant variability in the parameter. No extractable or bioaccessible arsenic was observed.

Table 20. Extractable and bioaccessible fraction of arsenic and lead in bead samples expressed as a percentage of the total content.

Bead Group	Percentage of Total Lead as Extractable	Percentage of Total Lead as Bioaccessible
AA	0.48	0.13
AC	3.36	16.36
BD	0.31	0.15
BE	0.79	0.11
BI	3.29	1.70
DA	0.14	0.06
DB	NA	NA
DC	NA	NA
DD	NA	NA
EA	NA	NA
FH	0.43	0.26
GA	NA	NA
GB	NA	NA
GC	NA	NA
GD	NA	NA
Overall Average	1.3	2.7

NA = not available because results were below detection limits

Environmental Half-Life

The environmental half-life is a parameter that describes the persistence of glass beads once they are released to the environment and is considered site specific. It is assumed that the glass beads are extremely stable and remain intact under typical environmental conditions, with the exception of beads removed by mechanicals means that might result in crushing of beads. Beads removed from the base material (paint, thermoplastic) by vehicle traffic are assumed to be intact, as are beads released into a storage yard.

Toxicity Factors

The toxicity factors are used to define, for each constituent, the potential for adverse health effects based on the magnitude of exposure for each receptor and pathway for each constituent. Contaminant speciation and complexation are a significant consideration in assigning a value for toxicity parameters.

Arsenic speciation in leachate from beads was measured and indicated that the dominant species is arsenic (V) in laboratory experiments (table 13). Although specific toxicity data are not available for particular arsenic species, studies have indicate that arsenic (III) is a generally more toxic form of arsenic. The full toxicological profile for arsenic is available from the Agency for Toxic Substances and Disease Registry (ATSDR) at http://www.atsdr.cdc.gov/toxprofiles/tp2.pdf. The ATSDR profile for lead is available at http://www.atsdr.cdc.gov/toxprofiles/tp13.pdf. Table 21 summarizes the toxicological parameters used in this study's modeling approach for arsenic.

Bead-Specific Exposure Parameters

Parameters that are bead specific reflect exposure mechanisms that depend on the properties of the beads under evaluation. The following subsections describe bead-specific parameters used in the assessment, including the concentration of the beads in the bead/soil source material, the concentration of metals in beads, and the leaching rate of metals from the glass beads.

Mass of Beads in Bead/Soil Source

The quantity of beads present in the environment as a result of bead loss during storage and application is an important parameter in the risk evaluation. The fraction of beads in the source material affects the magnitude of the exposure to humans. The following section presents estimates of bead loss, as well as field measurements of the bead fraction observed at an active bead storage facility.

Table 21. Toxicity data for glass bead assessment.

Constituent	Chemical Abstracts Service (CAS) No.	Exposure Point Concentration (EPC)	Units	Oral Reference Dose (RFDo) (mg/kg-d)	Absorbed Dermal Reference Dose (ADRFD) (mg/kg-d)	Inhalation Reference Concentration (RFCi) (mg/m^3)	Oral Slope Factor (SFO) (mg/kg-d)$^{-1}$	Inhalation Unit Risk (IUR) (μg/m^3)$^{-1}$	Inhalation Slope Factor (SFI) (mg/kg-d)$^{-1}$
Arsenic (at 54 ppm)	7440-38-2	22.8	mg/kg	3.00E-04	1.00E-02	1.50E-05	1.50E+00	4.30E-03	NA
Arsenic (at 62 ppm)	7440-38-2	26.1	mg/kg	3.00E-04	1.00E-02	1.50E-05	1.50E+00	4.30E-03	NA

NA = not applicable

Notes: Toxicity data from the EPA(21)

EPC—exposure point concentration in bead/soil assuming 42-percent beads in the source.

Arsenic concentrations of 54 and 62 ppm are the arithmetic average and 95-percent upper confidence limit (UCL95%), respectively.

Table 22 provides available data for estimating the bead concentrations in environmental media for various bead loss scenarios. The estimates presented in table 22 are based on the bead workflow elements and release potential outlined in table 17. The release potential values have been converted from English to SI units for use in the model equations.

The estimated bead concentration in the soil of a storage yard assumes that an area of 4,050 m^2 is used to store and transfer beads and that the beads are mixed into the soil to a depth of 150 mm. If approximately 4.5 kg were spilled daily for 250 days each year, a total of 1,125 kg of beads would be mixed into the soil annually, resulting in a bead concentration in soil of approximately 1,500 ppm after 1 year.

Bead loss to the environment may also occur during application of the beads onto pavement markings. During application, bead loss is expressed as a percentage of the total beads applied. The total bead load applied is a regulated quantity in some states. Table 23 presents an estimate of bead mass loss rate in kg/km, based on typical pavement marking paint and bead application rates. The application scenarios are shown in English units, with the final bead mass loss rate converted to SI units. Actual bead mass loss depends on the number and width of the pavement markings, operational characteristics of the application equipment, speed of application, and other factors.

The bead load estimate above is based on a four-lane undivided highway with a central turning lane, and the following 6-inch lines:

- Left shoulder—continuous.
- Lane 1 and 2 divider—dashed.
- Left double line for central turn lane—continuous/dashed.
- Right double line for central turn lane—continuous/solid.
- Lane 3 and 4 divider—dashed.
- Right shoulder—continuous.

Based on worker interviews and field observations, typical bead loss percentages are assumed to be 15 percent of the applied load. With a total estimated bead application rate of 1,150 lb/mi (see table 17), the resulting 15 percent bead loss rate is approximately 49 kg/km. The quantity of beads lost to the roadside can be used to provide an estimate of soil concentrations at residential locations near roads. Assuming that all beads are blown to one side of the road, and that they are mixed into the soil to a depth of 50 mm and to a width beside the road of 2 m, then the total mixing soil volume is 100 m^3/km. For a typical silty loam soil with a density of approximately 1.28 g/cc or 1.28×10^6 g/m^3 or 1,280 kg/m^3, the mixing mass of soil for each kilometer is 128,000 kg. The resulting bead concentration in the roadside soil would be 49 kg of beads in 128,000 kg of soil or 385 ppm.

Table 22. Estimates of bead loading to soil per year.

Scenario (Soil Location)	Affected Area (m^2)	Affected Depth (m)	Soil Density (kg/m^3)	Soil Mass (kg)	Typical Bead Loss (kg/event)	Release Frequency (events/yr)	Annual Bead Mass Released (kg)	Estimated Bead Concentration in Soil (kg_{bead}/kg_{soil})	Estimated Bead Concentration in Soil (mg_{bead}/kg_{soil} or ppm)
Storage Yard	4,050	0.15	1,280	777,600	4.5	250	1,125	0.0015	1,462
Rural Roadside During Application	2,000	0.05	1,280	128,000	49	1	49	0.0004	385
Roadside Due to Line Degradation	2,000	0.05	1,280	128,000	69	1	69	0.0005	538
Roadside Total	2,000	0.05	1,280	128,000	118	1	118	0.0009	923

Notes: Assumes storage yard area is approximately 1 acre or 4,050 m^2.

Assumes area affected for the roadside scenario is approximately 2 m wide, approximately 50 mm deep and 1 km long.

Soil density is that for silty loam (1,280 kg/m^3).

Bead mass for the storage yard assumes 4.5 kg per day over 250 days each year, or an annual release of 1,125 kg.

Bead mass for the roadside during application assumes 1,150 lb/mi application rate for six continuous 6-inch-wide lines with a bead loss of 15 percent the release is 175 lb/mi.

Bead mass for line degradation assumes 25 percent of the bead load on the line (85 percent of total applied load) is released in a year, or approximately 69 kg/yr per kilometer of roadway.

Bead mass for the total roadside is sum of the releases from the original line application and line degradation, per kilometer of road, assuming both occur during the same year.

Table 23. Estimated glass bead application and loss rate for line applications.

Line Width (inches)	Paint Volume Application Rate (gallon/line-mi)	Bead Application Concentration (lb/gal)	Bead Line Mass Application Rate (lb/line-mi)	Number of Lines per Roadway	Bead Roadway Mass Application Rate (lb/roadway-mi)	Bead Loss Percentage (%)	Bead Mass Loss Rate—English Units (lb/mi)	Bead Mass Loss Rate—SI Units (kg/km)
4	12	10	120	6	720	15	108	30
6	16	12	192	4	770	15	115	32
6	16	12	192	6	1,150	15	175	49

Notes**:** All quantities are estimates based on data from several State transportation departments. Site-specific information is used where available to refine the estimates.

In general, lines are replaced when reflectivity has dropped to 25 percent of the original value, which is assumed to occur within 3 years within the model calculations. Therefore, during 1 year, approximately 25 percent of the original line load will be released to the environment. For the example presented in table 22, the total applied load is 324 kg/km, with 275 kg/km adhering to the lines and 49 kg/km lost to the roadside initially. An additional loss of approximately 69 kg/km may occur over a period of a year through line degradation.

Field investigations have measured the fraction of beads in soil at one bead storage yard to provide perspective on the estimated bead concentrations (table 15). The storage yard has been used for at least 20 years and indicated a range of bead fractions (by weight) of 20 percent to approximately 78 percent and averaging 42 percent, or 420,000 mg/kg. The field measurements indicate that the estimated bead loss calculation presented in table 22 may be an underestimate by approximately an order of magnitude. However, it is not clear to what depth the beads were mixed into the soil during field measurements, which could account for the discrepancy.

In actuality, the mass balance of contaminants in the beads has not been included in the modeling methodology. The methodology currently proposes that the total mass of metals in the released beads is available for both direct contact and migration to groundwater individually. In reality, the bead mass lost to leaching would no longer be available for ingestion, dermal contact, or inhalation, thereby reducing the exposure concentration of metals for the direct contact receptor. Similarly, bead mass removed from the marking crew storage yards by wind scour or ingestion would no longer be subject to leaching. These conservative assumptions provide an additional margin of protectiveness in the calculations.

Concentration of Metals in Glass Beads and Leaching Potential

The evaluation of long-term exposures requires an understanding of the long-term releases from beads to the environment. Most significantly, metals may migrate from glass beads through interactions with precipitation and migrate to the groundwater. The modeling of bead leaching over a period of time similar to the long-term exposure duration of the receptors provides the most representative assessment of risk.

In the environment, beads are incorporated into the soil matrix, and any interactions with infiltrating water would be complex and include partitioning of contaminants among the beads, soil, and water in the pore spaces of the soil/bead matrix. As contaminants in beads go into solution, they may interact with soil particles and adsorb to the surface. Over time, contaminants may repeat this process, with the general effect of retarding the movement of some portion of the contaminants from freely moving with the infiltrating water through the soil column and into the underlying groundwater system. In addition, some portion of the contamination will remain in the soil matrix and never reach the groundwater. For calculation of groundwater protection screening levels, it is conservatively assumed that contaminants leaching from beads are not retained or retarded by the soil matrix, and instead travel unimpeded to a groundwater aquifer that is used for drinking water.

To determine long-term groundwater concentrations, it is important to understand the magnitude and rate of contaminant leaching from beads. The residential receptor is assumed to ingest groundwater over a period of 30 years; therefore, an average concentration over that period of time is most representative of the exposure scenario.

The results of leaching experiments may be used to estimate exposure over a lifetime by assuming that the leachable mass in beads enters the environment during a 1-year period. Experimental results may also determine whether beads in the environment longer than 1 year are inert and are not a source of further contamination to groundwater.

Calculating the groundwater concentration requires an estimate of either the mass of contamination entering the aquifer, which can be based on the mass of contaminants that can be leached, or the concentration of contaminants in the leachate. These estimates can be made through general assumptions regarding the leaching potential of beads or through experimental analysis. For the development of groundwater screening levels, the mass of contamination leaving the beads and entering groundwater on an annual basis may be calculated from the experimental data, which are discussed in the following sections.

An additional consideration is the physical location of the bead contamination within the bead structure. If contamination is coating the bead surface, it may leach quickly, leading to high initial water concentrations that quickly decline. Contamination within the bead matrix may provide lower initial water concentrations that persist longer. Continuing laboratory studies may provide data to clarify leaching dynamics.

The leaching rates used in the evaluation are necessary to describe the following processes: leaching rate of contaminants from glass beads to groundwater, leaching rate of contaminants to soil, and leaching of contaminants in a mixture of soil and beads to groundwater. Two older studies are available for determining the leaching rates of metals from glass beads: the TAMU study published in 2011 and NJIT/RU study.(22, 23) The TAMU study evaluated the leachability of metals from glass beads present in an up-flow column system as a function of pH, short-term exposures to high-intensity ultraviolet light, short-term exposures to high temperatures, and particle size. The NJIT/RU study also evaluated leaching in batch reactors as a function of pH and particle size. In addition, the NJIT/RU study evaluated leaching using the simulated precipitation leaching procedure and toxicity characterization leachate procedure, and a long-term leaching experiment conducted over a period of 160 days.

Section 2 of this report presents findings of the most recent study conducted on a large sample of beads from across the United States to provide a more representative study of beads actually in use on roads. Laboratory characterization of the State transportation department provided beads indicated a total arsenic concentrations ranging from 11 to 82 ppm with an overall average of 54 ppm. Total lead ranged from 3 to 199 ppm, with an overall average of 71 ppm. Statistical analysis of these datasets with EPA software is summarized in table 24 for arsenic and lead.(24) The 95-percent upper confidence intervals for arsenic and lead are 62.14 and 118.6 ppm, respectively. Estimates of human health risk are presented for exposure to both the mean and 95-percent upper confidence limit (UCL95%) concentrations in source materials for comparison.

Table 24. Summary of statistics for bead analysis.

Parameter	Arsenic	Lead
Minimum	11	3
Maximum	82	199
Arithmetic Average	54.4	71.47
UCL95%	62.14	118.6
Distribution	Normal	Gamma

Notes: All concentrations in ppm.
UCL95% is the 95-percent upper confidence limit on the mean concentration.
Statistics are based on the average concentrations in glass beads (table 7).
The EPA software ProUCL version 4.1, was used to generate the statistics.(24)

The potential leaching of metals was evaluated by comparing the total metals analysis to the extractable metals in laboratory experiments. Similarly, the bioaccessible fraction of metals was determined by comparing total and bioaccessible measurements. Extractable arsenic was not detectable in all samples and was similarly not detectable in the bioaccessibility analysis. Extractable lead was measured at up to 3.4 percent of the total measurement, and bioaccessible concentration was up to 16.4 percent of the total (see table 20). The time series analysis of column leaching studies indicated that lead concentrations were all below detection, and arsenic leachate concentrations were below detection within 48 hours (table 25 and table 26). The laboratory data indicate that there is a low likelihood of significant leaching of arsenic and lead from pavement-marking beads.

Table 25. Summary of TTI/TAMU leaching studies for arsenic—December 2012.

Arsenic Data (ppm)		**Sampling Time (hours)**							
Bead Group	**Total Arsenic by KOH**	**0**	**1**	**2**	**4**	**8**	**12**	**24**	**48**
AA	130	0.59	0.12	0.15	0.17	BQL	0.14	0.20	ND
BD	138	0.13	BDL	BDL	BDL	BDL	0.12	0.29	ND
BE	74	BDL	BDL	ND	ND	ND	BDL	0.18	ND
BI	54	BDL	BDL	ND	BDL	BDL	BQL	0.13	ND
DA	129	BDL	ND	ND	BDL	BDL	BDL	ND	ND
DB	130	BDL	BDL	ND	ND	ND	BDL	0.14	ND
DC	146	0.27	BDL	BDL	BDL	BDL	BDL	BDL	ND
DD	122	BDL	BDL	ND	ND	ND	BDL	BDL	ND
EA	97	0.13	BDL	ND	BDL	BDL	ND	ND	ND
FH	45	0.12	ND	ND	ND	ND	ND	ND	ND
GA	57	0.10	ND	ND	ND	ND	ND	ND	ND
GB	55	0.16	ND	ND	ND	ND	ND	ND	ND
GC	45	0.26	BDL	ND	ND	ND	ND	ND	BDL
GD	56	0.14	BDL	BDL	ND	ND	ND	ND	ND

KOH = potassium hydroxide
ND = not detected
BDL = below detection limit
BQL = below quantitation limit

Table 26. Summary of TTI/TAMU leaching studies for lead—December 2012.

Lead Data (ppm)		Sampling Time (hours)							
Bead Group	**Total lead by KOH**	**0**	**1**	**2**	**4**	**8**	**12**	**24**	**48**
AA	21	ND	ND	ND	ND	ND	ND	ND	ND
BD	17	BQL	ND	ND	ND	ND	ND	ND	ND
BE	6	ND	ND	ND	ND	ND	ND	ND	ND
BI	4	BQL	ND	ND	ND	ND	ND	ND	ND
DA	8	BQL	BDL	ND	BDL	ND	ND	ND	ND
DB	6	ND	ND	ND	ND	ND	ND	ND	ND
DC	10	BQL	ND	ND	ND	ND	ND	ND	ND
DD	ND	ND	ND	ND	ND	ND	ND	ND	ND
EA	ND	ND	ND	ND	ND	ND	ND	ND	ND
FH	124	BQL	ND	ND	ND	ND	ND	ND	ND
GA	ND	ND	ND	ND	ND	ND	ND	ND	ND
GB	20	ND	ND	ND	ND	ND	ND	ND	ND
GC	8	ND	ND	ND	ND	ND	ND	ND	ND
GD	66	ND	ND	ND	ND	ND	ND	ND	ND

KOH = potassium hydroxide
ND = not detected
BDL = below detection limit
BQL =below quantitation limit

RISK EVALUATION RESULTS

The estimate of human health risk from glass bead exposures was based on the residential and worker scenarios. Exposure pathways included in the evaluation were incidental ingestion and inhalation of re-suspended particulates. Although the laboratory data indicate a low likelihood of metal leaching from beads, the groundwater ingestion pathway has been evaluated for completeness.

Toxicity data used in the risk evaluation of arsenic are presented in table 21, and the results of the risk evaluation for beads in soil are presented in table 27. The exposure of receptors to arsenic at the average concentration resulted in risks of 8.8E-7, 2.5E-6, and 5.4E-7 for the adult, child, and worker, respectively. All carcinogenic risks are within the EPA acceptable risk range of E-6 to E-4. The majority of risk is via the ingestion pathway with insignificant risk owing to inhalation. The hazards for arsenic were all below the threshold hazard of 1, indicating a low likelihood of adverse human health effects due to exposure to beads released to the environment. These calculations were based on a source that was 42-percent beads.

Also presented in table 27 are results for exposures at the UCL95% arsenic concentration of 62 ppm for comparison. All risks and hazards are within the acceptable range and are not likely to present a health hazard. These calculations also assumed that the source material was 42-percent glass beads in the soil.

The potential for leaching of arsenic to groundwater is evaluated in table 28. Laboratory experiments yielded conflicting results regarding the leaching of arsenic and lead from glass beads. The risk evaluation was based on the most conservative leachate concentration observed (speciated arsenic (V) at 15 μg/L). Additional conservatism is included in the calculation because these leachate concentrations were assumed to persist for the duration of the exposures (up to 30 years in the case of the adult resident). The estimated groundwater concentration of 0.63 μg/L is below the Federal Maximum Contaminant Level of 10 μg/L but exceeds the EPA RSL of 0.045 μg/L. The estimated risk associated with arsenic in groundwater was 1.4E-5, which is within the acceptable risk range, even with the inclusion of conservative assumptions in the calculations. The results indicate that adverse human health impacts are unlikely via the groundwater pathway.

Table 27. Summary of glass bead risks for arsenic.

Exposure Pathway	Adult Resident		Child Resident		Industrial	
	ILCR	HQ	ILCR	HQ	ILCR	HQ
Arsenic (54 ppm)						
Bead Ingestion	8.8E-07	4.6E-03	2.5E-06	3.2E-02	5.2E-07	3.3E-03
Bead Inhalation	6.2E-11	2.7E-03	2.5E-11	3.0E-03	9.8E-11	1.9E-03
Totals	*8.8E-07*	*7.3E-03*	*2.5E-06*	*3.5E-02*	*5.2E-07*	*5.2E-03*
Arsenic (62 ppm)						
Bead Ingestion	1.0E-06	5.2E-03	2.9E-06	3.7E-02	6.0E-07	3.7E-03
Bead Inhalation	7.1E-11	3.1E-03	2.8E-11	3.4E-03	1.1E-10	2.2E-03
Totals	*1.0E-06*	*8.3E-03*	*2.9E-06*	*4.0E-02*	*6.0E-07*	*5.9E-03*

ILCR = incremental lifetime cancer risk
HQ = hazard quotient
ppm = parts per million
Notes: Beads were assumed to represent 42 percent of the bead/soil source.
Arsenic concentrations of 54 and 62 ppm are the arithmetic average and UCL95%, respectively (table 24).

Table 28. Estimated groundwater risk for arsenic.

Constituent	MCL (μg/L)	Tap Water RSL (μg/L)	Concentration in Leachate (μg/L)	Estimated Groundwater Concentration (μg/L)	Estimated Groundwater Risk
Arsenic	10	0.045	15	0.63	1.40E-05

Notes: Tap water RSL is based on carcinogenic effects to an adult/child at a risk level of 1E-6.

Maximum contaminant level (MCL) is a federally promulgated standard that accounts for economic and human health considerations.

Concentration in leachate is an upper bound based on speciated arsenic analysis of bead sample DC. The majority of samples indicated < 0.7 μg/L of extractable arsenic.

Estimated groundwater concentration assumed that the bead source is diluted to 42 percent of the soil matrix and a DAF of 10 in the aquifer.

Groundwater concentration is calculated as: Leachate Conc (μg/L) × 0.42 × (1/10) = 0.63 μg/L.

Estimated groundwater risk is based on the tap water RSL, and is calculated as:
Tap water RSL (μg/L) × Groundwater Concentration (μg/L)/1E-6.

Table 29 presents the bead screening levels for arsenic based on the exposure scenarios and pathways evaluated. Results are presented assuming a source that is 100-percent beads, as well as a source that is 42-percent beads diluted with uncontaminated soil. Screening levels are generated based on both carcinogenic and non-carcinogenic effects, with the lower value selected as the final screening level. For all scenarios (residents and industrial) the carcinogenic exposure via bead ingestion was the most significant pathway. Screening levels based on non-carcinogenic exposures were approximately an order of magnitude less stringent than those for carcinogenic effects. For an undiluted source, screening levels for the adult, child, and industrial worker were 252, 90, and 421 ppm, respectively. When considering a source that is 42-percent beads, the screening levels are 600, 220, and 1,000 ppm, respectively. The final screening level recommendation of 220 ppm is based on a child exposure to source material that is 42-percent beads.

The evaluation of lead used EPA models for adults and children as presented in table 30 and table 31. The exposures to lead and resulting blood lead levels are compared with the acceptable level of 10 μg of lead per dL of blood. The ALM indicated a blood lead concentration of approximately 1.9 μg/dL, and the ALM calculated screening level was 580 ppm. The IEUBK model for child lead exposure estimated a blood lead level of ~0.6 μg/dL, and the IEUBK calculated screening level was > 1,000 ppm. The adult and child lead modeling indicates that adverse health effects are not likely due to lead exposures. These results are based on the UCL95% concentration of 118 ppm for lead in undiluted beads, which represents a conservative exposure that is unlikely to be exceeded.

Table 29. Summary of glass bead screening levels for arsenic.

Exposure Pathway	Adult Resident			Child Resident			Industrial		
	Carcinogenic	Non-Cancer	Screening Level	Carcinogenic	Non-Cancer	Screening Level	Carcinogenic	Non-Cancer	Screening Level
Undiluted Bead Source									
Ingestion	2.6E+02	5.0E+03	2.6E+02	9.1E+01	7.0E+02	9.1E+01	4.4E+02	7.0E+03	4.4E+02
Inhalation	3.7E+06	8.4E+03	8.4E+03	9.2E+06	7.7E+03	7.7E+03	2.3E+06	1.2E+04	1.2E+04
Screening Level	*2.6E+02*	*3.1E+03*	***2.6E+02***	*9.1E+01*	*6.5E+02*	***9.1E+01***	*4.4E+02*	*4.4E+03*	***4.4E+02***
Diluted Bead Source (42% beads)									
Ingestion	6.2E+02	1.2E+04	6.2E+02	2.2E+02	1.7E+03	2.2E+02	1.0E+03	1.7E+04	1.0E+03
Inhalation	8.7E+06	2.0E+04	2.0E+04	2.2E+07	1.8E+04	1.8E+04	5.6E+06	2.8E+04	2.8E+04
Screening Level	*6.2E+02*	*7.5E+03*	***6.2E+02***	*2.2E+02*	*1.5E+03*	***2.2E+02***	*1.0E+03*	*1.0E+04*	***1.0E+03***

Notes: All units are ppm.
Values in bold are the final screening values.
Carcinogenic target incremental lifetime cancer risk (ILCR) was 1.0E-5.
Target HI was 1.0.
Beads were assumed to represent 42 percent of the bead/soil source (table 15).

Table 30. Calculations of adult blood lead concentrations.

Variable	Description of Variable	Units	GSDi and PbBo from Analysis of NHANES 1999–2004	GSDi and PbBo from Analysis of NHANES III (Phases 1&2)
PbS	Soil lead concentration	µg/g or ppm	118	118
$R_{fetal/maternal}$	Fetal/maternal PbB ratio	—	0.9	0.9
BKSF	Biokinetic Slope Factor	µg/dL per µg/day	0.4	0.4
GSD_i	Geometric standard deviation PbB	—	1.8	2.1
PbB_0	Baseline PbB	µg/dL	1.0	1.5
IR_S	Soil ingestion rate (including soil-derived indoor dust)	g/day	0.050	0.050
IR_{S+D}	Total ingestion rate of outdoor soil and indoor dust	g/day	0.050	0.500
W_S	Weighting factor; fraction of IR_{S+D} ingested as outdoor soil	—	0.750	0.750
K_{SD}	Mass fraction of soil in dust	—	0.500	0.500
$AF_{S,\,D}$	Absorption fraction (same for soil and dust)	—	0.17	0.17
$EF_{S,\,D}$	Exposure frequency (same for soil and dust)	days/yr	350	350
$AT_{S,\,D}$	Averaging time (same for soil and dust)	days/yr	365	365
PbB_{adult}	**PbB of adult worker, geometric mean**	**µg/dL**	**1.4**	**1.9**
$PbB_{fetal,\,0.95}$	95th percentile PbB among fetuses of adult workers	µg/dL	3.3	5.7
PbB_t	Target PbB level of concern (e.g., 10 µg/dL)	µg/dL	**10.0**	**10.0**
$P(PbB_{fetal} > PbB_t)$	**Probability that fetal PbB > PbB_t, assuming lognormal distribution**	**Percent**	**0.0%**	**0.8%**

NHANES = National Health and Nutrition Examination Survey
— indicates unitless
Notes: Absorption fraction is based on maximum bioaccessible lead measurements for bead group AC.
Source: http://www.epa.gov/superfund/lead/products.htm#alm
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Table 31. Calculations of adult lead screening levels.

Variable	Description of Variable	Units	GSDi and PbBo from Analysis of NHANES 1999–2004	GSDi and PbBo from Analysis of NHANES III (Phases 1&2)
$PbB_{fetal, 0.95}$	95th percentile PbB in fetus	µg/dL	10	10
$R_{fetal/maternal}$	Fetal/maternal PbB ratio	—	0.9	0.9
BKSF	Biokinetic Slope Factor	µg/dL per µg/day	0.4	0.4
GSD_i	Geometric standard deviation PbB	—	1.8	2.1
PbB_0	Baseline PbB	µg/dL	1.0	1.5
IR_S	Soil ingestion rate (including soil-derived indoor dust)	g/day	0.050	0.050
$AF_{S, D}$	Absorption fraction (same for soil and dust)	—	0.16	0.16
$EF_{S, D}$	Exposure frequency (same for soil and dust)	days/yr	350	350
$AT_{S, D}$	Averaging time (same for soil and dust)	days/yr	365	365
PRG	**Screening Level**	**ppm**	**1,051**	**580**

NHANES = National Health and Nutrition Examination Survey
— indicates unitless
Notes: Absorption fraction is based on maximum bioaccessible lead measurements for bead group AC,
Source: http://www.epa.gov/superfund/lead/products.htm#alm

GUIDANCE FOR DECISIONMAKING

The risk evaluation methods outlined in this report have been developed to provide reasonably conservative screening levels for protection against adverse human health effects. The exposure evaluation has documented the current understanding of potential human interaction with beads during use by workers and after release to the environment.

The determined screening levels for arsenic and lead are above the current maximum content of 200 ppm arsenic and 200 ppm lead adopted in MAP-21, the Moving Ahead for Progress in the 21st Century Act. Therefore, the existing legislation is determined to be protective of human health when all currently available data are considered.

The analysis includes a number of conservative assumptions:

- Bead leaching observed over 48-h laboratory experiments are representative of long-term releases from beads in the environment.
- Bead concentrations are represented by using UCL95% statistics from the laboratory results.
- Bioaccessible and extractable fractions of metals from beads are represented by upper bound estimates from the laboratory results.
- The fraction of beads in the bead/soil matrix are represented by the average observed in the field.

Environmental exposures are likely to be lower than those estimated in this risk evaluation. Because the application of conservative assumptions does not result in unacceptable risk to human health, less intense exposures would be similarly protective.

Although current risk levels are minimal, field observations of bead workflow processes did identify easy-to-implement practices that would further reduce exposure. In the occupational setting, employees were observed handling the beads without gloves or masks. Concern was raised during the visits and during the model peer-review process that employees may be exposed to high levels of silica from bead dust that could lead to silicosis. Wearing gloves and respirators to protect against potential silica exposures would have the added benefit of reducing exposure to arsenic and lead.

The model also predicted potential concern regarding the impact of bead storage facilities on residential groundwater owing to leaching of arsenic and lead from the beads that may occur within some climates. Current practices of bead storage prevent rainfall from leaching arsenic and lead from stored beads to groundwater. Efforts to reduce bead spillage during transfer would also reduce the likelihood that bead contaminated media could affect groundwater. Existing locations with long-term histories of bead (and or cullet) storage and transfer may present a challenge to groundwater where shallow groundwater tables are present.

Although application of the beads does result in bead loss to the surrounding environment, long line applications in which bead loss may reach up to 30 percent under poor application practices or conditions does not appear to present a risk to human health or the environment. During long line applications (roadway center and edge line markings), bead loss occurs over a long distance and the beads quickly scatter. Long line application is also performed using bead drop equipment in a manner that does not expose employees to the lost beads. Short line applications (cross walks and intersections), however, do result in greater worker exposure and higher concentrations of spilled beads accessible to the general public. Efforts should be made to reduce excess bead loss during short line applications. Employees putting down beads should wear gloves to reduce exposure, and beads should be dropped so that the majority land on the binder (paint, thermoplastic, or epoxy). In particular, efforts should be made to reduce excess bead loss in short line applications in locations with curbs and gutters because of the potential slipping hazard.

Line removal presents a separate set of potential risks. To minimize exposure to arsenic and lead from glass beads during marking removals, employees should wear gloves, eye protection, and respirators if they are performing removal techniques that generate dust. Grinding, sand-blasting, or water blasting systems used to remove the lines should be equipped with vacuum recovery systems to reduce dust removal. Additional investigations into dust exposures during marking removal are advised.

As a final comment, arsenic and lead in glass beads may be a minor concern for environmental health and safety compared with other components in pavement-marking systems. A thorough review of the risk posed by residential and occupational exposures to components in other marking systems is advised to ease potential concerns regarding environmental and worker safety.

ACKNOWLEDGMENTS

Completion of this research would not have been possible without the following individuals whom we gratefully acknowledge:

- Dr. William James from the TAMU Center for Chemical Characterization.
- Karen Mangalgiri and Heidi Wood from the Boulanger Research Group for their help and advice in research design, data acquisition, and data interpretation.
- Drs. Thabet Tolyamat, Timothy Taylor, and Mallik Nadagouda from EPA.
- Carl Andersen and Terry Arnold, FHWA.
- Paul Vinik, FDOT.
- All the support staff at TTI and the TAMU Zachry Department of Civil Engineering business office for their help in project administration.

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