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Chapter 9

BACKGROUND VERSUS RISK-BASED SCREENING LEVELS - AN EXAMINATION OF ARSENIC BACKGROUND SOIL CONCENTRATIONS IN SEVEN STATES

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ABSTRACT

Arsenic is often present in soils naturally or from historical anthropogenic activities. Arsenic is commonly a constituent of potential concern at environmental remediation sites, even where there is no reason to suspect a release. Site risks are frequently driven by arsenic, and risk-based screening levels below background are not uncommon. However, determining whether arsenic concentrations are consistent with background typically requires an extensive background data set. The ability to gain access to representative background locations owned by third parties is problematic at best in any characterization study. Consequently, many sites undergo characterization and potentially remediation for arsenic concentrations in soil that may in reality be representative of background (natural or anthropogenic). This study examines a large soil arsenic background data set to provide insight on typical concentrations of arsenic that are naturally occurring or represent anthropogenic background.

Between 1995 and 2001, over 1,600 background soil samples were collected from 189 sites in Kentucky, Maryland, New York, Ohio, Pennsylvania, Virginia, and West Virginia. Samples were collected using strict Quality Assurance/Quality Control procedures under a United States Environmental Protection Agency (USEPA) Superfund Administrative Order on Consent (AOC) and were analyzed by USEPA-approved laboratories. All data were verified and 10% underwent detailed data validation. Arsenic concentrations in samples retained for statistical analysis ranged from 1.1 mg/kg to 89 mg/kg. Data are evaluated by state and by geology and are compared to USEPA and state risk-based screening levels (RBSLs). Some standard background threshold values (BTVs) are derived for each state and distinct geology. The BTVs are greater than RBSLs. This extensive, regional data set should be considered by all stakeholders involved in relevant risk-based decisions related to arsenic in soils. The consideration of this data set and the BTVs may aid in the appropriate identification of arsenic in soils below typical background concentrations. In turn, the use of BTVs may aid in identifying where risks are truly elevated relative to background, and thus where remediation may or may not be appropriate.

Keywords: arsenic, background, risk-based cleanup, statistics, remediation

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1. INTRODUCTION

Arsenic is present in soils across the United States at concentrations that may be natural or due to historical anthropogenic activities such as pesticide application or the use of pressure treated wood. Regulatory or screening criteria for arsenic that are risk-based are often well below these background concentrations. Many sites that are regulated under United States Environmental Protection Agency (USEPA) or state programs therefore undergo cleanup actions for arsenic in soil that may in fact be related to background rather than site-related activities. The Agency for Toxic Substances Disease Registry (ATSDR) reports that 1,149 out of 1,684 sites on the National Priority List (NPL) contain arsenic (ATSDR, 2007). It is possible that for many of these sites, arsenic concentrations are consistent with local background, which may be due to naturally occurring concentrations or anthropogenic activity not related to site operations.

This study examines an existing large dataset containing over 1600 background soil samples that were collected and analyzed for arsenic under a USEPA Superfund Administrative Order on Consent (AOC). The samples were collected between 1995 and 2001 from seven states (Kentucky, Maryland, New York, Ohio, Pennsylvania, Virginia, and West Virginia). The results of the samples are evaluated statistically by state and by distinct geology. Typical background threshold values (BTVs) were also derived for various sub-sets of the data. The BTV is a concentration in soil that is representative of the sample results and may be used to describe the background conditions for a particular area or geologic characteristics. The datasets and BTVs were compared to typical risk-based screening levels.

2. MATERIALS AND METHODS

Data collection and laboratory methods are discussed, followed by statistical methods.

2.1 Data Collection and Laboratory Methods

The data used for this evaluation were collected under a Superfund AOC between the USEPA and a confidential utility company from over 250 sites across seven states. As part of the characterization effort, background soil samples were collected from the majority of sites from areas that were not impacted by site-related activities. Background soil samples were collected using strict Quality Assurance/Quality Control (QA/QC) procedures under the AOC and were analyzed by USEPA-approved laboratories. Data from 189 sites in seven states (Kentucky, Maryland, New York, Ohio, Pennsylvania, Virginia, and West Virginia) are included in this study. Sites lacking background data were not included in this study. Samples were collected between 1995 and 2001. Figure 1 presents the locations of the 189 sites.

Sampling was performed by USEPA-approved contractors in accordance with USEPA-approved work plans under the AOC. QA/QC samples (field duplicates, equipment blanks, trip blanks, matrix spikes, temperature blanks) were collected as required by the program. Samples were analyzed for arsenic using method SW 846-6010A/7000A by USEPA-approved laboratories. Data verification was performed, and traditional data validation was also conducted

by a qualified consulting firm on 10% of the program's data. Data were qualified as necessary. Data were managed in a database by the validation consultant for reporting and statistical evaluations. From this database, all analytical results for arsenic in soil samples that were collected at background locations were extracted for use in the evaluations described in this paper. Background data were available from 189 sites in the seven states listed above.

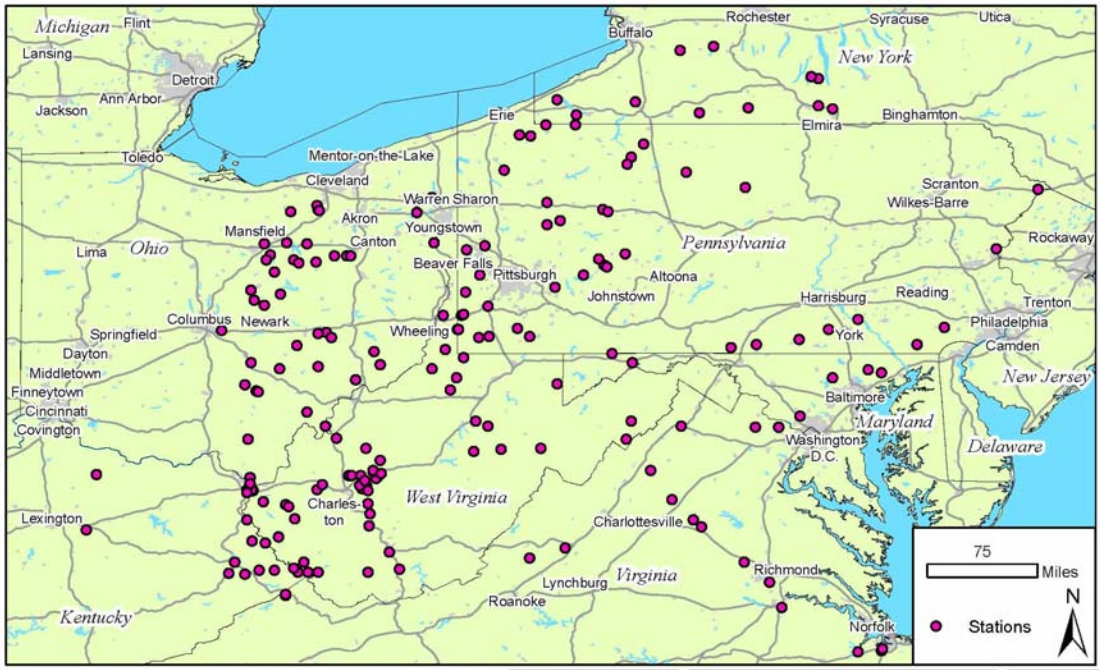

Figure 1. Site Locations

2.2 Statistical Methods

The data presented here were originally collected to achieve certain objectives under the AOC. The sampling was not intended to provide a representative dataset characterizing arsenic in soils in a certain geographic or geologic province. However, now that the data have been obtained, they do provide an opportunity to examine the patterns of occurrence of arsenic in background soils. Over 1,600 background soil samples were collected and analyzed for arsenic. The evaluation presented here relies on statistical methods to examine this very large dataset. Detected concentrations ranged from 1.1 mg/kg to 418 mg/kg. Few results (47 out of the dataset) were reported as not detected, with detection limits ranging from 1 mg/kg to 1.4 mg/kg. Where field duplicate samples were collected, the arithmetic average of the duplicates was used, except for locations where one result was reported as detected and the other not detected. In this case, the detected result was used for the statistical evaluations.

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2.2.1 Evaluation of Data Representativeness

Prior to evaluating the entire dataset, the data were examined to identify any samples that might bias the results or might not be representative. Arsenic concentrations in select samples from three sites appeared to be elevated in comparison with the rest of the dataset, based on a visual inspection of the data. Based on the characterization reports for these three sites, it was suspected that the background samples in question may have been collected from areas impacted by pesticides, herbicides, or other non-utility operations. Therefore, the samples in question (total of 14) were not included in the statistical analyses and were removed from this background dataset. Background samples from the three sites that did not appear elevated in comparison with the rest of the data set were retained for statistical evaluation. Detected concentrations of arsenic ranged from 1.1 mg/kg to 89 mg/kg in the samples retained for statistical evaluation.

2.2.2 Datasets

In addition to considering the entire dataset, several data subsets were assembled from the remaining 1,625 soil samples. They included seven state-specific datasets, five geology-specific datasets, and the full dataset. These thirteen datasets were further subdivided by sample depths as follows: a) all depths – compiled surface and subsurface soil samples; b) surface soil samples – samples from depths of 0 to 2 feet below ground surface; c) subsurface soil samples – samples from depths of greater than 2 feet below ground surface. Table 1 lists the datasets.

The geology at each of the 189 sites was determined based on regional (not site-specific) information. The geology of the bedrock that lies at or near the land surface at each site was identified using the Generalized Geologic Map of the Conterminous United States, a map compiled by the United States Geologic Survey (USGS). This map provides a wide range of geologic information, including bedrock and surficial geology, faults, major calderas, impact structures, and the limits of continental glaciation within the continental United States (Reed and Bush, 2005). The geologic information represented in the map was downloaded as Geographic Information System (GIS) polygon shapefiles from the online USGS National Atlas (www.nationalatlas.gov). The site locations, as point shapefiles, were overlain on these polygon shapefiles using ArcMapTM Software (ESRI®, 1999-2006). The geology from the polygon shapefiles was then associated with each of the point shapefiles. In this way, the map was used to assign the bedrock geology to each site. The geology at most of the sites was mapped as Paleozoic sedimentary rocks, as expected based on their locations in the Valley and Ridge and Allegheny Plateau Physiographic Provinces. Some of the other very infrequent bedrock types were combined based on geologic similarity, to eliminate datasets with only a few samples. The following classes of bedrock geology were developed from the dataset:

Crystalline rocks (includes geology mapped as Late Proterozoic and lower Paleozoic mafic rocks, Lower Mesozoic mafic rocks, Middle Proterozoic gneiss)

Early Paleozoic and older sedimentary rocks (includes geology mapped as Late Proterozoic and lower Paleozoic sedimentary rocks, Late Proterozoic sedimentary rocks, and Lower Paleozoic (Cambrian and Ordovician) sedimentary rocks)

Middle Paleozoic (Silurian, Devonian, and Mississippian) sedimentary rocks

Late Paleozoic and Mesozoic sedimentary rock (includes geology mapped as Upper Paleozoic (Pennsylvanian and Permian) sedimentary rocks, and Lower Mesozoic (Triassic and Jurassic) sedimentary rocks)

Quaternary and other recent units (includes geology mapped as Neogene sedimentary rocks, and Quaternary deposits)

2.2.3 Statistical Evaluation

Various statistics were calculated for each of the thirty-nine datasets, as presented in Table 1. The purpose of the statistics is to provide some characteristics and an overview of each dataset. This analysis included calculating summary statistics, the interquartile range (IQR), the 95th percentile, an upper tolerance limit (UTL), and a BTV. In addition, histograms were generated for the full dataset as well as each state to provide a way to visualize the datasets and data ranges. The statistics and the histograms are described in more detail below.

Histograms – The compiled dataset, as well as the state-specific datasets, were plotted as histograms and are presented in Figure 2 (full dataset) and Figures 3 through 9 (for each state). Histograms were created using a proxy value of one-half the detection limit for non-detects. Consistent bin sizes were used for all histograms. Analytical values of 0 to 36 mg/kg were divided into 18 bins, each spanning 2 mg/kg. A final bin, representing values greater than 36 mg/kg was also included. On the state-specific datasets, state-specific RBSLs and the BTVs have been indicated on the histogram for reference.

Summary Statistics - Summary statistics included the number of samples (after averaging of duplicates), frequency of detection (FOD), minimum detected concentration, maximum detected concentration, and median. The median was calculated using a proxy value of one-half the detection limit for non-detects using Intercooled Stata 8.1 Software (Stata Corporation, 2003).

The Interquartile Range (IQR) - The IQR describes the range of values between the 25th and 75th percentile. A binomial method was used to estimate confidence intervals that assumes no underlying distribution, as discussed in Statistical Methods for Environmental Pollution Monitoring by Richard O. Gilbert. To calculate the percentiles, the data points (including both detected and not detected values) were ranked from smallest to largest, and the following formula was used to calculate the rank of each percentile (Gilbert, 1987):

$$k = p(n+1)$$

k = the rank of the percentile
p = the percentile value (i.e. 0.99 for the ninety ninth percentile)
n = the number of observations

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Table 1. Summary Statistics for Arsenic Background Concentrations in Soil

Data Set	FOD	% Detected	Minimum Detect (mg/kg)	Maximum Detect (mg/kg)	Median (mg/kg)	IQR (mg/kg)	95th Percentile (mg/kg) (a)	UTL (mg/kg) (b)	Selected BTV (mg/kg) (c)	RBSL (mg/kg)
All Samples										
All samples	1578 : 1625	97%	1.1	89.0	7.6	7.3	21.4	21.8	21.4	0.39 (d)
Surface samples	902 : 916	98%	1.1	67.7	7.3	6.3	19.3	19.8	19.3	0.39 (d)
Subsurface samples	676 : 709	95%	1.3	89.0	8.4	8.7	23.7	24.5	23.7	0.39 (d)
By State										
Kentucky, all	103 : 103	100%	1.6	32.3	6.0	3.7	15.9	20.7	15.9	0.39 (d)
Kentucky, surface	57:57	100%	1.6	32.3	6.2	3.6	15.6	20.7	15.6	0.39 (d)
Kentucky, subsurface	46:46	100%	2.4	31.5	5.7	3.6	16.8	17.2	16.8	0.39 (d)
Maryland, all	33:42	79%	1.5	13.7	3.2	4.2	9.2	10.6	9.2	0.39 (d)
Maryland, surface	28:32	88%	1.8	13.7	4.1	3.9	10.1	11.7	10.1	0.39 (d)
Maryland, subsurface	5:10	50%	1.5	3.4	1.1	2.4	3.3	4.2	3.3	0.39 (d)
New York, all	80 : 101	79%	1.1	40.3	8.9	10.3	24.2	24.8	24.2	13 (e)
New York, surface	42:50	84%	1.1	40.3	7.6	10.8	22.8	23.4	22.8	13 (e)
New York, subsurface	51:51	100%	2.2	25.4	10.1	10.1	24.7	24.8	24.7	13 (e)
Ohio, all	304 : 313	97%	1.6	71.3	11.2	6.9	25.5	26.7	25.5	6.8 (f)
Ohio, surface	94 : 143	66%	4.0	61.9	10.1	5.2	21.7	22.8	21.7	6.8 (f)
Ohio, subsurface	161 : 170	95%	1.6	71.3	12.8	9.3	27.9	29.6	27.9	6.8 (f)
Pennsylvania, all	405 : 408	99%	1.3	67.7	10.3	7.2	23.4	24.4	23.4	12 (g)
Pennsylvania, surface	219 : 220	100%	2.3	67.7	9.3	6.3	23.7	25.1	23.7	12 (g)
Pennsylvania, subsurface	186 : 188	99%	1.3	34.6	11.4	8.6	23.0	24.4	23.0	12 (g)
Virginia, all	129 : 144	90%	1.2	40.9	4.2	5.1	14.9	16.2	14.9	0.39 (h)
Virginia, surface	91 : 98	93%	1.2	33.5	4.3	5.0	13.6	15.1	13.6	0.39 (h)
Virginia, subsurface	38:46	83%	1.3	40.9	3.7	5.4	17.1	20.1	17.1	0.39 (h)
W Virginia, all	503 : 514	98%	1.1	89.0	5.9	5.2	18.1	18.9	18.1	8.64 (i)
W Virginia, surface	314 : 316	99%	1.1	40.5	5.8	5.4	15.0	15.7	15.0	8.64 (i)
W Virginia, subsurface	189 : 198	95%	1.3	89.0	5.9	5.2	21.9	23.5	21.9	8.64 (i)

Table 1 (continued). Summary Statistics for Arsenic Background Concentrations in Soil

Data Set	FOD	% Detected	Minimum Detect (mg/kg)	Maximum Detect (mg/kg)	Median (mg/kg)	IQR (mg/kg)	95th Percentile (mg/kg) (a)	UTL (mg/kg) (b)	Selected BTV (mg/kg) (c)	RBSL (mg/kg)
By Geology										
Crystalline, all	17:19	89%	1.3	11.9	2.7	3.4	7.8	9.7	7.8	0.39 (d)
Crystalline, surface	15:15	100%	1.3	11.9	4.2	3.3	11.9	11.9	11.9	0.39 (d)
Crystalline, subsurface	2:04	50%	2.6	2.7	1.7	2.0	2.7	2.8	2.7	0.39 (d)
Early Paleozoic and older Sedimentary, all	138 : 147	94%	1.2	40.9	5.9	5.4	15.5	16.7	15.5	0.39 (d)
Early Paleozoic and older Sedimentary, surface	87 : 92	95%	1.2	22.7	5.9	5.1	13.1	14.3	13.1	0.39 (d)
Early Paleozoic and older Sedimentary, subsurface	51:55	93%	1.3	40.9	6.0	7.2	18.6	21.3	18.6	0.39 (d)
Mid-Paleozoic Sedimentary, all	414 : 421	98%	1.1	71.3	11.9	8.3	25.8	26.8	25.8	0.39 (d)
Mid-Paleozoic Sedimentary, surface	214 : 214	100%	1.1	61.9	10.6	6.9	23.4	30.0	23.4	0.39 (d)
Mid-Paleozoic Sedimentary, subsurface	200 : 207	97%	1.6	71.3	13.3	9.9	27.4	28.9	27.4	0.39 (d)
Late-Paleozoic and Mesozoic Sedimentary, all	966 : 983	98%	1.1	89.0	7.0	6.4	19.9	20.5	19.9	0.39 (d)
Late-Paleozoic and Mesozoic Sedimentary, surface	554 : 558	99%	1.1	67.7	6.9	5.7	18.2	18.8	18.2	0.39 (d)
Late-Paleozoic and Mesozoic Sedimentary, subsurface	412 : 425	97%	1.3	89.0	7.1	7.3	22.0	23.0	22.0	0.39 (d)
Quaternary and other recent, all	43:55	78%	1.4	11.9	3.0	3.6	8.0	9.0	8.0	0.39 (d)
Quaternary and other recent, surface	32:37	86%	1.4	10.5	3.2	3.0	7.1	8.2	7.1	0.39 (d)
Quaternary and other recent, subsurface	11:18	61%	1.9	11.9	2.7	6.4	9.4	12.0	9.4	0.39 (d)

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Table 1 (continued). Summary Statistics for Arsenic Background Concentrations in Soil

Notes:
BTV - Background Threshold Value.
FOD - Frequency of Detection = Number of detected samples: Number of total samples.
RBSL – Risk-Based Screening Level.
IQR - Interquartile range, the difference between the 75th and 25th percentiles. Reflects the range and variability of the dataset.
UTL - Upper Tolerance Limit.
Summary Statistics include detected value only. All datasets tested for normality; none were normally distributed.

(a) Calculated with ProUCL (USEPA, 2007a) using the 95% Percentile (z) if FOD<100% and the 95% percentile if FOD=100%.
(b) Calculated with ProUCL (USEPA, 2007a) using nonparametric statistics: 95% KM UTL with 95% Coverage if FOD<100% and 95% UTL with 95% Coverage if FOD=100%.
(c) ProUCL (USEPA, 2007a) provides a number of statistical options for BTVs. In this case, the 95th percentile is selected as an example of a BTV.
(d) USEPA, 2008a. Regional Screening Levels (SL) for Chemical Contaminants at Superfund Sites. September 12, 2008. http://www.epa.gov/region09/superfund/prg/index.html. SL for residential soil, based on incidental ingestion, inhalation, and dermal contact and a target risk level of 10^{-6}. Selected for Kentucky based on state guidance, which referred to the former USEPA Region 9 Preliminary Remediation Goals. Selected for geology and all soil because these data sets are not state-specific and the SL is a generic risk-based value.
(e) NYSDEC, 2006. New York State Regulations. Subpart 375-6: Remedial Program Soil Cleanup Objectives (SCO). §375-6.8 Soil Cleanup Objective Tables. http://www.dec.ny.gov/regs/15507.html. SCO for unrestricted use property. Based on rural background because the calculated SCO is lower than background. http://www.epa.state.oh.us/derr/vap/rules/vaprules.html.
(f) OEPA, 2009. Ohio Voluntary Action Program Generic Numerical Standard (GNS), March 2009. Ohio Administrative Code Rule 3745-300-08. Table 1. http://www.epa.state.oh.us/derr/vap/rules/vaprules.html. GNS for residential soil, based on incidental ingestion, inhalation, and dermal contact and a target risk level of 10^{-5}.
(g) PADEP, 2001. Pennsylvania Code Title 25, Chapter 250. Table 4a - Medium Specific Concentrations (MSCs) for Inorganic Regulated Substances in Soil: Direct Contact Values. http://www.depweb.state.pa.us/ocrlgs/cwp/view.asp?A=1459&Q=518871. MSC for residential soil, based on the lower of calculated values for incidental ingestion and inhalation and a target risk level of 10^{-5} or a leaching to groundwater value. The ingestion calculated value is the lower value and is therefore the selected value.
(h) VDEQ, 2009. Virginia Voluntary Remediation Program Risk Assessment Guidance, Table 2.5. January 21, 2009. http://www.deq.state.va.us/vrprisk/. Tier 2 value for residential soil, based on incidental ingestion and inhalation and a target risk level of 10^{-6}.
(i) WVDEP. West Virginia Voluntary Remediation and Redevelopment Act Guidance Manual. Version 2.1. http://www.wvdep.org/item.cfm?ssid=18&ss1id=33. DeMinimis Residential Standard is the higher of the background concentration (8.64 mg/kg) and the risk-based concentration (0.39 mg/kg).

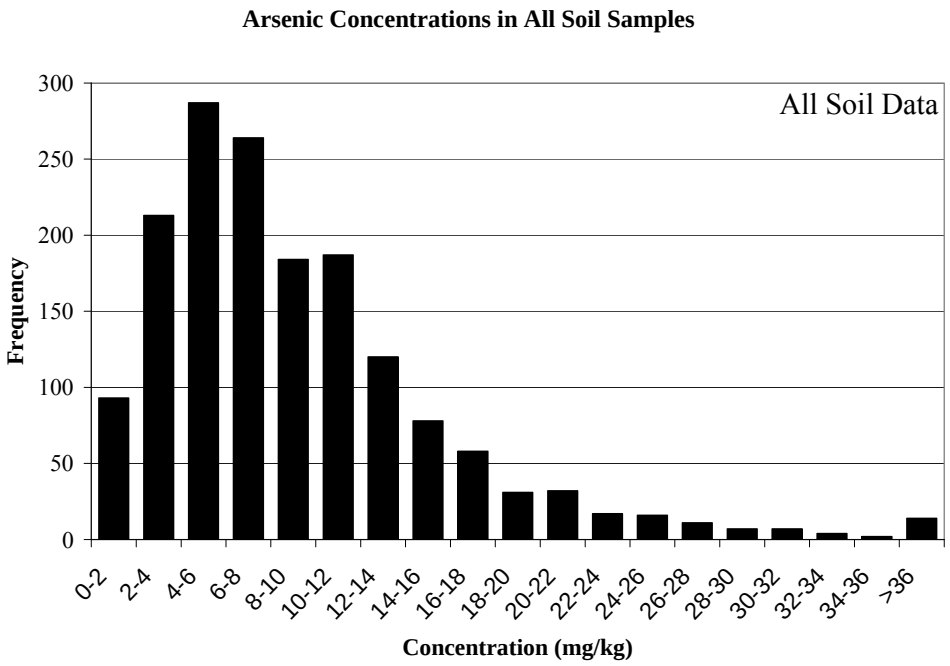

Figure 2. Arsenic Concentrations in Soil Samples

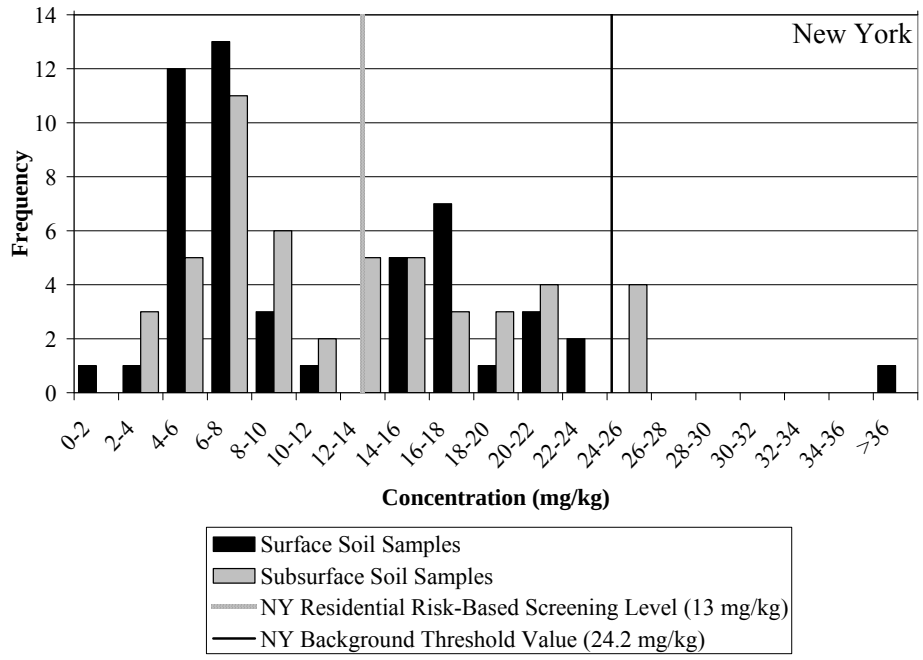

Figure 3. Arsenic Concentrations in New York Soil Samples Compared to BTV and RBSL

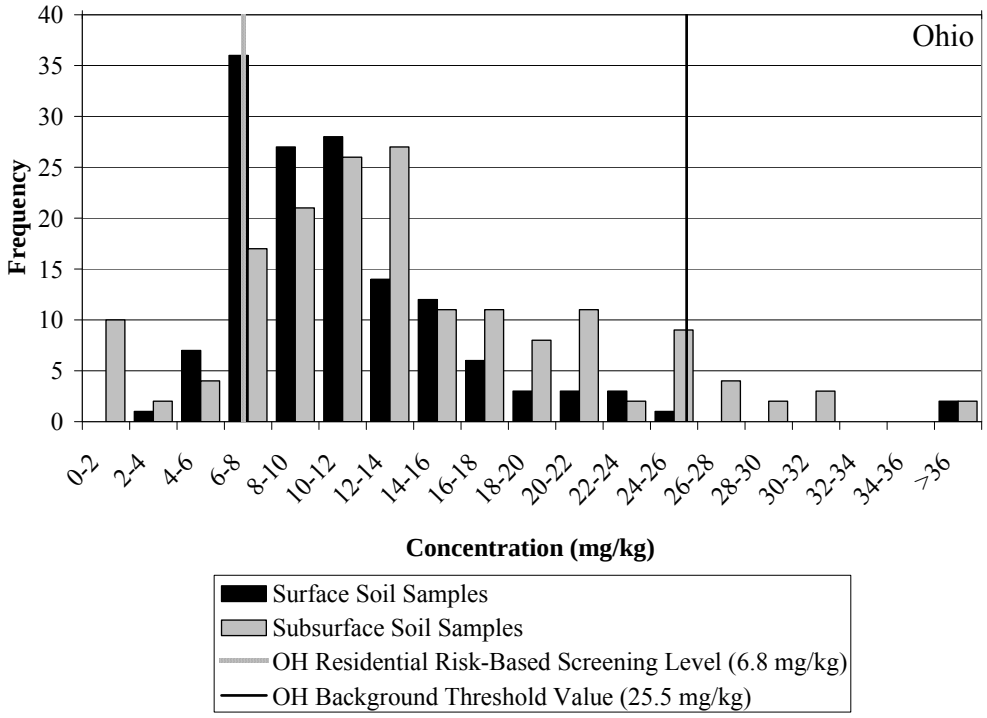

Figure 4. Arsenic Concentrations in Ohio Soil Samples Compared to BTV and RBSL

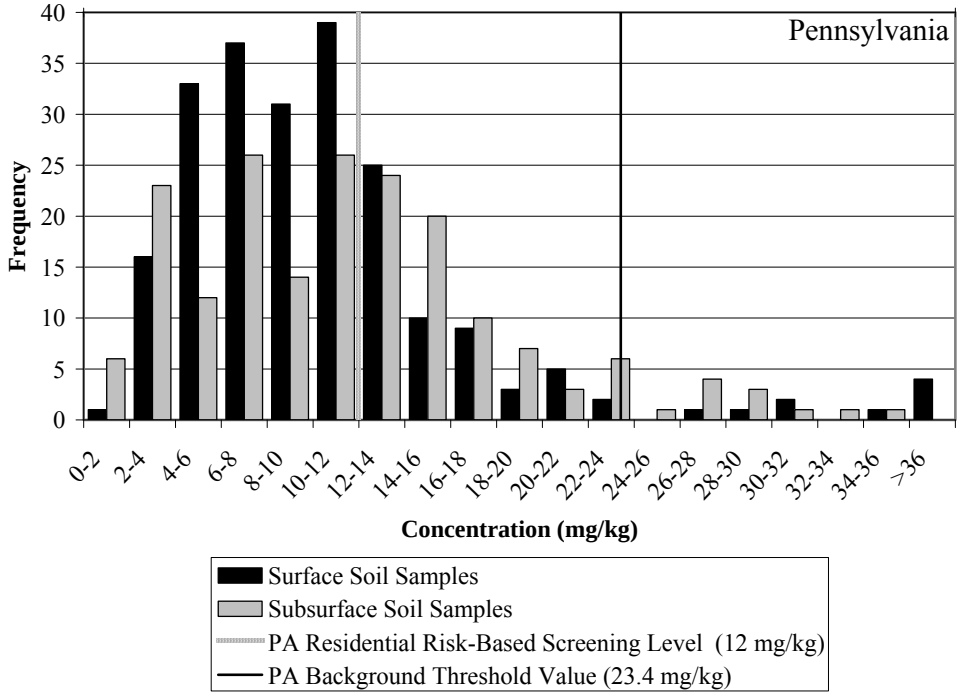

Figure 5. Arsenic Concentrations in Pennsylvania Soil Samples Compared to BTV and RBSL

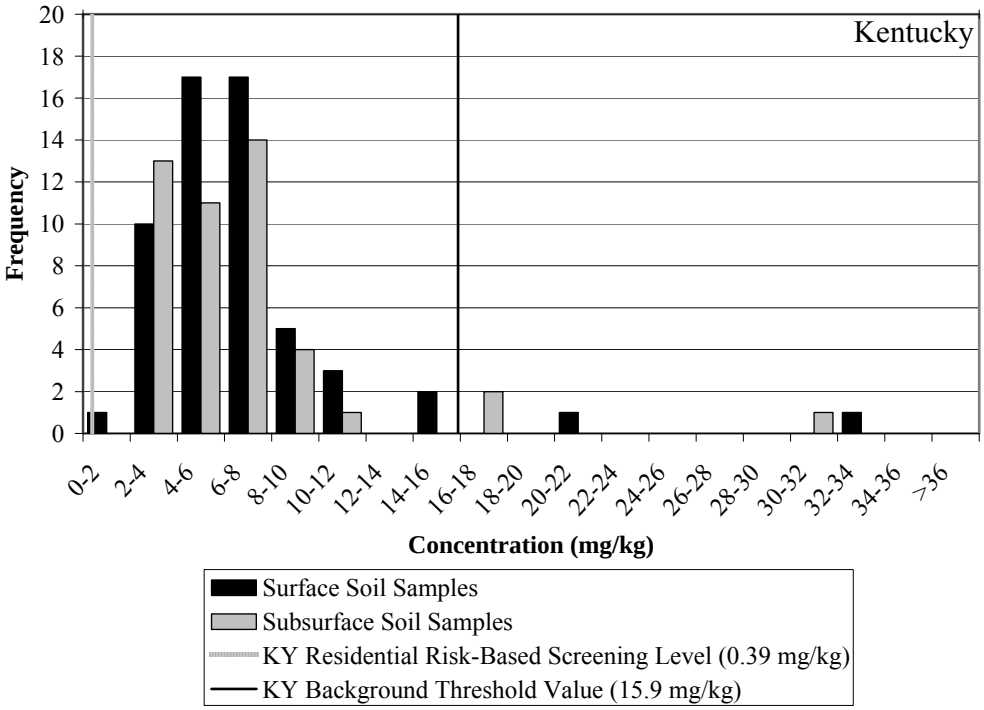

Figure 6. Arsenic Concentrations in Kentucky Soil Samples Compared to BTV and RBSL

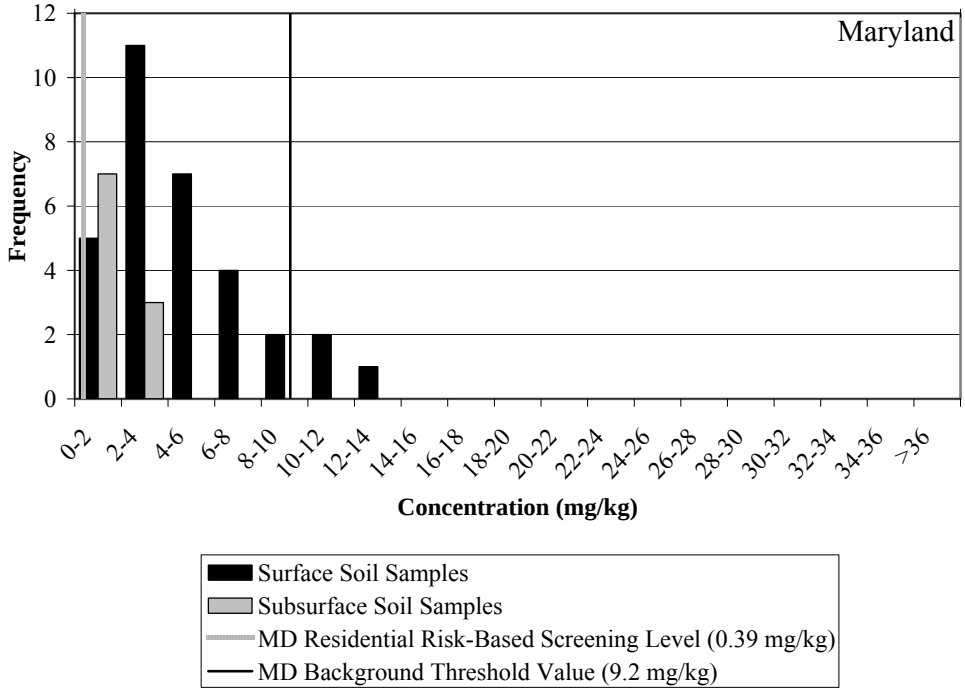

Figure 7. Arsenic Concentrations in Maryland Soil Samples Compared to BTV and RBSL

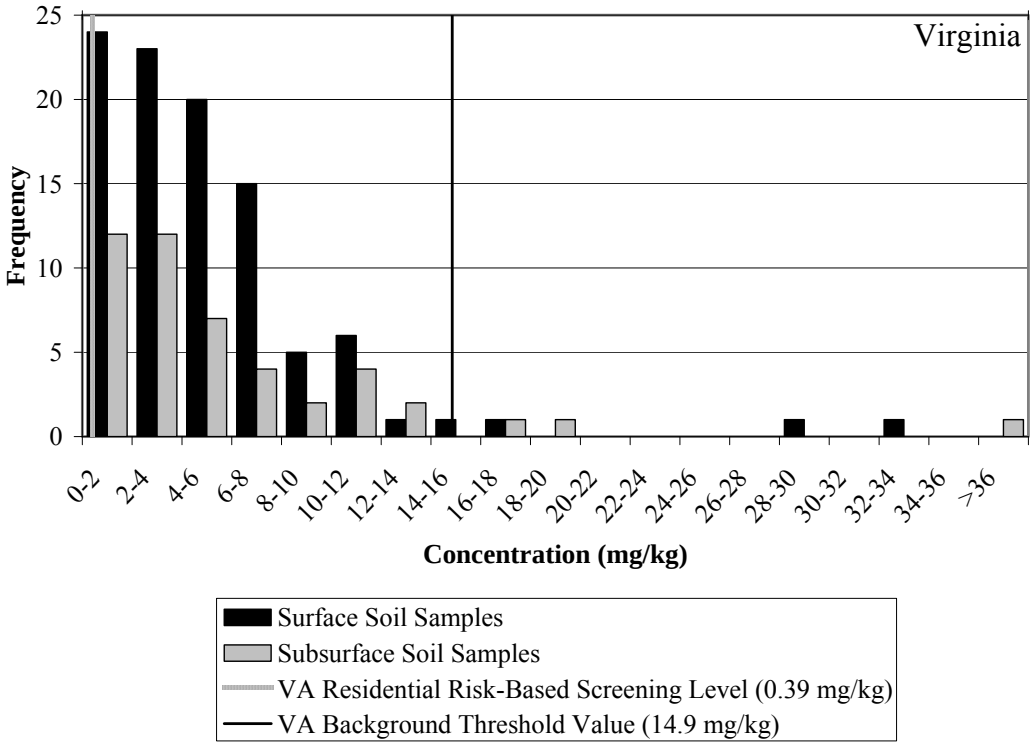

Figure 8. Arsenic Concentrations in Virginia Soil Samples Compared to BTV and RBSL

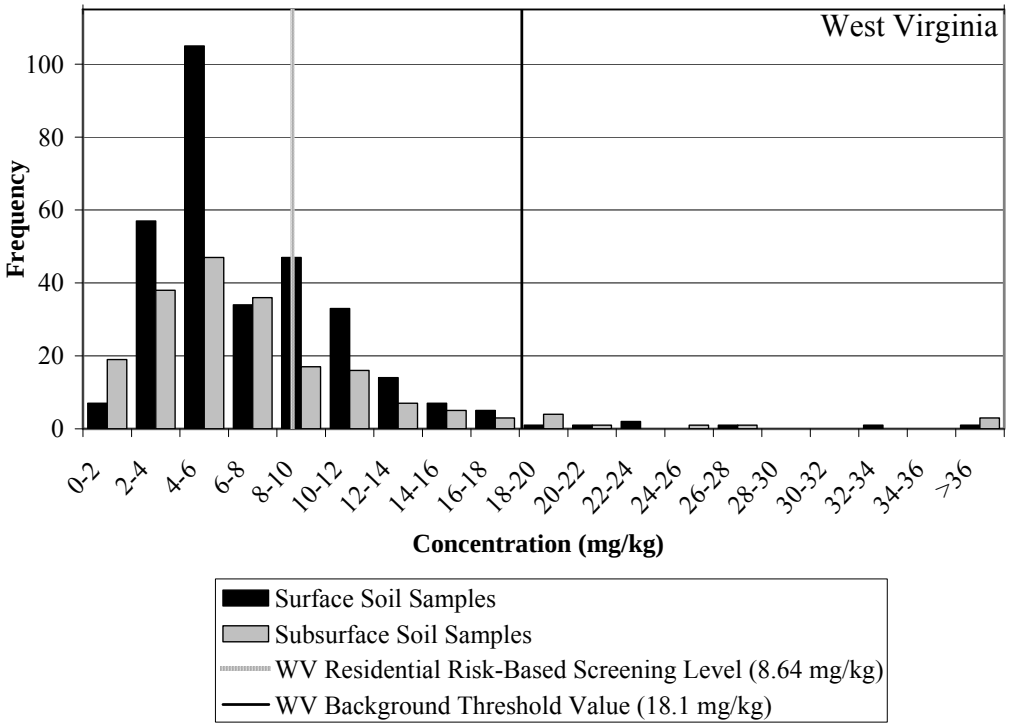

Figure 9. Arsenic Concentrations in WV Soil Samples Compared to BTV and RBSL

A linear interpolation was performed between ranked values to achieve the background statistic, as the k value resulting from this calculation is not usually an integer. The IQR was calculated using a proxy value of one-half the detection limit for non-detects using Intercooled Stata 8.1 Software (Stata Corporation, 2003).

95th Percentile – The non-parametric 95th percentile was calculated using ProUCL (USEPA, 2007a). One of two different methods was used depending on the FOD. When the FOD was equal to 100%, the 95th percentile was calculated using the non-parametric percentile calculation, k=p (n+1), as described in the preceding section (USEPA, 2007b). When the FOD was less than 100%, the Kaplan-Meier method was used to calculate the 95th percentile (USEPA, 2007b).

Upper Tolerance Limit (UTL) – The UTL is the upper bound on the tolerance interval, an interval generated to provide a predictive framework for future observations. Like the prediction interval, the tolerance interval spans the range of values within which future observations are predicted to occur with a confidence of (1-α)*100%. However, the tolerance interval differs from the prediction interval in that it includes a coverage of P (100%) of all potential future measurements (while the prediction interval is based on a coverage of 100% of a fixed and finite number of future measurements). The tolerance interval is more appropriate than the prediction interval for situations where the potential number of future observations is large or unknown, and achieving 100% coverage may not be possible (Gibbons, 1994). The UTL values presented in Table 1 describe an interval with a coverage of 95% and a confidence of 95% calculated using ProUCL (USEPA, 2007b). A nonparametric UTL cannot exactly achieve a specified confidence (1-α). Instead, the nonparametric UTL attempts to select a value of r such that the following expression gets as close as possible to (1-α).

$$\sum_{i=0}^{i=r} \binom{n}{i} p^i (1-p)^{(n-i)}$$

p = probability of success

n = sample size

The rth ordered statistic represents the value of the UTL. This method is only applicable to data sets with FOD = 100% (USEPA, 2007b). For datasets with FOD less than 100%, the UTL is calculated from the statistics generated from the Kaplan-Meier method as follows (USEPA, 2007b):

$$UTL = \hat{\mu} + K * \sqrt{\sigma^2}$$

K = the tolerance factor K (n, α, p), which is based on the non-central t-distribution.

Background Threshold Value (BTV) – The BTV is a value that characterizes the background dataset, and can be used instead of population comparisons for background evaluations, for example, for screening purposes. Values that are below the BTV would be considered representative of background; values above might be above background. There are numerous

statistics that can be used to calculate an appropriate BTV. For the sake of simplicity, the 95th percentile has been selected for this evaluation to serve as the BTV. However, it should be recognized that by definition, 5% of all true background samples would be interpreted as above background using this statistic, so this is conservative for a risk-based approach.

Hypothesis Testing – Because a number of differences between data subsets are readily observed in the summary statistics, selected hypothesis testing was performed to evaluate whether these observed differences are significant. However, the soil sampling program was not designed for the purposes of conducting hypothesis testing, so a number of adjustments were made to the dataset to remove obvious biases and interferences. For example, only surface soil samples were collected at some stations; only subsurface at others. The number of samples collected at each station varied from one up to 38. In addition, at the scale of this study (7 states), multiple samples collected at a single station are not necessarily independent with respect to hypothesis testing. These interferences were controlled by selecting data only from stations where both surface and subsurface samples are available, and by selecting a single representative value (the median was selected) for each depth (surface, subsurface) at these stations. This operation reduces the dataset to a total of 117 stations (out of 189) with a representative concentration for both surface and subsurface arsenic.

Because the datasets were typically not normally distributed, non-parametric methods were used for hypothesis testing. The Wilcoxon Rank Sum test (WRS, also known as the Mann-Whitney U) was used to compare two groups of data; the Wilcoxon Signed-Rank Test (WSRS) was used for paired data, such as the surface and subsurface sample pairs (Gilbert, 1987). The software Stata 8.1 (Stata Corporation, 2003) was used for these calculations. The null hypothesis for all these tests is that the two groups being compared are similar. If the null hypothesis is rejected (at a significance level of approximately 0.05), it is assumed that the differences between the groups are statistically significant.

Risk Based Screening Level (RBSL) - RBSLs have been compiled from applicable state or federal guidance for the various datasets from the following sources:

The United States Environmental Protection Agency. Regional Screening Levels (SL) (USEPA, 2008a). The screening level for arsenic in residential soil of 0.39 mg/kg, based on incidental ingestion, inhalation, and dermal contact and a target risk level of 10^{-6} was selected as the screening level for the full dataset and the geology-based datasets because these are non-state specific. This screening level is a generic risk-based value. It was also selected as the screening level for the Kentucky and Maryland datasets because state values are not available. State guidance references USEPA for screening levels.

New York State Regulations: New York Department of Environmental Conservation (NYSDEC) Remedial Program Soil Cleanup Objectives (NYSDEC, 2006). The soil cleanup objective (SCO) for arsenic of 13 mg/kg for unrestricted property was used as the screening level for the New York datasets. The SCO for arsenic is based on rural New York background concentrations.

Ohio Environmental Protection Agency (OEPA) Voluntary Action Program Generic Numerical Standard (OEPA, 2009). The generic numerical standard for arsenic in residential

soil of 6.8 mg/kg, based on incidental ingestion, inhalation, and dermal contact and a target risk level of 10^{-5} was used as the screening level for the Ohio datasets.

Pennsylvania Department of Environmental Protection (PADEP) Medium Specific Concentrations (MSC) for Inorganic Regulated Substances in Soil: Direct Contact Values (PADEP, 2001). The MSC for arsenic in residential soil of 12 mg/kg was used as the screening level for the Pennsylvania datasets. The MSC is based on the lower of calculated values for incidental ingestion and inhalation and a target risk level of 10^{-5} or a leaching to groundwater value. The ingestion calculated value is the lower value and is therefore the selected MSC.

Virginia Department of Environmental Quality (VDEQ) Voluntary Remediation Program Risk Assessment Guidance (VDEQ, 2009). The Tier 2 value for arsenic in residential soil of 0.39 mg/kg, based on incidental ingestion and inhalation and a target risk level of 10^{-6} was used as the screening level for the Virginia datasets. Note that the Tier 2 values are based on the USEPA SLs (USEPA, 2008a).

West Virginia Department of Environmental Protection (WVDEP). Voluntary Remediation and Redevelopment Act Guidance Manual. Version 2.1 (undated) and West Virginia Legislative Rule §60-3 (Voluntary Remediation and Redevelopment Rule), dated June 1, 2008. Per the guidance manual, the DeMinimis standard for arsenic is the higher of the risk-based screening level in the regulations (0.39 mg/kg, based on USEPA, 2008a) and the natural background concentration presented in the guidance manual (8.64 mg/kg). Therefore, the natural background concentration of 8.64 mg/kg was used as the screening level for the West Virginia datasets.

3. RESULTS AND DISCUSSION

Table 1 presents the calculated statistics, including summary statistics (sample number, FOD, minimum detected concentration, maximum detected concentration, median), IQR, 95th percentile, and UTL for the datasets listed above. The FOD was high for the majority of datasets; only four datasets had fewer than 70% of arsenic results reported as detected. With the exception of one dataset (crystalline, subsurface, with only 4 results) all datasets contained at least 10 samples and at least 5 detected results. Figure 2 presents a histogram for the full dataset.

Some general observations can be made from the various statistics calculated. Where these observations are supported by hypothesis testing to evaluate their significance, this is noted. Where hypothesis testing has not been performed, care should be taken in the use and interpretation of these observations as they are simple observations only, not based on formal testing to determine their statistical significance.

Over the entire dataset, the arsenic concentrations in subsurface samples tend to be greater than in surface samples (median of 8.4 mg/kg for subsurface compared to 7.3 mg/kg for surface; BTV of 23.7 compared to 19.3, respectively). The same pattern is present for most individual states, but not for Kentucky or Maryland. Hypothesis testing suggests these differences are not significant (WRS p=0.8787; WSRS p=0.2766; null hypothesis not rejected).

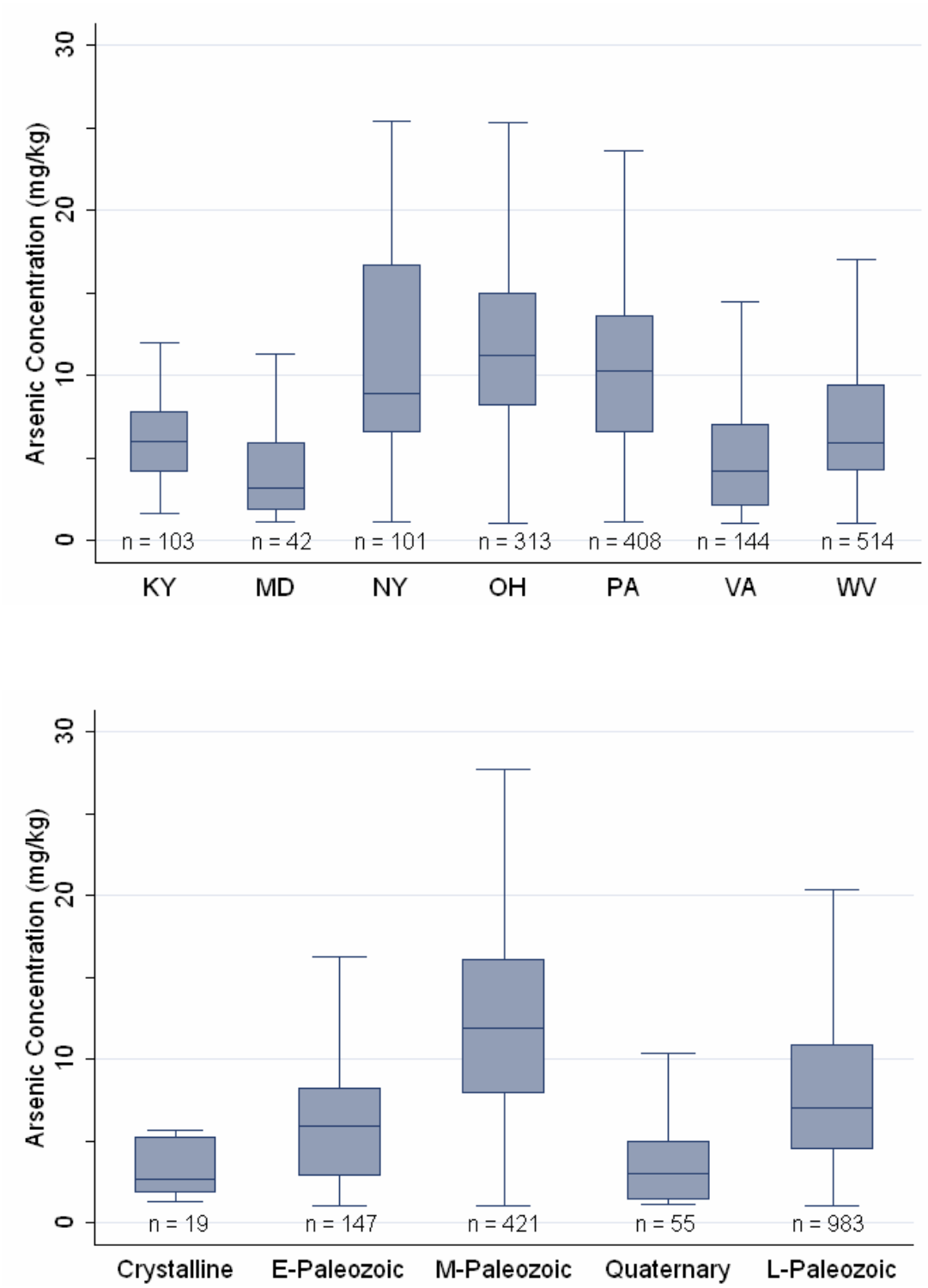

Figure 10. Side-by-side box plots showing the variation in arsenic concentrations over the different states (above, Figure 10a) and geologic classifications (below, Figure 10b) (results beyond the limits of the whiskers ("outside values") not shown).

BTVs range quite a bit across the different states, from a minimum of 9.2 mg/kg in Maryland to a maximum of 25.5 mg/kg in Ohio (all depths combined). BTVs are similar for Ohio, Pennsylvania, and New York (23.4 to 25.5 mg/kg); BTVs are also similar for Kentucky, Virginia, and West Virginia (14.9 to 18.1 mg/kg). The BTV for Maryland is lower, but Maryland is also the state with the fewest samples collected. Side-by-side box plots in Figure 10a show the ranges in arsenic concentrations between states (for the full dataset of 1625 results). The most obvious reason for the variations in arsenic concentrations is due to differences in the underlying geology. Spearman rank correlation tests indicate that there is interdependence among arsenic concentration, bedrock geology, and state (p values ranging from 0.0000 to 0.0062).

While the regional nature of the geologic evaluation does not allow for the identification of specific lithology or mineralogy, nor the distinction between glaciated vs. non-glaciated areas, all of which will influence soil chemistry, it does show distinct differences. BTVs for the different geologic groupings range from 7.8 mg/kg for crystalline rocks to 25.8 mg/kg for Mid-Paleozoic sedimentary rocks (all depths combined). The higher BTVs are associated with Paleozoic sedimentary rocks, reflecting the presence of arsenic in these depositional environments

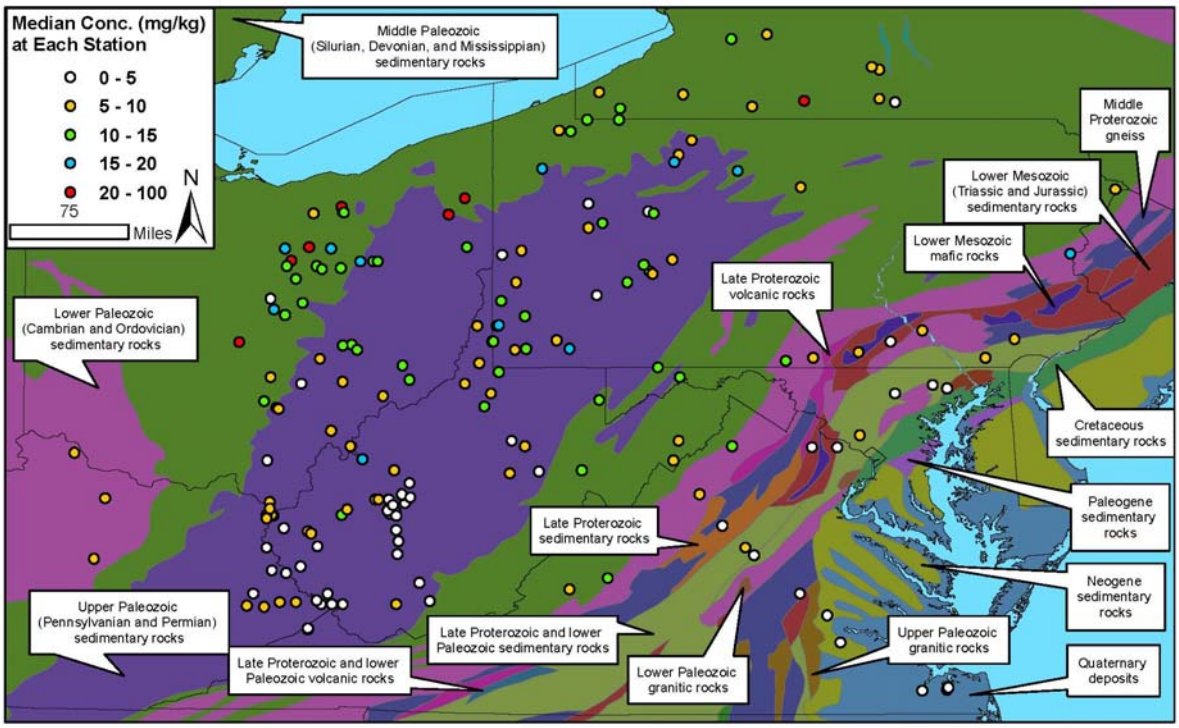

Figure 11. Geologic map showing median arsenic concentration at each station

(including coal deposits). However, it should also be recognized that the datasets for the other geologies are smaller (n=19 for crystalline rocks, n=55 for Quaternary/recent units), so the differences may also reflect a lack of a representative dataset. Side-by-side box plots in Figure 10b show the ranges of arsenic concentrations for each geologic classification (for the full dataset of 1625 results). Hypothesis testing indicates that arsenic concentrations are different in each geologic region (WRS p values ranging from 0.0000 to 0.0527), except that the Lower and Upper Paleozoic regions are similar (p=0.2615), and the Crystalline and Quaternary are similar (p=0.6689). In the case of the latter, it is more likely the test has insufficient power due to the small numbers of samples. Figure 11 shows the median concentration of arsenic at each station, overlain on the GIS-based geologic classifications.

Of the seven states included in this study, two have background-based screening levels for arsenic (New York, 13 mg/kg; West Virginia, 8.64 mg/kg). The remaining five states use RBSLs for arsenic. The RBSLs range widely; Kentucky, Maryland, and Virginia use the USEPA SL of 0.39 mg/kg (USEPA, 2008a), Ohio (OEPA, 2009) uses a value of 6.8 mg/kg, and Pennsylvania uses a value of 12 mg/kg (PADEP, 2001). The RBSLs are all based on the cancer slope factor of 7.3 (mg/kg-day)-1. The cancer slope factor is based on an epidemiological study of a Taiwanese population that was exposed to high levels of arsenic in drinking water (USEPA, 2008b). Use of a cancer slope factor based on high level exposure in drinking water may be overly conservative for low-level exposure to arsenic in soil, which is also likely to be less bioavailable than arsenic in drinking water. The wide variation in the RBSLs is due mainly to the target risk level, with the USEPA values based on 10-6 and the Ohio and Pennsylvania values based on 10-5. Exposure assumptions also vary; the USEPA values are based on a 350 day per year exposure and account for soil ingestion, dermal contact, and inhalation, while the Ohio value is based on the same pathways but at a lower exposure frequency of 250 days per year. The Pennsylvania value is based on the ingestion pathway alone (a separate inhalation-based value is calculated and the lower is selected as the MSC, with ingestion representing the lower value for arsenic) at an exposure frequency of 250 days per year. The wide variation in RBSLs, along with the conservative cancer slope factor, highlights the importance of considering background when setting cleanup objectives for a site. The comparison of BTVs to RBSLs presented on Table 1 and Figures 3 through 9 shows that the selected BTVs are higher than the applicable RBSL for each of the seven state datasets, again, highlighting the importance of background.

The findings presented here are consistent with several other national or regional studies which show background arsenic concentrations in soils commonly to be greater than RBSLs. Several national and regional soil background studies conducted by the USGS have shown similar results. Perhaps the most widely used database is that of Shacklette and Boerngen (1984), which reported data for over 1,200 soil samples from across the country, with results ranging from non-detect to 97 mg/kg. The USGS began the Geochemical Landscapes Project (http://minerals.cr.usgs.gov/projects/geochemical_landscapes/index.html) in 2003 to expand the Shacklette and Boerngen (1984) database. To date, two pilot studies have been conducted under this project, a regional scale study and a national scale study. The regional pilot study focused on a transect in northern California from Marin County (north of San Francisco) to the Nevada border (Goldhaber et al., 2005). The national pilot study included the collection of soil samples along two continental transects in North America: a north-south transect extending from the US-Mexico border near El Paso, Texas into northern Manitoba, Canada which included 105

sampling sites; and an east-west transect extending from the Maryland coast to near San Francisco, CA which included 160 sampling sites. At each site, a sample was collected from a depth of 0 to 5 centimeters as well as from the O, A, and C soil horizons. Arsenic concentrations in the 0 to 5 centimeter samples ranged from not detected to 20 mg/kg (Smith et al., 2005). Other national studies include the USGS's National Geochemical Survey (USGS, 2007), and a survey of 34 states conducted by the Association for the Environmental Health of Soil (AEHS, 1998). There are also likely to be other studies conducted on a state or regional basis (e.g., MDEQ, 2005).

Based on these national studies and the regional data presented here, it is apparent that arsenic concentrations across much of the United States are elevated with respect to residential RBSLs. Several states have recognized the importance of background with regards to remediation involving arsenic in soil. Some of these include:

California Environmental Protection Agency (CalEPA) Department of Toxic Substances Control (DTSC) has set an arsenic background concentration of 6 mg/kg to be used at Los Angeles Unified District school sites (CalEPA, 2005).

Illinois Environmental Protection Agency (IEPA) defaults to a background concentration for arsenic of 13 mg/kg for metropolitan areas or 11.3 mg/kg for non-metropolitan areas in its Tiered Approach to Corrective Action Objectives (IEPA, 2007).

Massachusetts Department of Environmental Protection (MADEP) has established a direct contact soil standard of 20 mg/kg for arsenic for several scenarios based on background (MADEP, 2008).

New Jersey Department of Environmental Protection (NJDEP) via the New Jersey Administrative Code (N.J.A.C.) has established a residential direct contact soil remediation standard of 19 mg/kg for arsenic, based on natural background (N.J.A.C, 2008).

NYSDEC has set an arsenic SCO of 13 mg/kg, based on rural background concentrations, because the calculated residential risk-based screening level for arsenic is lower than the background concentration (NYSDEC, 2006).

WVDEP (Voluntary Remediation and Redevelopment Act Guidance Manual. Version 2.1) uses a background concentration of 8.64 mg/kg as the residential DeMinimis Standard for arsenic.

4. CONCLUSIONS

The database of soil background concentrations of arsenic and the statistical evaluation presented in this paper show that for this study, background concentrations of arsenic in Kentucky, Maryland, New York, Ohio, Pennsylvania, Virginia, and West Virginia soils are greater than typical residential RBSLs for soil.

Clearly many sites undergoing cleanup under state or USEPA programs have arsenic as a primary or secondary constituent of concern. The number of on-going arsenic background

studies and the number of states defaulting to arsenic screening levels based on background rather than risk highlights the importance of understanding background concentrations when considering arsenic remediation. The results of the analysis performed in this paper, combined with the body of literature regarding arsenic in soil, should be reviewed by stakeholders at sites involving arsenic remediation. Remediation to RBSLs can be costly and may not be warranted where site concentrations are similar to background levels.

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