

## TECHNICAL MEMORANDUM

TO: Dave Bradley, Washington State Department of Ecology

FROM: Eric Weber, L.G. and Kris Hendrickson, P.E.

DATE: December 6, 2006

RE: **ADDITIONAL INFORMATION ON ARSENIC AND LEAD MOBILITY IN AREA-WIDE CONTAMINATION-IMPACTED SOIL (ADDENDUM TO SEPTEMBER 14, 2006 TECHNICAL MEMORANDUM RE: ARSENIC AND LEAD MOBILITY IN AREA-WIDE CONTAMINATION-IMPACTED SOIL)**

Information was presented to the Washington Model Toxics Control Act Science Advisory Board (SAB) on the mobility of arsenic and lead associated with area-wide contamination impacted soil. Information was conveyed in a series of presentations, most recently on October 23, 2006. A Landau Associates technical memorandum dated September 14, 2006 was also submitted to the SAB that summarized existing data and analysis on arsenic and lead mobility.

The September 14 technical memorandum presents information on four lines of evidence that, taken together, indicate concentrations of arsenic below 200 mg/kg and lead below 1,000 mg/kg are unlikely to pose a significant threat to groundwater. However, there may be some conditions, especially for arsenic, that increase leaching to the extent that site-specific demonstration of protection of groundwater may be appropriate. The four lines of evidence are.

- The expected limited mobility of arsenic and lead as a result of their chemical properties and field and laboratory studies that support this conclusion for tested soils.
- The extensive soil profile data available for the Tacoma Smelter Plume area and former orchards in central Washington which indicates the vertical extent of elevated arsenic and lead concentrations in undisturbed soil is limited to shallow soil.
- The groundwater data from the Tacoma Smelter Plume area that indicates existing concentrations of arsenic and lead have not impacted shallow groundwater. Limited groundwater data from former orchard areas is inconclusive.
- Literature values of arsenic distribution coefficients indicate that a representative coefficient for arsenic is much higher than the EPA and MTCA default value of 29 L/Kg. For example, the median value of arsenic distribution coefficients from a recent EPA publication is 2,510 L/Kg. If this value is used in the conservative equilibrium partition model, than an arsenic concentration of 251 mg/kg would be protective of groundwater.

During the October 23 presentation, the SAB raised a number of questions concerning information that was presented. This technical memorandum addresses these questions.

## RELATIONSHIP BETWEEN SOIL TYPES IN TOKUNAGA (2005) STUDY AND WASHINGTON STATE

- **September 14<sup>th</sup> Technical Memorandum:** Landau (2006) presents a conceptual model that supports the conclusion that arsenic and lead generally have low mobility in shallow soils. This conclusion was based in part on results from a Japanese study (Tokunaga (2005)). The study reported that several soil types had high arsenic sorption capacities that equate to soil concentrations ranging from 2,850 to 21,130 mg/kg.
- **Questions Raised at the October 23<sup>rd</sup> Board Meeting:** At the October 23<sup>rd</sup> meeting, the SAB questioned whether the study results were applicable to Washington. The SAB asked Ecology/Landau to explain how the soils in Washington compare with the soils in the Tokunaga study.
- **Additional Information:** Soils in the Tokunaga study are from Japan. The soil types are described as forest soil, red-yellow soil, Kuroboku soil pumice and gley soil. The chemical composition and water content, shown in Table 1, indicate that the soil types in the Tokunaga sorption experiment represent a wide range of soil conditions; however we were not able to correlate these soil types directly with soil descriptions from county soil surveys in Washington. However, Beaulieu and Savage (2005) completed an in-depth study of arsenic adsorption at five locations on south Vashon and Maury Islands. They measured the chemical composition of soil (collected from 0 to 36 inches depth below ground surface) at about 50 to 60 % SiO<sub>2</sub>, 10 to 15 % Al<sub>2</sub>O<sub>3</sub>, 5 % Fe<sub>2</sub>O<sub>3</sub> and organic content ranging from 5 to 20 %.<sup>1</sup> Soil pH ranged from 4.8 to 6.14. This soil type does not clearly match any of the soil types presented by Tokunaga (2005). Beaulieu and Savage (2005) concluded that these soil conditions (oxidizing and mildly acidic) promoted arsenic adsorption on soil colloids with aluminum oxyhydroxides as the major adsorbing substrate. They also concluded that transformation of soil conditions to a reducing or alkaline environment could increase arsenic mobility.

## IMPACT OF SMELTER EMISSIONS ON SOIL PH

- **September 14<sup>th</sup> Technical Memorandum:** Landau (2006) noted that soil pH affects arsenic mobility and that arsenic typically has low mobility in shallow soils in the acid to neutral range.
- **Questions Raised at October 23<sup>rd</sup> Board Meeting:** At the October 23 meeting, the SAB enquired about the pH of precipitation associated with smelter emissions and how that might affect arsenic mobility.
- **Additional Information:** The Tacoma Smelter emissions caused the precipitation downwind to be more acidic. A study at the University of Washington during 1984 (when the smelter was operating) measured precipitation pH of approximately 4.4 (at the closest site in West Seattle) (Vong 1985). The background pH was measured at 5.4. The decline in pH was attributed to smelter emissions. This acidic pH value was attributed to high sulfur dioxide content of smelter emissions. Precipitation for rainfall in western Washington is reported by the United States Geologic Survey at about 5.4. While the pH of rainfall is more

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<sup>1</sup> Organic carbon content was as high as 50% in one sample and 34% in another. In these samples, the percentage of other constituents was lower than the ranges given to accommodate the high organic content.

acidic than background, it is not appreciably more acidic than western Washington soil. Consequently, the acidifying affect of smelter-affected rainfall may be limited.

#### APPLICABILITY OF CRECELIUS STUDY TO OTHER AREAS

- **September 14<sup>th</sup> Technical Memorandum:** Landau (2006) summarized the results of a leaching study completed by Eric Crecelius, then at the University of Washington. Crecelius et al. (1985) reported maximum arsenic and lead concentrations (As = 393 and Pb = 586 mg/kg) in the 0-2 inch depth interval and declined to background levels at the 10-12 inch or 23-26 inch depth intervals (varied by location). Pore water concentrations at the 10-12 inch depth interval were low or undetectable (< 0.4 µg/L).
- **Questions Raised at October 23<sup>rd</sup> Board Meeting:** At the October 23rd meeting, the SAB inquired about the pH of pore water from the Crecelius study (1985). The Board was also interested in the general applicability of this study to Puget Sound area soil.
- **Additional Information:** For Crecelius' study, the soil pH was measured at different intervals in the soil profile and ranged from 3.4 (extremely acid) to 5.1 (strongly acid). Pore water pH was not reported. The Crecelius study was conducted at an apparently undisturbed plot of land approximately 600 ft south of the southern border of Point Defiance Park, within 1 mile of the former Tacoma Smelter. Soil is described as Sinclair (moderately deep, moderately well drained soil formed in glacial till) and Indianola (deep excessively drained soil formed in sandy outwash). These soil types may be more permeable (i.e. higher sand and gravel content) than typical Puget Sound soils. Organic carbon content of these soils was relatively low for surface soil, between about 0.2 and 6.5 %. Arsenic soil concentrations at this location are likely to be higher than other area-wide impacted locations due to the proximity to the smelter. The soil pH also appears to be somewhat more acid than typical Puget Sound soil. A more permeable surface soil with low organic carbon content would likely be more oxidized, possibly decreasing arsenic mobility. More permeable soil and higher soil concentrations may increase arsenic mobility. Overall, it appears that the soil conditions are reasonably representative of upland conditions in Puget Sound and therefore should be useful in evaluating arsenic mobility.

#### RELATIONSHIPS BETWEEN SOIL CONCENTRATIONS AND GROUNDWATER CONCENTRATIONS

- **September 14<sup>th</sup> Technical Memorandum:** Ecology and Landau Associates have not identified studies evaluating the impacts of widespread arsenic and lead soil contamination on ground water quality. However, Landau Associates (2006) reviewed available monitoring data for wells on Vashon and Maury Islands and found no consistent relationship between surface soil concentrations and ground water concentrations. Landau noted that two wells in the central portion of Vashon and Maury Islands (areas with highest soil concentrations) had arsenic concentrations above 10 µg/L. However, Landau Associates noted that these two wells were relatively deep (about 300 ft) suggesting that the elevated levels of arsenic in the wells are from a natural source. An evaluation by King County Department of Natural Resources Groundwater Division reached the same conclusion.
- **Questions Raised at October 23<sup>rd</sup> Board Meeting:** At the October 23rd meeting, SAB members inquired about the depth of wells on Vashon and Maury Islands that were part of King County's long-term monitoring program. They also asked that Landau Associates look

at specific springs and/or wells and compare groundwater concentrations with soil concentrations.

- **Additional Information:** The depth of wells that are part of King County's long-term groundwater monitoring program are between 67 ft and 691 ft depth. Wells less than 200 ft deep are likely screened in the glacial advance outwash aquifer, commonly referred to as the Principal Aquifer. Deeper wells are likely screened in sand and gravel lenses in older interglacial silt and clay deposits. The depths of individual wells are shown on Figure 1. Most of the wells are located outside of the area of higher arsenic and lead soil concentrations located on Maury Island and the south end of Vashon Island. The distribution of arsenic in soil in the 0-6 inch depth intervals are shown on Figures 2 and 3. These figures show the 90<sup>th</sup> percentile and median of the arsenic concentration respectively.<sup>2</sup> Lead concentrations show similar trends with the absolute concentration being roughly 3 to 5 times higher. Note that wells W-04 and W-07, the two wells that had elevated arsenic concentrations, are located in the central to north part of the island (see Figure 1) where arsenic concentrations are relatively low. The arsenic at these wells is likely to be from natural sources and related to dissolution of iron hydroxides in a deeper, anaerobic aquifer.

To further evaluate the effect of soil arsenic concentrations, we looked at the Dockton Water Association (DWA) springs. DWA is located on the south end of Maury Island and gets its water from springs and wells. The Dockton Spring is located at about Elevation 55 ft. They supply about 35 gpm from well points spread over about 10 acres of the watershed near Dockton Park. The Hake Spring is located at about Elevation 175 ft, MSL and supply between 5 and 7 gpm (Geraghty and Miller 1995). The location of the Dockton and Hake Springs are shown on Figures 4 and 5. Figure 4 also shows arsenic concentrations in soil. Figure 5 shows lead concentrations in soil.

The geology of the south end of Maury Island is dominated by three geologic units: glacial till (Qvt); advance outwash sand (Qva); and older (pre-Vashon) silt, clay and sand (Qpvu). The surface distribution of these geologic units is shown on Figures 4 and 5. The glacial till is a dense deposit that impedes infiltration. The principal aquifer is in the Qva where groundwater infiltrates from the surface, particularly where the glacial till is absent, and forms on top of the less permeable Qpvu deposits. The stratigraphy of these geologic units is shown in cross section on Figures 6 and 7.

The Dockton Spring discharges directly from the Qva Principal Aquifer (near Well 22 on Figure 7). Recharge to the spring is from infiltrating precipitation, particularly where the till is absent. The Hake Spring appears to represent discharge that flows directly off the surficial deposit of glacial till in this area. Discharge at both the Dockton Spring and the Hake Spring likely represents relatively recent recharge from infiltrating precipitation. At the Hake Spring, discharge appears to represent groundwater interflow directly off of the till. At the Dockton Spring, discharge is from infiltration to the principal aquifer. The average velocity through the advance outwash unsaturated zone was estimated at about 20 ft/month (Pacific Groundwater Group 2000). Given the high soil arsenic concentrations and the shallow nature of these springs, both water sources should be considered susceptible to mobile arsenic

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<sup>2</sup> These plots are constructed using Thiessen Polygons. A polygon is constructed around each data point so that any point within the polygon is closer to the original data point than any other data point. A data distribution associated with each polygon is constructed by selecting the 9 nearest neighbors. The 90<sup>th</sup> percentile and median is selected from the data distribution for each polygon. See Pacific Groundwater Group 2005 for additional explanation.

contamination. However, arsenic was not detected in samples from either spring. The Dockton Spring was sampled 4 times between 1990 and 2002. The Hake Spring was sampled 5 times during the same time period.<sup>3</sup> The reported detection limit for the first sample at each spring was 0.1 mg/L. The detection limit was not reported for the remaining samples.

## DISTRIBUTION OF SOIL ARSENIC OVER TIME

- **September 14<sup>th</sup> Technical Memorandum:** Landau (2006) summarized several studies that examined the relationship between soil depth and arsenic and lead concentrations.
- **Questions Raised at October 23<sup>rd</sup> Board Meeting:** At the October 23<sup>rd</sup> meeting, the SAB asked whether there was information showing the distribution of soil arsenic with depth over time.
- **Additional Information:** Unfortunately, we could not find data describing arsenic distribution over time. However, it is known that the majority of arsenic was originally deposited in the upper six inches. Recent soil profile data from both the Tacoma Smelter Plume area and orchards in eastern Washington indicate that both arsenic and lead has been redistributed in the soil column over the last 20 to 80 years. In the Tacoma Smelter Plume area, elevated concentrations of arsenic generally do not occur below 2 ft in the absence of soil disturbance. In former orchard areas, elevated concentrations of arsenic may occur to a depth of over 4 ft.

## ARSENIC MASS BALANCE

- **September 14<sup>th</sup> Technical Memorandum:** Landau (2006) provided the results of initial modeling performed using the MTCA/EPA Partitioning Model. However, the technical memorandum does not include a discussion of mass-balance approaches.
- **Questions Raised at October 23<sup>rd</sup> Board Meeting:** At the October 23<sup>rd</sup> meeting, the SAB inquired whether a mass balance approach was useful in evaluating arsenic mobility.
- **Additional Information:** We looked at mass balance using two approaches. The first approach was to look at how long it would take to leach half the arsenic from the upper 6-inches of soil using the batch flush model. The second approach looked at estimates of total arsenic and lead loading and compared them to current concentrations to see if there was evidence that appreciable mass was lost.
  - **Batch Flush Model:** A relatively simple but informative approach to evaluating contaminant depletion in soil is the batch flush model (Zheng et al. 1991, Gehlar and Wilson 1974). The batch flush model assumes contaminant concentrations decline exponentially in proportion to the retardation factor which is a function of the distribution coefficient. This is an approximate method with significant limitations however; it can be useful in evaluating distribution coefficients. Batch flush model calculations are presented in Attachment 1. Assuming a distribution coefficient of 29 L/kg, it was

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<sup>3</sup> Arsenic data for both the Dockton and Hake springs is presented on King County's IMAP website. [http://www.metrokc.gov/gis/mapportal/iMAP\\_main.htm](http://www.metrokc.gov/gis/mapportal/iMAP_main.htm).

estimated that it would take 18.2 years for half of the arsenic to be removed from one cubic foot of soil, 6-inches thick. If a distribution coefficient of 1,580 L/kg is used, it would take over 990 years to remove half of the arsenic from one cubic foot of soil 6-inches thick.

- Arsenic and Lead Loading – Agricultural Soil: The Area-Wide Task Force Report (2003) summarized agricultural loading calculations completed by Dr. Frank Peryea at Washington State University. Annual loading rates from lead arsenate sprays were estimated to increase from approximately 55 kg lead/ha-year and 20 kg arsenic/ha-year (49 lb/acre-year lead and 18 lb/acre-year arsenic) in 1905 to 215 kg lead/ha-year and 80 kg arsenic/ha-year (191 lb/acre-year lead and 71 lb/acre-year arsenic) in 1947 (Peryea 1989). His estimates were based on per-acre rates of application reported by Overley (1950) and Benson et al (1968) for the time period 1905 to 1947. Peryea prepared a report for the Wenatchee School District in 1991. This report provides a rough estimate of soil loading with lead and arsenic from lead arsenate insecticide sprays in Washington apple orchards (Peryea 1991). The estimated total amount of arsenic applied was 841 kg/acre (1850 lbs/acre) and lead was 2291 kg/acre (5040 lb/acre). These loading rates would result in maximum predicted soil concentrations of approximately 1900 mg/kg arsenic and 5,200 mg/kg lead. Based on Peryea's analysis, the total amounts estimated agree well with the values calculated for the two sites with most heavily arsenic and lead enriched orchard soil that were included in his early evaluation of six orchard sites (Peryea 1989).

Peryea notes in his 1991 report that exact agreement between loading estimates and measured concentrations would not be expected. This is because off-target lead arsenate applications would vary within an orchard, with soils under trees preferentially enriched because of spray drift, dripping, and stem flow, while areas between trees would receive only spray drift. Peryea has also completed analysis of the chemical composition of agricultural-grade acid lead arsenate (unpublished paper) and found that the arsenic concentration was lower and the lead concentration higher than expected for pure acid lead arsenate. This is consistent with the lower loading rates observed in the field testing relative to the predicted loading amounts (Area-wide Task Force 2003).

A similar calculation was presented in the National Academy of Sciences report on arsenic (National Research Council 1977). They estimated arsenic loading rates at 30 to 60 pounds per acre of lead arsenate. They estimated that this application rate over 60 years would result in 194 to 389 ppm arsenic in the upper 6 inches of soil.

## EQUILIBRIUM PARTITIONING MODEL

- September 14<sup>th</sup> Technical Memorandum: Landau (2006) provided the results of initial modeling performed using the MTCA/EPA Partitioning Model. .
- Questions Raised at October 23<sup>rd</sup> Board Meeting: At the October 23<sup>rd</sup> meeting, the SAB discussed the results of the equilibrium partitioning model. The Board requested additional information on the applicability of the  $K_d$  values in the Allison and Allison (2005) report. They also asked for additional information on modeling parameters or assumptions (e.g. unlimited source) that might lead to results that over- or under-predict real-world conditions.

- **Additional Information:** In general, the model overestimates the concentration of arsenic in groundwater. As discussed in the meeting, the partitioning model assumes that the soil concentration used in the calculation is constant throughout the soil column. However, the soil concentration decreases with depth and arsenic resorbs deeper in the soil column. If these facts were taken into account, the groundwater concentration would be lower than the model suggests. The model also assumes equilibrium partitioning between soil and liquid phase. Equilibrium would generate the highest possible concentration of arsenic in the water. Therefore, the actual groundwater concentration must be equal to or less than the concentration predicted by the model. If significant leaching was occurring, the source concentration would decline. The concentration would be less than calculated with the model if the source no longer contributed contamination to the site.

The dilution factor (DF) used in the model is based on a 30-acre source size and includes mixing in the aquifer downgradient of the source. In the case of the smelter, with a larger source size than assumed, the DF should be assumed smaller if average concentrations are used as input to the model. A smaller DF would result in a greater estimated concentration in groundwater. However, for a source size smaller than assumed, perhaps an orchard, the DF should potentially be larger, resulting in a smaller estimated concentration in groundwater.

The distribution coefficient probably has the greatest impact on the equilibrium partition equation result. The MTCA default value for arsenic is 29 L/kg, while median literature values are estimated as high as 2,510 L/kg (Allison and Allison 2005). Most of the literature describing arsenic distribution coefficients does not provide specific corresponding information on factors that affect the coefficient value such as pH, soil type, and concentration. There is information that indicates that arsenic (III) is more mobile than arsenic (V). However, we did not find specific information that would help us narrow the range of distribution coefficients applicable to Washington State

## ARSENIC MIGRATION RATES

- **September 14<sup>th</sup> Technical Memorandum:** Landau (2006) did not discuss arsenic migration rates.
- **Questions Raised at October 23<sup>rd</sup> Board Meeting:** At the October 23rd meeting, the SAB inquired about potential maximum arsenic migration rates
- **Additional Information:** The primary migration process for a dissolved solute in the subsurface is advection (or movement with the bulk motion of groundwater flow). Solutes that tend to adsorb to the solid matrix will be retarded, i.e. will migrate at a rate slower than the average groundwater velocity. Retardation is often estimated by the following equation.

$$R = 1 + (\rho / n) * K_d$$

R = retardation factor

$\rho$  = bulk density of soil (given as 1.5 kg/L)

n = porosity of soil (given as 0.3 mL water / mL soil)

$K_d$  = distribution coefficient (default for arsenic given as 29 L/kg)

For the parameters given above, retardation for arsenic is 146. That means that arsenic would travel 146 times slower than the average water velocity. Vertical unsaturated groundwater flow velocities on Maury Island (through advance outwash soil) were estimated at about 20 ft/month or about 240 ft/year (Pacific Groundwater Group 2000). Assuming a retardation factor of 146, arsenic would migrate vertically in the unsaturated zone at about 1.4 ft/year. If a mean  $K_d$  for arsenic of 1,580 L/kg (Allison and Allison 2005) was used, the retardation factor would be 7,954. The calculated vertical migration rate would be 0.03 ft/year or about 3 ft in 100 years.

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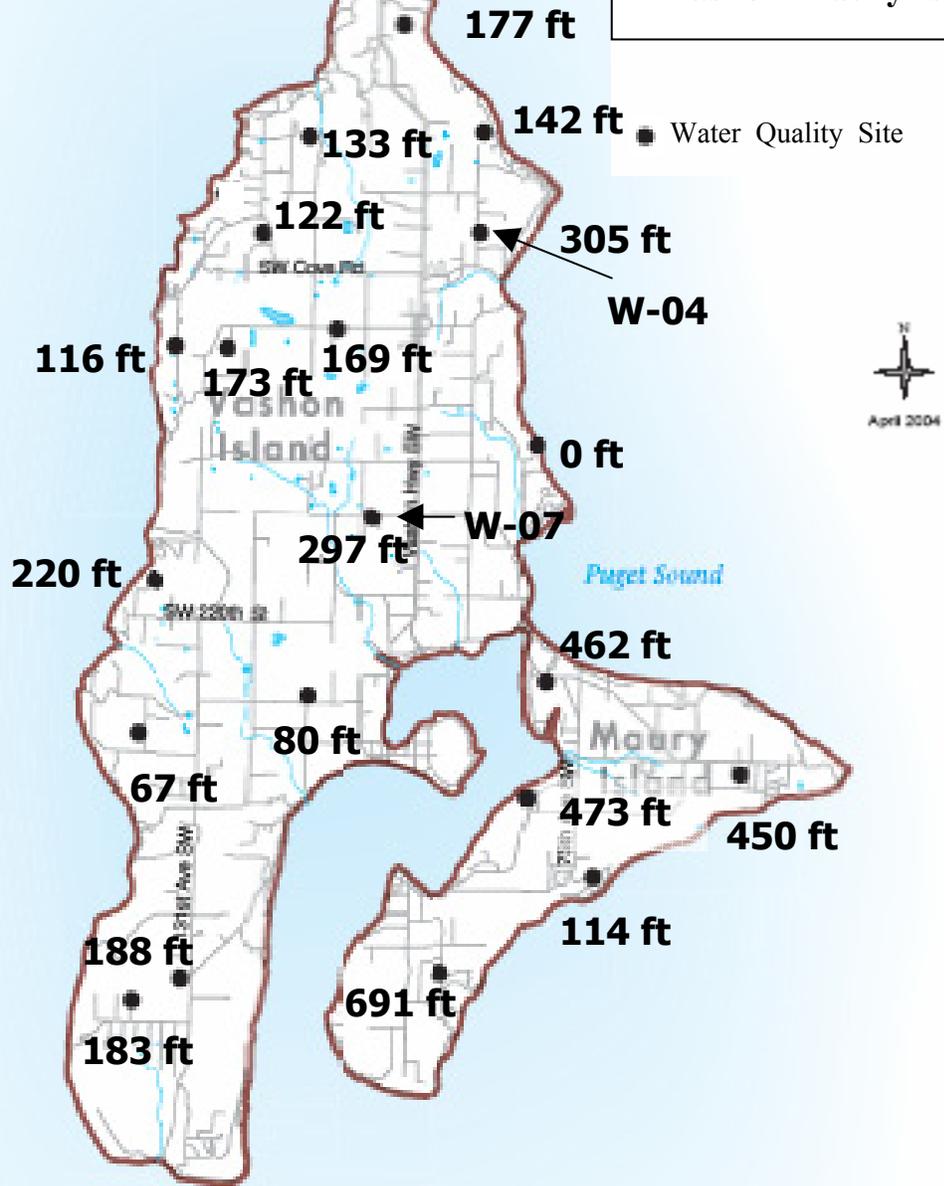
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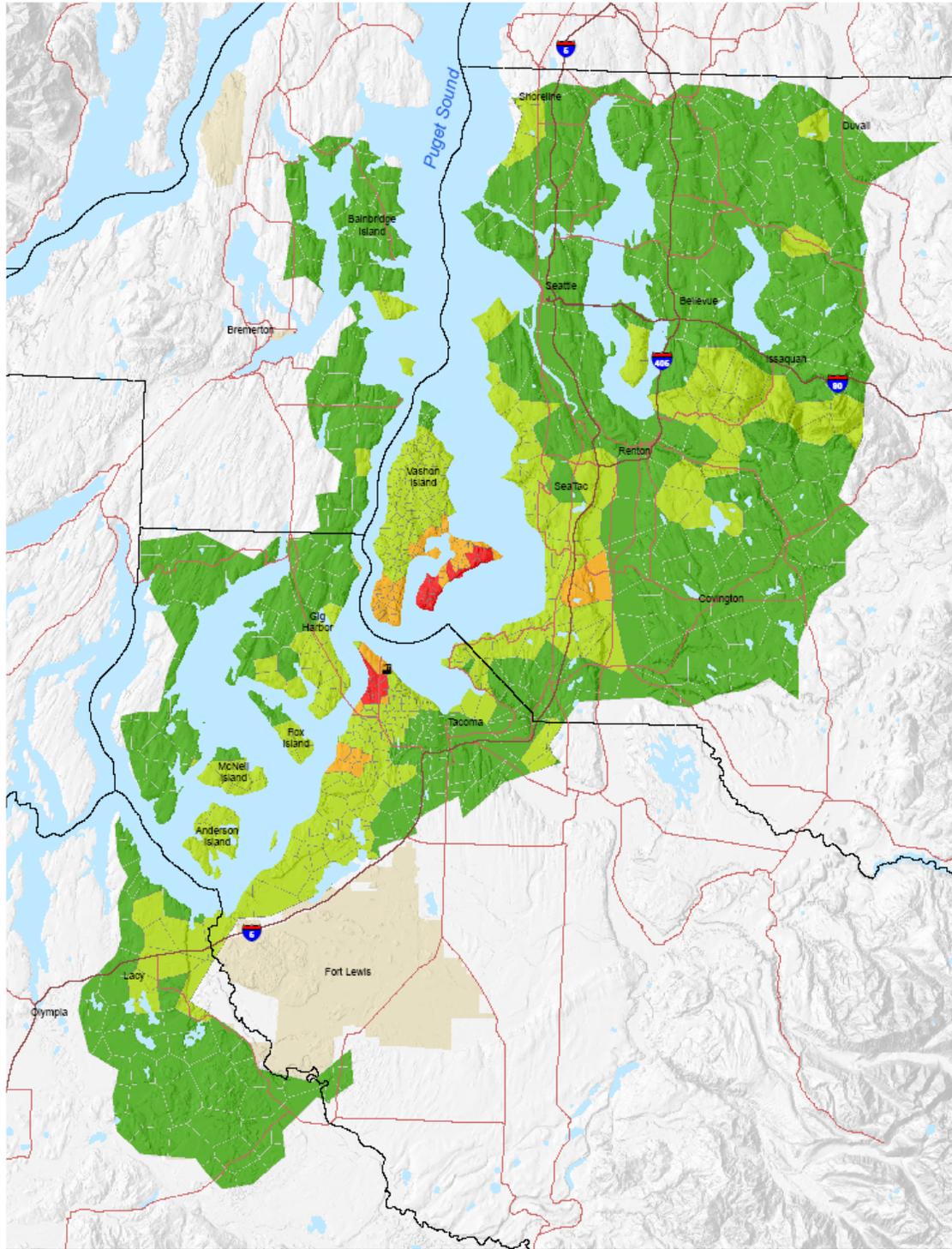
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**Well Depths of  
Water Quality Sites on  
Vashon-Maury Island**



**Area A: Vashon-Maury Island  
Monitoring Locations**





**Arsenic Concentrations 0-6" 90th Percentile (mg/kg)**

<ul style="list-style-type: none"> <li><span style="display: inline-block; width: 15px; height: 10px; background-color: #008000; margin-right: 5px;"></span> 0.0 - 20.0</li> <li><span style="display: inline-block; width: 15px; height: 10px; background-color: #90EE90; margin-right: 5px;"></span> 20.1 - 100.0</li> <li><span style="display: inline-block; width: 15px; height: 10px; background-color: #FFD700; margin-right: 5px;"></span> 100.1 - 200.0</li> <li><span style="display: inline-block; width: 15px; height: 10px; background-color: #FF0000; margin-right: 5px;"></span> 200.1 - 1050.0</li> </ul>	<ul style="list-style-type: none"> <li><span style="display: inline-block; width: 10px; height: 10px; background-color: black; margin-right: 5px;"></span> Tacoma Smelter Stack</li> <li><span style="display: inline-block; border-bottom: 1px solid black; width: 20px; margin-right: 5px;"></span> County Boundaries</li> <li><span style="display: inline-block; border-bottom: 1px solid red; width: 20px; margin-right: 5px;"></span> Highways</li> <li><span style="display: inline-block; border-bottom: 1px solid brown; width: 20px; margin-right: 5px;"></span> Major Roads</li> <li><span style="display: inline-block; width: 15px; height: 10px; background-color: lightblue; margin-right: 5px;"></span> Puget Sound &amp; Lakes</li> <li><span style="display: inline-block; width: 15px; height: 10px; background-color: #D2B48C; margin-right: 5px;"></span> Military Bases - Inaccessible</li> </ul>
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0 Miles 10

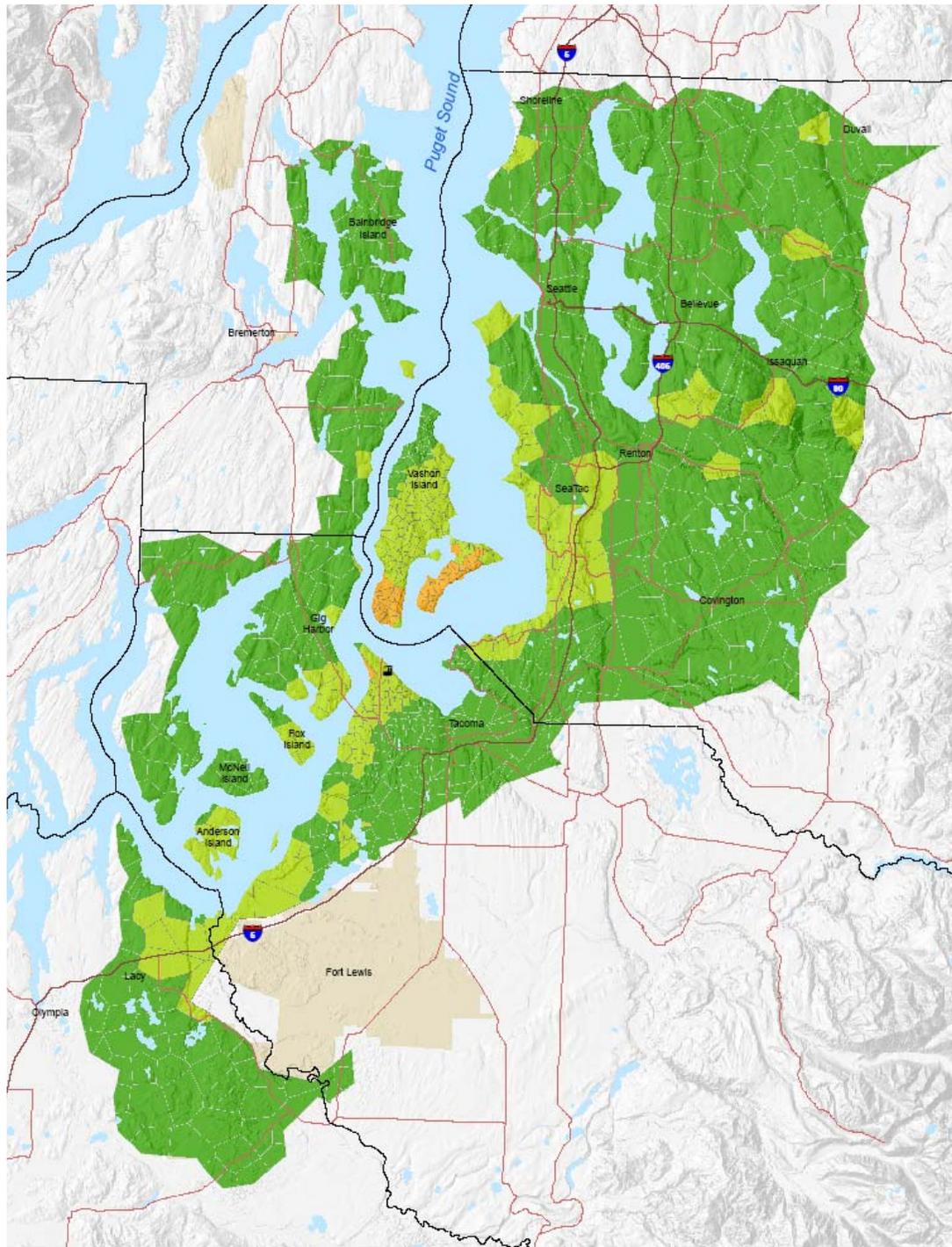
Source: Pacific Groundwater Group



Area-Wide Implementation  
Project, Washington  
Department of Ecology

**Arsenic Concentrations in Soil  
90th Percentile, 0-6 inches**

Figure  
**2**



<b>Arsenic Concentrations 0-6"</b>	Tacoma Smelter Stack
<b>Median Values (mg/kg)</b>	County Boundaries
0.0 - 20.0	Highways
20.1 - 100.0	Major Roads
100.1 - 200.0	Puget Sound & Lakes
200.1 - 1050.0	Military Bases - Inaccessible

0 Miles 10

Source: Pacific Groundwater Group

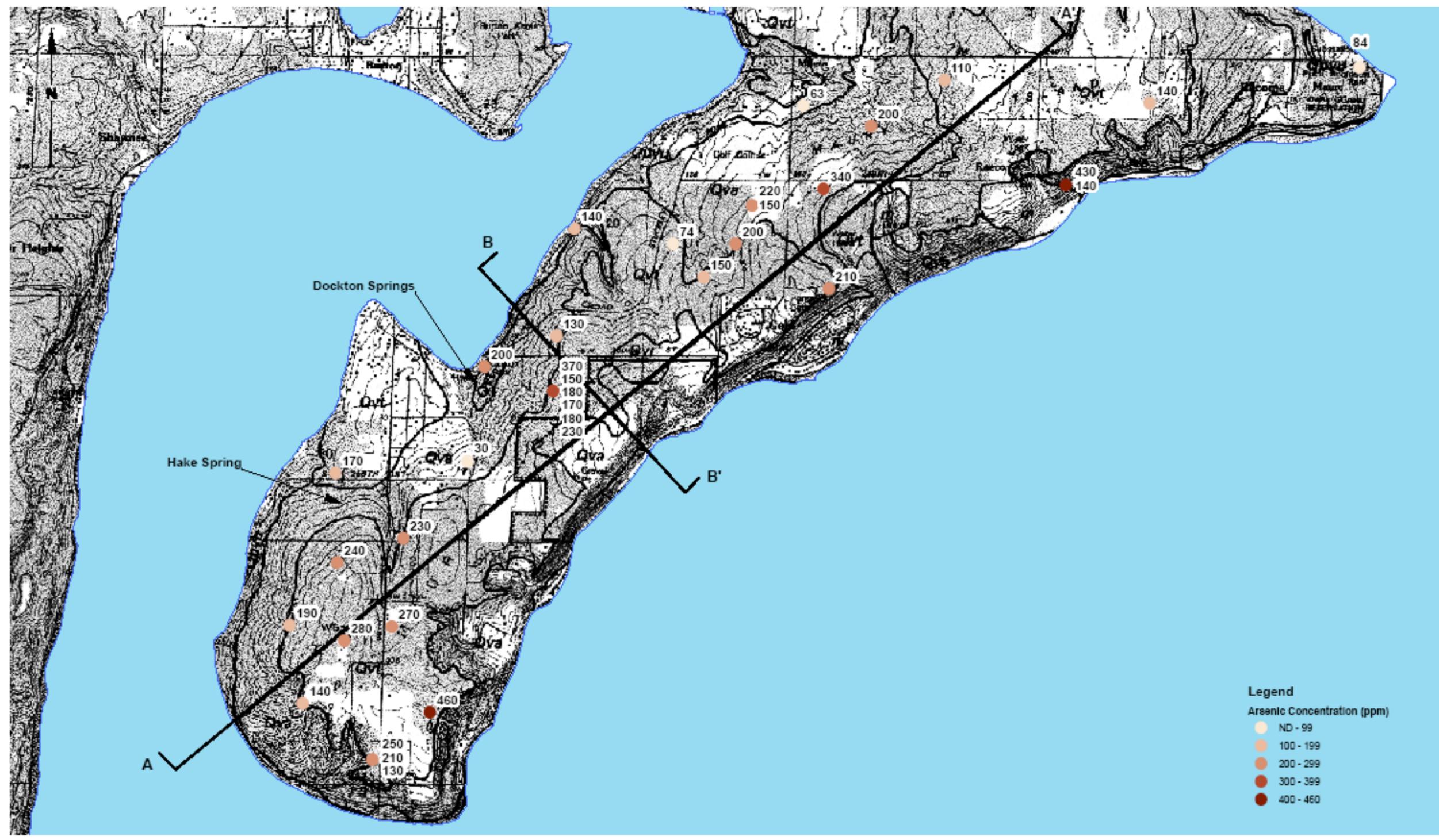


Area-Wide Implementation Project, Washington Department of Ecology

**Arsenic Concentrations in Soil Median, 0-6 inches**

Figure 3

Ecology | I:\DATA\PROJECT\1136\Soil to GWIR\Tech Memo Addendum\Figure 4.dwg "Figure 4" 12/1/2006



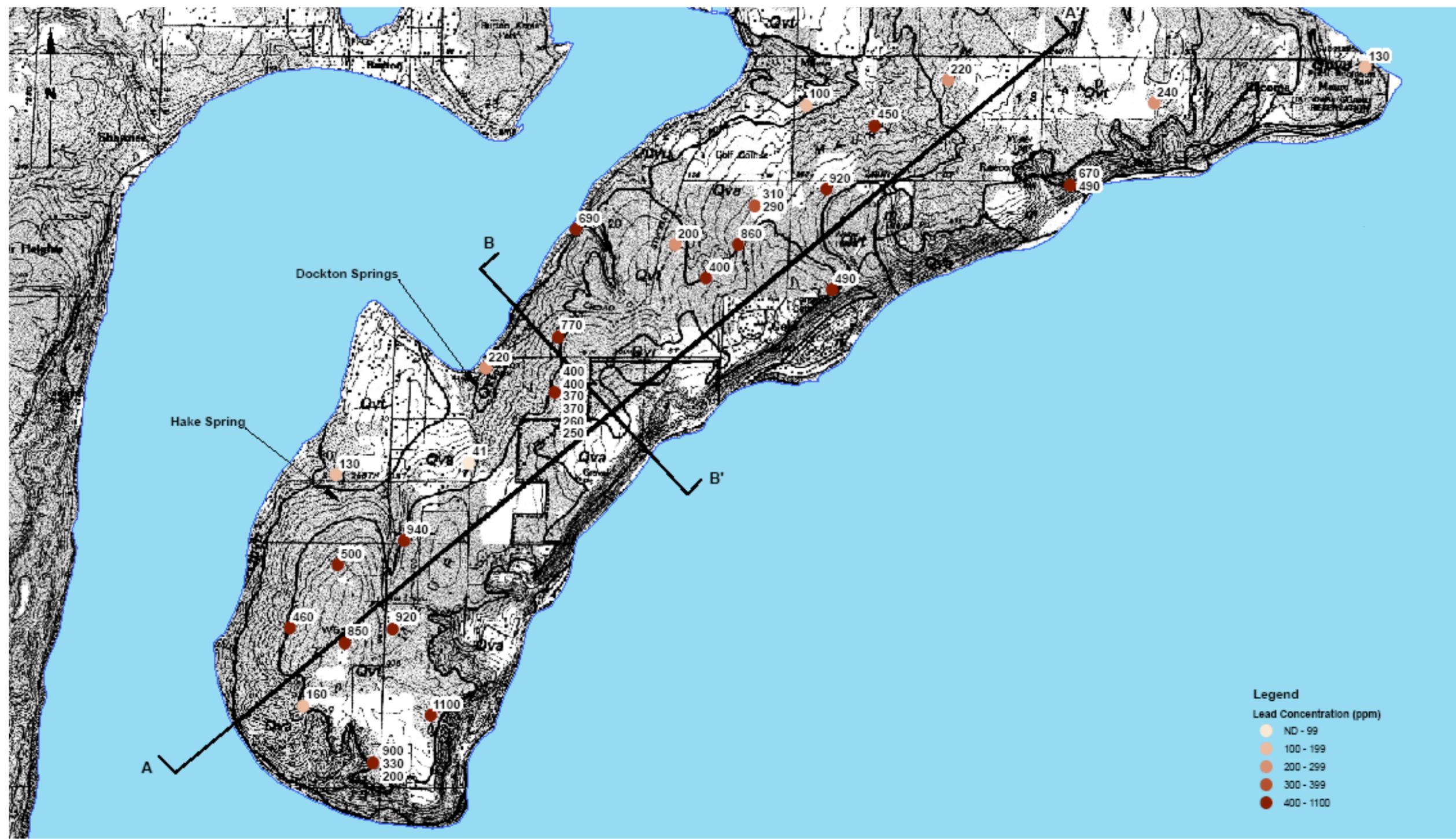
Source: Public Health Seattle King County 2000 and Pacific Groundwater Group 2000

Area-Wide Implementation  
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**Maury Island  
 Arsenic Concentrations**

Figure  
**4**

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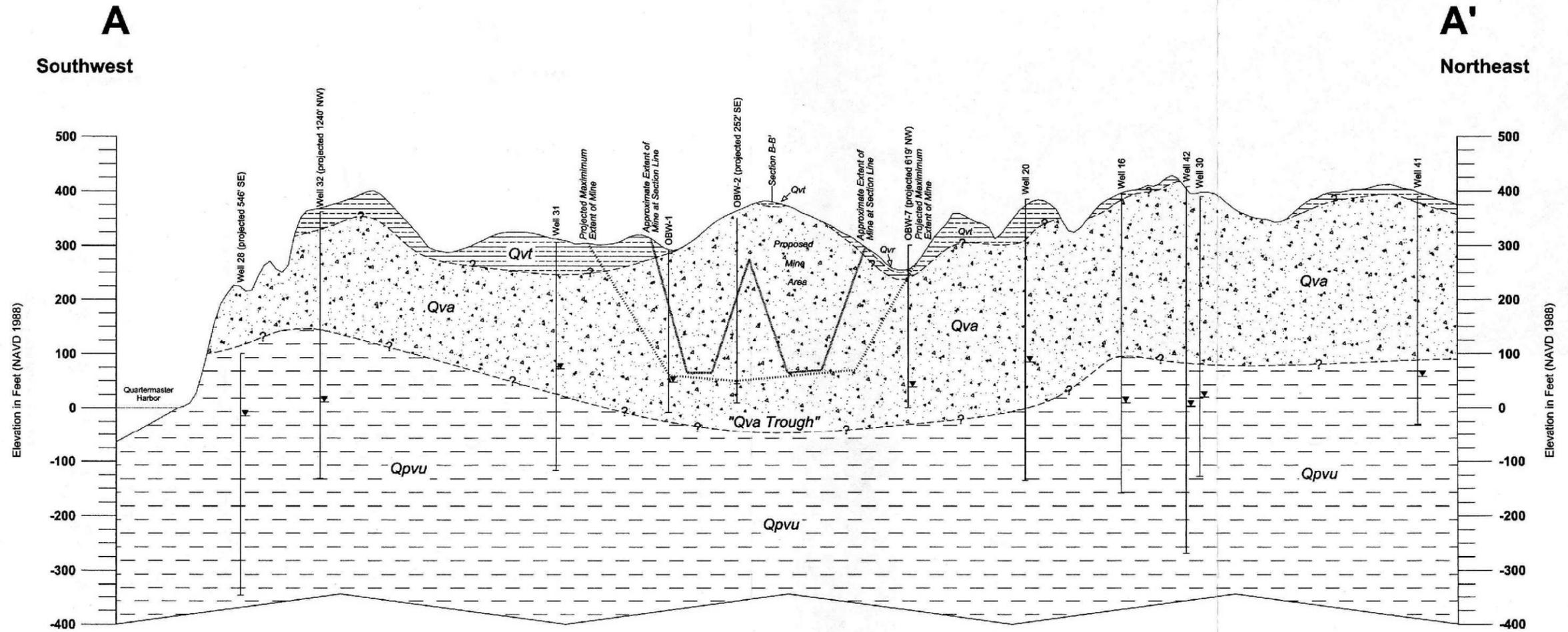


Source: Public Health Seattle King County 2000 and Pacific Groundwater Group 2000

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Project, Washington  
Department of Ecology

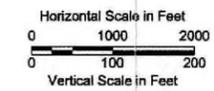
**Maury Island  
Lead Concentrations**

Figure  
**5**



**Legend**

- Qvr - Vashon Recessional Outwash
  - Qvt - Vashon Till
- Qva - Vashon Advance Outwash
  - Qpvu - Undifferentiated Pre-Vashon Sediments



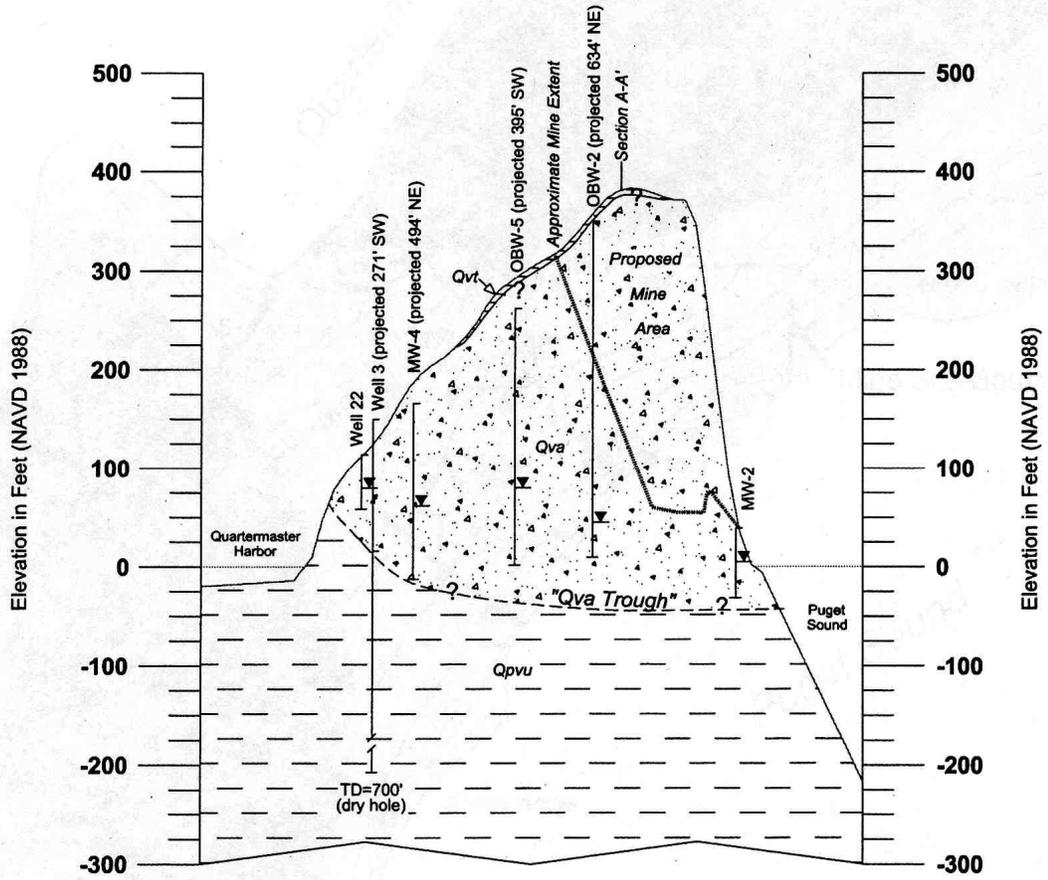
Source: Pacific Groundwater Group 2000

Area Wide Implementation Project  
Washington Department of Ecology

**Cross Section A – A'**

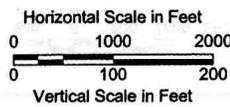
Figure  
**6**

**B** Northwest **B'** Southeast



**Legend**

-  Qvt - Vashon Till
-  Qva - Vashon Advance Outwash
-  Qpvu - Undifferentiated Pre-Vashon Sediments



Source: Pacific Groundwater Group 2000

**TABLE 1**  
**CHEMICAL COMPOSITION OF SOIL SAMPLES (AFTER TOKUNAGA 2005), %**

Soil	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	org-C	Water	Comments on Soil Type
PY Pseudogleyed yellow-brown forest soil	4.06	14.95	67.91	0.30	4.63	high Fe, low pH (2.84)
RY Red-yellow soil	15.18	54.36	20.31	0.49	4.62	high Si
YB Yellow-brown forest soil	21.04	32.86	11.78	0.70	29.33	high water content, even after air drying
KS Kuroboku soil	19.45	37.98	15.02	7.33	13.49	high org. carbon
KP Kanuma pumice	34.34	46.67	2.73	0.10	11.31	high Al, high surface area
TG Thionic gley soil	20.62	47.74	8.14	0.81	8.34	low pH, high total S (3.1%)

**Technical Memorandum re: Mass Balance of  
Arsenic Contamination in Washington State**

## Technical Memorandum

TO: Eric Weber  
FROM: Annika Deutsch  
DATE: 17 November 2006

### **RE: Mass Balance of Arsenic Contamination in Washington State**

#### **INTRODUCTION**

The purpose of this memo is to determine the length of time it would take to leach half of the arsenic contamination out of a set amount of soil. The set of variables is provided below:

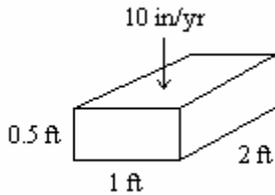


Figure 1. Volume of contaminated soil with rate of penetration of rain

Therefore:     A     = surface area of soil (given as 2 ft<sup>2</sup>)  
                  V     = volume of soil (given as 1 ft<sup>3</sup>)

The time to remove half of the arsenic contamination from this soil volume can be estimated using the simple mixed linear reservoir or batch flush model (Zheng et al. 1991, Gehlar and Wilson 1974). The batch flush model calculates the number of pore volumes<sup>1</sup> necessary to reduce an initial concentration (C<sub>i</sub>) to a final concentration (C<sub>f</sub>) by the following calculation:

$$\text{Equation 1: } PV = -R * \ln ( C_f / C_i )$$

Where:        PV     = number of pore volumes.  
                  C<sub>f</sub>     = final concentration of contamination (mg/L)  
                  C<sub>i</sub>     = initial concentration of contamination (mg/L)  
                  R     = retardation factor

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<sup>1</sup> A pore volume is the amount of water occupied in the soil volume.

Equation 2:  $R = 1 + (\rho / n) * K_d$

- $\rho$  = bulk density of soil (given as 1.5 kg/L)
- $n$  = porosity of soil (given as 0.3 mL water / mL soil)
- $K_d$  = distribution coefficient (default for arsenic given as 29 L/kg)

As the final and initial concentrations in Equation 1 are in the form of a ratio, the quantities do not need to be known. As a reference, the initial concentration in the top six inches of soil in Tacoma is approximately 271 mg/kg (Crecelius et al. 1985).

Equation 2 can be solved for the retardation factor which is approximately 146 (dimensionless) based on the default  $K_d$  value of 29 L/kg. With this retardation factor, Equation 1 can be solved with a concentration ratio of 0.5, according to the initial set of variables. In this case, the number of pore volumes is calculated as approximately 101.2.

The pore volume is the amount of space in soil that is available to be filled with water at a given time. Essentially, when the soil is completely saturated, the pore volume is equal to the porosity times the volume of soil. Therefore, Equation 3:  $1 PV = n * V * 0.5$

Equation 3 can be solved for the volume of pore space (or water when saturated) in this amount of soil. There are 0.3 ft<sup>3</sup> in one pore volume. If it requires 101.2 PVs to reduce the amount of arsenic contamination by one half, it will take 30.4 ft<sup>3</sup> (i.e., 101.2 \* 0.3 ft<sup>3</sup>).

If we assume infiltration is 10 in/yr (or 0.83 ft/yr), the volume of rain over 2 ft<sup>2</sup> is calculated at approximately 1.7 ft<sup>3</sup>/yr<sup>2</sup>. The time required to flush 30.4 ft<sup>3</sup> of rainwater through this cubic foot of soil is calculated as approximately 18.2 years. Therefore, half of the arsenic contamination in this soil is estimated to be removed over the course of 18.2 years.

## LIMITATIONS

There are limitations to this method of estimating the time to remove adsorbed arsenic contamination. Perhaps the most evident limitation is that the soil is assumed to be saturated. Unsaturated soil will have a lower pore volume resulting in a shorter time to flush one pore volume of clean water through the soil. However, unsaturated flow through a soil will not necessarily contact all of the soil particle. Also, the method is dependant on the use of a distribution coefficient. For instance, Allison and Allison (2005), give a minimum distribution coefficient value of 1.99, maximum of 20,000, and a mean of 1,580 L/Kg. Different distribution coefficient values result in different time estimates to

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<sup>2</sup> Ten inches per year is probably low for infiltration in western Washington and high for eastern Washington. The calculated time for removal of half of the arsenic would be less for greater infiltration rates and more for smaller infiltration rates.

reduce adsorbed contamination.. For instance, using Allison and Allison's  $K_d$  value of 1,580 instead of 29,, the amount of time would lengthen from 18.2 to approximately 992 years to reduce the concentration by half.

The method is also dependent on equilibrium. The assumption is made that arsenic desorbs to equilibrium as each new pore volume of rainwater reaches the soil. In this respect, an estimate of 18.2 years for removal of half the arsenic in the soil may be low.