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Chapter 8

AN INVESTIGATION OF THE NATURAL AND ANTHROPOGENIC CONTRIBUTIONS OF ARSENIC TO URBAN FILL SOIL

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ABSTRACT

Arsenic in urban/historic fill soil, originating from both natural and anthropogenic sources, is a continuing concern from a human health risk point of view. This concern is heightened in urban gardens where the soil is to be used for growing vegetables for consumption.

The presentation explores the origin of arsenic present in New England urban/historic fill soil and will derive an understanding of the relative contribution of the natural and anthropogenic components using available data sets. These data sets include more than 5,000 urban soil samples from the Central Artery/Tunnel Project in Boston statistically analyzed using ProUCL 4.0. Data also includes more than 2,700 samples of a natural/rural background data set from a comprehensive study of rock and stream sediment arsenic in New England analyzed by the U.S. Geological Survey (USGS) (Ayotte and Robinson, 2007), supported by other available data sets resulting in a broad base of up to approximately 10,000 individual sample results. These multiple data sets will be reviewed and summarized such that there are a mean/median and upper values presented for natural soils and rocks and a mean/median and upper values presented for anthropogenic impacted soils, with and without outliers. From this compilation will be derived an understanding of the numerical differential between them. Finally, we will apply standard human health risk calculations, provided by the Massachusetts Department of Environmental Protection (MassDEP) (Office of Research and Standards, 2007), to illustrate the magnitude of potential effects of the natural soil and the anthropogenic–containing soil. The derived mean, median, and upper percentage values will be considered in the context of the human health risk assessment calculations. In conclusion, the

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exercise will identify the risk significance of the anthropogenic contribution relative to the natural soil and provide an understanding of the overall affect associated with background in the urban environment.

Keywords: Arsenic, anthropogenic

1. INTRODUCTION

The purpose of this investigation is to identify naturally and anthropogenic occurring concentrations of arsenic in soils in the Boston metropolitan area. Lead was included as a companion contaminant of concern. The investigation was undertaken by reviewing, summarizing, and working with readily available and relatively robust existing soil data sets. The identification of soil metal background concentrations is necessary in understanding what portion of the metals in a sample of urban/historic fill may be naturally occurring and defined as natural “background” concentrations. This understanding then provides the information needed to identify the anthropogenic component of the metals concentrations found in historic fill soil and also to understand relative risk-related impacts. From a regulatory perspective, natural conditions are not considered to pose an unacceptable risk in and of themselves regardless of the contaminant concentrations present.

Due to possible non-documentable anthropogenic influences, the data sets used cannot be claimed to represent purely natural soil results, with the exception of deep, uncontaminated clays and the referenced results of natural mineral/rock formations. However, we represent that this data assessment has resulted in moving relatively close to understanding the natural component for a number of metals, particularly in regard to the mean values for arsenic coupled with lead. Furthermore, the focus of a natural soil and urban fill metals assessment is logically directed to arsenic coupled with lead. These metals, in general, appear to exhibit the greatest human health risk significance based on our experience with risk characterizations at a multitude of urban/ historic fill sites.

2. MATERIALS AND METHODS

The following three data sets were readily available and utilized in this analysis:

Data for Natural Soil Located Immediately below Historic Fill: This data set was gathered from soil sampling and analysis results at a number of construction sites located in Boston and Cambridge. Data in this set is for soil that, by its location, visual assessment, and pre-characterization sampling and analysis site information, was identified as natural and was sampled and analyzed for reuse following the removal of overlying historic/urban fill. The data is from soil expected to be relatively proximate to the original ground surface and under any organic layer, and tended to be relatively granular in nature. This data was believed to be the most representative of natural material of the several data sets considered with the exception of the marine clay (the third data set discussed below). The total number of samples with arsenic and lead results in this data set was 375. The exact locations are confidential per client request to allow use of the data.

Data for Central Artery/ Tunnel (CA/T) Soils: Data from the Central Artery/Tunnel Project, consisting of more than 6,000 soil samples, were sorted into two subsets of data and carefully adjusted to approximate the natural soil component. The two subsets, representing the 0-to17-foot-zone below grade and the >30-foot zone, were carefully reviewed. Some of the results were purged from the sets (as described below) to arrive at two data sets considered to represent the natural component of the metals. After reviewing the samples in the master data set, the total number of arsenic results was 3,523 while the number of lead results was 4,956. Following adjustment, more than 1,300 samples remained in the two sets and are considered as representative of natural soil. The >30-foot zone was appropriately believed to be largely representative of natural soil, while the shallower zone, even after adjustment, likely included results affected by an assortment of anthropogenic influences. Nevertheless, it was carried forward in the analysis since it was a considerable number of data points and could be advantageously contrasted with the other data. The 0-to-17-foot-zone was used rather than a 0-to-15-foot zone (MassDEP soil criteria: soil categories S-1, S-2, S-3 of the Massachusetts Contingency Plan) (Deparment of Environmental Protection, 2007) in order to capture a large number of split spoon soil boring samples programmatically collected in the 15-to-17-foot interval. Samples from >30 feet were generally assumed to be natural and were also presumed to include marine clay or a fine grained soil component. The data was used with permission of the project, with no identification herein of the exact locations upon client request.

Data for Marine Clay: This data set is from marine clay presumed to be entirely natural material deposited over a considerable period of time. This material was overlain by granular soil, a thin organic layer, and historic fill. The total number of marine clay samples was 240. The exact locations are confidential per client request to allow use of the data.

These three data sets were then tabulated along with two of the data sets from the MassDEP document (Office of Research and Standards, 2002), which were considered by MassDEP when selecting natural soil background maximums concentrations. The tabulation added weight to the overall analysis results and allowed closer comparison with the MassDEP's previously selected numbers. The CA/T data set of the MassDEP document is an initial portion of the more than 6,000 results mentioned above.

The remaining available samples from the first three data sets, with outliers removed and summing in the two data sets from prior MassDEP work, totals more than 2,600 individual arsenic analyses and more than 3,000 individual lead analyses. More exact counts are provided in the tables below under the results and discussion section.

In regard to data management, the sample sets were reviewed and adjusted as follows:

Any metals data set with greater than 50% non-detects was not viewed as viable for our analysis and was not carried forward. This decision did not affect any arsenic or lead data sets. This approach eliminated antimony, selenium, silver, and thallium from the natural and CA/T soil data sets. These evaluations were focused on Resource Conservation and Recovery Act RCRA 8 or priority pollutant 13 lists of metals.

For management of the natural soils data set, the presence of volatile organics or polycyclic aromatic hydrocarbons was used to discriminate potentially affected soils and remove these from the data set. While the presence of organics does not necessarily mean the metals are anthropogenic, it was believed this approach would result in a more representative data set.

In managing the CA/T data set, most samples with lead in excess of 20 milligrams per kilogram mg/kg were rejected, as we surmised that 20 mg/kg is a natural background limit for lead. A review was conducted for the presence of other contaminants, particularly semivolatile organic compounds (SVOCs), and of lead at concentrations well above 100 mg/kg. This review was used to remove samples that appeared to be historically influenced or were likely part of sites of a release. These findings were also applied across the other metals tabulations to adjust the other metals data sets. As the MassDEP natural background concentration for lead is set at 100 mg/kg, this was initially used as a discriminator, with 20 mg/kg appearing to offer a more conservative threshold value based on the patterns in the results suggesting releases. We reviewed the data for surrounding samples initially removed as outliers/ anthropogenic influenced samples or sites of release, and surmised the high results, including lead concentrations, behaved more akin to a release than natural phenomenon. While this approach is questionable in certain respects, the results suggest a reasonably good fit with the other data sets and that the approach resulted in useful information.

Finally, the selected method of removing "outliers" (Department of Toxic Substances Control, 2007) was applied to further adjust the data assuming natural soil would exhibit a normal distribution. This method was selected from the literature and had been extensively applied to school sites in California with arsenic issues. The method removed outliers in a consistent mathematical manner. Data sets with and without these outliers are presented as the mathematical approach does not guarantee of definition of an outlier. The method uses quartiles. The data set is divided by the median number and then each sector is divided again giving a median number for the group above and the group below the overall median. Any number 1.5 times the range between the secondary (25% and 75%) medians is considered to be an outlier in either the high or low direction.

3. RESULTS AND DISCUSSION

Tables 1, 2, and 3 illustrate the treatment of the data sets for arsenic and lead, with and without outliers. This presentation is following the removal of those samples believed to be contaminated based on concentration patterns of other contaminants as described above and high lead levels. Note that the 0-to-17-foot CA/T data set had the largest number of outliers, a probable reflection of the residual anthropogenic influence not captured by the other adjustments. Since the computed number of outliers was consistently lower in the other data sets, and may have even included some natural soil results, less credence can be placed on the 0-to-17-foot set. It is suggested that the removal of outliers from that set may have made it reasonably comparable to the other sets. Hence, it was included in the analysis and the relative values portray a reasonably good fit.

The lowest metal concentrations were evident in the shallow and more granular soil, which was presumed to be natural, followed by the purged urban fill, mainly natural deeper soil, and natural marine clay. The mainly natural deep soil would have included a marine clay component and the purged urban fill was from a zone similar to the natural and just below it. This progression of increasing concentration suggests a consistent pattern of increased metals concentration with depth as the clay/fine grained component increases.

For contrast and verification of results, we provide a comparison against the MassDEP 2002 background document data sets for natural soils (Table 4). For metals, it is noted that the data from Haley & Aldrich (H&A) and the MassDEP (Office of Research and Standards, 2002) was introduced for a comparative review, carrying over the median/geometric mean, which differs from the median and the arithmetic mean of the other sets. That is the reason for bolding the values in the table. Also, we did not investigate the outlier issue in the two "borrowed" data sets in this comparison. Although the two data sets from the 2002 document are not entirely comparable, we believe they are in fact mathematically proximate and may reasonably be displayed together. The geometric mean/median placement of the results in our mean column is noted in bold to be cautioned as not directly comparable. Generally, metals results are higher in the deeper finer grained soil.

In considering the results for arsenic, it can be surmised the MassDEP set most likely reflects more samples in the "arsenic belt" west of the Boston Metro area, while the data provided by the H & A data set is comparable by location to the natural and two purged CA/T sets (Table 4). The lead results in the MassDEP

Table 1. Natural Soil Collected Below Urban Fill by CDM (Concentrations in mg/kg)

Parameters	Arsenic	Lead
Detects	334	292
Non-Detects	3	51
Total	337	343
Number of Outliers	6	1
Deduct Outliers	331	342

Original Set	Arsenic	Lead
Mean	4.9	7.3
Median	4.4	7.6
80%	7.0	11.0
90%	9.2	13.0
95%	10.0	15.0

Outliers Removed	Arsenic	Lead
Mean	4.8	7.3
Median	4.3	7.6
80%	6.8	11.0
90%	8.8	12.0
95%	10.0	15.0

and H & A data set tend to be higher. This finding suggests there may be a quantity of anthropogenic material in these sample sets, or an outlier effect, and these sets did not appear to have outliers removed in any described manner. The MassDEP natural maximum values appear in the last column and results equal to or greater than these are illustrated for all the metals.

The remaining metal sets are relatively consistent for each parameter as well, with the following variations noted:

- Barium: H & A and CDM consistent, marine clay higher, MassDEP set lower
- Chromium: Relatively consistent, MassDEP set lower
- Copper: H & A and MassDEP higher in 90% and 95% categories, possible anthropogenic/outlier influence
- Nickel: MassDEP lower and H & A higher than our three sets
- Vanadium: MassDEP lower than CDM natural set
- Zinc: H & A and MassDEP higher in 90% and 95% categories, possible anthropogenic/outlier influence

Table 2. CA/T Soil Data Sets (0-to-17 feet) (Concentration in mg/kg)

Parameters	**Arsenic**	**Lead**
Detects	1018	831
Non-Detects	52	542
Total	1070	1373
Number of Outliers	46	3
Deduct Outliers	1024	1370

Original Set	**Arsenic**	**Lead**
Mean	6.1	8.0
Median	4.6	7.0
80%	9.0	13.0
90%	12.0	16.0
95%	15.0	18.0

Outliers Removed	**Arsenic**	**Lead**
Mean	5.2	7.9
Median	4.4	6.9
80%	8.0	13.0
90%	10.0	16.0
95%	12.0	18.0

As a further consideration and comparison, the USGS collected a large data set consisting of 1,597 stream sediment and 1,279 rock samples (2,876 total samples) in their quest for better identification of arsenic sources in the New England area. This was in response to problematic concentrations of arsenic in potable water wells (Ayotte and Robinson, 2007). In summary, the natural rock average was 7 mg/kg and the stream sediment average was 5.5 mg/kg. They note that the stream sediment might be expected to contain some anthropogenic influence, particularly from the agricultural sector. The 5.5 mg/kg total arsenic value is close to the result extracted from the 0-to-17 foot value from the CA/T data set at 5.2 mg/kg. There is, moreover, consistency with these average results and all the soil results described above as they range from 4.7 mg/kg to 12 mg/kg total arsenic.

Table 3. CA/T Soil Data Sets (> 30 feet) (Concentration in mg/kg)

Parameters	**Arsenic**	**Lead**
Detects	326	215
Non-Detects	17	142
Total	343	357
Number of Outliers	9	0
Deduct Outliers	334	357

Original Set	**Arsenic**	**Lead**
Mean	8.1	7.1
Median	4.6	5.2
80%	9.0	12.0
90%	14.0	15.0
95%	16.0	17.0

Outliers Removed	**Arsenic**	**Lead**
Mean	7.5	7.1
Median	6.6	5.2
80%	11.6	12.0
90%	14.0	15.0
95%	15.0	17.0

4. CONCLUSIONS

The MassDEP maximum background soil detection for arsenic of 20 mg/kg for natural and urban fill soil is well supported by the above findings. While the derived natural soil numbers only bring one into a range of values due to limitations in identification and management of outliers, the results do provide valuable information. The data helps us understand background detection concentrations in the Boston Metro Area, as well as lend considerable overall support to the MassDEP selections in the 2002 document. While we believe natural lead in soil is generally less than 20 mg/kg, we suggest that the 100 mg/kg MassDEP number appears to be a reasonable maximum.

Table 4. Comparison of Data Sets Inclusive of MassDEP (2002) Sets

PARAMETERS (Total Samples in Group)	Sample Sources	Samples by Source	RESULTS				MassDEP (2002) Natural Background Number
			Mean	Median	90%	95%	
ARSENIC (2,653)	Natural	331	4.8	4.3	8.8	10	20
	CA/T 1	1024	5.2	4.4	10	12	
	CA/T 2	334	7.5	6.6	14	15	
	Marine Clay	236	12	12	14	16	
	DEP (1995)	139	*4.7*	4.8	17	24.5	
	H&A 2001	589	*5.5*	5.6	11	13	
BARIUM (1,125)	Natural	334	31	27	62	74	50
	CA/T 1	-	-	-	-	-	
	CA/T 2	-	-	-	-	-	
	Marine Clay	237	86	88	100	100	
	DEP (1995)	64	*15*	16	45	52.8	
	H&A 2001	490	*35*	36	80.9	89.3	
CHROMIUM (2,700)	Natural	333	19	16	37	42	30 (total)
	CA/T 1	1052	19	16	40	45	
	CA/T 2	342	37	37	60	63	
	Marine Clay	237	45	46	50	52	
	DEP (1995)	147	*10*	11	29	39	
	H&A 2001	589	*22*	22	44	50	
COPPER (1,647)	Natural	172	15	16	27	29	40
	CA/T 1	1010	16	14	28	32	
	CA/T 2	340	23	24	34	37	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	103	*7.7*	7.3	38	56	
	H&A 2001	22	*26*	27	48	65	
LEAD (3,029)	Natural	342	7.3	7.6	12	15	100
	CA/T 1	1370	7.9	6.9	16	18	
	CA/T 2	357	7.1	5.2	15	17	
	Marine Clay	236	11	11	12	13	
	DEP (1995)	141	*20*	19	99	158	
	H&A 2001	583	*15*	24	79	112	
NICKEL (1,750)	Natural	280	15	14	25	30	20
	CA/T 1	1002	16	14	31	37	
	CA/T 2	343	28	29	43	45	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	103	*4.6*	5.1	17	23	
	H&A 2001	22	35	35	68	70	
VANADIUM (73)	Natural	43	33	26	56	61	30
	CA/T 1	-	-	-	-	-	
	CA/T 2	-	-	-	-	-	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	30	*7.6*	10	29	39	
	H&A 2001	-	-	-	-	-	
ZINC (1,772)	Natural	281	38	37	63	71	100
	CA/T 1	1017	46	42	81	93	
	CA/T 2	340	69	71	99	104	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	112	*29*	28	116	131	
	H&A 2001	22	*67*	59	103	106	

NOTES: DEP (1995) and H&A (2002) from (Office of Research Standards, 2002). Italic mean values are "geometric mean or median" which differ from the mean. Shaded at or in excess of MassDEP (2002) selected number.

For further reference and information, the mean of the 0-to-17-foot CA/T samples for arsenic and lead, inclusive of all samples, was computed to be 8.9 mg/kg and 310 mg/kg respectively. This most closely fits in comparison to the ranges for natural soil derived above as shown in the Tables, per the adjusted 0-to-17-foot data set. These urban fill averages were derived using all values and ProUCL 4.0 as provided by U.S. Environmental Protection Agency. Our comparison with the derived natural component 0 to 17 feet suggests that anthropogenic arsenic and lead contribute approximately 8.9-5.2/8.9 =42 % and 310-7.9/310=97% to the urban/historic fill average respectively. This relationship also represents that portion of the potential human health risk impact of each. Furthermore, for arsenic, the 5.2 mg/kg and 8.9 mg/kg results, were applied to MassDEP Method 3 risk calculations per their short form. This application results in an excess lifetime cancer risk (ELCR) of 4E-06 and 7E-06 respectively, exclusive of the vegetable growing scenario. The 90% level of 10 mg/kg is close to the allowable no significant risk threshold of 1E-05 (ELCR).

As a final note, no data set can be viewed as purely natural other than the marine clay. Use of large data sets brings a certain perspective to the natural and historic fill environment and assists in understanding the magnitude of the source of metals present in natural soil and urban/historic fill. The data sets presented above are complementary and provide a range of natural soil metals concentrations in the Boston metro setting.

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