TACOMA SMELTER PLUME SITE

FINAL REPORT
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TRACE ELEMENT ANALYSES
for
SELECTED SOIL SAMPLES
VASHON-MAURY ISLAND AND KING COUNTY MAINLAND

prepared by

Gregory L. Glass
Environmental Consultant
Seattle, Washington

for

Tacoma-Pierce County Health Department
and
Washington State Department of Ecology

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EXECUTIVE SUMMARY

This report describes the study design and results of trace element analyses of selected soils from Vashon-Maury Island and King County Mainland areas in the Tacoma Smelter Plume Site. Additional trace element analyses are currently being performed for selected soil samples from Pierce County. Those additional analyses will be completed during 2003.

Analyses for multiple trace elements in 234 soil samples collected from King County areas surrounding ASARCO's former Tacoma Smelter, plus 8 unrelated soil samples from former orchard properties in eastern Washington, demonstrate that trace element chemistry in soils can be used effectively for source identification. The Tacoma Smelter is identified as the major source for the observed regional distribution of arsenic in shallow soils in central Puget Sound.

The ASARCO Tacoma Copper Smelter located in Ruston, Washington operated for approximately 100 years. It specialized in the toll smelting of complex (e.g., high arsenic content) ores and concentrates. Smelter operations ceased in 1986. The Tacoma Smelter was the dominant regional source of arsenic emissions. The smelter also emitted a significant quantity of lead, and lesser amounts of other metals associated with copper smelting.

Since 1999, the Washington State Department of Ecology, in cooperation with local health departments, has been investigating the regional extent of soil contamination from smelter emissions. The areas included are called the Tacoma Smelter Plume Site under Washington's Model Toxics Control Act (MTCA). Soil sampling and analysis for arsenic and lead, the two smelter contaminants of primary concern for human health, is being performed in two phases: i) sampling in relatively undisturbed forested locations, and ii) sampling in child-use areas (e.g., schools, parks, camps, and daycare centers) in identified regions of higher soil contamination. These two phases are referred to as Footprint and Child-Use Areas studies.

This two-phased approach has been applied to three geographic areas downwind of the smelter: Vashon-Maury Island (approximately 50 square miles); King County mainland areas from West Seattle to the Pierce County line, extending inland about 10 miles (approximately 200 square miles); and Pierce County areas north and west of I-5 (approximately 200 square miles). As a result, the Tacoma Smelter Plume Site investigations include six studies so far.

The results from the Footprint studies demonstrate elevated soil arsenic and lead concentrations, with a gradient of decreasing concentrations with increasing distance from the smelter and an association with annual wind patterns. Ecology reviewed a number of additional types of studies that could help confirm the source(s) for soil arsenic and lead contamination, and in particular the role of Tacoma Smelter emissions. Analysis of additional trace elements in soil samples was selected as the first source identification approach. Volatile trace elements are known to occur in smelter emissions and have been studied in various environmental media at a number of other smelter sites.

The initial trace element studies included 234 samples from 60 locations within the King County portion of the Tacoma Smelter Plume Site. Archived samples from the Vashon-Maury Island Child-Use Areas study and the King County Mainland Footprint Study were used; a few additional samples from undisturbed areas on Vashon-Maury Island were also collected. This study therefore includes soil samples from both undisturbed and disturbed (developed) locations. Eight unrelated samples from former orchard properties in eastern Washington, where lead arsenate was used, were also collected and analyzed to determine how well trace element analyses can discriminate between potential sources for arsenic and lead in soils.

Budget constraints limited the number of analyses that could be included in this study. A small initial group of samples from each of the two King County studies, as well as the orchard samples, were analyzed for an extended list of 35 or 36 elements. The results were evaluated in order to select a small number of "best trace elements" to be analyzed in the majority of soil samples. Antimony, bismuth, and indium were chosen as the main targeted trace elements and were analyzed in all samples. Smaller groups of samples were also analyzed for silver and mercury in an exploratory evaluation of how those additional trace elements performed.

The major findings of this study include the following:

- Ten or more elements appear to be enriched in soils near the smelter and to be associated with arsenic concentrations.

- In addition to arsenic, the primary tracer of smelter impacts, three elements selected for detailed investigation in this study - antimony, bismuth, and indium - are effective tracers of smelter impacts on a regional scale (e.g., to distances of more than 20 miles).

- All pairwise correlations for seven elements - arsenic, lead, antimony, bismuth, indium, silver, and mercury - are statistically highly significant. Those correlations are particularly strong for trace elements antimony, bismuth, and indium. The strong correlation pattern indicates similar spatial distributions for multiple elements and argues for a common source.

- The characteristic trace element-to-arsenic ratios are shown to be much higher (by approximately an order of magnitude) in soils impacted by smelter emissions than in orchard soils affected by applications of lead arsenate. Orchard soils also show a different pattern of pairwise correlations among trace elements. Trace element analyses can therefore be used to discriminate between smelter versus orchard sources.

- Trace elements demonstrate different mobilities (downward) in the soil column. This mobility is greatest for arsenic and least for lead, with the other targeted trace elements intermediate between these two end members of the mobility sequence.

- The trace elements selected for detailed investigation show similar patterns in both undisturbed and disturbed soils. Like arsenic, trace elements show an overall gradient with distance from the smelter, plus considerable local variability (especially for properties with disturbed soils). Evaluations of trace element-to-arsenic ratios versus distance show different patterns for different elements. Bismuth demonstrates the most stable results among targeted trace elements.

- The most frequent anomalous results are a moderate number of high lead values. Some of those borings are also high in antimony; a non-smelter source for antimonial lead may be implicated at those locations. Only a very small number of results for other trace elements are identified as anomalous. Trace element concentrations generally vary consistently with arsenic values at sampling locations with spatially anomalous arsenic results.

- Trace elements appear useful on a local as well as a regional spatial scale. Trace element results generally mirror the varying patterns for arsenic in multiple borings on one property (albeit with moderate variations in trace element-to-arsenic ratios), with only a few significantly divergent values.

1.0 INTRODUCTION

1.1 TACOMA SMELTER PLUME INVESTIGATIONS: OVERVIEW

The ASARCO Tacoma Copper Smelter located in Ruston, Washington operated for approximately 100 years. It specialized in the toll smelting of complex (e.g., high arsenic content) ores and concentrates. Smelter operations ceased in 1986. The Tacoma Smelter was the dominant regional source of arsenic emissions; for many years, it was the sole domestic supplier of arsenic for the United States. The smelter also emitted a significant quantity of lead, and lesser amounts of other metals associated with copper smelting.

The smelter property and the largely residential areas in Ruston and North Tacoma to a distance of about one mile are being cleaned up under the Superfund program, overseen by the U.S. Environmental Protection Agency, Region 10. Those cleanup activities are not expected to be completed for several years.

Since 1999, the Washington State Department of Ecology, in cooperation with local health departments, has been investigating the regional extent of soil contamination from smelter emissions. These studies are being conducted under the state's Model Toxics Control Act (MTCA); the areas included are called the Tacoma Smelter Plume Site under MTCA. Soil sampling and analysis for arsenic and lead, the two smelter contaminants of primary concern for human health, is being performed in two phases. First, samples from relatively undisturbed wooded locations are collected to establish upper bounds for the likely magnitude and extent of soil contamination from smelter emissions. Second, samples are collected from child-use areas (e.g., schools, parks, camps, and daycare centers) in identified regions of higher soil contamination to determine potential exposures to young children, a population of special concern, and the need for early actions to reduce exposures to contaminated soils. These two phases are referred to as Footprint and Child-Use Areas studies.

This two-phased approach has been applied to three geographic areas downwind of the smelter: Vashon-Maury Island (approximately 50 square miles); King County mainland areas from West Seattle to the Pierce County line, extending inland about 10 miles (approximately 200 square miles); and Pierce County areas north and west of I-5 (approximately 200 square miles). As a result, the Tacoma Smelter Plume Site investigations include six studies so far.

The results from the Footprint studies demonstrate elevated soil arsenic and lead concentrations, with a gradient of decreasing concentrations with increasing distance from the smelter and an association with annual wind patterns. The spatial patterns for lead indicate contributions from one or more non-smelter sources at some locations, especially in the heavily urbanized areas of the Tacoma Smelter Plume Site. In discussions with multi-party study design Work Groups, Ecology reviewed a number of additional types of studies that could help confirm the source(s) for soil arsenic and lead contamination, and in particular the role of Tacoma Smelter emissions. Analysis of additional trace elements in soil samples was selected as the first additional source identification approach. Volatile trace elements are known to occur in smelter emissions and have been studied in various environmental media at a number of other smelter sites. Previous investigations of the Tacoma Smelter provide some limited information regarding the occurrence of trace elements at the smelter and in environmental samples.

This report describes the study design and results of trace element analyses of selected soils from Vashon-Maury Island and the King County Mainland. Additional trace element analyses are currently being performed for selected soil samples from the Pierce County Footprint Study. Those additional analyses will be completed during 2003. The Pierce County results will be provided and evaluated in a supplement to this report.

Report organization. Sections 1.2 through 1.5 provide background information on trace elements in copper smelting and Tacoma Smelter operations. The selection of samples and trace elements for analysis are described in Section 2.0. Laboratory analysis methods, data validation results, and analytical results are summarized in Sections 3.0 and 4.0 (see Attachments for complete data listings). Section 5.0 presents a series of data evaluations organized around a set of primary issues of interest. The overall study conclusions are summarized in Section 6.0, and cited references are listed in Section 7.0.

1.2 TRACE ELEMENTS IN COPPER SMELTING

The basic fact that copper smelter emissions can be enriched in various trace elements has been known for a very long time. An early text by Peters (1907), for example, comments as follows: "The substances contained in the gases that issue from the chimneys of a smelting plant must, of course, depend largely on the composition of the ores and fluxes which are treated in its furnaces. Any volatile constituent of the ore is likely to be present in the gases..." and "...the gases that escape from the central stack of a copper plant...consist mainly of heated atmospheric air, of the nitrogen which has lost its accompanying oxygen in passing through the furnaces, of the ordinary products from the combustion of carbonaceous fuel, of steam, of (ordinarily) minute proportions of volatile sulphides and oxides such as of arsenic and antimony, and of sulphur dioxide, often with minute proportions of sulphur trioxide". In discussing possible effects of smelter emissions, Peters (1907) also comments: "Volatile Sulphides, etc. - These substances are volatilized during roasting or smelting, and are carried out by the draft before the temperature has fallen sufficiently to cause their condensation to the solid form again. They are not gases in the sense in which this word is ordinarily employed. They are metallic, or semi-metallic, vapors, in which the particles of the original material are present, although in a state of extreme division. Among the commonest of these volatile substances are lead and zinc sulphides, arsenic and antimony trioxides, arsenides and antimonides of metals, sulphates and oxides of lead, oxide of zinc, etc.".

Fulton (1915) provides an extended discussion of "Metallurgical Smoke" including characterization of the gaseous, flue dust, and fume components of smelter smoke. The results of chemical analyses for fume samples from multiple smelters are presented, demonstrating an increased knowledge of the composition of such materials. Elemental constituents of the compounds identified in Fulton (1915) include silver, gold, zinc, antimony, lead, bismuth, copper, arsenic, tellurium, selenium, cadmium, and thallium. Complaints about "smelter smoke" in the early 1900s led to several lawsuits against smelter companies (summarized in Fulton 1915), including claims of damages from trace element emissions. Holmes et al. (1915) provide one of the most detailed early evaluations of the emissions of trace elements, particularly lead and arsenic, from the period of the early smelter lawsuits.

Other early reports address issues of the removal and marketing of various trace elements associated with copper smelting, confirming a detailed understanding of the co-occurrence of these elements. Addicks (1917) identifies the following list of elements commonly associated with copper and their status as by-products in copper refining: gold, silver, platinum, palladium, lead, nickel, antimony, bismuth, arsenic, cobalt, selenium, and tellurium. Komakine (1917) discusses the smoke problems at major Japanese copper smelters and methods of controlling fume containing copper, tin, lead, arsenic, and antimony. Trace element contents in refined copper have remained an industry concern; in its 1993 annual report, ASARCO (1993) notes the installation of a new facility at one of its copper refineries to improve the removal of impurities, principally antimony and bismuth, from electrolytic copper. Navarro and Alguacil (2002) also identify removal of arsenic, antimony, and bismuth impurities from copper electrolytes as a primary objective of copper refining.

Recovery of trace elements at non-ferrous smelters is a primary method for the commercial production of a number of elements (see, for example, U.S. Bureau of Mines 1965). The sixteenth annual report from ASARCO (1914) notes that the company gave "great attention during the past few years to the production and sale of many other metals"; a list of metals being refined and sold included gold, silver, copper, lead, zinc, nickel, platinum, arsenic, bismuth, cadmium, tellurium, selenium, and palladium. Marketing announcements from many present-day smelting companies list various trace elements recovered from ores and concentrates and available for sale. Ayres et al. (undated) identify a number of metals that are largely obtained as by-products from nonferrous smelters, including copper smelters. They list metals of economic importance (gold and silver), highly toxic metals (arsenic, cadmium, and thallium), metals with small but significant market niches (antimony, bismuth, selenium), and metals that may become important in specialized electronic applications (bismuth, germanium, indium, rhenium, tellurium, thallium).

Geochemically, arsenic is often accompanied by other trace elements. Boyle and Jonasson (1973) review arsenic geochemistry and identify the following list of elements with which arsenic is often found: copper, silver, gold, zinc, cadmium, mercury, uranium, tin, lead, phosphorus, antimony, bismuth, sulfur, selenium, tellurium, molybdenum, tungsten, iron, nickel, cobalt, and the platinum group metals. Davies (1980) lists common trace metal constituents of chalcopyrite, an important copper mineral, including silver, cobalt, germanium, indium, manganese, nickel, selenium, and tin. Nelson (1977) provides a list of volatile elements contained in copper, lead, and zinc concentrates, including antimony, arsenic, bismuth, cadmium, copper, indium, lead, selenium, tellurium, thallium, and zinc. Wolfe (1981) describes the metal content in a typical copper smelter flue dust as including various concentrations of copper, zinc, lead, arsenic, iron, bismuth, tin, cadmium, germanium, silver, and gold. A USGS report (du Bray 1995) classifies and describes various types of ore deposits, noting that soils downwind from smelters processing such ores can contain elevated abundances of a number of metals.

Nriagu and Pacyna (1988; see also Nriagu 1992) provide summaries of trace element emission factors for various anthropogenic source categories. For the source category copper-nickel production, quantitative emission factors are given for the following elements: arsenic, cadmium, copper, indium, manganese, nickel, lead, antimony, selenium, tin, vanadium, and zinc. Dudka and Adriano (1997) review and summarize information on soil contamination from smelter emissions. They identify smelters as the main sources of atmospheric emissions of arsenic, copper, cadmium, antimony and zinc on a global scale, with substantial contributions of chromium, lead, selenium, and nickel. Davies (1980) also summarizes studies of trace element soil contamination near smelters, coal-fired powerplants, and other point sources.

Black & Veatch (1988b) provides a listing of 20 elements in addition to arsenic that are identified as potential airborne contaminants from copper smelting. Those elements are identified based on documented smelter products, detection in various smelter materials or collected dusts, or detection in environmental samples.[1]

Newhook et al. (2003) summarize ambient air monitoring data for copper smelters and refineries and zinc plants in Canada. Emissions from those facilities are identified as resulting in potential exposures to a number of elements. This report focuses on arsenic, cadmium, chromium, nickel, and lead releases. Copper smelting is noted to result in particularly high ambient concentrations among the facilities studied.

Mehta (1981) provides assay data for a number of copper smelter flue dusts, as part of an

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[1] The potential airborne contaminants are classified, based on estimated mass loading, as follows: primary constituents - copper, arsenic; secondary constituents - lead, antimony, nickel, mercury, bismuth; tertiary constituents - selenium, tellurium, gold, silver, platinum, palladium, iridium, osmium, rhodium; and potential airborne - cadmium, indium, gallium, molybdenum, chromium.

EPA-spnsored study of methods to treat arsenic-containing wastes. Elements reported to occur in these flue dusts include arsenic, bismuth, cadmium, copper, lead, antimony, tin, tellurium, zinc, molybdenum, silver, and gold.

Schwitzgebel et al. (1978) performed sampling at multiple locations at a primary copper smelter in the U.S. (not the Tacoma Smelter), with primary analyses by atomic absorption spectrophotometry plus extensive trace element analyses (using semiquantitative spark source mass spectrometry, which is cited as having detection limits of 0.1 to 1.0 ppm for solids). Samples were collected of reverberatory furnace concentrate feedstocks, matte, and slag, as well as inlet and outlet gas streams for the reverberatory furnace electrostatic precipitator (ESP). The concentrates showed arsenic, copper, iron, titanium, calcium, potassium, sulfur, silicon, aluminum, magnesium, and sodium to be present at >1,000 ppm, bismuth, lead, barium, antimony, molybdenum, selenium, zinc, nickel, and fluorine at 50 to 1,000 ppm, and various additional elements (e.g., cadmium, silver, gold, tungsten, chromium, rare earth metals) in the low ppm range. Additional analyses for trace elements in reverberatory furnace matte and slag supported evaluations of trace element partitioning and supported preliminary mass balance calculations. (Measurements of additional materials streams to complete a rigorous mass balance calculation were lacking). Multi-element analyses were also performed for ESP inlet and outlet gas streams, as well as collected ESP dusts. The authors conclude that appreciable material composed of toxic trace elements passes through the ESP in the vapor state at the ESP operating temperature and condenses to form particulates upon cooling.

Parker (1978) confirms that copper smelting also provides a means of recovery of important quantities of gold, silver, selenium, tellurium, arsenic, and platinum-group metals (platinum and palladium included in this study, but also including iridium, osmium, rhodium, and ruthenium, all known to occur in copper ores). This Bureau of Mines study determined the occurrence of these byproduct trace elements in various copper ores and evaluated their distribution during copper smelting operations. Some of the sources providing concentrates to the Tacoma Smelter are identified as having among the highest levels of trace elements. Volatile elements such as arsenic, selenium, and tellurium (among those studied) are noted as potentially being lost through gaseous or other emissions during copper smelting. The occurrence of recoverable quantities of bismuth in "leady residues" such as some ESP dusts, which are shipped from copper smelters to lead smelters for further processing, is also noted.

Tayler (1976) characterizes the particulates from the offgases of the reverberatory furnace and converter processes at the Kennecott copper smelter in Utah. Chemical differences between the coarse and fine fractions of flue dusts were demonstrated; Tayler notes that some of the fine fraction particulates are not captured by the ESP and are eventually emitted to the atmosphere. Volatile elements are found to concentrate in the fine as opposed to the coarse fraction. Sampling (cascade impactor) includes gas streams beyond the ESP, representative of smelter emissions. Chemical analysis of the emissions sample from the reverberatory furnace showed quantifiable concentrations (all >0.1 percent by weight, or 1,000 ppm) of arsenic, bismuth, copper, iron, molybdenum, lead, antimony, selenium, tin, tellurium, and zinc. The concentrations of volatile elements arsenic, bismuth, and lead were much higher in the emissions sample (beyond the ESP) from the converter process. Agglomeration processes for the fine particulates as the gas streams reach and transit the ESPs are demonstrated.

Lastra-Quintero et al. (1987) performed chemical and mineralogical analyses on ESP dusts (after water soluble components had been removed) from the Kidd Creek copper smelter in Canada. Elements identified in the dusts included lead, zinc, copper, iron, arsenic, cadmium, tin, bismuth, cobalt, and indium.

Henderson et al. (1998), in a study of soil contamination surrounding the copper-zinc smelting complex at Flin Flon, Manitoba, Canada, cite a compliance testing report by the facility's operator (Hudson Bay Mining and Smelting Company). That report identifies smelter stack dust as containing high concentrations of zinc, iron, copper, lead, cadmium, and arsenic, with low to trace amounts of mercury, chromium, cobalt, nickel, and manganese. Henderson et al. (1998) also note that the smelting complex at Flin Flon produces zinc, copper, cadmium, lead concentrates, and silver, gold, selenium, and tellurium by-products refined offsite. McMartin et al. (1999) state that emissions from this smelter have varied depending on ore composition over time and improvements to smelting and control processes, but historically were dominated by zinc, iron, and lead, with lesser quantities of arsenic, copper, cadmium, and mercury, and trace amounts of silver, aluminum, magnesium, manganese, selenium, antimony, nickel, chromium, and cobalt.

Based on air sampling in workers' areas in a copper smelter, and single particle analyses by SEM, Michaud et al. (1996) similarly demonstrated differences in composition between coarse and fine fractions of collected particulates. Volatile elements were found to be enriched in the fine fraction, including lead, bromine, sulfur, zinc, tin, indium, arsenic, selenium as well as copper and cadmium. Samples from near the reactor (furnace) versus the converters showed some differences in composition, identifying certain elements as being primarily associated with one or another of the steps in copper smelting. Volatile elements were also often found to be enriched on the surface of fine particulates, consistent with adsorption of those volatile elements onto particles.

Germani et al. (1981) report the results of a study of trace elements at five primary copper smelters in Arizona and provide an excellent general theory (in combination with Small et al. 1981) of the occurrence of some trace elements at enriched concentrations in smelter emissions. They also note that the trace element composition of particulate emissions shows large variability from one smelter to another. Samples of feedstock concentrates were obtained and analyzed for approximately 35 elements (using neutron activation analysis and atomic absorption spectrometry). The authors note that special emphasis was placed on analyses for volatile elements usually associated with sulfide ores (including arsenic, selenium, antimony, cadmium, indium, zinc, and lead). Additional samples from ores, precipitator dusts, and in-plume (airborne) sampling of stack emissions (see Small et al. 1981) allowed comparisons to be made of trace element concentrations through the smelting process. Enrichment factors for concentrates (i.e., elemental ratios in concentrates versus crustal materials) were calculated normalized to aluminum; trace elements associated with sulfides, including iron, cobalt, copper, zinc, sulfur, arsenic, selenium, silver, cadmium, indium, antimony, tungsten, gold, and lead, showed enrichment factors >10 in the concentrates. Germani et al. (1981) provide a classification of elements according to their fractionation in the smelting process. They conclude that there are three main factors contributing to the large enrichment of trace elements in copper smelter plumes: 1) the enrichment of sulfide-related elements in the concentrates compared to original ores; 2) high smelting temperatures leading to volatilization of many elements; and 3) inefficiencies of typical pollution control devices such as electrostatic precipitators for capturing elements that may be in the vapor phase or present on small particulates. The differing compositions of trace elements in smelter plumes are attributed to differences in feedstock concentrates (derived from copper ore differences), varying operating conditions among smelters, and differences in the pollution control devices installed at each smelter.

Small et al. (1981) collected and analyzed samples from within the plumes of 5 copper smelters in Arizona, using a light twin-engine airplane for sampling. All 5 smelters are located in rural areas where the smelter emissions are the dominant pollution source. While the plumes could be tracked to distances of more than 100 km downwind from the smelters, particulate samples were collected within the first 8 km distances to ensure sufficient filter loadings for analysis. Most elements were analyzed using neutron activation analysis; lead was analyzed using atomic absorption spectroscopy. Variability in composition of trace elements in the plumes was studied at two smelters by collecting repeated samples over a period of approximately one week. Ambient (background) concentrations of many elements were found to be much lower than concentrations observed in the plumes. Enrichment factors (compared to crustal, normalized to aluminum) were used to evaluate patterns in trace element occurrence. The time series samples over one week at two smelters showed a marked consistency in enrichment factors for multiple elements, with somewhat larger variability for more volatile elements; that finding supports the representativeness of comparisons in results among the 5 smelters. Most chalcophilic elements (including sulfur, copper, zinc, arsenic, selenium, silver, cadmium, indium, antimony, tungsten, and gold) were demonstrated to be strongly enriched in the smelter plumes. Large differences were found in the patterns of trace elements from one smelter to another. The authors suggest that these differences make smelter plumes sufficiently distinctive that they can be identified from trace element chemistry. Other sources such as coal-fired powerplants and municipal incinerators (high temperature processes whose feedstocks include materials with above de minimis trace element concentrations) also have enriched chalcophilic element concentrations, but the authors show that elements such as copper, arsenic, antimony, selenium, indium, and cadmium are particularly enriched in smelter emissions compared to these other sources. Small et al. (1981) conclude that smelter emissions may contribute substantially to the atmospheric cycles of several elements on a local or, possibly, even regional scale.

Chaubal and Nagamori (1983) and Chaubal (1989) report on computer modeling of the elimination of arsenic, antimony, and bismuth during copper converting operations. The authors describe these impurities as being "detested in copper smelting". These three trace metals are cited as being primarily eliminated by volatilization in the initial slag-making phase of converting operations (and therefore may be emitted as fugitive emissions during converter rollouts).

The U.S. Environmental Protection Agency (1998), in its proposed rule for National Emission Standards for Hazardous Air Pollutants (NESHAPs) for the source category of primary copper smelters, notes that emissions of listed hazardous air pollutant metals from copper smelters are sufficiently large to qualify those facilities as major sources under the Clean Air Act. Trace elements originally occur in copper ore deposits; the specific list of trace elements emitted at a copper smelter, and their quantities, depend on the ores being processed. The USEPA proposed rule identifies arsenic, antimony, bismuth, cadmium, lead, selenium, magnesium, aluminum, cobalt, tin, nickel, tellurium, silver, gold, and palladium, as well as beryllium and chromium, as among the possible metals associated with copper smelting. (See also USEPA 2001).

The information from toxics release inventory reports (see the www.epa.gov/tri website) for operating smelters in the U.S. provides current information on estimated releases for a number of trace elements. Emission controls are much improved at modern U.S. smelters compared to those in earlier years; consequently, recent emissions estimates do not indicate the magnitude of historic emissions resulting in residual soil contamination near smelters.

1.3 APPLICATIONS OF TRACE ELEMENT STUDIES

The number of studies of trace element contamination in the environment near smelters, or other major point sources, is large and growing. This is an area of active current research, as illustrated by the Kola geochemistry project (see Reimann 2002) and Canada's multi-year Metals in the Environment - Research Network (see MITE-RN 1998 to present) project. Selected studies are described in this section to illustrate the application of trace element chemistry for environmental impact and source identification.[2]

In a study of soils around the largest point source of metals emissions in Sweden, the Ronnskar copper smelter, Nordgren et al. (1986) collected two replicate composite (10:1) soil samples from 21 locations ranging from 2.4 km up to 55 km from the smelter. Sampling locations were in relatively undisturbed coniferous forest areas that surrounded the smelter. A total of 17 elements was analyzed. Nordgren et al. (1986) present a summary (log-log scaled) plot showing the results for nine elements that all showed decreasing concentrations with

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[2] The list of elements analyzed in each study differs. The absence on an element from a discussion of results here may reflect only the fact that it was not analyzed in that study. Therefore, the identification of elements associated with studied emission sources may not be complete because of the study design.

increasing distance from the smelter: arsenic, chromium, copper, iron, lead, nickel, selenium, vanadium, and zinc. All nine elements demonstrated high R-squared values for regression of concentration versus distance. Elements known to occur in smelter emissions (e.g., copper, zinc, arsenic, and lead) were among those analyzed; other elements in smelter emissions (e.g., mercury and cadmium) were not included as analytes in this soil study. The nine smelter-related elements were all grouped together in the first factor in a multivariate statistical analysis by the authors.

Beckman (1978) notes that elevated levels of heavy metals including lead, mercury, arsenic, and cadmium have been reported in various environmental media sampled near the Ronnskar smelter. Beckman cites mean annual air emissions estimates for the period 1967-1978 for arsenic, lead, cadmium, and mercury of 115, 485, 12, and 2 tons per year. Johnson et al. (1992) sampled sediments from 12 lakes at distances up to 80 km from the Ronnskar smelter. They demonstrated that sediment concentrations for mercury, lead, cadmium, copper, and arsenic showed a significant pattern of decreasing concentrations with increasing distance from the smelter.

Gabriel and Patten (1994) investigated the use of honey mesquite, a widely occurring plant species in the Sonoron Desert ecosystem surrounding the large primary copper smelter in San Manuel, Arizona, as a bioindicator for the magnitude and extent of contamination from smelter emissions. Leaf and bark samples from honey mesquite, as well as soil samples (surface and 25 cm depth), were collected from distances up to 25 km from the smelter, as well as at a control location. All samples were analyzed for 27 elements using neutron activation analysis. For each matrix sampled, patterns of uniformly high pairwise correlations among subsets of the 27 elements analyzed were evaluated. Trends in concentrations versus distance from the smelter were evaluated. Elemental enrichment factors were also calculated (compared to crustal values, normalized to aluminum). While the resulting element subsets for each individual data evaluation differed somewhat, the authors conclude that their results demonstrate a general grouping of "smelter-related" elements characterized by high volatility and enrichment in sulfide phases of copper concentrates (compare Germani et al. 1981). That group of "smelter-related" elements includes, among others, copper, arsenic, antimony, indium, and chromium. Some of the specific data evaluation results for these elements are discussed in terms of possible differences in transport distances and fates in soils once deposited from smelter emissions.

In a similar follow-up study, Gabriel and Patten (1995) collected and analyzed honey mesquite leaves during a year of smelter operations and a year of smelter shutdown (for conversion to a new smelting technology, during which trial smelting runs resulted in some short-term emissions). The trace element patterns for operating and non-operating periods were compared to evaluate the sensitivity of the honey mesquite plant as a pollution bioindicator. The results showed large reductions (up to 95 percent) in leaf concentrations of "smelter-related" trace elements including copper, arsenic, indium, antimony, zinc, and tungsten.

Ragaini et al. (1977) sampled ambient air particulate filters (high volume samplers), soils

(0-2, 10-12, and 20-22 cm depth intervals), and grasses (analyzed unwashed) from areas within several miles of the Bunker Hill lead smelter and associated facilities in Kellogg, Idaho. A total of 36 elements was analyzed in the collected samples, using a combination of neutron activation and X-ray fluorescence methods. (See Roberts 1973 for the complete results of ambient air particulates analyses). Evaluation of enrichment factors (compared to crustal values, normalized to scandium), soil depth profiles, synchronous variation with lead in ambient air particulate samples, and comparative results for soils versus ambient air particulates were used to identify smelter-related elements, which included cadmium, arsenic, lead, indium, selenium, antimony, zinc, mercury, silver, gold, nickel, and possibly copper.

Lynch et al. (1980) collected 100 soil samples (0-2.5 cm depth interval) from the community near the Trail, British Columbia, Canada lead smelter and from a reference community (Nelson, B.C.) and analyzed them for 30 elements. The smelter area soils were found to be enriched in lead, zinc, copper, cadmium, arsenic, and antimony. Ambient particulate samples collected at one location in each community over a one-year period showed enrichment by the same elements (copper data excluded because of contamination from the motors in ambient high volume samplers).

Pagenkopf and Maughan (1984) investigated atmospheric deposition of metals near the East Helena, Montana lead smelter, following reports of cattle losses from lead poisoning. Snow cores were collected and analyzed over a region of more than 80 square miles surrounding the smelter, with data from the 91 day sampling period extrapolated to estimate annual deposition amounts. Substantial deposition of lead, zinc, arsenic, and cadmium was demonstrated, with a spatial pattern indicating the smelter was the source. Soil sampling along three transects to distances of 8 miles from the smelter also revealed elevated concentrations for these four elements, and nonlinear decreases with distance from the smelter.

Galbraith et al. (1995) studied the relationship of soil metals contamination and vegetation in areas within about 10 miles of the Anaconda copper smelter in Montana. The Anaconda smelter operated from 1884 and 1980. Soil samples from 0-5 cm were collected from 40 locations; at half of those locations, additional samples at 0-15 cm were also collected. Significantly elevated concentrations of arsenic, cadmium, copper, lead, and zinc were reported, with the upper 5 cm depth interval showing higher levels than the deeper soil cores. All five elements were documented to occur in smelter emissions in substantial amounts.

Henderson et al. (1998) discuss the results from a series of studies around the Flin Flon copper/zinc smelting complex in Manitoba, Canada. Interpretations of the concentrations of metals in soils around the smelter are aided by two factors: 1) the lack of other significant anthropogenic sources for metals in the remote Flin Flon location, and 2) the availability of an extensive regional geochemical database for soils resulting from a surficial geological mapping and geochemical prospecting project. The geochemical database provides a context in which to assess the effects of prolonged smelter emissions, in an area where the natural geological variation in trace element concentrations is well known. Henderson et al. (1998) cite arsenic, cadmium, copper, mercury, lead, and zinc as elements demonstrating concentrations decreasing with distance from the smelter and exceeding regional background levels to distances of as much as 100 km or more. McMartin et al. (1999) provide additional information on the patterns of soil contamination revealed by this study, including estimates of the maximum anthropogenic contribution (percent) by trace metal and zone (distance range). This recent study confirms the results reported in several earlier investigations of the Flin Flon smelter (see Franzin et al. 1979 [bulk precipitation and snow sampling]; Zoltai 1988 [peat sampling]; Pip 1991 [soils and garden produce]). All of these studies confirm the Flin Flon smelter as a dominant regional source of trace element contamination of the surrounding region.

Soil samples were collected along two transects at distances up to 27.5 km and 42.5 km from the Horne copper-zinc smelter at Rouyn-Noranda, Quebec, Canada (Dumontet et al. 1992). Elevated concentrations of cadmium, lead, copper, and zinc were reported, with greater contamination in the more frequent downwind direction. These trace elements in 0-15 cm soil samples showed statistically significant exponential decay with distance from the smelter and a high degree of correlation. Concentrations were found to decrease rapidly with depth, based on comparisons of results from 0-15 cm and 15-30 cm.

McMartin et al. (2002) compare soil sampling results from regions around three Canadian smelters: Flin Flon, Manitoba; Trail, British Columbia; and the Horne Smelter at Rouyn-Noranda, Quebec. These comparisons are based on recent studies with sampling at distances up to 200 km, 50 km, and 69 km for the three smelters, respectively. The humus, B-horizon, and C-horizon of soil profiles were sampled and analyzed separately to examine contaminant depth profiles and mobility. Copper, lead, and mercury are shown to exhibit similar patterns of elevated concentrations in humus samples at all three sites, with exponentially decreasing concentrations versus distance that reasonably reflect estimated emissions. Locations closest to the smelters occasionally have elevated metals concentrations in B-horizon samples, indicating some downward leaching in the region of highest concentrations. Anthropogenic soil contamination is evaluated based on the humus-to-C-horizon ratios for trace elements. C-horizon values represent uncontaminated mineral soils; allowance is made for the natural enrichment of trace elements in organic-rich humus layers.

Trace elements were analyzed in samples from ploughed horizons of agricultural soils near two large and long-operating smelters in the north of France: a lead-zinc smelter founded in 1894 and a zinc smelter operating since 1869 (Sterckeman et al. 2002). Soils near the lead-zinc smelter were found to be contaminated by silver, arsenic, bismuth, cadmium, copper, mercury, indium, nickel, lead, antimony, selenium, tin, thallium, and zinc. The same elements, but in different proportions, were also found to be elevated in soils near the zinc smelter, where chromium contamination was also documented. Control soil samples from similar agricultural plots described as distant from potential sources (although at distances less than those shown to be affected by smelter emissions in other studies) were collected and analyzed to determine background concentrations for trace elements in soils. All soil samples were 20-to-1 composites from the top 20 cm; selected locations were sampled to about 2 m to evaluate vertical mobility.

Several trace elements, such as silver and indium, reported at low (absolute) concentrations were nevertheless shown to be present near the smelters at large multiples of background levels (i.e., they demonstrated large enrichment factors). In contrast to the major contaminants of concern - cadmium, lead, and zinc - from these smelters, which showed elevated levels to depths of up to 2 m, the minor trace elements were elevated only within the top 30 cm of soils. The areas sampled were spatially limited, with maximum distances of 4 km and 2.1 km from the two smelters. The inter-element correlations and patterns of concentrations versus distance were different for the two facilities studied. The data from the lead-zinc smelter showed concentration gradients with distance and identified the smelter as the source for trace element contamination. The data from the zinc smelter, with a more limited sampling area, did not show a clear distance relationship even though they were elevated above background levels; the authors discuss possible confounding factors affecting this spatial pattern.

The region surrounding a mining and smelting complex in the Kola Peninsula of far northwestern Russia, near Russia's borders with Finland and Norway, has been the subject of a large number of studies over the past decade (see Reimann 2002). That group of studies includes geochemical characterization of trace element concentrations in diverse environmental media. (See http://www.ngu.no/Kola/publist.html for an extensive list of project publications). A pilot project (Niskavaara et al. 1996) collected samples from 10 different environmental media and analyzed them for up to 40 elements. Sampling of soils (Ao-horizon, humus), terrestrial moss, snow, and stream water was recommended to most clearly define pollutant-related elements including arsenic, cadmium, cobalt, chromium, copper, molybdenum, nickel, sulfur, antimony, and vanadium.

Gregurek et al. (1998) report the results of analyses for up to 44 elements in spring snowpack samples collected near the Kola Peninsula metals processing facilities. Enrichment factors were calculated for snow filter residues compared to pristine northwestern Finland samples; they showed elevated concentrations for many elements near the processing facilities. Samples collected at Monchegorsk, site of a nickel-copper-cobalt smelter complex, included the highest enrichment factors among all snowpack samples for arsenic, cadmium, molybdenum, lead, antimony, and vanadium. Multiple elements at each of the three regions sampled show a similar pattern of decreasing concentrations with increasing distance from the plant. Concentrations of rhodium, palladium, platinum, gold, and tellurium were higher near Monchegorsk than the other two sampling regions, attributed by the authors to differences in the composition of ores processed at the various facilities. This is supported by differences in ratios among the elements near the various sources (Gregurek et al. 1999). Those five trace elements were highly correlated at all three sites.

Reimann et al. (1997) collected and analyzed multiple topsoil (0-5 cm) samples from each of eight catchments (watersheds) in the Kola Peninsula region; two of the catchments were at the locations of smelter or ore roasting facilities. Samples near those facilities were shown to be enriched in a number of elements, including silver, arsenic, bismuth, cadmium, cobalt, chromium, copper, iron, nickel, lead, antimony, selenium, tellurium, and vanadium.

Reimann et al. (2000) describe a regional geochemistry survey covering a 188,000 square kilometer area surrounding the Kola industrial facilities. They note that volatile elements such as lead, cadmium, silver, arsenic, and selenium whose ore contents and stack emissions are much lower than primary elements such as nickel and copper, nevertheless show similar "halos" of enrichment around the major emissions sources. The spatial extent of these halos is from tens of km to 150 km. Reimann et al. (2000) also note that the enriched soils within these halo areas appear to account for most of the mass of trace elements emitted over time, and are thus a long-term reservoir.

Haugland et al. (2002) collected samples of soil and vegetation from four locations, at distances of 7 to 28 km, near the Severonickel copper-nickel smelter on the Kola Peninsula (at Monchegorsk), as well as from a background location at over 150 km. Those samples were analyzed for ten selected elements. The trace elements silver, arsenic, cobalt, iridium, nickel, and antimony showed enrichment in soils and spatial patterns identifying the smelting complex as the source. Soil depth profiles for trace elements were also determined. Contamination by some elements in deeper horizons was noted. Many statistically significant positive correlations for pairs of elements were also observed. The authors note that the region is one of the most contaminated regions in the northern boreal forest zone, with visible effects of air pollution on vegetation recorded at distances up to 80 km and traces of pollutants detectable at up to 200 km; the total area affected by air pollution is cited at over 10,000 square km.

Nieminen et al. (2002) compared concentrations of selected metals in peat bog cores from a location near a copper-nickel smelter (southwest Finland, 2.4 km from the smelter complex) and an unimpacted reference location (eastern Finland). Annual emissions of copper, nickel, zinc, lead, and arsenic for 1985-1999 from the Harjavalta smelter complex are provided. The five selected trace elements were shown to be enriched in the peat bog core located near the smelter complex. Precipitation samples (rain and snow) collected near the smelter complex were similarly found to be enriched (arsenic not analyzed) in the selected trace elements.

The Sudbury, Ontario (Canada) region has a long history of copper and nickel mining and smelting. Three smelters operated within a distance of approximately 20 km. Dudka et al. (1995) collected and analyzed 73 soil samples from the 0-20 cm depth interval in a reconnaissance survey of regional soil trace element impacts. Copper and nickel, the two primary metals in smelter emissions, were highly elevated and showed a spatial pattern associated with the smelter operations. Other trace elements that were enriched in soils included cadmium, cobalt, chromium, iron, manganese, and zinc. (Note: poor results for analyses of lead in lab QA/QC reference materials led to the exclusion of all lead results). Of these, cadmium had a different spatial pattern than the other elements which could not be explained. In a followup study of the chemical form and mobility of trace elements in soils, Adamo et al. (2002) collected 20 soil samples and analyzed them by sequential extraction as well as total analysis methods. Copper, nickel, and cadmium were the trace elements with the greatest soil impacts; other trace elements were modestly elevated in only some of the samples. The Ontario Ministry of the Environment (2001) recently released a compendium of results for trace metal analyses in soil and vegetation samples in the Sudbury region. The data reported are from sampling programs between 1971 and 2000. Among other findings, elevated soil concentrations for copper, nickel, arsenic, cobalt, and less frequently selenium are documented.

Kluge et al. (1991) collected soils over a study area of about 580 square km centered on the Freiberg/Saxony region of Germany, where smelting of lead-zinc-silver ores occurred. The soil samples were analyzed for 15 trace elements. Using factor analysis, the authors concluded that soil impacts from smelter emissions and native mineralization were characterized by the elements lead, silver, copper, tin, and zinc. Smelter impacts accounted for the largest fraction of total variance in the data set.

Karczewska et al. (1998) report on soil contamination near the copper industry region of Legnica and Glogow, Poland. A summary of earlier studies notes that copper, lead, zinc, cadmium, and arsenic were reported in smelter emissions and soil and snow samples in the vicinity of the smelters.

A national-scale survey of concentrations of 14 metals in forest floor humus layers was conducted for the Czech Republic (Suchara and Sucharova 2002). Samples were collected on a 20-km grid scale with a total of 192 locations sampled. Several regions of elevated concentrations were identified in this survey, one of which was a mining and smelting area near the town of Pribram. Elements noted as being enriched in that mining/smelting region included arsenic, cadmium, copper, mercury, lead, and zinc. The authors conclude that forest soils, including the organic-rich humus layer, are a long-term repository for atmospherically-deposited contaminants and provide a suitable sampling medium for identifying regional-scale impacts.

Chatterjee and Banerjee (1999) collected soil and other environmental samples near a lead smelter in Calcutta, India and analyzed the samples for 20 elements. Soils were found to be contaminated by lead, cadmium, silver, copper, zinc, arsenic, molybdenum, tin, and mercury. These elements showed significant positive correlations and similar patterns of decreasing concentrations with distance from the facility, indicating a common emission source from the smelter stack.

Asami et al. (1992) collected 24 samples near the Kunitomi smelter in Hokkaido, Japan. That smelter operated from 1890 to 1976, producing mainly copper, lead, and bismuth. Substantially elevated levels of copper, lead, bismuth, and antimony were found in smelter soils compared to background surface soils throughout Japan.

In a study of the distribution of arsenic in soils near the Garfield, Utah smelter, Ball et al. (1983) found the usual pattern of exponentially decreasing arsenic concentrations with increasing distance, as well as an association with wind frequencies. The authors note that antimony is a trace constituent of smelter stack emissions. A strong linear relationship between arsenic and antimony concentrations in soils over the study area (extending to 22 km from the stack) was demonstrated.

Trace element analyses have also been applied to ambient air and precipitation studies. Source apportionment studies to identify the primary emissions sources affecting ambient particulates can combine chemical analysis and air trajectory analysis approaches. For example, Gullu et al. (1995) studied the concentrations of 38 elements in ambient particulate samples from upstate New York. A high arsenic-to-selenium ratio was used to identify smelter contributions; days with high arsenic-to-selenium ratios were shown through back-trajectories to be associated with air masses arriving from Canadian copper smelter regions (e.g., Rouyn-Noranda). Multivariate factor analyses of the elemental chemistry data identified a separate factor representing copper smelters, with high factor loadings for the elements arsenic, indium, cadmium, and antimony. Blanchard and Stromberg (1987) collected and analyzed rain samples from two sites in southeastern Arizona near a number of smelters, over a period of 13 months. Multivariate factor analysis identified a factor associated with smelters based on arsenic, antimony, cadmium, copper, lead, and zinc concentrations. The mean values for each trace element-to-copper ratio for precipitation samples were similar to the average ratios calculated for in-plume samples at five Arizona smelters by Small et al. (1981), supporting the association of that factor with smelter emissions.

Extensive sampling and analysis of shallow sediments in Lake Coeur d'Alene, Idaho, downstream from the historically important Silver Valley mining district and the mining and smelting operations of the South Fork of the Coeur d'Alene River, showed enrichment by multiple trace elements (Horowitz et al. 1995). Marked enrichment was noted for silver, arsenic, cadmium, mercury, lead, antimony, and zinc. Sediment core dating and chemical profiling of sediment samples resulted in estimated dates for the onset of sediment contamination that are consistent with the 1880-1890 timeframe for the start of mining and ore-processing in the Silver Valley district.

1.4 TACOMA SMELTER OPERATIONS

The basic operations of the ASARCO Tacoma Smelter are described in PSAPCA (1981) and USEPA (1983). Selected studies providing relevant information on trace elements associated with smelter operations are discussed below.

NEA, Inc. (1984) performed a receptor modeling study to investigate sources contributing to high ambient air arsenic measurements in areas surrounding the Tacoma Smelter. Multi-element analyses of potential source materials were completed as part of that study. For example, samples were analyzed for up to 30 elements from the following materials: Herreshoff roaster charges and calcines; slag; various electrostatic precipitator and baghouse flue dusts; arsenic product; dustfall from various locations at the smelter; copper ore concentrates (one type); smelter process emissions (several locations); and ambient air particulates. The XRF analytical method used had limited sensitivity to detect low concentrations (detection limits generally several hundred parts per million). Nevertheless, the results reported by NEA confirm the presence of trace elements such as nickel, zinc, arsenic, selenium, silver, cadmium, antimony, lead, and bismuth in smelter feedstock materials. Various flue dust and process emission samples are shown to include the following trace elements, among others: chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, molybdenum, silver, cadmium, indium, tin, antimony, tellurium, mercury, lead, and bismuth. Multi-element analyses of Tacoma Smelter slag are also reported by Keystone/NEA (1991).

PSAPCA (1974) provides some information on smelter emissions from stack tests or ASARCO reports. For example, PSAPCA cites mercury content of ores and stack particulate emissions at 25 ppm (average value, range of 1 ppm to 94 ppm) and 825 ppm, respectively. Estimates for annual stack emissions in tons/year are given for arsenic, lead, mercury, and cadmium for 1971-1973. An increased frequency in meteorological controls and physical control system improvements resulted in substantial reductions in particulate emissions over that period. In 1973, estimated tall stack emissions (in tons) were: arsenic, 133; lead, 48; cadmium, 1.2; and mercury, 0.28. For that same year, Labbe (1973) provides estimates of anticipated discharges to air (in tons) as follows: arsenic, 133; cadmium, 1.2; copper, 5.8; lead, 82; nickel, 0.1; selenium, 0.2; silver, 0.1; and zinc, 14.

Varner (1983) provides data on annual stack emissions of arsenic, lead, and mercury at the Tacoma Smelter. Data for arsenic and lead cover 1960 and 1970 through 1983; data for mercury cover 1973 through 1983. A historical report on arsenic emissions for 1953 is also cited. Annual arsenic emissions were reported at up to 500 tons per year, or more, in the 1960s and earlier, declining by about 90 percent in the last years of smelter operation. Stack emissions of lead declined over the same period from more than 200 tons per year to about 10 to 20 tons per year. Stack emissions of mercury decreased from over 900 pounds in 1974 to a little over 100 pounds by 1983. If the proportion of mercury to arsenic in stack emissions was roughly constant, the arsenic emissions data for pre-1973 years suggests that mercury emissions could have been as much as several tons per year for the 1960s and earlier.

Nelson and Roberts (1975) report partial chemical analyses for Tacoma Smelter roaster charge on several days. Measurable concentrations, showing little variability over time for the short periods represented by the data, are given for 9 elements: lead, copper, arsenic, antimony, nickel, sulfur, cadmium, mercury, and selenium. Nelson and Roberts (1975), in the course of testing the performance on an existing electrostatic precipitator (ESP) and a pilot baghouse for controlling emissions from the roaster gas streams at the smelter, compiled data on downstream emissions of metals from these control systems. The existing ESP system was shown to be much less efficient at capturing fine particulates, where volatile elements such as arsenic, lead, cadmium, and antimony were particularly enriched. Measurements of total (filter plus impinger) loadings downstream of the ESP resulted in approximate element ratios as follows: arsenic (nominal value of 1,000): lead (331): antimony (76): copper (51): nickel (22): cadmium (8): selenium (4).

The USEPA conducted tests to determine mass emission rates and particle size distributions for six selected elements from the roaster/reverberatory furnace and converter gas streams at the Tacoma Smelter (Statnick 1974). The total emission rates (in pounds per hour) were: arsenic, 58.05; lead, 24.65; zinc, 15.7; copper, 4.825; cadmium, 1.32; and chromium, 0.065. For these elements, the measured emissions in relation to arsenic showed ratios of 0.42 (lead), 0.27 (zinc), 0.08 (copper), 0.02 (cadmium), and 0.001 (chromium). The composition of particulate emissions was found to be reasonably stable across particle sizes.

ASARCO reported to PSAPCA on monitoring conducted on the roof of the converter building during October 1974, to characterize fugitive emissions released to the ambient air from converter operations (Labbe 1975). Data for multiple sampling runs (each collected for approximately 18-20 hours) are provided for arsenic, lead, zinc, cadmium, and mercury; some or all of the results for cadmium and mercury were apparently below detection limits. Since total particulate loadings (in mg/m3) are also given, the concentrations for elements can be derived; arsenic concentrations, for example, ranged from about 14,000 ppm to 82,000 ppm. The lead:arsenic ratios for 15 sampling runs ranged from 0.43 to 1.9, with an average value of 1.01.

Control of fugitive emissions released during converter operations, especially when the converters were in "rollout mode", was the focus of a testing program for the efficiency of an air curtain hooding system at the Tacoma Smelter (PEDCo 1984). As part of that testing program, analyses were performed for arsenic, lead, selenium, cadmium, antimony, and bismuth during various stages of converter operations and for various particle size fractions of the fugitive particulate emissions. The majority of the total measured releases of these elements occurred in the finest size fraction (< 3.4 um). Comparisons of total converter cycle measurements and specific "rollout mode" measurements support the finding that most of the total fugitive converter emissions occurred during converter rollouts. The elemental fractions in total particulate emissions, while variable from run to run and across converter operating modes, generally showed arsenic and lead to be greatest (at times each exceeding 10 percent of total particulate mass), followed by antimony (around 1 percent), with bismuth, cadmium, and selenium lower (at tenths of a percent).

In July 1984 a fire in the main stack of the Tacoma Smelter resulted in deposition of particulates in surrounding neighborhoods. Austin (1984) reports the results of PSAPCA's analyses of 11 collected samples for arsenic, copper, lead, zinc, and antimony; an analysis submitted to PSAPCA by ASARCO is also included. The average elemental ratios for PSAPCA's analyses for arsenic: lead: copper: zinc: antimony were 1.00: 1.10: 0.40: 0.20: 0.0011. ASARCO's results for these ratios were 1.00: 0.83: 0.22: 0.13: 0.06.

Unfortunately, the extensive files of the Puget Sound Clean Air Agency (formerly the Puget Sound Air Pollution Control Agency) for the Tacoma Smelter, including various source test results, have been discarded (Nehen 2002) and are therefore not available for review.

The Tacoma Smelter operated three NPDES monitored outfalls (PSAPCA 1981). Those three outfalls discharged only noncontact cooling water and surface water that was collected from throughout the smelter property. Monitoring data showed large mass discharges for arsenic, zinc, copper, antimony, lead, and cadmium. The presence of these trace elements in high quantities in the outfalls was attributed primarily to the incorporation of particulates and dusts in surface water runoff from smelter property.

1.5 PREVIOUS TACOMA SMELTER STUDIES

Numerous studies have been performed addressing various environmental media in the region surrounding the Tacoma Smelter. A large proportion of these studies have focused on arsenic, lead, and less frequently cadmium as the primary smelter-related contaminants of potential concern. Some investigations have included analyses of a larger number of trace elements. A chronology of many of the studies completed by 1991 is provided in Bechtel Environmental, Inc. (1992). In this section, selected investigations that provide relevant trace element information are identified and briefly discussed.

Crecelius et al. (1974) note that Tacoma Smelter stack dust was characterized by the Puget Sound Air Pollution Control Agency as containing 30 to 40 percent arsenic, 20 to 30 percent lead, 2 percent antimony, and smaller amounts of zinc, copper, mercury, and other metals. Their early report of soil sampling conducted by several entities included results for analyses of 15 surface soil samples (0-3 cm) for antimony, showing significantly elevated values for areas up to several miles from the smelter. Arsenic and lead analytical results were also reported. Crecelius et al. (1975) also showed elevated antimony occurred in sediment cores near the Tacoma Smelter. Core dating established the onset of increased antimony concentrations in sediments to be consistent with the start of Tacoma Smelter operations. In some locations the elevated antimony in sediments was concluded to result from windborne transport of smelter air emissions rather than from tidal currents of materials released to water (e.g., slag disposal or direct water discharges from smelter outfalls). (See also Crecelius 1974 and 1975).

Ratsch (1974) collected soil (0-2 inches) samples, primarily from gardens, along two transects heading south and southwest from the Tacoma Smelter. Cadmium, lead, and mercury, as well as arsenic, showed elevated concentrations in soils, decreasing with increasing distance from the smelter. Copper was also noted to be highly elevated near the smelter.

Heilman and Ekuan (1977) performed what is probably the most extensive trace element analysis study of soils near the Tacoma Smelter. They sampled soils from 70 residential gardens (five located in Puyallup as controls), covering parts of Vashon-Maury Island and areas in Ruston and North Tacoma (primarily south and southeast of the smelter, with few sites in the primary downwind direction, southwest). Analyses were performed by two laboratories for up to 37 elements. Data for each element were plotted versus distance from the smelter. The authors conclude that the following elements had elevated soil concentrations near the smelter: arsenic, cadmium, lead, copper, mercury, zinc, tin, platinum, molybdenum, antimony, sulfur, thallium, gold, and chlorine, and to a lesser degree palladium, tellurium, tantalum, tungsten, and bismuth. The general form of the concentration versus distance relationship for the most clearly smelter-related elements was an exponential decay curve.

PSAPCA (1974) provides a summary of various studies near the Tacoma Smelter, focusing on arsenic, lead, cadmium, and mercury results. In addition to these four elements, maximum antimony, copper, and zinc concentrations are reported for horse pasture grass based on 5 samples. Elevated concentrations of these elements are documented. PSAPCA also analyzed the fallout of eight elements - arsenic, lead, cadmium, copper, nickel, antimony, selenium, and mercury - in three containers set out for a period of 120 days (March 1 to June 27, 1975) at three school locations near the Tacoma Smelter (see Roberts 1975). Measurable quantities of all eight elements were reported for all three locations, with implied deposition rates from tens of pounds per square mile per year for trace elements such as cadmium and mercury up to thousands of pounds per square mile per year for the more abundant elements (copper, arsenic, and lead). The ratios for mass collected for trace elements versus arsenic at the three locations were as follows: copper - 4.2 to 4.3 plus a high outlier[3] of 22.1; lead - 0.64 to 2.72; selenium - 0.06 to 0.12; antimony - 0.04 to 0.10; nickel - 0.02 to 0.06; cadmium - 0.006 to 0.007; and mercury - 0.005 to 0.008. The deposition ratios for these seven trace elements at three school locations close to the Tacoma Smelter are thus seen to be reasonably stable, except for the single high copper outlier.

GCA (1974) operated three high-volume air sampling stations near the Tacoma Smelter for three months. Daily samples were collected for total particulates measurement. A total of 35 of those daily filters were subsequently analyzed for 13 elements (not all analyzed in all filters): arsenic, bismuth, cadmium, copper, iron, mercury, indium, manganese, nickel, lead, antimony, samarium, and zinc. Samarium was not detected in any analysis; all other elements were quantified in at least one filter. A pattern of significant correlations among elements was demonstrated. Measured concentrations for multiple elements - arsenic, cadmium, copper, iron, lead, and mercury - were characterized as greatly in excess of normal urban values.

McClannan (1974) performed an air monitoring study during periods of smelter operation and strike periods when the smelter was shut down. Analyses of total suspended particulate matter collected by Hi-Vol stations near the Tacoma Smelter included cadmium, mercury, manganese, lead, antimony, selenium, and zinc, in addition to arsenic. Measured concentrations for all elements but manganese showed marked increases during periods of smelter operations compared to during the strike. Concentrations also decreased with greater distance from the smelter, and the monitored elements all showed synchronous variations over time. Most concentrations were elevated compared to values collected at the University of Washington campus in Seattle. McClannan concluded that these results demonstrated impacts in Ruston and

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[3] Throughout this report, the term "outlier" is used only to identify apparently anomalous results. Statistical outlier tests were not performed. The use of the term outlier is thus intended to convey a discussion point rather than a statistically rigorous finding.

North Tacoma from low-level (fugitive) emissions sources at the Tacoma Smelter.

Lowry (1983) sampled soils (0-6 inches) in gardens in areas surrounding the Tacoma Smelter to distances of more than 5 miles, and in Puyallup (a control area). Arsenic and cadmium were analyzed in all samples. The areas near the smelter showed statistically significantly higher concentrations than Puyallup, with values decreasing as distance from the smelter increased.

As part of a large-scale soil sampling program for Ruston and North Tacoma, Black & Veatch (1988a) analyzed 31 soil samples for a list of elements in addition to arsenic. Analytes included antimony, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc. Soil samples were 4:1 composite samples, 27 for surface soils at 0-1" and 4 for depth profiles at two locations and two additional depths, 4-6" and 10-12". Based on elevated concentrations and a pattern of significant pairwise correlations, elements in addition to arsenic found to be associated with smelter releases included selenium, lead, mercury, silver, cadmium, antimony, and copper.

Bechtel Environmental, Inc. (1992) collected and analyzed additional soil samples to extend the data set from Black & Veatch (1988a) investigations. In addition to arsenic, analyses for antimony, cadmium, copper, lead, mercury, and silver were performed for 26 soil samples. The 26 samples included 14 surface samples (4:1 composites, 0-1" depth interval) and 12 depth profile samples (6-10" and 12-16" depth intervals collected from a single core at each of 6 locations). Elevated concentrations for these metals were reported.

Researchers from the University of Washington in Seattle conducted a number of precipitation chemistry studies in areas downwind from the Tacoma Smelter. Several of those studies included analyses for selected trace elements, in addition to arsenic and sulfur (the major elements known to characterize smelter emissions). Larson et al. (1975) report the results of regional sampling (at 43 collection sites) of precipitation from a single storm, including analyses of 11 samples for arsenic, antimony, cadmium, copper, bismuth, and zinc. Rain chemistry impacts associated with the smelter were detected to a distance of about 40 km, and arsenic and antimony were found to be good elemental tracers of the plume to about 25 km. The other metals showed spatial patterns not characteristic of a single source (for example, two of the most distant collection sites had among the highest values for bismuth, copper, and cadmium); locations near the smelter (Fox Island, Maury Island) did, however, have elevated concentrations.

Knudson et al. (1977) statistically analyzed data from a similar single-storm study using factor analysis methods. Analyzed elements included arsenic, antimony, cadmium, lead, copper, zinc, and manganese. The authors note that single-element isopleth maps of the spatial distributions of metals associate arsenic, antimony, copper, and cadmium with the Tacoma Smelter. These same four elements are highly intercorrelated and identified as a prominent grouping in the factor analysis. Thus, smelter emissions are identified as an important factor affecting rain chemistry in the region; other important factors are interpreted as sea-salt background and urban sources.

Vong and others continued studies of rainfall chemistry in western Washington, particularly as it related to acid precipitation and smelter emission effects. For example, Vong et al. (1987) report that single storm precipitation sampling data for 38 collection sites show spatial patterns for arsenic, lead, copper, indium, and antimony that can be associated with the Tacoma Smelter as an important source. Vong et al. (1987) cite data from aircraft sampling in the smelter plume in 1986 showing an arsenic to antimony ratio similar to the 8:1 value in the single storm rainfall data set. Multivariate statistical evaluations of data from two storm monitoring events identified a factor including arsenic, lead, antimony, and copper (as well as sulfate), interpreted as representing the effects of Tacoma Smelter emissions (see also Vong et al. 1988).

2.0 OBJECTIVES AND STUDY DESIGN

2.1 PURPOSE OF TRACE ELEMENT STUDY

Historic studies, as well as the recent series of studies conducted by Ecology and local health departments, have demonstrated a widespread occurrence of elevated soil arsenic and lead concentrations in areas surrounding the Tacoma Smelter. The spatial pattern of these elevated soil concentrations has shown a gradient with distance from the smelter (see, for example, Washington State Department of Ecology 2002) and a relationship to annual wind frequencies.

Ecology and other members of the study design work groups for recent investigations of the extent of soil contamination considered various approaches to providing additional evidence regarding the source(s) for documented elevated soil arsenic and lead levels. For example, lead isotope analyses in soils, trace element analyses in soils, chronologic sediment core analyses (in freshwater lakes or Puget Sound marine sediments), analyses of peat bog samples, and emissions transport and deposition modeling studies were all identified as possible approaches.[4] Trace element analyses of soil samples was selected as the first approach for collecting additional information for source identification.

The fact that smelter emissions contain various elements, present in smelter feedstocks, that are volatilized during high-temperature smelting processes is well established. Where release, transport, and deposition of these elements results in a sufficiently large increase in otherwise occurring soil concentrations (or in other media), these volatilized elements should be useful in evaluating the smelter as a principal source for contaminants of primary concern for health threats, such as arsenic or lead. Soils should be a relatively long-term environmental sink for deposited contaminants; the rates of mobilization and loss of deposited elements from smelter emissions are slow. Soils therefore represent an accumulation of smelter contaminants over the nearly 100-year period of smelter operations. This accumulation in soils over time improves the detectability of elements that are emitted by the smelter in comparatively smaller amounts.

Trace element studies have been performed at a number of smelters (see Section 1.3), as well as at other high-volume, high-temperature sources (e.g., coal-fired powerplants and large municipal incinerators). The usefulness of trace element analyses for source identification has been demonstrated in those studies. Many of the reviewed trace element studies at smelters

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[4] Since the Tacoma Smelter is no longer operating, other approaches involving measurements of current emissions (air particulates analyses, deposition collection and analysis, air trajectory analyses) are not applicable.

involved facilities located in rural areas where other potential sources are all but absent. The purpose of the trace element analyses of soils near the Tacoma Smelter was to investigate their usefulness in identifying the Tacoma Smelter as a principal source for elevated soil arsenic and lead in the highly developed and urbanized central Puget Sound region. The Tacoma Smelter is believed to be the dominant regional source of arsenic emissions, although several other minor and localized sources can be identified. In contrast, other substantial regional-scale sources for lead besides the Tacoma Smelter are known, especially emissions from the use of leaded gasoline and from weathering or removal of leaded paints. Little is known about the comparative magnitude of releases from the smelter and from other possible sources for additional trace elements in smelter emissions. The ideal trace elements for smelter source identification are those that have significant smelter emissions, insignificant losses from fate and mobility processes during transport and once deposited to soils, no other significant sources (individually or cumulatively), naturally occurring concentrations that are low and relatively unvarying, and available analytical methods that can quantify to low levels (e.g., at or below typical background concentrations). How well smelter trace elements work for source identification in the presence of "urban plume" emissions from a multitude of sources was a question to be addressed in this study.

In community meetings, local citizens have asked on several occasions what smelter-emitted contaminants besides arsenic and lead occur in their soils. The trace element analyses in this study provide some additional information on the presence of additional contaminants. The main focus of the study, however, is to address source identification questions and not to perform human health or ecological risk assessments for an expanded list of soil contaminants related to smelter operations.

2.2 TRACE ELEMENT STUDY PHASES

Samples for trace element analyses were selected during the course of two studies on the magnitude and extent of soil arsenic and lead contamination: the Vashon-Maury Island Child-Use Areas study (see PHSKC and Glass 2001) and the King County Mainland study (see Washington State Department of Ecology 2002). In each case, the trace element samples represent a subset of all samples collected and initially analyzed for arsenic and lead, the two smelter contaminants of primary concern for human health. Samples for trace element analyses were selected only after review of the arsenic and lead results (see Section 2.3). The field sampling activities for these two studies occurred sequentially: from August 28 to November 8, 2000 for the Vashon-Maury Island study, and from February 21 to June 26, 2001 for the King County Mainland study.

Two groups of soil samples were selected and sent for trace element analyses within each of the two major studies; thus, there are a total of four sample groups for the King County trace element study. The two sample groups within each study are distinguished by their size and the number of trace elements analyzed. A small initial group of samples[5] was analyzed for an extended list of up to 36 elements. The larger, main group of samples was then analyzed for a targeted, small list of trace elements selected based on evaluations of the results from the first sample group (see Section 2.4). This approach was adopted so that a group of "best trace elements" for the Tacoma Smelter and specific study region could be selected based on site-specific information. Budget constraints limited the number of elements that could be analyzed for the main sample groups.

To manage sample archiving requirements and provide for timely completion of the trace element study, the small initial sample group was chosen based on a limited number of the earliest results for arsenic and lead analyses. The sequencing for sample collection was therefore arranged to include some locations likely to have among the highest soil contamination levels early in the study. The larger, main group of samples for trace element analyses was selected in increments as the arsenic and lead results for additional samples became available.

Information on Tacoma Smelter operations and from previous environmental studies in areas surrounding the smelter suggested a partial list of elements that were likely to be associated with smelter emissions. This information was not comprehensive in identifying all potentially useful trace elements, nor did it support a ranking of potential trace elements according to their utility for source identification. A review of the literature indicated that the best trace elements for source identification were very likely to be source-specific; therefore, the results from studies at other smelters were of indirect rather than direct application. Compared to most other smelters that processed ores from one or a few local mines (with less variable composition), the Tacoma Smelter - operating as a toll smelter - processed materials from a large number of diverse sources. This introduced additional complexity and uncertainty into the task of identifying best trace elements. Ecology and the study design work groups therefore adopted the approach of analyzing a small initial group of samples for many elements so that the best trace elements could be identified with site-specific information. The two-phase approach added modestly to the costs for trace element analyses. The uncertainty in selecting best trace elements from the limited available information on the Tacoma Smelter without collecting additional site-specific data was of much greater concern.

The two-phase approach was repeated in the second study (King County Mainland) for two reasons: 1) depending on the magnitude of their emissions and fate and mobility processes, certain trace elements could lose effectiveness at greater distances from the smelter source, and 2) emissions of some trace elements within the much more heavily developed mainland study area could mask the effects of smelter emissions of those trace elements. Some geologic variability in naturally-occurring concentrations of elements by region was also deemed possible.

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[5] The initial sample groups were referred to as "first ten" samples in the study designs, since the intent was to select ten samples for extended trace element analyses. However, since the two initial sample groups actually had 11 and 18 samples, that terminology is not used here to avoid confusion.

The analysis of a small initial group of region-specific samples was therefore repeated to provide data to confirm the Vashon-Maury Island selection of best trace elements, or to identify alternatives.

2.3 SELECTION OF SOIL SAMPLES FOR TRACE ELEMENT ANALYSES

A subset of the samples from the Vashon-Maury Island Child-Use Areas study and the King County Mainland study was chosen for trace element analyses. The design goal was to analyze approximately 10 to 15 percent of all samples from these two studies. A set of selection principles was used to guide sample selection. The small initial sample groups for extended trace element analyses had slightly more restrictive selection criteria. The general principles for sample selection are described first, followed by a description of the limitations for selecting the small initial sample groups in each study.

To meet the source identification objectives of the study, the following principles were used in selecting trace element samples:

1. Samples with a broad range of arsenic and lead concentrations should be included, with samples well-distributed across those ranges. The range of concentrations should extend down to near background levels. Low concentrations are required to confirm low trace element values in the absence of elevated arsenic and lead concentrations. A broad range of concentrations will support analyses of correlations (i.e., proportional response) among elements.

2. Samples should be selected from widespread locations to provide good spatial coverage of the Tacoma Smelter Plume area. This will support evaluations of the spatial range over which trace elements are effective for source identification, including the possible effects from non-smelter sources.

3. Multiple samples should be selected from adjacent depth intervals within a boring location. Differences in mobility of arsenic versus other trace elements would result in the separation of different elements within the soil column, affecting evaluations of their degree of association. Selecting samples from adjacent depth intervals will allow for an assessment of differential mobility. Arsenic is believed to be more mobile in soils than most other smelter-related trace elements. Therefore sample selection should focus on depth intervals above the maximum arsenic interval where applicable (i.e., where other than the top two depth intervals are selected).

4. Samples selected for the trace element analyses should include some "anomalous" results to check on trace element levels. Anomalous results could include samples with highly atypical lead-to-arsenic ratios (e.g., high-arsenic, low-lead results or low-arsenic, high-lead results) or samples with reasonably typical ratios

occurring in atypical and unexpected locations. Analysis of these samples will help determine if trace elements are discriminating among possible sources.

5. Samples should represent both relatively undisturbed (forested) and disturbed properties. The Vashon-Maury Island Child-Use Areas study included both undisturbed and disturbed sampling locations (such as camps, parks, school playgrounds, and residence-based child care centers); the King County Mainland study included only undisturbed locations. While undisturbed locations provide the clearest evidence related to soil impacts from smelter emissions, developed and disturbed properties are of greatest concern for human exposures and remedial actions. The trace element data set should provide an opportunity to evaluate how well trace elements work in both settings. Selected samples should also include both "normal" (decreasing concentrations with depth) and "inverted" (increasing concentrations with depth) depth profiles for arsenic and lead. Inverted profiles are more common at developed properties, as a result of soil disturbance during property development activities.

6. Where opportunities arise, some samples should be selected from multiple borings at a single property or decision unit (DU). This will be especially appropriate if different borings have markedly different arsenic and lead levels. Including samples from multiple borings in this manner will support evaluations of how well trace elements work on a local scale. This approach is essentially a "property as its own control" design.

The two small initial sample groups were selected and analyzed to determine a set of "best trace elements". That is, they focused on the question of how well various trace elements worked to identify the smelter as a source in the absence of confounding factors. Samples selected for these two sample groups therefore represented primarily undisturbed locations with normal depth profiles, and excluded anomalous results. They were still chosen to reflect a broad range of arsenic and lead concentrations. They also included multiple depth intervals at each selected boring, but only a single boring per sampled location. Given the small number of samples included, their spatial coverage was necessarily somewhat limited, but each sample group still represented a range of locations.

Ecology recognized an opportunity within this first Tacoma Smelter trace element study to compare the behavior of trace elements in smelter-impacted soils versus other soils with elevated arsenic and lead concentrations. The historic use of lead arsenate at orchards to control the coddling moth and other pests has been well documented. Numerous sites in Washington, a primary producing area for apples and other tree fruit, are known to be affected and to have residual soil contamination with arsenic and lead, at concentrations similar to those in smelter-impacted areas of Puget Sound. Ecology decided to add samples from two former orchard properties in Eastern Washington (i.e., from soils known to be affected by a non-smelter source for arsenic and lead) to the small initial sample group from the King County Mainland study for extended trace element analyses. The main objective for these additional samples was to investigate how well trace element analyses discriminated between these two different sources for soil arsenic and lead.

A map showing all locations on Vashon-Maury Island and the King County Mainland where samples were analyzed for trace elements, after the initial analyses for arsenic and lead, is provided as Figure 1.[6] A summary of the characteristics of selected samples is provided in Table 1. Some details of sample selection in the two studies are described below.

Vashon-Maury Island Child-Use Areas Study. Collection of undisturbed samples was planned at only four properties (the "forest fringe" samples; see PHSKC and Glass 2001) within the child-use areas study. It was difficult to assure early sampling at these few undisturbed areas; moreover, given their locations it was not certain that they would provide highly elevated soil arsenic and lead concentrations. To provide undisturbed soil samples with a large range of arsenic and lead concentrations at an early enough date for extended trace element analyses of the small initial sample group for this study, Ecology and PHSKC decided to resample four locations where high levels of soil contamination had been found in the first Vashon-Maury Island study of undisturbed properties (see PHSKC and Glass 2001, Attachment C). At each of the four properties, nine samples were collected (three depth intervals in each of three borings). The 36 resulting resamples were analyzed only for arsenic, which was deemed sufficient for sample selection for the trace element study. (A strong association between arsenic and lead concentrations had already been established in the initial Vashon-Maury Island study).

Nine of the 36 resamples, representing all four locations, were selected for extended trace element analyses. The maximum arsenic concentrations from the four locations ranged from 120 to 230 ppm[7], with specific depth-interval concentrations down to 33 ppm. Two additional samples from Point Robinson (location 42) were included in the first sample group, with arsenic concentrations of only 10 and 16 ppm, to extend the lower end of the range for arsenic levels. The extended trace element analysis sample group therefore included 11 samples, with distances from the Tacoma Smelter tall stack of 3.0 to 8.8 miles and directions (bearings, clockwise from due north) of -7 to 41 degrees (see Figure 1). The five locations extend in an approximately NNE to SSW alignment along the southern edge of the Vashon-Maury Island landmass.

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[6] Note: some of the location code numbers are repeated in the two studies. Therefore an unambiguous identification requires the study designation as well as the location number.

[7] ppm = parts per million. All analysis results in this report are expressed on a dry weight basis for the size fraction <2mm.

The larger, main sample group for targeted trace element analyses included an additional 155 samples, for a total from the Vashon-Maury Island Child-Use Areas study of 166 samples. Approximately one-quarter of these samples (n=41) represent undisturbed sampling locations (either resamples from the first study or forest fringe samples), and three-quarters (n=125) samples from one of the types of child-use areas reflecting some degree of property development and soil disturbance (see Table 1). Selected samples are from 27 locations in all (see Figure 1); one location (number 42) was included in both the small initial sample group and the larger main sample group, and three locations (numbers 6, 39, and 42) contributed both undisturbed (forest fringe) and disturbed (child-use area) samples. The sample locations provide broad spatial coverage across the general south-to-north gradient (high-to-low concentrations) for soil contamination.

The 166 samples selected for trace element analyses represent a little more than 10 percent of the 1,619 samples in the Vashon-Maury Island Child-Use Areas study (1,503 for child-use areas, 80 for forest fringe areas, and 36 resamples from the initial study).

Several characteristics of the selected samples are identified on Table 1. All but three of the 59 borings from which trace element analysis samples were selected include the first two depth intervals. The majority of borings (37 of 59) have samples selected from three or more adjacent depth intervals. At 15 of the 27 locations, two or more borings from the same DU have samples selected for trace element analyses, allowing comparisons of trace element performance on a local scale.

King County Mainland Study. All King County mainland samples were collected from relatively undisturbed locations. A small initial sample group for extended trace element analyses was selected from five locations along the western (nearshore) margin of the mainland study area (see Figure 1), with 2 samples from adjacent depth intervals in a single boring selected at each location (n=10 samples total). The five locations extend in an approximately N to S alignment, with distances from 8.9 to 19.8 miles from the smelter stack and bearing directions from about 16 degrees to 86 degrees (i.e., West Seattle to Federal Way). The maximum arsenic concentrations by location ranged from 17 ppm to 140 ppm, with individual depth interval samples extending down to 9.1 ppm arsenic.

An additional 8 samples collected from former orchard properties in the Yakima, Washington area (see Peck 2001) were included in the small initial sample group for extended trace element analyses. These 8 samples were from two adjacent surficial depth intervals (0-2 inches and 2-6 inches, matching the Tacoma Smelter Plume sampling protocols) in each of two borings at each of two properties. Previous sampling at both locations had confirmed the presence of elevated arsenic and lead levels.

The larger, main sample group from the King County mainland consisted of 58 samples from an additional 28 locations. Thus, the total set of mainland samples included 68 samples from 33 locations (see Figure 1). These selected trace element sample locations provided broad spatial coverage over the mainland study area of approximately 200 square miles. The most distant location was almost 25 miles from the smelter stack.

The 68 selected trace element samples represent almost 12 percent of the total of 576 soil samples collected in the King County Mainland study. As shown in Table 1, 31 of 33 borings include the first two depth intervals, and only 2 of 33 borings include samples from more than two depth intervals. In all cases, selected samples from a location came from only a single boring; no "within-location" comparisons are available for the mainland. The set of trace element samples from the King County Mainland study therefore represents a simpler, more homogeneous design than those from the Vashon-Maury Island Child-Use Areas study.

Summary. The total data set for trace element analyses thus consists of 234 soil samples from 60 locations within the Tacoma Smelter Plume site in King County, Washington plus 8 unrelated samples from former orchard properties in Eastern Washington. The selection of samples satisfied the identified principles for selection, including (as will be seen) performing trace element analyses for some anomalous samples based on initial arsenic and lead results.

2.4 SELECTION OF TRACE ELEMENTS FOR ANALYSIS

2.4.1 Extended Trace Element Analyses

Various reports on Tacoma Smelter operations and environmental investigations in areas surrounding the Tacoma Smelter were reviewed to compile a preliminary list of potential trace elements for analysis. This review was expanded to include reports from the literature on other smelters and smelting processes (see Section 1). A previous Ecology-sponsored study (see Black & Veatch 1988b, Table 3-1) had summarized similar information on trace elements likely to be associated with copper smelter emissions, and provided a point of departure for the current effort.

Preliminary recommendations were also discussed with the analytical lab performing the trace element analyses (Battelle Marine Sciences Laboratories: E. Crecelius), with respect to both analytical capabilities and knowledge of potential smelter trace elements. The result was a final set of 36 elements to be analyzed as an extended trace element study for the two small initial sample groups (including samples from former orchard properties in Eastern Washington). A listing of these 36 elements (ordered by atomic number) is provided in Attachment A. This list reflects a compilation of elements with some rationale for being associated with smelter emissions as well as additional "exploratory" elements.

2.4.2 Targeted Trace Element Analyses

The results of analyses for the extended trace element list are provided in Attachment D.

The evaluation of these results to select "best trace elements" was based on the preliminary results as reported by Battelle; data validation reviews were not performed until after all of the trace element sample analyses were completed, and then only for 7 of the 36 elements (see Section 3.0).

Two basic evaluation approaches were used to assess the results of the extended trace element analyses. These two approaches correspond to evaluations of the strength and the specificity of association of a trace element with smelter emissions. The strength of association was determined by the enrichment factor for a trace element. The specificity of association was determined by the correlation structure of a trace element with arsenic, the primary smelter contaminant of concern, and with other trace elements showing large enrichment factors.

Enrichment factors as used here are a measure of the degree to which the soil concentration of an element exceeds a typical or reference concentration, such as a background concentration. A normalization of enrichment factors, using a conservative element believed to be relatively unaffected by anthropogenic sources, has often been used; that approach has also recently been critiqued (see Reimann and Caritat 2000). The extended trace element list includes likely conservative trace elements, but the analyses of the larger sample groups are limited to selected "best trace elements" and do not include conservative elements. Normalization of the larger sets of results are therefore in any event not possible from the reported data. A simpler version of enrichment factors was used for this study, in which the sample concentrations for any trace element are normalized to the value reported for that element for the sample in the initial sample group with the lowest arsenic concentration.[8] A number of analyzed elements show enrichment factors of more than tenfold using this approach, while others - cerium, for example - show essentially no enrichment over the full range of arsenic concentrations (more than tenfold to more than twentyfold in the two initial sample groups).

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[8] As discussed in Section 2.3, the lowest arsenic concentrations in the two initial sample groups were about 10 ppm in the original OnSite analyses, and reflect locations known to be downwind from the Tacoma Smelter. The samples may still include minor impacts from smelter emissions, even though they approach expected regional background values, and the calculated enrichment factors may be biased low to some degree. This does not affect the selection of "best trace elements" for the study.

The specificity of association with smelter emissions was measured by the pairwise correlation results among trace elements, including arsenic.[9] Higher correlations between elements with substantial enrichment factors reflect a closer, more proportional association over the full range of observed soil concentrations.[10] Higher correlations are interpreted as showing more dominant smelter impacts, versus impacts from other possible sources (including anthropogenic releases and geochemical variability). (Possible effects on correlations from different mobilities of elements in soil were judged qualitatively; reducing the data set to maximum values in only five borings produces limitations in measures of statistical significance for correlations).

Based on these strength and specificity evaluations of the extended trace element analyses, multiple elements appear to be good candidates for tracers of smelter emissions. At least ten elements appear to be effective tracers: antimony, arsenic, bismuth, cadmium, copper, indium, lead, mercury, silver, and tin. Some additional elements demonstrate possible (but less certain) associations with smelter emissions, with enrichment factors and correlations that are lower than those of the major group of ten elements listed above.

Three "best trace elements" were selected for primary analyses of the larger sample groups, considering both enrichment factor and correlation results. These three "best trace elements" are antimony, bismuth, and indium.[11] The expected background soil concentrations for these three elements are low (well below 1 ppm; see Encyclopedia Britannica 1980, Ermolenko 1966, Kabata-Pendias and Pendias 1992, and Meador et al. 1994). For the initial sample group from Vashon-Maury Island, where the maximum enrichment factor for arsenic based on Battelle results was about 17, the maximum enrichment factors for antimony, bismuth, and indium were about 50, 68, and 27, respectively. The pairwise correlation coefficients for these three elements versus the list of ten good candidate trace elements were also notably high and statistically significant. The evaluations of results for the mainland samples confirmed selection of antimony, bismuth, and indium as the three primary elements for analysis in the larger group of mainland samples. These three trace elements were thus analyzed in all 234 samples from King County selected for the trace element study.

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[9] Trace element samples for the small initial sample groups were selected to provide an approximately uniform distribution of values over the selected range. Pairwise correlations were therefore calculated based on the reported results rather than log values.

[10] It is possible for two elements to both show large enrichment factors within a group of samples, but with a pattern that produces a low correlation between them. It is also possible for elements with more modest enrichment factors to show the highest correlations, for example if the smelter is the only significant source but the mass emissions over time are comparatively small. The enrichment factors and correlations therefore conceptually measure different aspects of the trace element results.

[11] It is noteworthy that antimony and bismuth are both Group V elements occurring in the same column of the periodic table as arsenic.

A review of general literature sources describing uses of antimony, bismuth, and indium did not identify any likely large sources of air emissions other than the smelter. (Sources reviewed included the Encyclopedia Britannica; the Encyclopedia of Chemical Processing and Design; the Kirk-Othmer Encyclopedia of Chemical Technology; Ullmann's Encyclopedia of Industrial Chemistry; the US Geological Survey Minerals Yearbooks and Mineral Commodity Summaries; and Chow 1995). The former secondary lead smelter on Harbor Island was identified as a likely localized source for antimony emissions whose spatial range of impacts was very small compared to the Tacoma Smelter (see Kimbrough and Suffet 1995; Eckel et al. 2002).

A decision was also made to investigate the performance of a fourth trace element in analyses of each of the larger sample groups. For the Vashon-Maury Island sample group, the fourth trace element was mercury; for the King County mainland sample group, the fourth trace element was silver. A subset of the Vashon-Maury Island sample group (26 of 155 samples) was analyzed for mercury. All of the mainland sample group (58 samples) was analyzed for silver. These two additional trace elements were selected based on evaluations of the initial extended analyses. Mercury, for example, had a maximum enrichment factor of about 41 for the first group of 11 samples from Vashon-Maury Island, as well as a strong pattern of high pairwise correlation coefficients. Different fourth elements were selected for the two larger sample groups to expand the information collected on smelter trace element performance.

Finally, arsenic was analyzed for the same samples analyzed for the fourth selected trace elements in the two larger sample groups. This provided data to compare results between the two labs (OnSite and Battelle) for arsenic, involving two different analytical methods, separate sample aliquots from the sample jars, and a separation in time of analysis since sample collection. Consistent and highly comparable results for these arsenic reanalyses would support evaluations of the reported Battelle trace element results together with the original OnSite arsenic and lead results, as one data set. Lead was not included as a Battelle analyte for the larger sample groups, and arsenic was not analyzed by Battelle for all samples (due to budget constraints).

3.0 LABORATORY ANALYSES AND DATA VALIDATION

The evaluations of trace element analyses include the results of initial analyses by OnSite Environmental, Inc. for arsenic and lead (see Sections 4.0 and 5.0). The OnSite laboratory analyses and data validation reviews for the Vashon-Maury Island samples are described in PHSKC and Glass (2001); similar methods were used for the analysis and validation of King County Mainland samples (see Washington State Department of Ecology 2002 and the Ecology website for a summary of mainland results). OnSite performed all analyses on sieved samples (<2mm) and reported all results on a dry weight basis. A microwave digestion procedure was used. Arsenic analyses were performed by graphite furnace atomic absorption (GFAA) methods, and lead analyses by ICP methods.

The Battelle Marine Sciences Laboratories, located in Sequim, Washington performed the additional trace element analyses. OnSite stored all samples after completion of initial analyses, pending the selection of samples for trace element analyses. The selected samples were then sent to Battelle under chain of custody. The four groups of samples selected for trace element analyses (see Section 2.2) were received at Battelle Sequim on 12/06/00, 2/23/01, 6/1/01, and 10/04/01 to 11/19/01. After trace element analyses were completed, Battelle stored the samples until after data validation reviews were completed. Ecology approved disposal of the samples once data validation results were available, in November 2002.

Consistent with earlier Tacoma Smelter Plume site investigations, and the requirements of Washington's Model Toxics Control Act (MTCA), all Battelle analyses were performed on the <2mm size fraction of samples and reported on a dry weight basis. Rather than analyzing samples for percent moisture, Battelle dried a portion of each sample before analysis. Battelle also used a different digestion procedure than OnSite. The hot plate digestion protocol used by Battelle is longer than the microwave digestion protocol and is generally considered somewhat more rigorous.

Most elements were analyzed by Battelle using ICP-MS methods. Exceptions were silver, which was analyzed by GFAA to avoid possible interferences, and mercury, which was analyzed by cold vapor atomic absorption (CVAA) methods. These methods were selected based on the anticipated concentration ranges for trace elements (down to background levels) to provide suitably low detection limits, minimizing not detected results.

Not all samples were analyzed for all trace elements. Of the planned analyses, Battelle provided results for all but one: a sample from Vashon-Maury Island (sample 1-1100-1-1-3) was not analyzed for silver. Battelle included a number of quality assurance/quality control (QA/QC) provisions supporting evaluation of the quality of the reported results. Analyses of blank samples, multiple standard reference materials (as lab control samples), matrix spike/matrix spike duplicate samples, and lab duplicate samples were performed. No field duplicate samples were submitted for analyses.[12] The trace element analyses for a large number of elements resulted in some limitations for the QA/QC program (see EcoChem 2002). For example, method detection limit studies were not available for some elements, some elements lacking calibration curves were reported as relative magnitudes (instrument responses), and standard reference materials did not have certified values for some trace elements. All such limitations were considered during data validation reviews.

For each of the four sample groups, Battelle reported all results, including QA/QC results, in a spreadsheet format (submittals on 2/12/01, 5/04/01, 7/18/01, and 12/06/01). Data reports were initially sent to Ecology and PHSKC. Ecology subsequently decided to submit the results for independent data validation reviews, which were performed by EcoChem, Inc., located in Seattle, Washington. Battelle then provided data deliverables to EcoChem for data validation. The reviews of the two small sample groups with extended trace element analyses were limited in scope (no transcription checks or recalculations performed), and based on Ecology request were limited to only 7 of the trace elements analyzed. The two large sample groups analyzed at Battelle for three primary tracers and associated analyses received full data validation (Level 4).

EcoChem conducted data validation reviews using quality control criteria documented in the analytical methods and in EPA's *National Functional Guidelines for Inorganic Data Review*. In cases where Battelle reported results from more than one analysis for a sample, EcoChem determined which results should be used. EcoChem documented the conclusions of data validation reviews in a series of reports matching the sample groups (see EcoChem 2002) and provided electronic deliverables to Ecology for use with Ecology's EIM database system. Additional data quality flags were assigned as a result of data validation reviews. A number of results were flagged as estimated values (J flag) based on evaluations of accuracy and precision QA/QC results or hold times. Results were flagged as not detected (U/UJ flag) in cases where an element was detected in a blank sample and also in a soil sample at less than 5 times the blank hit (i.e., where no method detection limit had been established by the lab). The frequency of not detected flags varied by trace element. None of the Battelle results, or the earlier OnSite results for selected tracer samples, were rejected based on data validation reviews. Data completeness was therefore nearly 100 percent, with only a single silver value missing from the planned trace element analyses.

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[12] Samples from relatively closely spaced borings (tens of feet separation) in decision units at several Vashon-Maury Island child-use areas were analyzed as part of the trace element study. The results from these multiple locations within decision units help characterize local variability, but are not true duplicate samples.

4.0 ANALYTICAL RESULTS

For data evaluations, the results of Battelle trace element analyses were combined with the results of initial analyses for arsenic and lead by OnSite Environmental, Inc. and information on sampling locations. Ecology provided a complete data spreadsheet listing these results using information from its EIM data management system and sampling location information provided by PHSKC. That data listing included the following: sample ID information (study, location number, DU, boring, and depth); distance (miles) and direction (bearing angle from due north, clockwise, in degrees) of sampling locations from the former Tacoma Smelter tall stack in Ruston, Washington; arsenic and lead results from OnSite; and arsenic, lead, antimony, bismuth, indium, mercury, and silver results from Battelle. Data validation flags associated with the results for each element analyzed were also included.

The data spreadsheet provided by Ecology was given an extensive QA check before data evaluations were performed. A few sample ID transcription errors that had been noted as occurring with sample shipment from OnSite to Battelle and in Battelle data reporting were checked and confirmed to have been corrected.

The data set used for all evaluations is provided in two formats as Attachments to this report. Attachment B lists the results by individual sample, with the four sample groups submitted for trace element analyses kept as separate blocks within the spreadsheet. Each row represents one sample submitted for analysis; Attachment B lists results for 234 smelter site sampling locations and 8 former orchard locations. The ordering of samples within each block is by sample location, then DU within location, then boring within DU, then depth within boring. Analytical results and associated data quality flags are presented across spreadsheet columns.

Attachment C provides a listing of analytical results for the 92 borings for which smelter site samples were submitted (former orchard results omitted). The maximum concentrations for each trace element in each boring (regardless of depth) are listed, with borings in rows and analytical results and flags in columns. Using maximum concentrations within borings to summarize the results reduces the effects of differential mobilities on the degree of association between trace elements.

A summary of the analytical results for all 242 samples, by trace element and by sampling area, is provided in Table 2. Grouping the data by Vashon-Maury Island, the King County Mainland, and former orchard properties (in Eastern Washington) highlights some simple comparisons among the results. Both OnSite and Battelle results are included. For each trace element and sampling area, information listed includes: the number of samples analyzed; the number of not-detected results, based on data validation flags (U/UJ); the range of concentrations for not-detected results; the minimum and maximum concentrations for detected and quantified results; and the ratio of maximum-to-minimum quantified results. Based on these data summaries, several characteristics of the analytical results are notable.

The smelter samples selected for trace element analyses represent a range of more than two orders of magnitude for arsenic and lead concentrations, using the initial OnSite results. The maximum values of 230 ppm and 900 ppm for arsenic and lead, respectively, occur on Vashon-Maury Island; maximum values of 180 ppm and 619 ppm for the King County Mainland are only modestly lower. The maximum arsenic concentration among trace element samples, 230 ppm, is about one-half the maximum concentration reported in the Phase I Vashon-Maury Island study (of relatively undisturbed forested properties).

The ratios of maximum-to-minimum quantified values for arsenic (135) and for lead (130) on Vashon-Maury Island are comparable, but on the mainland the ratio for lead (92) is substantially higher than for arsenic (24). The targeted trace elements also have substantial enrichment as shown by the ratios of maximum-to-minimum concentrations, which indicate ranges in results from one to more than two orders of magnitude. In all cases, the ratios for King County Mainland samples are less than for Vashon-Maury Island samples. Among the targeted trace elements, bismuth and antimony have the highest ratios (i.e., enrichment factors).

Most of the not-detected concentration ranges represent values that are quite low within the range of quantified results. The major exception is antimony, where the highest not-detected values are significantly elevated within the range of quantified results (as a result of some relatively high blank hits; see EcoChem 2002). Silver also shows this pattern but to a lesser degree than antimony. Table 2 also illustrates how the number and frequency of not-detected results vary, not only among trace elements but also between sampling areas. The differences between sampling areas reflect the fact that sample groups for different areas were submitted and analyzed separately (and therefore had separate QA/QC analyses associated with them).

The maximum trace element concentrations, other than lead, for orchard samples are seen to be relatively low compared to smelter samples, even accounting for the lower maximum arsenic concentration (77.8 ppm) for orchard samples.

Table 2 also lists the number of analyses for each element. OnSite analyzed all 234 smelter samples for arsenic, but only 225 for lead. The 9 missing lead analyses reflect resampled Phase I Vashon-Maury Island locations for which only arsenic analyses were performed (see Section 2.3); the arsenic results alone were considered a sufficient basis for sample selection for the trace element study. Since those 9 samples were part of the initial sample group submitted for trace element analyses, lead results for them are available from the Battelle analyses. None of the former orchard samples were analyzed by OnSite.

Somewhat less than half of the smelter samples (but all of the mainland samples) were analyzed for arsenic at Battelle. The only Battelle lead analyses were performed on the small initial sample groups, representing less than ten percent of all smelter samples.

The three primary targeted trace elements - antimony, bismuth, and indium - were analyzed by Battelle for all 234 smelter samples. Mercury and silver were analyzed in fewer samples. As shown on Table 2, most of the mercury results are from Vashon-Maury Island and most of the silver results are from the mainland (where, in fact, all samples were analyzed for silver). Both the sample counts and spatial coverage for mercury and silver are therefore noted to be different than for antimony, bismuth, and indium. The ranges of OnSite arsenic results for the subsets of samples analyzed for mercury and silver were checked; in both cases, the more limited data sets still cover the full range of arsenic results.

All of the former orchard samples were analyzed for all seven trace elements listed on Table 2.

The data validation reviews of Battelle results covered only seven primary targeted analytes; all of those results were listed on the data spreadsheet provided by Ecology (see Attachments B and C). The results for the extended trace element analyses of the initial sample groups from Vashon-Maury Island (35 elements) and the King County Mainland (36 elements) are provided as Attachment D. The data as reported by Battelle include all QA/QC results as well as study sample results (see Battelle Marine Sciences Laboratories 2001); Attachment D lists only the study sample results.[13] The main evaluation of the extended trace element analyses was for selection of a small set of targeted trace elements (see Section 2.4.2) for which the larger sample groups would be analyzed.

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[13] The results for arsenic, lead, antimony, bismuth, indium, mercury, and silver for the small initial sample groups are included in Attachments B and C as well as Attachment D.

5.0 DATA EVALUATIONS

5.1 INTER-LAB ARSENIC COMPARISONS

All of the selected trace element samples from the Tacoma Smelter Plume site have original arsenic results from OnSite; only a subset have arsenic results from Battelle. Most evaluations of the trace element results were intended to be performed in comparison to the complete set of OnSite arsenic results. Before those evaluations were performed, the paired arsenic results from the two labs were compared to confirm that such cross-lab results would be meaningful.

An X-Y scatterplot (see Figure 2) was used to visually compare the paired results for the 105 selected trace element samples with arsenic values from both labs (no orchard samples included).[14] The inter-lab results are highly collinear, with only two notable outlying points. For Mainland sample 65-1-1-2[15], OnSite reported 57 ppm and Battelle only 22.8 ppm (60 percent lower). For Vashon-Maury Island sample 22-1-1-4, OnSite reported 52 ppm and

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[14] Unless otherwise noted, data evaluations use the detection limit for not-detected results.

[15] Where a specific sample is referenced in this report, it will be identified by study and referenced by the coding "location-DU-boring-depth". Thus Mainland 65-1-1-2 refers to a sample from the King County Mainland study at location 65, DU number 1 (default value for the mainland, where only one undisturbed DU per location was sampled), boring number 1, depth number 2 (i.e., 2-6 inches). When a location for a maximum concentration in a boring is referenced, the last component of the sample code (depth) is dropped. For the example given above, the location for maximum concentrations is therefore referenced by Mainland 65-1-1.

Battelle only 4.23 ppm (almost 92 percent lower).[16] The range of OnSite arsenic results for the 105 samples with matching Battelle arsenic results is 1.6 to 230 ppm, matching the full range for all 234 selected trace element samples.

A regression analysis was performed to statistically evaluate the inter-lab results. Linear regression produced a best-fit equation of

$$\text{Arsenic-Battelle} = 1.031\ \text{Arsenic-OnSite} + 3.77\ \text{ppm}$$

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[16] This sample was not one of the five samples for which multiple reanalyses were performed from the Vashon-Maury Island study (see PHSKC and Glass 2001). For 3 of the 5 samples, the original "anomalous" values for arsenic or lead were not confirmed by multiple reanalyses. The OnSite lead result for sample 22-1-1-4 was only 5.6 ppm, which would give a very low lead:arsenic ratio for smelter-impacted soils. The original reported value of 52 ppm arsenic may be suspect.

with an R-squared value of 94.8 percent (n=105 samples; no outlier values excluded).[17] The regression equation, as well as the X-Y scatterplot, show that Battelle values were slightly higher than OnSite results. For arsenic in the range of 50 to 200 ppm, the regression equation results in Battelle arsenic values being higher by about 10.6 to 5 percent. There were only 12 samples analyzed at both labs for lead, but the inter-lab results for lead show very similar results. Linear regression results in an R-squared value of 98 percent for lead (range of OnSite lead results: 13 to 580 ppm) and a slight high bias for Battelle compared to OnSite results. The high bias for Battelle results for both arsenic and lead points to a somewhat stronger digestion procedure as the likely cause for higher values.

The highly consistent inter-lab results support use of the OnSite arsenic and lead results in evaluating trace element values reported by Battelle. The small degree of positive bias for Battelle results does not affect pairwise correlation analyses among elements; trace element-to-arsenic or -lead ratios may be biased slightly high for the study as a whole, with similar degrees of bias from sample to sample.

The set of original OnSite lead results is missing values for the 9 samples selected for trace element analyses from Vashon-Maury Island resampling of Phase I (undisturbed) locations (see Section 2.3 discussion). The Battelle lead results for those 9 samples were added (without bias correction) to the OnSite results, as surrogates for the missing values, to produce a complete set of lead concentrations for evaluation. The missing lead values correspond to some of the highest OnSite arsenic results for the selected trace element sample set. Those 9 Battelle results are likely to include a small degree of positive bias compared to the remaining OnSite lead results. This should not markedly affect the results of data evaluations; the use of simple (uncorrected) surrogate values was deemed beneficial compared to accepting missing values for samples with among the highest arsenic results.

5.2 PAIRWISE RELATIONSHIPS AMONG TRACE ELEMENTS

The degree of association (or proportionality in concentrations) among the various candidate smelter trace elements is the evaluation of greatest interest for this study. Pairwise correlation/regression analyses were performed to investigate the associations among the target trace elements analyzed for the larger sample groups. In this section, the results for samples

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[17] The distributions of arsenic results from both labs are right-skewed. However, a linear regression model showed better fit than regression based on LOG values (R-squared of 94.8 percent versus 82.1 percent). The linear R-squared value was only marginally better if the two noted outlier values were omitted.

from the Tacoma Smelter Plume site are discussed. Comparable results for samples from former orchard properties are discussed in Section 5.5 below.

A matrix of pairwise correlation coefficients based on individual sample results was first calculated for the list of target elements: arsenic, lead, antimony, bismuth, indium, silver, and mercury. All pairwise correlation coefficients for the first five listed elements are based on 234 samples; coefficients involving silver (except for mercury) are based on 78 samples, and those involving mercury (except for silver) are based on 47 samples. The silver-mercury pairing is based on only 20 samples.

The distributions for all trace elements are right-skewed; LOG transformations produce approximately normal distributions. Therefore, parametric correlation coefficients were calculated using LOG concentration values. All 21 pairwise results are statistically highly significant ($p<0.00005$), with correlation coefficients ranging from 0.646 to 0.917. Thus, all of the selected target trace elements show a very strong degree of association. The range of arsenic concentrations (OnSite lab analyses) is 1.6 to 230 ppm.

An examination of the correlation matrix shows some interesting differences among elements, even though all results are statistically highly significant. Arsenic has the worst pattern of correlations with other elements, including 3 of the 4 lowest coefficients overall (arsenic versus lead, mercury, and silver). Bismuth shows the best pattern overall, with all 6 coefficients greater than 0.8. Mercury has a similarly strong pattern versus all elements other than arsenic. The subset of antimony, bismuth, indium, and mercury has uniformly high pairwise coefficients (all greater than 0.8). Mercury-antimony, mercury-silver, and bismuth-indium pairings show the strongest association, with coefficients greater than 0.9.

Evaluating the pairwise correlations among trace elements based on individual sample results does not account for different mobilities among elements in the soil column. One possible explanation for arsenic having the worst pattern of correlations could be a greater mobility post-deposition for arsenic than for the other trace elements. Therefore, a second correlation matrix was calculated using the maximum concentrations, from the selected trace element samples, for each trace element in each boring (n=92). Mercury was dropped for this second analysis (small sample size). For the correlations based on maximum concentrations, pairings involving silver are based on 38 values and all others are based on 92 values.

Examples of the strong associations between trace elements (maximum concentrations, LOG scales) are provided in two-element scatterplots as Figure 3 (maximum arsenic versus maximum antimony) and Figure 4 (maximum bismuth versus maximum indium).

The correlation matrix based on maximum concentrations in borings was also calculated using LOG concentrations to achieve more-nearly normal distributions. The results are provided in Table 3. The range of maximum arsenic concentrations (OnSite lab analyses) was 4.4 to 230 ppm, nearly identical to the range for individual samples. All 15 pairwise correlation coefficients are again statistically highly significant ($p<0.00005$),[18] with values ranging from 0.604 to 0.945. Arsenic no longer has a pattern of notably lower correlations, although the arsenic-lead pairing has the lowest overall coefficient of 0.604. Lead has the lowest coefficients of any element paired with arsenic, bismuth, indium, and silver, and the second lowest for antimony. (This may reflect some lead contributions from sources other than the smelter, to a degree greater than for other trace elements, although it should be borne in mind that all of the lead correlations are still statistically highly significant). The triplet of antimony, bismuth, and indium retains the pattern of uniformly high pairwise correlations, and in fact has the three highest correlations. The bismuth-indium pairing shows the highest overall correlation of 0.945.

Correlations were also calculated separately for Vashon-Maury Island and King County Mainland results and for undisturbed and disturbed locations on Vashon-Maury Island, using maximum concentrations by boring. (Silver was analyzed only in samples from five borings on Vashon-Maury Island, and is omitted in the following discussion because of this small sample size). For all of these data subsets, the pairwise correlations remained statistically significant.[19] Thus, the strong associations among trace elements are preserved across study areas and types of sampling locations. Some distinctions were noted among the correlations for data subsets. Except for the arsenic-lead pairing, arsenic correlations with other trace elements were stronger on Vashon-Maury Island than on the mainland, and stronger for disturbed than undisturbed locations on Vashon-Maury Island. On Vashon-Maury Island, lead had notably lower correlations in samples from disturbed locations (almost three-fourths of the borings) versus undisturbed locations; all of the mainland samples were from undisturbed locations. The antimony-bismuth-indium triplet retained the pattern of very strong pairwise correlations in both undisturbed and disturbed locations on Vashon-Maury Island. On the mainland, antimony correlations were generally weaker (except with lead) than on Vashon-Maury Island. These distinctions reflect relatively minor differences, since all of the results were statistically significant.

Regression analyses were also performed for each of the other trace elements against

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[18] Nonparametric correlations show similarly significant results.

[19] Most significance values were at $p<0.00005$. The only result with $p>0.01$ was for arsenic-lead at undisturbed Vashon-Maury Island locations, with $p=0.0265$. One boring (location 6, DU 4, boring 4) in that subset of samples has an anomalous maximum lead of 250 ppm with maximum arsenic of 23 ppm, and an atypical depth profile for undisturbed soils. If it is omitted, the remaining 14 borings would have a correlation with $p=0.003$.

arsenic, again using LOG concentrations to achieve more nearly normal data distributions. The resulting regression equations are of the form

$$\text{trace element concentration} = \text{constant x (arsenic concentration)}^{\text{exponent}}$$

which results in a best-fit curve (not a straight line, unless the exponent is equal to 1) for the X-Y scatterplot of trace element versus arsenic data in original concentration units (not LOG units). The ratio of a trace element to arsenic depends on the arsenic concentration with this curvilinear best-fit equation.

The best-fit regression equations for maximum concentrations by boring (n=92 for lead, antimony, bismuth, and indium; n=38 for silver) are as follows:

$$\text{lead} = 8.547\ \text{arsenic}^{0.72}$$

$$\text{antimony} = 0.138\ \text{arsenic}^{0.986}$$

$$\text{bismuth} = 0.0214\ \text{arsenic}^{1.154}$$

$$\text{indium} = 0.0075\ \text{arsenic}^{0.844}$$

$$\text{silver} = 0.0227\ \text{arsenic}^{0.735}$$

The trace element-to-arsenic ratios for arsenic values of 20, 50, 100, and 200 ppm, representative of the range of arsenic data in the selected trace element samples, were calculated using these regression equations. The results are summarized in Table 4 (top third), which also lists the regression R-squared values. These results identify characteristic ratios versus arsenic for the various trace elements. If smelter emissions and deposition to soils for two elements were in the identical ratio as the concentrations of those elements in background soils, then there would be enrichment of soil concentrations but no change in the characteristic trace element-to-arsenic ratio. The differences in ratios as arsenic concentrations change, as shown in Table 4, can be understood as a mixing model between background ratios and smelter emission/deposition ratios (ignoring differential fate and mobility for the moment). The limiting ratio as arsenic concentration increases should be the smelter emission/deposition ratio. Considering this mixing model, different sources with different emission/deposition ratios for any pair of elements would be less distinguishable at concentrations approaching background levels and increasingly distinguishable as soil concentrations increase above background levels. Comparisons of these ratios for smelter-impacted soils versus orchard-impacted soils are discussed in Section 5.5.

Another simple measure of a typical trace element-to-arsenic ratio for impacted soils is the median ratio among all data (i.e., among all borings with lab analyses and maximum concentrations for both elements). The median values for the Tacoma Smelter Plume borings are consistent with the ratios given in Table 4, but not as illuminating with respect to a mixing model interpretation. The median ratios for trace elements versus arsenic are: lead, 2.68; antimony, 0.123; bismuth, 0.038; indium, 0.0040; and silver, 0.0074.

The high correlations between arsenic and other trace elements mean that low arsenic concentrations are paired with low concentrations for the other trace elements. These low concentrations provide an estimate for background levels in regional soils. Measured by either the median of all results for samples in which arsenic concentrations were below 10 ppm, or by the range of concentrations for the 10 lowest reported trace element results, these approximations for background levels are very consistent with values reported in the literature for these trace elements (see Encyclopedia Britannica 1980; Ermolenko 1966; Kabata-Pendias and Pendias 1992; Meador et al. 1994; and Sterckeman et al. 2002). The best-fit regression equations versus arsenic also can be used to estimate background trace element-to-arsenic ratios. For arsenic at 5 ppm, these calculated background ratios are: lead, 5.44; antimony, 0.135; bismuth, 0.027; indium, 0.0058; and silver, 0.015. All of these background ratios except bismuth are higher than the typical ratios for impacted soils around the Tacoma Smelter (see above). In the mixing model of smelter impacts, this suggests that the dominant arsenic emissions from the smelter will reduce the background values for most other trace element-to-arsenic ratios (see Table 4), even as both arsenic and other trace elements show enrichment compared to background levels. The bismuth results indicate that the smelter emissions may be even more enriched for bismuth than for arsenic.

5.3 COMPARATIVE DEPTH PROFILES

A comparison of the depth profiles for different trace elements supports an analysis of the comparative mobility of those trace elements in soils. Differences in contaminant mobility will result in a separation of air-deposited elements in the soil column. As noted above, this can affect evaluations of correlations and ratios among the trace elements.

Samples for trace element analyses were selected from 92 borings. Of those 92 borings, 87 included samples from both of the first two sampled depths, 0-2 inches and 2-6 inches (see Table 1). Interpretations of contaminant mobility in soils are more difficult at disturbed locations, since both natural mobility and physical disturbance of soils can affect the resulting concentrations by depth intervals. The relative importance of those two factors can vary from one location to another. The trace element study includes 46 borings at undisturbed locations - 15 on Vashon-Maury Island and 31 on the King County Mainland (see Table 1) - at which both the 0-2 inch and 2-6 inch samples were analyzed. The 46 undisturbed borings with trace element analyses, and their spatial coverage, are deemed sufficient for the comparative evaluations of contaminant mobility among trace elements to be based on only the results for undisturbed samples.

Analytical results for arsenic, lead, antimony, bismuth, and indium are available for all

46 borings. (The arsenic data are from OnSite analyses; most of the lead results are from OnSite analyses, supplemented by a few Battelle results for resampled locations on Vashon-Maury Island [see Section 5.1]; all other trace element data are from Battelle analyses). Data are also available for silver at 35 of the 46 borings, omitting only the borings from forest fringe DUs on Vashon-Maury Island. Only a small number of borings provide depth profile information for mercury, which is therefore not considered further. Comparative depth profile evaluations were thus carried out for six elements: arsenic, lead, antimony, bismuth, indium, and silver.

All not-detected results were included in the evaluations, using the reported detection limit concentrations. The not-detected results appear to be consistent with the overall depth profile patterns.

A graphical approach was first used to investigate the comparative depth profiles among different trace elements. The concentrations for the two depth intervals at all borings for single trace elements were plotted on X-Y scatterplots. The proportion of results plotting on either side of the x=y line provides a simple visualization of which depth interval most frequently has higher concentrations. The distances from the x=y line indicate how far the ratios of concentrations deviate from 1.00 (i.e., how unequal the concentrations are at the two sampled depth intervals). The set of these scatterplots suggests that arsenic (see Figure 5) shows the greatest comparative mobility downward in the soil column, and lead (see Figure 6) the least, among the six trace elements evaluated.

A second graphical analysis approach provides a better visualization of the comparisons between trace elements. The first scatterplots (e.g., Figures 5 and 6) illustrate the ratios between concentrations at two depths for single elements. The second approach also uses scatterplots, but this time each axis is the ratio of concentrations for the first depth (0-2 inches) versus the second depth (2-6 inches) for a given trace element. That is, it illustrates the "ratio-of-two ratios", with each plotted point representing paired results of two elements for two samples from the same boring. As an example: assume in a given boring the lead concentrations at 0-2 and 2-6 inches are 420 and 300 ppm, respectively, and the arsenic concentrations are 150 and 214 ppm, respectively (i.e., arsenic shows comparatively greater downward mobility than lead). Then the two ratios for lead and arsenic are 420/300 = 1.4 and 150/214 = 0.7, respectively. The plotted point reflecting the four initial measurements would plot on the lead-ratio side of the x=y line and show for that boring that lead had comparatively less mobility than arsenic. (The higher the ratio for 0-2 inch versus 2-6 inch results, the lower the downward mobility). The "ratio-of-two ratios" for lead versus arsenic in the example would be 1.4/0.7 = 2, indicating less mobility for lead than for arsenic.

Each individual trace element had a broad range of ratios for concentrations in the top two depth intervals; in some borings, the 0-2 inch concentration was greater, while in others, the 2-6 inch concentration was greater. Location-specific factors apparently result in this range of depth profile patterns. The "ratio-of-two ratios" scatterplots provide a direct visual comparison for paired results for two trace elements, across all borings, regardless of which depth interval has the higher concentration for either trace element. That is, they plot comparative mobilities. Thus, in a manner similar to interpreting the first, simpler set of scatterplots for a single element, the proportion of plotted data on each side of the x=y line and the distances of the plotted points from the x=y line show which of two trace elements has comparatively greater mobility and how great the differences between the two elements are.

Figure 7 provides an example of the two-element scatterplots for comparative depth profiles, based on arsenic and bismuth results for the 46 undisturbed borings with data for the 0-2 inch and 2-6 inch depth intervals.

The results of these graphical approaches to evaluating depth profiles for the various trace elements show the greatest mobility for arsenic and the least for lead, with the other elements intermediate between arsenic and lead. To further characterize the comparative mobilities among the six trace elements evaluated, a median value for the ratio of each trace element depth-ratio to that for each of the two end-members in the mobility sequence (arsenic and lead) was calculated. That is, for arsenic the median result for all borings was calculated for the concentrations

$$\frac{\text{(trace element i, 0-2") / (trace element i, 2-6")}}{\text{(arsenic, 0-2") / (arsenic, 2-6")}}$$

and similarly for lead. (Note: on the "ratio-of-two ratios" scatterplots this is equivalent to finding the constant-ratio line that divides the set of plotted points into two subgroups of equal size, one on either side of the line). The resulting comparative mobility sequence and calculated median values, from greatest to least mobility, are as follows:

	arsenic >	indium >	antimony >	silver >	bismuth >	lead
(based on arsenic)	(1.00)	(1.13)	(1.21)	(1.25)	(1.58)	(1.64)
(based on lead)	(0.61)	(0.72)	(0.78)	(0.89)	(0.90)	(1.00)

This comparative mobility sequence shows a strong degree of correlation with atomic weights for the six elements. Small differences among the calculated median values may not reflect stable differences of adjacent members of this mobility sequence. Nevertheless, the results confirm that the six trace elements exhibit a range of degrees of mobility in soils. Using a derived database of maximum concentrations in borings, to lessen the effects of differential mobilities on data evaluations, is supported by these results.

5.4 SPATIAL PATTERNS

Samples were selected to provide broad spatial coverage of the areas included in the Vashon-Maury Island Child-Use Areas Study and the King County Mainland Study (see Figure

1). The trace element study selected some samples on the basis of their anomalous lead-to-arsenic ratios, and/or their apparent divergence from the overall spatial pattern of arsenic or lead concentrations. This introduced a measure of bias into the selection process (i.e., some sample locations were targeted for inclusion based on anomalous results). The results for trace element analyses in anomalous samples are discussed in Section 5.6.

The general spatial pattern for each trace element was examined graphically, using the maximum concentrations by boring. Scatterplots were prepared for the maximum concentrations versus distance and direction from the Tacoma Smelter tall stack in Ruston, Washington. The overall spatial patterns for both arsenic and lead (using OnSite analytical results) were very similar to the spatial patterns shown by all sampling results from undisturbed locations on Vashon-Maury Island (from the initial study, not the Child-Use Areas study) and the King County Mainland (see the concentration by distance figures in Washington State Department of Ecology 2002).[20] The trace element sample set is therefore reasonably representative of the complete data set used previously to assess the spatial distribution of arsenic and lead in the region surrounding the smelter, despite the targeted inclusion of some anomalous samples. A number of anomalously high lead values, in particular, are notable at distances greater than 10 miles on the lead versus distance plot.

Figures 8 and 9 provide scatterplots of the maximum arsenic and maximum lead concentrations, respectively, versus distance from the smelter stack.

Similar scatterplots of maximum concentrations versus distance were prepared for antimony, bismuth, indium, and silver. As expected, given the high pairwise correlations of all six trace elements (see Section 5.2), their spatial patterns were very similar to the arsenic pattern and to each other. As an example, the scatterplot for maximum bismuth versus distance is provided in Figure 10.

Antimony, bismuth, indium, and silver all have bounding curves - straight lines, on log concentration versus linear distance plots, on or below which all plotted data points occur - that reflect exponential decay in maximum concentrations with increasing distance from the smelter stack. Such exponential decay has been found to be characteristic of the spatial pattern around major air emissions point sources, including the spatial pattern of soil arsenic around the Tacoma Smelter. Like arsenic and lead, the four additional trace elements show considerable variability in maximum concentrations at any given distance, especially shorter distances. This variability is a result of several factors: the influence of varying wind frequencies by direction; the effects of different degrees of soil disturbance at sampling locations (recall that both undisturbed and

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[20] The trace element study did not include samples representative of the highest results found on Vashon-Maury Island, with arsenic in the general range of 250 to 500 ppm. Thus, the concentration by distance scatterplot is somewhat truncated at the top compared to the summary scatterplot for all undisturbed sampling locations. Nevertheless, the overall spatial patterns of the two data sets are very similar.

disturbed locations are included in the trace element sample set); and the inherent localized variability in contaminant deposition and retention in soils, for example as influenced by elevation, slope aspect, slope magnitude, and vegetation. The concentration versus distance results when only undisturbed samples were evaluated showed the exponential decay pattern much more clearly.

The characteristic ratios of trace element-to-arsenic maximum concentrations were discussed in Section 5.2, based on regression analyses of concentrations (see also Table 4). The stability or trend in such characteristic ratios is a matter of considerable interest for the question of how well trace elements perform for source identification in different parts of the Tacoma Smelter Plume site. A number of factors could affect trace element-to-arsenic ratios spatially. First, in-plume processes that resulted in different airborne particle size distributions for different trace elements, or that affected fate processes differently, could result in different patterns of deposition with distance. Detailed information of this type for the Tacoma Smelter plume is lacking; in-plume processes are a matter of current research interest for other smelters (see, for example, the description of projects at MITE-RN 1998 to present). Second, different trace elements in smelter emissions are at different magnitudes compared to soil background concentrations. The mixing model discussed in Section 5.2 noted how characteristic ratios would change as smelter soil arsenic impacts change, and soil arsenic concentrations from smelter emissions are a function of distance from the smelter. Thus, different trace elements may have different "effective distances" of use because of the magnitude of smelter emissions compared to background levels in soils. Third, ratios could show a trend or become more variable (i.e., "noisy") because of influences apart from smelter emissions, including changes in geologic materials and impacts on soils from other sources. Under those conditions, some trace elements may become ineffective for source identification. Note that these impacts may be selective; that is, some trace elements may be affected while others are not.

To assess the spatial patterns, if any, in characteristic trace element-to-arsenic ratios, regression analyses were performed of those ratios versus distance from the smelter tall stack for lead, antimony, bismuth, indium, and silver. The total data set includes maximum concentrations for 92 borings for the first four elements, but only 38 borings for silver (mostly on the mainland). The scatterplots of trace element-to-arsenic ratio versus distance identify a small number of high-outlier ratios. The results for such anomalous cases are discussed further in Section 5.6. Regression analyses were first performed using all results, and then by selectively omitting a small number of high-outlier cases to assess the general spatial patterns.

The results for bismuth, indium, and silver all showed no statistically significant trends in the trace element-to-arsenic ratios versus distance. A representative scatterplot for the maximum bismuth-to-arsenic ratios versus distance is provided in Figure 11. The regression line for bismuth, excluding a single high outlier ratio, was nearly flat (n=91; p=0.65; ratio = -0.00022 x Distance + 0.046). Indium had five high outlier ratios, three of which had very low arsenic concentrations (less than 10 ppm) with indium values near the detection limit. Excluding those five outliers, indium showed a small, statistically non-significant downward trend with distance (n=87; p=0.14; ratio = -0.000049 x Distance + 0.0048). There was a small trend of increasing ratios for silver when 2 high outliers were omitted (n=36; p=0.21; ratio = 0.00014 x Distance + 0.0063). Although not statistically significant, this trend toward higher ratios may suggest some additional sources for silver on the mainland. The smaller number of analyses for silver affects its p-value in comparison to those for the other trace elements.

In contrast to bismuth, indium, and silver, the regression results for antimony (see the data scatterplot in Figure 12) and lead were statistically significant, with opposite trends versus distance. Antimony had three high outlier ratios, two on Vashon-Maury Island and one on the mainland. Excluding those three results, the antimony-to-arsenic ratio showed a statistically significant downward trend with distance (n=89; p=0.001; ratio = -0.0053 x Distance + 0.200). The data for Vashon-Maury Island and the mainland were also examined separately, still excluding the three high outlier values. Both regression lines showed a notable, but statistically non-significant, downward trend with distance (p-values of p=0.08 and p=0.14 for Vashon-Maury Island and King County Mainland, respectively). Lead ratios had a different spatial pattern. Nine of the 92 lead ratios were high outliers (ratios greater than 10). Excluding those nine results, the lead-to-arsenic ratio showed a statistically significant and comparatively steep <u>increase</u> with distance (n=83; p=0.0003; ratio = 0.110 x Distance + 1.63). The lead results for Vashon-Maury Island only, excluding ratios greater than 10, showed essentially no relationship with distance (n=52; p=0.89), while the mainland results showed a small, statistically non-significant increasing trend with distance (n=31; p=0.31).[21]

The ratios for various trace elements included in this study to arsenic, the primary smelter contaminant of concern, thus show different spatial patterns. The statistically significant increase of the lead ratio with distance is likely a result of other sources of lead in the heavily urbanized parts of the mainland sampling region (e.g., from much higher traffic volumes and emissions from the use of leaded gasoline). The small, statistically non-significant trend of increasing ratios for silver is suggestive of other small-magnitude sources for silver in the urbanized area. Bismuth appears to be the most conservative of the trace elements, in the sense that it shows the least trend overall with distance. Indium has a small, statistically non-significant decrease with distance. Antimony has the strongest trend of decreasing ratios with distance; the consistency of that declining trend for both Vashon-Maury Island and King County Mainland data sets is suggestive of differences between antimony and arsenic for in-plume processes and deposition to soils. The (linear) regression equation for antimony-to-arsenic ratios shows approximately a 50 percent reduction in the antimony-to-arsenic ratio over a distance of 20 miles.

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[21] Three additional results can be considered low outliers with lead-to-arsenic ratios less than 1 (see Section 5.6). Excluding those 3 results in addition to the 9 high outliers gives nearly identical results. The overall regression versus distance is still highly statistically significant (n=80; p=0.0007; ratio = 0.103 x Distance + 1.77). The Vashon-Maury Island slope is essentially zero (n=49; p=0.95), and the King County Mainland trend is increasing ratios with distance (n=31; p=0.31).

The variable results for trace element ratios to arsenic are not consistent with some possible interpretations of soil arsenic spatial patterns. For example, if arsenic concentrations on Vashon-Maury Island, but not the mainland, were substantially affected by agricultural uses of arsenic (e.g., lead arsenate applications), then the ratios of most or all trace elements to arsenic would be lower on Vashon-Maury Island than on the mainland. This, however, is not the case.

It is interesting to note that a USGS national survey of streambed sediment concentrations of trace elements (Rice 1999) found that concentrations of cadmium, chromium, copper, lead, mercury, nickel, and zinc, but not arsenic or selenium, were higher in areas with urban versus non-urban land use.

The evaluations of trace element-to-arsenic ratios as a function of distance from the smelter show that different elements have different patterns. Those differences should be considered when using trace element ratios for source identification. Lead and antimony, from the group of five elements included in this study, show the largest trends across the study area. Those trends are opposite in direction and appear to be caused by different factors.

5.5 SOURCE DISCRIMINATION: ORCHARD RESULTS

Trace element analyses of 8 soil samples collected from former orchard properties (see Peck 2001) were included in this study. This limited set of samples was collected to support a pilot investigation of the ability of trace element analyses to discriminate among potential sources of soil arsenic and lead contamination.

The range of arsenic concentrations for the 8 orchard samples was 15.2 to 77.8 ppm. The arsenic enrichment factor (maximum/minimum concentration ratio) for the orchard samples is much lower than for smelter soils (see Table 2), where both lower and higher concentrations were reported, but the set of orchard soils includes a moderate degree of arsenic contamination above background levels. Lead concentrations are generally elevated in all of the orchard samples (range: 110 to 364 ppm lead). The other trace elements show modest degrees of enrichment from lowest to highest reported concentrations (see Table 2), compared to smelter samples.

Pairwise correlations among the target trace elements[22] and regression equations versus arsenic were evaluated for the orchard samples. These evaluations used LOG concentrations, the same as the procedure used for smelter samples. Since there are only 8 orchard samples, the

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[22] The orchard samples were analyzed for the extended trace element list (see Attachment A). Several elements not on the smaller target trace element list are associated with smelter emissions, and may provide additional power to discriminate between smelter and orchard sources for soil arsenic and lead.

evaluations were performed for individual samples rather than maximum concentrations within borings.

All pairwise correlations were positive, with coefficients ranging from 0.489 to 0.965. Of the 21 pairings, 12 were not significant at p=0.01 and 6 were not significant at p=0.05. Seven pairings had correlations of 0.9 or better. The significance values are affected by the small number of orchard samples, and may be affected by different fates and mobilities in orchard soils among the trace elements. The arsenic-lead pairing showed the highest correlation, consistent with the known occurrence of both elements (at fairly stable ratios) in the lead arsenate pesticides historically used at orchards. Indium-bismuth had the lowest correlation among all pairings. Antimony had the strongest overall pattern of correlations. The triplet of arsenic-lead-bismuth had uniformly strong pairwise correlations. Thus, the pattern of associations as shown by the correlation matrix differs in some respects between orchard soils and smelter soils.

The regression analyses produced the following best-fit equations:

$$\text{lead} = 15.3\ \text{arsenic}^{0.723}$$

$$\text{antimony} = 0.192\ \text{arsenic}^{0.396}$$

$$\text{bismuth} = 0.138\ \text{arsenic}^{0.209}$$

$$\text{indium} = 0.031\ \text{arsenic}^{0.163}$$

$$\text{silver} = 0.0245\ \text{arsenic}^{0.299}$$

In the same manner as with smelter samples, the orchard regression equations were used to calculate trace element-to-arsenic ratios for arsenic values of 20, 50, 100, and 200 ppm. The results are summarized in Table 4 (middle section). Each ratios column of Table 4 has a fixed concentration for soil arsenic. The results for smelter and orchard soils can therefore be compared by dividing the smelter result by the orchard result, entry by entry. The resulting values are comparative enrichment factors for trace elements in smelter soils versus orchard soils at various arsenic concentration levels. Lead is shown to be comparatively enriched in orchard soils; all other trace elements are enriched in smelter soils. Moreover, the degree of enrichment for trace elements other than lead increases with increasing arsenic concentrations, consistent with the mixtures model and greater trace element contents in the smelter emissions (see Section 5.3). Once arsenic concentrations reach 200 ppm, antimony, bismuth, indium, and silver have trace element-to-arsenic ratios that are approximately an order of magnitude or more greater in smelter-impacted soils than in orchard soils. Thus, the pilot study data indicate that trace elements likely can be used to discriminate between these two sources for soil arsenic and lead as long as arsenic concentrations are at least modestly enriched above background levels.[23]

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[23] The use of multiple trace elements, possibly including some only analyzed in this study

The Battelle results for antimony versus arsenic concentrations, for both smelter and orchard samples, are provided as a scatterplot in Figure 13. The results for individual samples are plotted, using LOG scales (compare to Figure 3, which uses maximum values for borings rather than individual sample results). The smelter and orchard samples are seen to have divergent trend lines.

The calculation of trace element-to-arsenic ratios for orchard soils using the regression equations, as summarized in Table 4, extends to arsenic concentrations of 200 ppm. This is well above the maximum arsenic value of 77.8 ppm for the 8 orchard samples. As a result, a measure of caution needs to be applied to the interpretations of the smelter versus orchard data. However, an independent evaluation of antimony versus arsenic concentrations in Washington orchard soils lends support to the results summarized in Table 4. Wagner (1993) performed neutron activation analyses for arsenic and antimony in 8 soil samples collected from the 0-20 cm depth interval at 8 orchard locations in Washington. Four of the eight samples had essentially background concentrations of arsenic; the other four had elevated levels. The range of arsenic concentrations was 2.8 to 168 ppm. The raw data show that total (uncorrected for background) antimony-to-arsenic ratios decrease as arsenic concentrations increase; the ratios for the background samples (arsenic less than 10 ppm) approach or exceed 0.1, while the ratios for three samples with arsenic greater than 100 ppm are 0.0071, 0.0079, and 0.0087. Ratios calculated in the manner of Table 4 from a best-fit regression equation for Wagner's data are very similar to those listed in Table 4 derived from the analyses of orchard soils in this study. Wagner gives the antimony-to-arsenic ratios for three commercial lead arsenate products, all with a nominal 20 percent arsenic content, as ranging from 0.0034 to 0.016. These source ratios are much smaller than the comparable smelter antimony-to-arsenic ratio (see Crecelius et al. 1974), which is about 0.1 (consistent with the values for affected soils shown in Table 4). Wagner calculates soil ratios for antimony-to-arsenic in the most affected soil samples in her study, first subtracting an estimated background level from the reported total antimony concentrations, and demonstrates that the results are consistent with the ratios known to occur in lead arsenate products.

5.6 ANOMALOUS RESULTS

The total set of trace element results shows a very strong degree of association of the

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for the extended trace element list, will provide the most powerful discrimination approach. Additional information on variances in the ratios, through analyses of a larger number of samples, would help quantify a discriminant function.

selected trace elements with arsenic and with each other. The samples selected for trace element analyses included some that were "anomalous" by virtue of their original arsenic and lead results (see Section 2.3). Those anomalous samples included both unusual lead-to-arsenic ratios and arsenic or lead concentrations that were atypical with respect to the overall spatial pattern for soil contamination. The additional trace element analyses also provide a small number of results that can be considered anomalous by virtue of their trace element-to-arsenic ratios or their spatial occurrence, as noted in discussions in previous sections. The results of trace element analyses on such anomalous samples provide useful information on how well they perform for source identification. Additional evaluations were therefore performed for anomalous results.

Different trace element mobilities downward in the soil column will independently contribute to apparent anomalies in the data (e.g., atypical trace element-to-arsenic ratios for single depth intervals; see Section 5.3). All evaluations of anomalous results were therefore based on maximum concentrations by boring (see Attachment C; n=92 borings total).[24] The patterns at disturbed sampling locations on Vashon-Maury Island may be substantially affected by soil disturbance, affecting the identification and limiting the interpretation of apparently anomalous results.

The general pattern of trace element results for samples easily identified as anomalous (by ratios or concentrations and spatial location) is the primary focus for these evaluations, rather than specific conclusions regarding sources for individual sampling locations. More detailed, location-specific information would be required to draw conclusions about sources contributing to specific samples. For example, information on the historic uses of a property and the proximity of other possible sources (e.g., firing ranges, large painted structures, traffic counts for nearby roadways, incinerators or other high-temperature processes, manufacture or use of metal alloys, or use of herbicides/pesticides at forest lands, agricultural lands, or along railroads or roadsides, among many others) would have to be compiled and carefully reviewed for a full assessment. Such detailed information is not available for the limited evaluations of anomalous

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[24] The maximum concentration for selected trace element samples in a boring is a simple surrogate variable used to reduce the effects of different mobilities for various elements. An alternative approach is to sum contributions above background levels over all depths (weighted by depth intervals) with elevated concentrations, thus estimating total deposition to soils. The second approach may reduce the number of apparent anomalous results and support better comparisons among elements. However, since only selected samples were analyzed for trace elements, total sums over all elevated depths cannot be calculated for this study.

results discussed here.

Anomalous results were identified by several graphical and numerical data evaluation approaches. The scatterplots of concentrations of other trace elements versus arsenic (e.g., see Figure 3), as well as the scatterplots of trace-element-to-arsenic ratios versus distance (e.g., see Figure 12), were used to visually identify atypical results, whose sample codes were then determined from the data listings. Another graphical technique normalized the maximum concentration data by dividing each result by the maximum value for that element (i.e., rescaling values between 0 and 1). This was done separately for the Vashon-Maury Island and King County Mainland sample sets. The normalized values for all trace elements (arsenic, lead, antimony, bismuth, indium, and silver) in all samples were then plotted together on a single line plot. Figure 14 illustrates this approach for multi-element plotting of normalized data, showing the result for some of the King County Mainland borings included in the trace element study.[25] Most values rose and fell synchronously on the normalized plots, consistent with the high correlation coefficients among the trace elements; anomalous results were those which deviated significantly from this synchronous behavior. The concentration data for each boring were also compared to spatial maps of regional arsenic and lead results (see Washington State Department of Ecology 2002) to identify results that were spatially atypical (high or low).

Numerical approaches for identifying anomalous results included developing rank-ordered listings of trace element concentrations and trace element-to-arsenic ratios, and examining the extreme values on those listings. Borings with patterns of consistently high or low trace element-to-arsenic ratios across elements were also identified using a spreadsheet listing of such ratios, with all results in the upper and lower percentiles of the distribution for each ratio highlighted.

Several categories of anomalous data, with a general description of their evaluation results, are discussed below. The locations for maximum concentration results discussed below are identified by study and location-DU-boring (refer to Attachment C for data and to Figure 1 for sampling locations).

- Anomalous lead-to-arsenic ratios. Ratios greater than 10 and less than 1 were used to identify anomalously high and low results, respectively. Nine results had high ratios: on the King County Mainland, 503-1-3 and 504-1-1; on Vashon-Maury Island, 6-3-2, 6-4-4, 7-2-2, 27-2-1, 30-1-3, 35-2-1, and 35-2-6. Three results had low ratios: on Vashon-Maury Island, 13-1-5, 33-2-3, and 39-1-3.

  Many of the trace element results are generally consistent with reported maximum arsenic concentrations. At King County Mainland location 503-1-3, antimony but no other trace element is significantly elevated, suggesting a contribution from a

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[25] The sequence numbers on the X-axis reflect the ordering of Mainland borings as given in the Attachment B data tables.

source with antimonial lead. Several borings at the Vashon-Maury Island schools complex (locations 6 and 7) had notably high lead values; location 7-2-2 also has a comparatively elevated indium versus arsenic concentration. Vashon-Maury Island location 30-1-3 is a good demonstration of how trace elements contribute to an understanding of likely sources; the lead concentration of 900 ppm is the highest for any trace element samples, but the antimony, bismuth, and indium results are consistent with the low arsenic concentration of 17 ppm, thus indicating a non-smelter source for this high lead result.

Vashon-Maury Island location 13-1-5 (disturbed soil at a child-use area), with a low lead-to-arsenic ratio, has elevated antimony, bismuth, and indium concentrations but comparatively low ratios versus arsenic for those additional trace elements. The maximum arsenic concentration of 110 ppm occurs in the deepest depth interval sampled, indicating an inverted depth profile at this boring. The data for this boring may therefore be limited by not extending deep enough to fully characterize the inverted profile. Alternatively, since the other elements have a consistent pattern with each other, the results may also indicate a second source for arsenic in addition to the smelter.

o Low arsenic spatial anomalies. Soil concentrations of arsenic and lead show substantial local variability. A number of borings were selected for trace element analyses where maximum arsenic concentrations were low compared to the regional spatial pattern. Examples include the following: on the King County Mainland, borings 21-1-1, 31-1-2, 58-1-2, 89-1-1, and 507-1-1; on Vashon-Maury Island, borings 4-1-4, 6-3-2, 7-2-2, 11-1-5, 13-1-4, 27-1-7, 27-7-1, 37-1-8, 39-1-1, 42-2-2, and 45-1-1. These low, spatially anomalous results reflect both soil disturbance at developed properties and topographic influences (e.g., elevations and slope aspects unfavorable for deposition). Other than high lead concentrations at Vashon-Maury Island locations 6 and 7 (the schools complex), all of the trace element results are consistent with these low arsenic results.

o High arsenic spatial anomalies. Only a few results were considered as possible high arsenic anomalies in comparison to the overall spatial pattern. On the King County Mainland, boring 84-1-3 (maximum arsenic of 180 ppm) is the farthest inland and the farthest south of the mainland results over 100 ppm. Trace element concentrations are elevated, with ratios versus arsenic that are typical for lead, moderately reduced for bismuth, indium, and silver, and markedly lower for antimony (which nevertheless has a maximum concentration about 6 to 10 times background). These results indicate a substantial smelter influence, with perhaps a secondary effect on arsenic (or arsenic and lead) from another source.

Another King County Mainland result, for boring 37-1-2 (West Seattle), has a maximum arsenic concentration of 86 ppm and is modestly high for its distance from the smelter (almost 20 miles). All of the trace element concentrations are elevated, similar to location 84. The lead and antimony ratios versus arsenic are moderately high; those for bismuth, indium, and silver are slightly elevated. These results also indicate a substantial smelter influence, with perhaps a secondary contribution from a source or sources for antimony and lead.

- Low lead spatial anomalies. The identified low lead anomalies include locations also identified as low arsenic anomalies (for example, King County Mainland 507-1-1 and Vashon-Maury Island 13-1-4, 27-1-7, 37-1-8, 42-2-2, and 45-1-1). The trace element results for these borings are consistent with the low arsenic and lead results.

- High lead spatial anomalies. High lead values were the most frequently observed anomaly, including the nine locations noted above as high lead-to-arsenic ratios and additional spatial anomalies. The following are among the prominent high lead anomalous locations: on the King County Mainland, 2-1-2, 37-1-2, 79-1-1, 84-1-3, and 503-1-3; on Vashon-Maury Island, 6-4-1, 6-4-4, 7-2-2, 27-2-1, 30-1-3, and 35-2-1. Many of the trace element results are consistent with the reported maximum arsenic results for these high lead borings. The mainland borings 503-1-3 and 79-1-1, as well as Vashon-Maury Island boring 27-2-1, have elevated antimony-to-arsenic ratios, which suggests another source of antimonial lead. King County boring 84-1-3, already discussed above, also has a high maximum arsenic concentration (i.e., several ratios for trace elements-to-arsenic are comparatively low).

  The cases where trace element results indicate a non-smelter source for spatially anomalous high lead, or high lead and antimony, are in contrast to the results for King County Mainland boring 60-1-2. That nearshore location (Normandy Park) has maximum concentrations for all of the trace elements at or near their highest value for any mainland boring.

  The results for Vashon-Maury Island location 6-4-1 are interesting. The concentrations for all trace elements are among the highest for the trace element study and the ratios versus arsenic are uniformly high. The maximum arsenic concentration of 61 ppm is well above background, but low when compared with all other trace elements. This pattern occurs only rarely in the data set. It is unlikely that a non-smelter source contributes lead, antimony, bismuth, and indium in proportions so similar to smelter emissions. The results for 6-4-1 are suggestive of "missing" arsenic from this boring, possibly a result of soil disturbance or of unusual arsenic mobility in soil at this location.

- Anomalous trace element-to-arsenic ratios. Examination of the trace element-to-arsenic results resulted in identification of only a small number of apparent outlier values: 12 for lead (9 high ratios, 3 low ratios; see list above); 3 for antimony (King County 503-1-3; Vashon-Maury Island 6-4-1, 35-2-1); 1 for bismuth (Vashon-Maury Island 6-4-1); 5 for indium (King County Mainland 504-1-1; Vashon-Maury Island 6-4-1, 7-2-2, 27-1-7, and 35-2-1); and 2 for silver (King County Mainland 58-1-2 and 504-1-1). Many of these cases have already been discussed above. A few additional comments are warranted. At King County boring 58-1-2, the silver result of 1.51 ppm - the highest mainland value - combined with a maximum arsenic value of only 36 ppm produces a silver-to-arsenic ratio almost an order of magnitude higher than typical ratios; results for other elements at that boring are unremarkable. A local source for silver is indicated. Three of the five borings with high indium-to-arsenic ratios have very low arsenic concentrations and indium values near the detection limit; only the results for King County Mainland 504-1-1 and Vashon-Maury Island 6-4-1 appear to reflect any appreciable elevation in ratios for indium.

Low trace element-to-arsenic ratios were much less prominent than high ratios.

The evaluations of anomalous results generally support the usefulness of the selected trace elements for source identification. Most of the trace element results are consistent with the reported maximum arsenic concentrations in borings, as well as consistent (i.e., proportional) with each other. The most frequent type of anomaly is high lead concentrations, at times accompanied by elevated antimony concentrations. The selected trace elements appear to be significantly influenced by other sources only rarely in this data set.

5.7 WITHIN-LOCATION RESULTS

For a number of locations, the set of trace element samples includes samples from multiple borings in a DU or multiple DUs at a single property. These within-location results were reviewed to determine how strongly the selected trace elements are associated with arsenic on a local scale. A strong pattern of association for trace elements with arsenic and with each other has been demonstrated on a regional scale. On the other hand, different mobilities for various elements result in some separation of trace elements versus arsenic in the soil column (i.e., within a single boring).

All of the locations with trace element samples from multiple borings are on Vashon-Maury Island. At 11 properties, samples were analyzed for trace elements in 2 to 4 borings from a single DU; 4 of those 11 properties also had samples from multiple borings for a second DU. Thus, there are 15 sets of within-DU borings to be evaluated (see Attachment C). All four of the undisturbed "forest fringe" DUs from the Vashon-Maury Island Child-Use Areas Study are included among those 15 DUs. The remaining eleven DUs have disturbed soils. (Each of the 15 DU data sets has samples of only one type, undisturbed or disturbed). The borings included in these evaluations of within-DU results have a broad range of maximum arsenic concentrations (4.4 to 150 ppm), with locations from the southern half of Vashon-Maury Island.

Five properties include samples from multiple DUs at a single location (see Attachment C). These five properties include 3 of the 4 locations with "forest fringe" samples; comparisons across DUs at those 3 properties therefore involve both undisturbed and disturbed sampling locations. The borings included in these evaluations of across-DU results have the same broad range of maximum arsenic concentrations (4.4 to 150 ppm) and also represent locations on the southern half of Vashon-Maury Island. The five data sets evaluated for across-DU results included between 2 and 4 DUs and between 4 and 7 borings.

The maximum concentrations of trace elements in borings were used for within-location evaluations. The results for each of the 15 within-DU and 5 across-DU data sets were graphed separately, using multi-element line plots of normalized concentrations (with each result normalized to the maximum value for that element in that data set) versus boring. All values were thus rescaled to between 0 and 1, and the lines for different elements traced rising and falling patterns that showed how consistently the elements varied from one boring to another (i.e., the graphs were similar in appearance to Figure 14 but focused on local areas). Tabled values of the trace element-to-arsenic ratios were also reviewed. Thus, both graphical and numerical approaches were used. In cases where maximum concentration data showed deviations from consistent patterns, the depth profile results for individual samples were reviewed.

Both within-DU and across-DU comparisons showed that the selected trace elements mirrored the local-scale variability in arsenic concentrations quite well. Their behavior is not perfectly proportional; the trace element-to-arsenic ratios for an element, across borings, are often variable even when the overall pattern of rising and falling concentrations is consistent with arsenic. Only a small number of cases were noted where a result deviated strongly from the overall pattern. The majority of such cases involved lead (e.g., at borings 6-4-4 and 28-2-5).

For several of the data sets, multiple trace elements showed a very consistent pattern across borings with arsenic results deviating somewhat from that pattern. Atypical or varying depth profiles for arsenic occurred at some of these locations (e.g., borings 27-1-2, 28-1-3, 39-1-3, and 39-1-4). The greater mobility of arsenic compared to the other trace elements means that arsenic tends to become more spread out over depths. Using the maximum concentration at any of the sampled depth intervals may be too simple an approach to always address these differences in mobility among the elements. (Calculation of the mass above background over the whole soil column, using depth-weighted calculations from reported concentration data, may be an alternate approach worth examining). It may also be the case that at locations with disturbed soils the depth intervals selected for trace element analyses were too few to fully characterize the relationship among elements.

6.0 CONCLUSIONS

Analyses for multiple trace elements in 234 soil samples collected from areas surrounding ASARCO's former Tacoma Smelter, plus 8 unrelated soil samples from former orchard properties in eastern Washington, demonstrate that trace element chemistry in soils can be used effectively for source identification. The Tacoma Smelter is identified as the major source for the observed regional distribution of arsenic in shallow soils.

The major findings of this study include the following:

- At least ten elements, and possibly more, show soil contamination patterns and associations identifying the smelter as a primary source.

- In addition to arsenic, the primary tracer of smelter impacts, three elements selected for detailed investigation in this study - antimony, bismuth, and indium - are effective tracers of smelter impacts on a regional scale (e.g., to distances of more than 20 miles).

- All pairwise correlations for seven elements - arsenic, lead, antimony, bismuth, indium, silver, and mercury - are statistically highly significant. Those correlations are particularly strong for trace elements antimony, bismuth, and indium. The strong correlation pattern indicates similar spatial distributions for multiple elements and argues for a common source.

- The characteristic trace element-to-arsenic ratios are shown to be much higher (by approximately an order of magnitude) in soils affected by smelter emissions than in orchard soils affected by applications of lead arsenate. Orchard soils also show a different pattern of pairwise correlations among trace elements. Trace element analyses can therefore be used to discriminate between smelter versus orchard sources.

- The high correlations between arsenic and other trace elements mean that low arsenic concentrations are accompanied by low concentrations for the other elements. The reported concentrations for other trace elements in this study for samples with low arsenic concentrations are consistent with literature values for their background levels (e.g., based on estimated crustal abundance).

- The (downward) mobility of trace elements in the soil column is observed to vary, resulting in some separation by depth for different elements. This mobility is greatest for arsenic and least for lead, with the other targeted trace elements intermediate between these two end members of the mobility sequence.

- The trace elements selected for detailed investigation show similar patterns in both undisturbed and disturbed soils. Like arsenic, trace elements show an overall gradient with distance from the smelter, plus considerable local variability (especially for properties with disturbed soils). Evaluations of trace element-to-arsenic ratios versus distance show different patterns for different elements. Lead ratios are higher in the more heavily urbanized King County Mainland, indicating additional non-smelter lead sources (e.g., leaded gasoline emissions). Antimony ratios show a trend of decreasing values with distance, both on Vashon-Maury Island and on the King County Mainland. This may reflect in-plume processes and changes in relative deposition from smelter emissions as a function of distance. Bismuth demonstrates the most stable ratio among targeted trace elements.

- The most frequent anomalous results are a moderate number of high lead values. Some of those borings are also high in antimony; a non-smelter source for antimonial lead may be implicated at those locations. Only a very small number of results for other trace elements are identified as anomalous. Trace element concentrations generally vary consistently with arsenic values at sampling locations with spatially anomalous arsenic results.

- Trace element results generally mirror the varying patterns for arsenic in multiple borings on one property (albeit with moderate variations in trace element-to-arsenic ratios), with only a few significantly divergent values. Trace elements therefore appear useful on a local as well as a regional spatial scale.

Additional trace element analyses are being performed for approximately 150 soil samples from the Pierce County Footprint Study, covering the portion of Pierce County north and west of I-5. That region includes areas southwest of the Tacoma Smelter in the second prominent downwind direction. Those additional analyses will be completed during 2003. The results will be provided and evaluated in a supplement to this report.

7.0 REFERENCES

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Table 1

Tacoma Smelter Plume Site

Summary of Samples Selected for Trace Element Analyses

UNDISTURBED SAMPLE LOCATIONS

												Number of DUs with Multiple Borings per DU		
				Depth Profiles:										
	Number of:			Two				Three		Four	Five	Two	Three	Four
	Samples	Borings	Locations	1/2	2/3	3/4	4/5	1/2/3	3/4/5	1/2/3/4	1/2/3/4/5			
Vashon-Maury Island	41	15	8	6				8			1	1	3	
King County Mainland	68	33	33	29	1	1		2						

DISTURBED SAMPLE LOCATIONS

												Number of DUs with Multiple Borings per DU		
				Depth Profiles:										
	Number of:			Two				Three		Four	Five	Two	Three	Four
	Samples	Borings	Locations	1/2	2/3	3/4	4/5	1/2/3	3/4/5	1/2/3/4	1/2/3/4/5			
Vashon-Maury Island	125	44	22	14		1	1	21	1	3	3	7	3	1

FORMER ORCHARD SAMPLE LOCATIONS

												Number of DUs with Multiple Borings per DU		
				Depth Profiles:										
	Number of:			Two				Three		Four	Five	Two	Three	Four
	Samples	Borings	Locations	1/2	2/3	3/4	4/5	1/2/3	3/4/5	1/2/3/4	1/2/3/4/5			
Yakima Area	8	4	2	4								2		

Table 2

Tacoma Smelter Plume Site

Trace Element Analyses
Summary of Results

		OnSite Analyses		Battelle Analyses						
Sample Locations		arsenic	lead	arsenic	lead	antimony	bismuth	indium	mercury	silver
Vashon-Maury Island										
(n=)										
	number of analyses	166	157	37	11	166	166	166	37	10
	number of NDs	3	9	2	0	48	18	24	7	0
	ND range	1.6 - 1.7	5.2 - 6.4	5.16 - 13.7	n/a	0.725 - 16.8	0.1 - 0.683	0.05	0.0393 - 0.169	n/a
	minimum quantified	1.7	6.9	4.23	16	0.591	0.1	0.0504	0.063	0.0891
	maximum quantified	230	900	238	681	68.1	18.7	1.5	2.57	1.69
	ratio: Max/Min	135	130	56	43	115	187	30	41	19
King County Mainland										
(n=)										
	number of analyses	68	68	68	10	68	68	68	10	68
	number of NDs	1	1	0	0	0	1	14	0	15
	ND range	5	6.8	n/a	n/a	n/a	0.1	0.05	n/a	0.049 - 0.345
	minimum quantified	7.5	6.7	9	27.5	0.57	0.205	0.0363	0.13	0.0879
	maximum quantified	180	619	217	705	27.7	9.05	0.916	1.56	1.51
	ratio: Max/Min	24	92	24	26	49	44	25	12	17
Former Orchards										
(n=8)										
	number of analyses	0	0	8	8	8	8	8	8	8
	number of NDs	n/a	n/a	0	0	0	0	0	2	0
	ND range	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.0106 - 0.0115	n/a
	minimum quantified	n/a	n/a	15.2	110	0.526	0.241	0.0456	0.0158	0.0528
	maximum quantified	n/a	n/a	77.8	364	1.19	0.347	0.0693	0.0483	0.099
	ratio: Max/Min	n/a	n/a	5.1	3.3	2.3	1.4	1.5	3.1	1.9

NOTES:
1. All concentrations in ppm, dry weight, on <2mm size fraction.
2. Where all samples are not analyzed, the ranges shown may not include analyses of samples over the full range of arsenic results.

Table 3

Tacoma Smelter Plume Site

Trace Element Correlations Based on Maximum Concentrations by Boring

		Inter-Element Correlations			
	Arsenic	Lead	Antimony	Bismuth	Indium
Lead	0.6037				
	(92)				
	0.0000				
Antimony	0.8030	0.7210			
	(92)	(92)			
	0.0000	0.0000			
Bismuth	0.8682	0.7465	0.8849		
	(92)	(92)	(92)		
	0.0000	0.0000	0.0000		
Indium	0.8407	0.6969	0.8878	0.9447	
	(92)	(92)	(92)	(92)	
	0.0000	0.0000	0.0000	0.0000	
Silver	0.7664	0.6734	0.6890	0.8260	0.8295
	(38)	(38)	(38)	(38)	(38)
	0.0000	0.0000	0.0000	0.0000	0.0000

NOTES:

1. Entry formats are:

0.6037	correlation coefficient
(92)	number of samples
0.0000	significance level (0.0000 means < 0.00005)

2. All data distributions are right-skewed; therefore correlations (parametric) are calculated using LOG concentrations.
3. Arsenic and lead results are from OnSite lab analyses; other results are from Battelle lab analyses.
4. For 9 samples without OnSite lead results, Battelle results are used instead as surrogate values.
5. Correlations are based on results from all Tacoma Smelter Plume locations (Vashon-Maury Island and King County Mainland; undisturbed and disturbed soils) with trace element analyses.

Table 4

Tacoma Smelter Plume Site

Trace Element-to-Arsenic Ratios
From Regression Equations

		Regression R-Squared (percent)	Element-to-Arsenic Ratio at Arsenic concentration (ppm) of:			
			20	50	100	200
Tacoma Smelter Plume Samples (n=92 borings)						
	Pb	36.4	3.69	2.86	2.35	1.94
	Sb	64.5	0.132	0.131	0.129	0.128
	Bi	75.4	0.034	0.039	0.043	0.048
	In	70.7	0.0047	0.0041	0.0037	0.0033
	Ag	58.7	0.0103	0.0081	0.0067	0.0056
Orchard Samples (n=8 samples)						
	Pb	93.2	6.67	5.18	4.27	3.53
	Sb	59.7	0.032	0.018	0.012	0.008
	Bi	76.1	0.0129	0.0063	0.0036	0.0021
	In	47.9	0.0025	0.0012	0.0007	0.0004
	Ag	57.0	0.0030	0.0016	0.0010	0.0006
			Comparative Enrichment, Smelter vs Orchard Soils			
	Pb		0.55	0.55	0.55	0.55
	Sb		4.1	7.3	10.8	16.0
	Bi		2.6	6.2	11.9	22.9
	In		1.9	3.4	5.3	8.3
	Ag		3.4	5.1	6.7	9.3

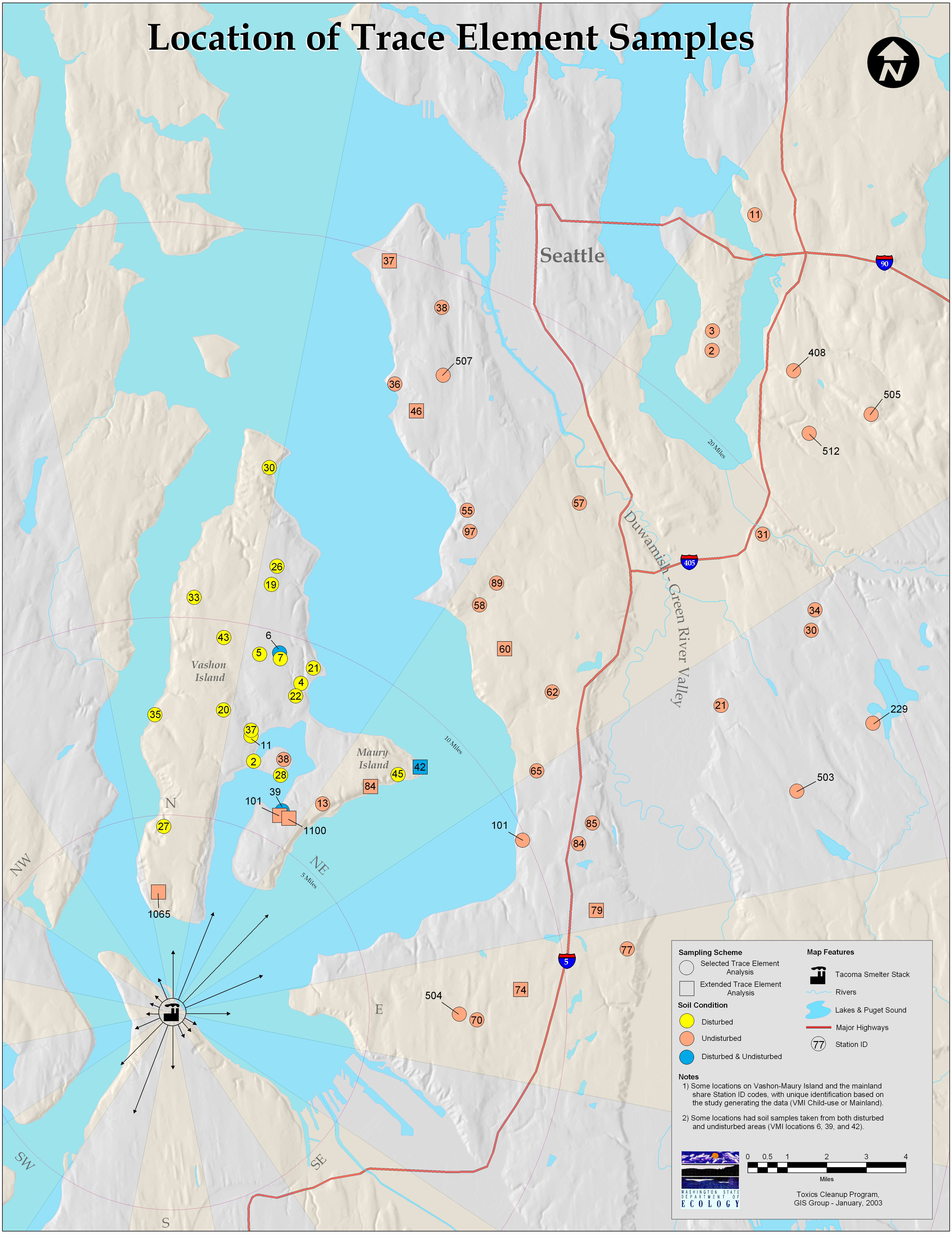
NOTES:

Comparative enrichment calculated as element-to-arsenic ratio for smelter soils divided by orchard soils.

All linear regression equations calculated using LOG concentrations.

Detection limit concentrations used for not-detected results.

Location of Trace Element Samples



Notes

1) Some locations on Vashon-Maury Island and the mainland share Station ID codes, with unique identification based on the study generating the data (VMI Child-use or Mainland).

2) Some locations had soil samples taken from both disturbed and undisturbed areas (VMI locations 6, 39, and 42).

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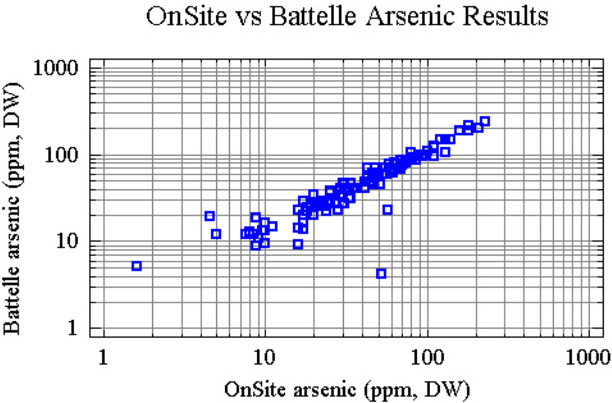
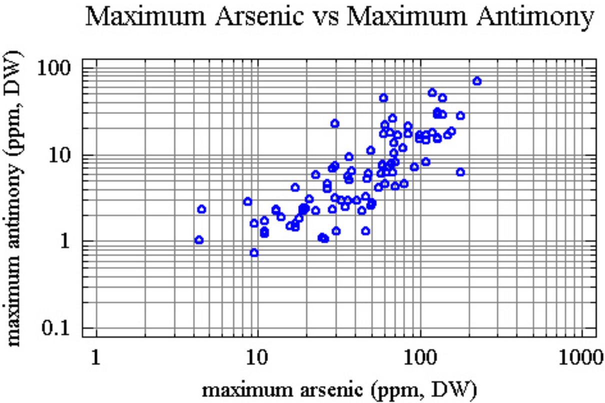
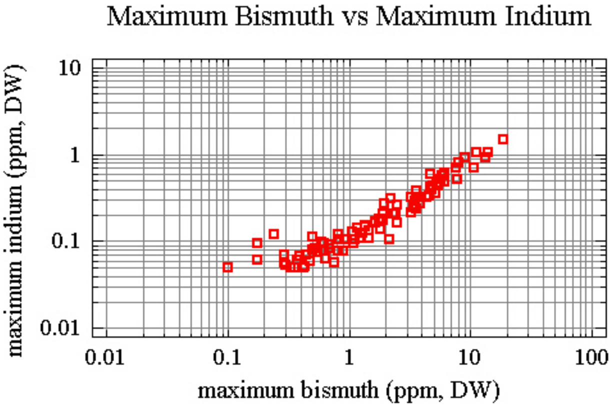
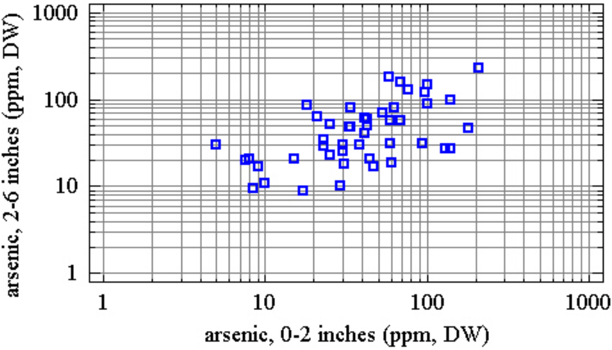
GIS Group - January, 2003


OnSite vs Battelle Arsenic Results
Battelle arsenic (ppm, DW)
1000
100
10
1
1
10
100
1000
OnSite arsenic (ppm, DW)

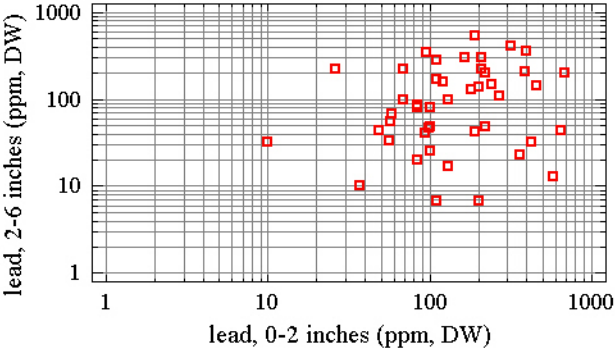

Maximum Arsenic vs Maximum Antimony
maximum antimony (ppm, DW)
100
10
1
0.1
1
10
100
1000
maximum arsenic (ppm, DW)


Maximum Bismuth vs Maximum Indium
maximum indium (ppm, DW)
10
1
0.1
0.01
0.01
0.1
1
10
100
maximum bismuth (ppm, DW)

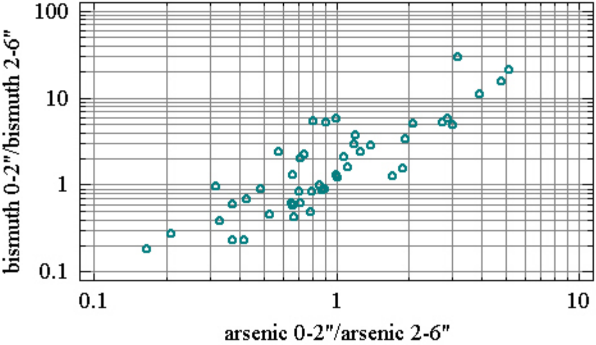
Depth Profile, Arsenic (0-2 vs 2-6 inches), Undisturbed Locations

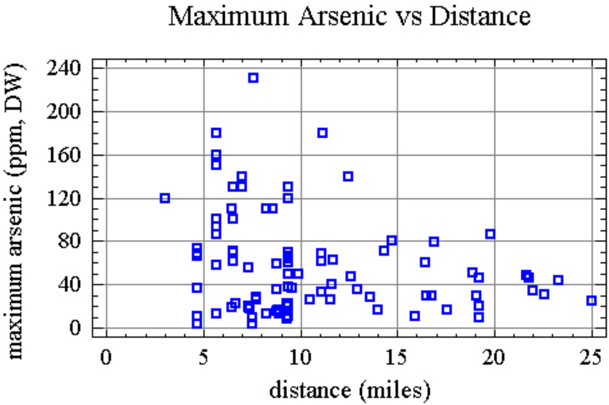


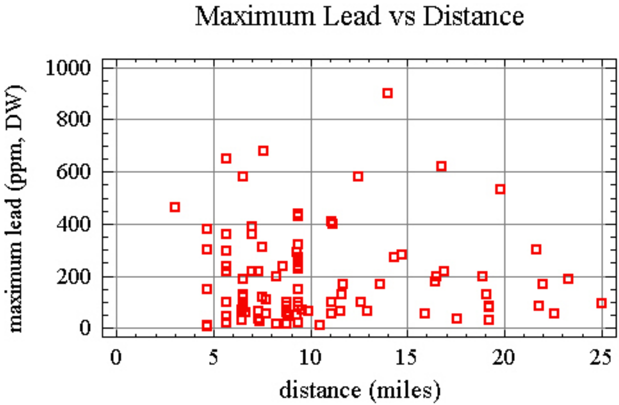
Depth Profile, Lead (0-2 vs 2-6 inches), Undisturbed Locations

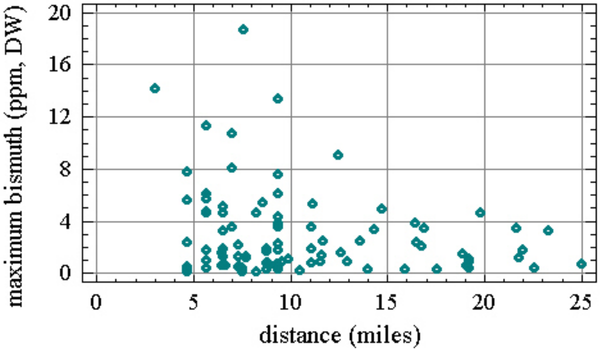


Comparative Depth Profiles, Arsenic vs Bismuth (Undisturbed)

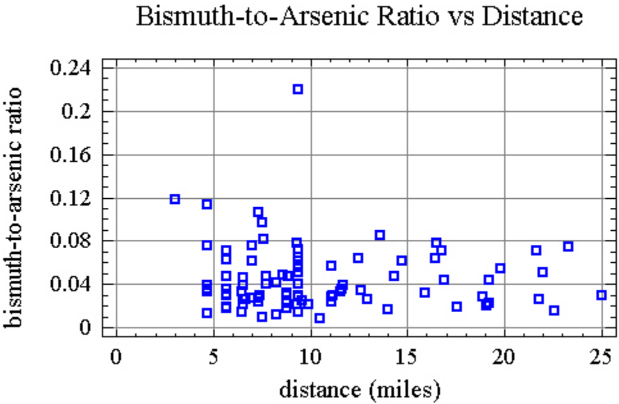


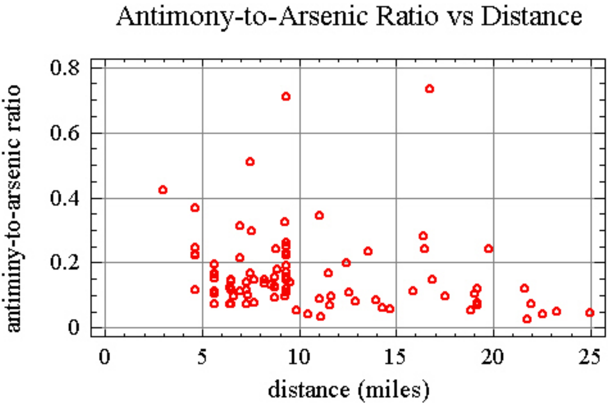

Maximum Arsenic vs Distance
maximum arsenic (ppm, DW)
240
200
160
120
80
40
0
0
5
10
15
20
25
distance (miles)

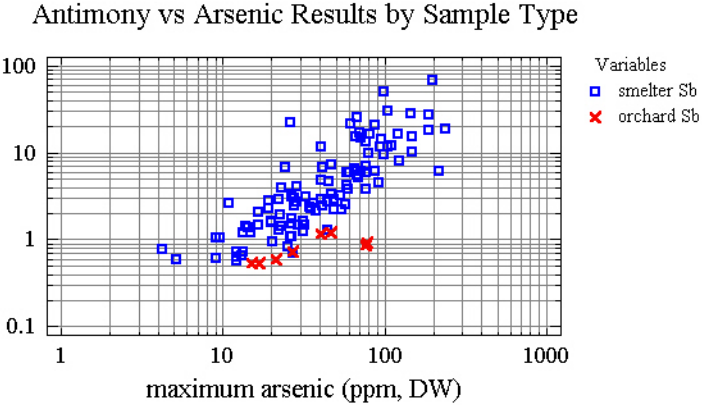

Maximum Lead vs Distance
maximum lead (ppm, DW)
1000
800
600
400
200
0
0
5
10
15
20
25
distance (miles)

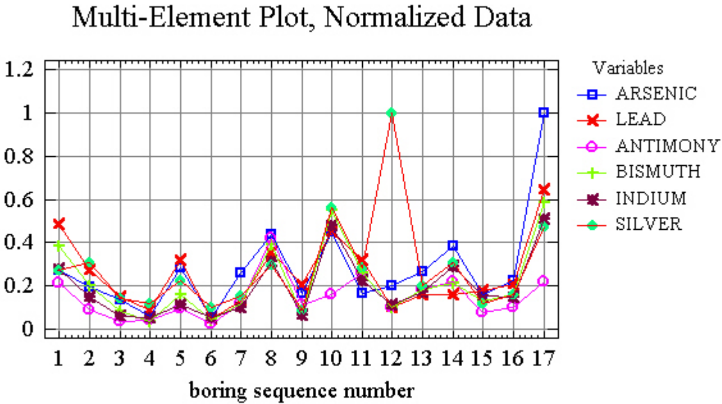


Maximum Bismuth vs Distance


Bismuth-to-Arsenic Ratio vs Distance


Antimony-to-Arsenic Ratio vs Distance
antiminy-to-arsenic ratio
0
0.2
0.4
0.6
0.8
0
5
10
15
20
25
distance (miles)


Antimony vs Arsenic Results by Sample Type
100
10
1
0.1
1
10
100
1000
maximum arsenic (ppm, DW)
Variables
smelter Sb
orchard Sb


Multi-Element Plot, Normalized Data
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
boring sequence number
Variables
ARSENIC
LEAD
ANTIMONY
BISMUTH
INDIUM
SILVER

ATTACHMENT A

List of Elements Analyzed
for
Extended Trace Elements Samples

Attachment A

List of Elements Analyzed for Extended Trace Elements Samples

element	atomic number	element	atomic number
vanadium	23	**antimony** (b)	**51**
chromium	24	tellurium	52
cobalt	27	iodine	53
nickel	28	cesium	55
copper	29	lanthanum	57
zinc	30	cerium	58
gallium	31	samarium	62
germanium	32	ytterbium	70
arsenic (b)	**33**	tungsten	74
selenium	34	platinum	78
bromine	35	gold	79
yttrium (a)	39	**mercury** (b)	**80**
molybdenum	42	thallium	81
ruthenium	44	lead	82
rhodium	45	**bismuth** (b)	**83**
palladium	46	polonium	84
silver (b)	**47**		
cadmium	48		
indium (b)	**49**		
tin	50		

(a) Yttrium reported for King County Mainland samples, but not Vashon-Maury Island samples.

(b) Elements shown in bold analyzed as targeted analytes in some or all samples in larger sample groups. Antimony, indium, and bismuth selected as three primary targeted trace elements and analyzed in all samples; mercury and silver analyzed for a subset of samples in a preliminary investigation of their performance as smelter trace elements. Arsenic analyzed for a subset of samples to provide data for between-lab comparisons.

	A	B	C	D	E	F	G	H	I
1	**Attachment B**								
2									
3	**Tacoma Smelter Plume Site**								
4									
5	**Targeted Trace Elements**								
6	**Analytical Results by Sample**								
7									
8									
9									
10									
11		**Study**	**Sample Code**		**Direction**	**Distance**		**Location**	**DU**
12					**(degrees)**	**(miles)**			
13		**King County**							
14		**Mainland**							
15									
16		Main sample	1-2-1-2-1		39.25	21.62		2	1
17		group	1-2-1-2-2		39.25	21.62		2	1
18			1-3-1-1-1		38.45	22.01		3	1
19			1-3-1-1-2		38.45	22.01		3	1
20			1-11-1-3-1		36.19	24.99		11	1
21			1-11-1-3-2		36.19	24.99		11	1
22			1-21-1-1-1		60.82	15.92		21	1
23			1-21-1-1-2		60.82	15.92		21	1
24			1-30-1-3-1		59.17	18.85		30	1
25			1-30-1-3-2		59.17	18.85		30	1
26			1-31-1-2-1		51.04	19.24		31	1
27			1-31-1-2-2		51.04	19.24		31	1
28			1-34-1-2-2		57.99	19.20		34	1
29			1-34-1-2-3		57.99	19.20		34	1
30			1-36-1-1-1		19.56	16.87		36	1
31			1-36-1-1-2		19.56	16.87		36	1
32			1-38-1-1-1		20.98	19.10		38	1
33			1-38-1-1-2		20.98	19.10		38	1
34			1-55-1-1-1		30.49	14.74		55	1
35			1-55-1-1-2		30.49	14.74		55	1
36			1-57-1-3-1		38.69	16.50		57	1
37			1-57-1-3-2		38.69	16.50		57	1
38			1-58-1-2-3		37.09	12.92		58	1
39			1-58-1-2-4		37.09	12.92		58	1
40			1-62-1-3-1		49.93	12.59		62	1
41			1-62-1-3-2		49.93	12.59		62	1
42			1-65-1-1-1		56.54	11.07		65	1
43			1-65-1-1-2		56.54	11.07		65	1
44			1-70-1-1-1		91.41	7.73		70	1
45			1-70-1-1-2		91.41	7.73		70	1
46			1-77-1-3-1		82.08	11.64		77	1
47			1-77-1-3-2		82.08	11.64		77	1
48			1-84-1-3-1		67.50	11.15		84	1
49			1-84-1-3-2		67.50	11.15		84	1
50			1-85-1-3-1		65.79	11.67		85	1
51			1-85-1-3-2		65.79	11.67		85	1

	A	B	C	D	E	F	G	H	I
52			1-85-1-3-3		65.79	11.67		85	1
53			1-89-1-1-1		37.14	13.62		89	1
54			1-89-1-1-2-1		37.14	13.62		89	1
55			1-97-1-3-1		31.82	14.31		97	1
56			1-97-1-3-2		31.82	14.31		97	1
57			1-101-1-2-1		63.91	9.89		101	1
58			1-101-1-2-2		63.91	9.89		101	1
59			1-229-1-2-1		67.61	19.19		229	1
60			1-229-1-2-2		67.61	19.19		229	1
61			1-408-1-1-1		44.12	22.61		408	1
62			1-408-1-1-2		44.12	22.61		408	1
63			1-503-1-3-1		70.52	16.78		503	1
64			1-503-1-3-2		70.52	16.78		503	1
65			1-503-1-3-3		70.52	16.78		503	1
66			1-504-1-1-1		90.37	7.28		504	1
67			1-504-1-1-2		90.37	7.28		504	1
68			1-505-1-3-1		49.48	23.28		505	1
69			1-505-1-3-2-1		49.48	23.28		505	1
70			1-507-1-1-1		23.07	17.53		507	1
71			1-507-1-1-2		23.07	17.53		507	1
72			1-512-1-3-1		47.77	21.79		512	1
73			1-512-1-3-2		47.77	21.79		512	1
74									
75		Initial Sample	1-37-1-2-1		16.16	19.79		37	1
76		Group	1-37-1-2-2		16.16	19.79		37	1
77			1-46-1-2-1		22.15	16.43		46	1
78			1-46-1-2-2		22.15	16.43		46	1
79			1-60-1-2-1		42.48	12.47		60	1
80			1-60-1-2-2		42.48	12.47		60	1
81			1-74-1-1-1		86.28	8.85		74	1
82			1-74-1-1-2		86.28	8.85		74	1
83			1-79-1-1-1		76.52	11.05		79	1
84			1-79-1-1-2		76.52	11.05		79	1
85									
86		**E. Washington**	ORCHARD-1A						
87		**Orchards**	ORCHARD-1B						
88			ORCHARD-2A						
89			ORCHARD-2B						
90			ORCHARD-3A						
91			ORCHARD-3B						
92			ORCHARD-4A						
93			ORCHARD-4B						
94									
95									
96		**Vashon-Maury**							
97		**Island**							
98									
99		Main Sample	1-2-1-7-1		6.64	72.12		2	1
100		Group	1-2-1-7-2		6.64	72.12		2	1
101			1-2-1-7-3		6.64	72.12		2	1
102			1-2-1-7-4		6.64	72.12		2	1

	A	B	C	D	E	F	G	H	I
103			1-2-1-7-5		6.64	72.12		2	1
104			2-4-1-4-1		8.89	68.69		4	1
105			2-4-1-4-2		8.89	68.69		4	1
106			2-5-1-2-1		9.28	76.36		5	1
107			2-5-1-2-2		9.28	76.36		5	1
108			2-6-2-6-1		9.38	73.3		6	2
109			2-6-2-6-2		9.38	73.3		6	2
110			2-6-2-6-3		9.38	73.3		6	2
111			2-6-3-2-1		9.38	73.3		6	3
112			2-6-3-2-2		9.38	73.3		6	3
113			2-6-4-1-1		9.38	73.3		6	4
114			2-6-4-1-2		9.38	73.3		6	4
115			2-6-4-3-1		9.38	73.3		6	4
116			2-6-4-3-2		9.38	73.3		6	4
117			2-6-4-3-3		9.38	73.3		6	4
118			2-6-4-4-1		9.38	73.3		6	4
119			2-6-4-4-2		9.38	73.3		6	4
120			2-6-4-4-3		9.38	73.3		6	4
121			2-6-4-4-4		9.38	73.3		6	4
122			2-6-4-4-5		9.38	73.3		6	4
123			2-6-5-1-1		9.38	73.3		6	5
124			2-6-5-1-2		9.38	73.3		6	5
125			2-6-5-1-3		9.38	73.3		6	5
126			2-6-5-3-1		9.38	73.3		6	5
127			2-6-5-3-2		9.38	73.3		6	5
128			2-6-5-3-3		9.38	73.3		6	5
129			2-7-2-2-4		9.31	73.07		7	2
130			2-7-2-2-5		9.31	73.07		7	2
131			1-11-1-5-1-1		7.29	74.28		11	1
132			1-11-1-5-2-1		7.29	74.28		11	1
133			1-11-1-6-1		7.29	74.28		11	1
134			1-11-1-6-2		7.29	74.28		11	1
135			1-11-1-6-3		7.29	74.28		11	1
136			1-13-1-4-1		6.45	54.05		13	1
137			1-13-1-4-2		6.45	54.05		13	1
138			1-13-1-5-3		6.45	54.05		13	1
139			1-13-1-5-4		6.45	54.05		13	1
140			1-13-1-5-5		6.45	54.05		13	1
141			3-19-1-3-1		11.07	77.02		19	1
142			3-19-1-3-2		11.07	77.02		19	1
143			2-20-1-4-1		7.72	80.51		20	1
144			2-20-1-4-2		7.72	80.51		20	1
145			2-20-1-4-3		7.72	80.51		20	1
146			2-20-1-4-4		7.72	80.51		20	1
147			2-21-1-1-1		9.37	67.73		21	1
148			2-21-1-1-2		9.37	67.73		21	1
149			2-21-1-1-3		9.37	67.73		21	1
150			2-21-1-2-1		9.37	67.73		21	1
151			2-21-1-2-2		9.37	67.73		21	1
152			2-21-1-2-3		9.37	67.73		21	1
153			2-21-1-2-4		9.37	67.73		21	1

	A	B	C	D	E	F	G	H	I
154			2-21-1-5-1		9.37	67.73		21	1
155			2-21-1-5-2		9.37	67.73		21	1
156			2-21-1-8-1		9.37	67.73		21	1
157			2-21-1-8-2		9.37	67.73		21	1
158			2-21-1-8-3		9.37	67.73		21	1
159			2-22-1-1-1-1		8.55	68.72		22	1
160			2-22-1-1-2-1		8.55	68.72		22	1
161			2-22-1-1-3-1		8.55	68.72		22	1
162			2-22-1-1-4-1		8.55	68.72		22	1
163			3-26-2-3-1		11.55	76.85		26	2
164			3-26-2-3-2		11.55	76.85		26	2
165			1-27-1-1-1		4.67	87.08		27	1
166			1-27-1-1-2		4.67	87.08		27	1
167			1-27-1-2-1		4.67	87.08		27	1
168			1-27-1-2-2		4.67	87.08		27	1
169			1-27-1-2-3		4.67	87.08		27	1
170			1-27-1-7-1		4.67	87.08		27	1
171			1-27-1-7-2		4.67	87.08		27	1
172			1-27-2-1-1		4.67	87.08		27	2
173			1-27-2-1-2		4.67	87.08		27	2
174			1-27-2-1-3		4.67	87.08		27	2
175			1-27-3-2-1		4.67	87.08		27	3
176			1-27-3-2-2		4.67	87.08		27	3
177			1-27-7-1-3		4.67	87.08		27	7
178			1-27-7-1-4		4.67	87.08		27	7
179			1-28-1-1-1		6.55	65.48		28	1
180			1-28-1-1-2		6.55	65.48		28	1
181			1-28-1-1-3		6.55	65.48		28	1
182			1-28-1-3-1		6.55	65.48		28	1
183			1-28-1-3-2		6.55	65.48		28	1
184			1-28-1-3-3		6.55	65.48		28	1
185			1-28-1-3-4		6.55	65.48		28	1
186			1-28-1-3-5		6.55	65.48		28	1
187			1-28-1-6-1		6.55	65.48		28	1
188			1-28-1-6-2		6.55	65.48		28	1
189			1-28-1-6-3		6.55	65.48		28	1
190			1-28-2-5-1		6.55	65.48		28	2
191			1-28-2-5-2		6.55	65.48		28	2
192			1-28-2-5-3		6.55	65.48		28	2
193			1-28-2-6-1		6.55	65.48		28	2
194			1-28-2-6-2		6.55	65.48		28	2
195			1-28-2-6-3		6.55	65.48		28	2
196			3-30-1-3-1		11.55	76.85		30	1
197			3-30-1-3-2		11.55	76.85		30	1
198			3-30-1-3-3		11.55	76.85		30	1
199			3-33-2-3-1		10.47	87.11		33	2
200			3-33-2-3-2		10.47	87.11		33	2
201			3-33-2-3-3		10.47	87.11		33	2
202			2-35-2-1-1		7.51	86.47		35	2
203			2-35-2-1-2		7.51	86.47		35	2
204			2-35-2-1-3		7.51	86.47		35	2

	A	B	C	D	E	F	G	H	I
205			2-35-2-6-1		7.51	86.47		35	2
206			2-35-2-6-2		7.51	86.47		35	2
207			2-35-2-6-3		7.51	86.47		35	2
208			1-37-1-8-1		7.37	74.47		37	1
209			1-37-1-8-2		7.37	74.47		37	1
210			1-37-1-8-3		7.37	74.47		37	1
211			1-38-3-1-1		6.95	66.22		38	3
212			1-38-3-1-2		6.95	66.22		38	3
213			1-38-3-2-1		6.95	66.22		38	3
214			1-38-3-2-2		6.95	66.22		38	3
215			1-38-3-2-3		6.95	66.22		38	3
216			1-38-3-3-1		6.95	66.22		38	3
217			1-38-3-3-2		6.95	66.22		38	3
218			1-38-3-3-3		6.95	66.22		38	3
219			1-39-1-1-1		3.03	82.96		39	1
220			1-39-1-1-2		3.03	82.96		39	1
221			1-39-1-1-3		3.03	82.96		39	1
222			1-39-1-3-1		3.03	82.96		39	1
223			1-39-1-3-2		3.03	82.96		39	1
224			1-39-1-3-3		3.03	82.96		39	1
225			1-39-1-4-1		3.03	82.96		39	1
226			1-39-1-4-2		3.03	82.96		39	1
227			1-39-1-4-3		3.03	82.96		39	1
228			1-39-1-4-4		3.03	82.96		39	1
229			1-39-1-4-5		3.03	82.96		39	1
230			1-39-6-2-1		3.03	82.96		39	6
231			1-39-6-2-2		3.03	82.96		39	6
232			1-39-6-2-3		3.03	82.96		39	6
233			1-39-6-3-1		3.03	82.96		39	6
234			1-39-6-3-2		3.03	82.96		39	6
235			1-39-6-3-3		3.03	82.96		39	6
236			1-39-6-4-1		3.03	82.96		39	6
237			1-39-6-4-2		3.03	82.96		39	6
238			1-42-2-5-1		8.78	44.61		42	2
239			1-42-2-5-2		8.78	44.61		42	2
240			1-42-2-5-3		8.78	44.61		42	2
241			1-42-3-1-1		8.78	44.61		42	3
242			1-42-3-1-2		8.78	44.61		42	3
243			1-42-3-1-3		8.78	44.61		42	3
244			1-42-3-2-1		8.78	44.61		42	3
245			1-42-3-2-2		8.78	44.61		42	3
246			1-42-3-2-3		8.78	44.61		42	3
247			2-43-1-2-1		9.53	82.38		43	1
248			2-43-1-2-2		9.53	82.38		43	1
249			1-45-1-1-1		8.26	46.39		45	1
250			1-45-1-1-2		8.26	46.39		45	1
251			1-45-1-6-1		8.26	46.39		45	1
252			1-45-1-6-2		8.26	46.39		45	1
253			1-45-1-6-3		8.26	46.39		45	1
254									
255		Initial Sample	1-42-2-2-1		8.78	44.61		42	2

	A	B	C	D	E	F	G	H	I
256		Group	1-42-2-2-2		8.78	44.61		42	2
257			1-84-1-1-1		7.56	48.64		84	1
258			1-84-1-1-2		7.56	48.64		84	1
259			1-101-1-2-1		3.03	82.96		101	1
260			1-101-1-2-2		3.03	82.96		101	1
261			1-1065-1-1-1		5.69	59.01		1065	1
262			1-1065-1-1-2		5.69	59.01		1065	1
263			1-1100-1-1-1		5.63	61.38		1100	1
264			1-1100-1-1-2		5.63	61.38		1100	1
265			1-1100-1-1-3		5.63	61.38		1100	1

	J	K	L	M	N	O	P	Q	R	S
1										
2										
3										
4										
5										
6										
7										
8										
9				**Concentrations (in ppm, dry weight):**						
10				**OnSite Lab:**					**Battelle Lab:**	
11	**Boring**	**Depth**		**Arsenic**	**Flag**	**Lead**	**Flag**		**Antimony**	**Flag**
12										
13										
14										
15										
16	2	1		33		210			1.63	J
17	2	2		49		300			5.91	J
18	1	1		23		110			1.52	
19	1	2		35		170			2.49	
20	3	1		25		94			1.08	
21	3	2		23		41			0.823	
22	1	1		9.9		57			1.21	J
23	1	2		11		55			1.19	J
24	3	1		25		200			1.46	
25	3	2		51		140			2.69	
26	2	1		8.4		10			0.633	J
27	2	2		9.6		32			0.724	J
28	2	2		16		48			1.92	J
29	2	3		47		81			3.27	J
30	1	1		63		210			9.92	J
31	1	2		79		220			11.7	J
32	1	1		30	J	130			3.11	J
33	1	2		30	J	97			2.43	J
34	1	1		34		110			1.23	
35	1	2		81		280			4.5	
36	3	1		30		200			7.19	J
37	3	2		25		6.8	U		2.11	J
38	2	3		25		41			2.65	J
39	2	4		36		64			2.9	J
40	3	1		34		69			3.31	J
41	3	2		48		100			5.09	J
42	1	1		69		100			6.12	J
43	1	2		57		79			1.43	J
44	1	1		29		110			2.26	
45	1	2		10		6.7			1.06	
46	3	1		41		130			2.88	
47	3	2		19		17			1.08	
48	3	1		58		400			5.83	J
49	3	2		180		360			6.03	J
50	3	1		21		120			3.35	J
51	3	2		63		160			5.45	J

	J	K	L	M	N	O	P	Q	R	S
52	3	3		55		170			6.1	J
53	1	1		23		110			2.71	J
54	1	2		29		170			6.72	J
55	3	1		53		270			4.24	J
56	3	2		71		110			3.84	J
57	2	1		43		58			2.21	J
58	2	2		50		67			2.55	J
59	2	1		7.5		84			0.736	J
60	2	2		20		85			2.35	J
61	1	1		31		56			0.703	J
62	1	2		18		33			1.27	J
63	3	1		5	U	95			0.57	J
64	3	2		30		350			1.49	J
65	3	3		22		619			21.9	J
66	1	1		7.9		69			0.645	
67	1	2		21		220			2.96	
68	3	1		44		190			2.21	J
69	3	2		21		42			1.75	J
70	1	1		17		37			1.6	
71	1	2		8.8		10			0.613	
72	3	1		47		84			1.27	
73	3	2		17		20			0.953	
74										
75	2	1		18		190			6.84	
76	2	2		86		530			20.7	
77	2	1		43	J	180			16.8	
78	2	2		60	J	130			6.19	
79	2	1		140		580			27.7	
80	2	2		27		13			3.14	
81	1	1		9.1		49			2.64	
82	1	2		17		43			4.1	
83	1	1		41		320			11.5	
84	1	2		62		410			21.2	
85										
86									0.528	
87									0.588	
88									0.526	
89									0.713	
90									1.19	
91									1.16	
92									0.85	
93									0.91	
94										
95										
96										
97										
98										
99	7	1		20		38			1.61	
100	7	2		22		32			2.12	
101	7	3		20		28			2.23	
102	7	4		23		49			2.14	

	J	K	L	M	N	O	P	Q	R	S
103	7	5		17		61			1.92	
104	4	1		13		45			2.3	U
105	4	2		7.5		12			1.45	U
106	2	1		19	J	24			1.34	U
107	2	2		23	J	49			2.23	U
108	6	1		21		36			2.46	U
109	6	2		64		86			6.9	
110	6	3		21		17			3.2	U
111	2	1		11		150			1.7	U
112	2	2		7.2		15			1.7	U
113	1	1		61		430			43.3	
114	1	2		19		32			2.2	
115	3	1		38		100			6.42	
116	3	2		30	J	48			3.88	U
117	3	3		3.3	J	5.9	U		0.725	U
118	4	1		15	J	26			1.77	U
119	4	2		21	J	220			4.02	U
120	4	3		16	J	250			5.75	U
121	4	4		17	J	88			3.46	U
122	4	5		23	J	53			2.06	U
123	1	1		70	J	240			13.4	
124	1	2		40	J	63			4.51	
125	1	3		7.9	J	7.2			1.42	
126	3	1		45		230			11	
127	3	2		50		98			4.06	
128	3	3		20		8.2			1.76	
129	2	4		1.6	U	5.5	U		0.765	
130	2	5		8.7		290			2.83	
131	5	1		19		36			2.23	
132	5	2		13		17			1.7	
133	6	1		39		66			4.01	
134	6	2		56		57			3.84	
135	6	3		24		17			2.44	
136	4	1		19		30			2.36	
137	4	2		13		21			2.12	
138	5	3		24		29			2.9	J
139	5	4		28		56			3.98	
140	5	5		110		69			7.98	
141	3	1		33		54			2.91	
142	3	2		24		30			2.71	
143	4	1		10		16			1.18	
144	4	2		17		20			1.59	
145	4	3		27		50			2.96	
146	4	4		26		54			3.93	
147	1	1		130	J	440			29.7	
148	1	2		45	J	58			4.73	U
149	1	3		6.7	J	5.4	U		0.862	U
150	2	1		20	J	91			6	
151	2	2		42	J	110			9.73	
152	2	3		120	J	320			17.4	
153	2	4		49	J	58			5.66	

	J	K	L	M	N	O	P	Q	R	S
154	5	1		20		22	J		2.4	U
155	5	2		9.4		8.2	J		1.74	U
156	8	1		55	J	130			10.5	
157	8	2		66	J	270			17.3	
158	8	3		13	J	7.2			0.884	U
159	1	1		110	J	240			14.4	
160	1	2		39	J	30			3.45	U
161	1	3		11	J	7.4			1.87	U
162	1	4		52	J	5.6	U		0.763	
163	3	1		27		65			4.47	U
164	3	2		17	J	29			2.04	J
165	1	1		69	J	300			25.3	
166	1	2		26	J	75			5.03	
167	2	1		42	J	150			7.66	
168	2	2		33	J	80			6.7	
169	2	3		67	J	20			2.32	
170	7	1		4.4		8			0.976	
171	7	2		3.1		7			1	
172	1	1		37	J	380			9.07	
173	1	2		24	J	200			6.76	
174	1	3		17	J	110			2.53	
175	2	1		74		300			16.5	
176	2	2		10		10			1.43	
177	1	3		6.2	J	5.6	U		0.629	
178	1	4		11		14			1.29	J
179	1	1		70		130			10.1	
180	1	2		37		61			7.88	
181	1	3		14		9.1			1.75	
182	3	1		40		49			4.53	
183	3	2		37		49			4.57	
184	3	3		26		33			2.81	
185	3	4		9.8		8.3			1.24	
186	3	5		62		120			0.591	
187	6	1		71		62			6.29	
188	6	2		66		79			8.08	
189	6	3		34		35			4.36	
190	5	1		130		580			15.5	
191	5	2		93		300			11.6	
192	5	3		12		26			2.59	
193	6	1		100		170			14.8	
194	6	2		62		190			12.5	
195	6	3		21		18			3.79	
196	3	1		16	J	110			1.42	
197	3	2		17	J	900			1.45	J
198	3	3		10	J	95			0.848	
199	3	1		5		11			0.99	
200	3	2		16		10			1.05	
201	3	3		26		6.4	U		0.891	
202	1	1		1.6	UJ	29			0.601	J
203	1	2		1.7		230			0.895	U
204	1	3		4.5		310			2.29	J

	J	K	L	M	N	O	P	Q	R	S
205	6	1		1.7	U	9.8			0.761	U
206	6	2		9.5		48			1.04	U
207	6	3		4.4		120			1.57	U
208	8	1		18		28			1.83	J
209	8	2		7.7		9.7			1.29	J
210	8	3		2.9		5.2	U		0.618	J
211	1	1		130		360			27.9	J
212	1	2		27		23			3.08	J
213	2	1		140		390			43.7	J
214	2	2		100		210			11.9	
215	2	3		11		11			1.67	J
216	3	1		76		220			14.6	J
217	3	2		130		49			6.9	J
218	3	3		7		5.9	U		1.09	J
219	1	1		9		18			1.17	J
220	1	2		8.4		8.8			1.23	J
221	1	3		13		22			2.19	J
222	3	1		19		32			2.01	U
223	3	2		44		46			3.03	U
224	3	3		58		40			5.93	U
225	4	1		86		360			16.8	U
226	4	2		62		260			15.3	
227	4	3		64		61			3.74	U
228	4	4		50		79			5.56	U
229	4	5		8.2		13			1.31	U
230	2	1		100	J	220			16.2	
231	2	2		150	J	200			11.2	
232	2	3		13	J	16			1.87	U
233	3	1		100	J	240			16.4	
234	3	2		89	J	150			9.38	J
235	3	3		16	J	6.9			2.78	U
236	4	1		94	J	100			6.91	
237	4	2		31	J	25			3.32	U
238	5	1		15	J	23			2.57	U
239	5	2		16	J	25			2.88	U
240	5	3		36	J	61			5.51	U
241	1	1		59	J	84			6.59	
242	1	2		58	J	79			7.2	
243	1	3		12	J	9.9			1.91	U
244	2	1		59	J	99			7.41	
245	2	2		31		47			4.63	
246	2	3		4.3		6	U		1.2	U
247	2	1		6.1		62			5.08	U
248	2	2		37		73			4.11	U
249	1	1		14	J	19			1.89	U
250	1	2		11	J	7.1			1.4	U
251	6	1		110	J	200			16.1	
252	6	2		97	J	130			13	U
253	6	3		10	J	8.3			2.04	U
254										
255	2	1		16		15			1.36	

	J	K	L	M	N	O	P	Q	R	S
256	2	2		10		16			1.48	
257	1	1		210					68.1	
258	1	2		230					18.8	
259	2	1		69					14.9	
260	2	2		160					17.9	
261	1	1		97					50.5	
262	1	2		120					10.1	
263	1	1		180					27	
264	1	2		46					5.98	
265	1	3		33					4.81	

	T	U	V	W	X	Y	Z	AA	AB
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11	**Arsenic**	**Flag**	**Bismuth**	**Flag**	**Indium**	**Flag**	**Lead**	**Flag**	**Mercury**
12									
13									
14									
15									
16	31.5	J	1.47	J	0.0706				
17	58.8	J	3.48	J	0.255				
18	26.8		1.12		0.0842				
19	41.3		1.81		0.136				
20	26.7		0.749		0.0576				
21	25		0.356		0.05	U			
22	13.2		0.312		0.05	U			
23	14.9		0.357		0.05	U			
24	29.1		1.31		0.0719				
25	44.7		1.47		0.107				
26	12.2	J	0.357	J	0.05	U			
27	13.2	J	0.42	J	0.05	U			
28	22.6	J	0.567	J	0.0506				
29	53	J	1.08	J	0.0953				
30	80.1	J	2.95	J	0.234				
31	105	J	3.52	J	0.29				
32	32.5	J	0.632	J	0.0643				
33	27.6	J	0.498	J	0.0566				
34	31.4		1.15		0.05	U			
35	91.5		4.96		0.441				
36	46.9	J	2.36	J	0.208				
37	37.5	J	0.81	J	0.0775				
38	36.5	J	0.806	J	0.0949				
39	40.3	J	0.93	J	0.105				
40	46.5	J	1.35	J	0.111				
41	69.1	J	1.65	J	0.161				
42	87.1	J	1.95	J	0.268				
43	22.8	J	0.535	J	0.0784				
44	35		1.18		0.141				
45	9.55		0.205		0.05	U			
46	48.7		1.46		0.135				
47	26.2		0.251		0.05	U			
48	76.4		4.96		0.411				
49	217		5.3		0.468				
50	26.5		0.82		0.0533				
51	67.3		2.13		0.185				

	T	U	V	W	X	Y	Z	AA	AB
52	70.8		2.47		0.263				
53	28.6		1.19		0.0863				
54	40.9		2.47		0.165				
55	58.5		3.38		0.246				
56	77.2		1.52		0.122				
57	54		1.08		0.0974				
58	57.3		1.11		0.104				
59	12.1		0.517		0.05	U			
60	34.6		0.886		0.0783				
61	26.9	J	0.473	J	0.05	U			
62	22.1	J	0.375	J	0.0588				
63	12.2		0.337		0.05	U			
64	32		1.87		0.106				
65	26.2		2.14		0.0813				
66	13.1		0.503		0.0553				
67	27.8		2.23		0.312				
68	48.2		3.27		0.211				
69	26.4		0.659		0.074				
70	19.9		0.331		0.05	U			
71	9		0.1	U	0.05	U			
72	44.4		1.22		0.109				
73	20.2		0.233		0.05	U			
74									
75	24.4		1.27		0.105		200		0.628
76	86.6		4.66		0.585		533		1.56
77	70.6		3.86		0.321		265		1.23
78	67.2		1.95		0.163		135		0.361
79	146		9.05		0.916		705		1.04
80	26.8		0.433		0.0771		27.5		0.13
81	10.8		0.362		0.0363		61.9		0.227
82	28.6		0.813		0.121		81.4		0.223
83	40.8		2.06		0.151		355		1.26
84	61.7		3.55		0.382		482		1.47
85									
86	16.7		0.242		0.0469		110		0.0115
87	21.3		0.241		0.05		112		0.0106
88	15.2		0.248		0.0456		129		0.0158
89	26.9		0.318		0.048		193		0.0165
90	47		0.33		0.0631		241		0.0483
91	40.2		0.279		0.0693		206		0.04
92	76.2		0.347		0.0559		364		0.0396
93	77.8		0.33		0.0574		361		0.0238
94									
95									
96									
97									
98									
99	19.7		0.463	U	0.0637				0.123
100			0.595		0.0714				
101			0.499		0.0867				
102			0.593		0.0986				

	T	U	V	W	X	Y	Z	AA	AB
103			0.571		0.0841				
104			0.623		0.0951				
105			0.276		0.0571				
106			0.286		0.0755				
107			0.494		0.0805				
108			0.701		0.0769				
109	77.2		1.82		0.178				0.291
110			0.4		0.0706				
111			0.446		0.0691				
112			0.361		0.0649				
113			13.4		0.924				
114			0.464		0.0713				
115			2.33		0.209				
116			0.97		0.141				
117			0.1	U	0.0651				
118			0.369		0.0658				
119			0.595		0.091				
120			0.679		0.0869				
121			0.687		0.0729				
122			0.218		0.0548				
123	76.1		3.9		0.274				0.489
124			1.03		0.119				
125			0.153		0.05	U			
126			3.62		0.327				
127			1.39		0.121				
128			0.173		0.05	U			
129			0.112		0.05	U			
130	19		0.683	U	0.0839				0.167
131			0.525		0.082				
132			0.425		0.0638				
133			1.35		0.151				
134	59.8		1.3		0.123				0.194
135			0.414		0.0566				
136			0.627		0.0763				
137			0.343		0.0581				
138	22		0.646		0.0813				0.0964
139	23.1		1.41		0.159				0.169
140	123		1.64		0.17				0.243
141			0.81		0.0699				
142			0.571		0.0784				
143			0.285		0.05	U			
144			0.438		0.057				
145			1.07		0.102				
146			1.28		0.126				
147	104		7.61		0.709				1.47
148			1.16		0.108				
149			0.1	U	0.05	U			
150			0.951		0.0907				
151			1.88		0.148				
152			6.11		0.488				
153			0.885		0.0866				

	T	U	V	W	X	Y	Z	AA	AB
154			0.3		0.0541				
155			0.1	U	0.05	U			
156			2.2		0.156				
157			4.34		0.326				
158			0.1	U	0.05	U			
159	96.2		5.41		0.432				0.716
160			0.477		0.0734				
161			0.1	U	0.05	U			
162	4.23		0.1		0.05	U			0.0931
163			0.912		0.105				
164	16.5		0.429		0.0776				0.194
165	67.6		7.81		0.518				0.924
166			1.57		0.18				
167			2.44		0.209				
168			1.67		0.171				
169			0.403		0.0662				
170			0.159		0.0504				
171			0.175		0.0962				
172			0.366		0.101				
173			0.504		0.114				
174			0.3		0.08				
175	81.3		5.65		0.519				0.57
176			0.25		0.0699				
177			0.1	U	0.05	U			
178			0.372		0.0603				
179			3.25		0.32				
180			1.78		0.215				
181			0.199		0.0687				
182			1.3		0.135				
183			1.34		0.146				
184			0.863		0.105				
185			0.231		0.0664				
186			0.114		0.0618				
187			1.37		0.169				
188			1.89		0.206				
189			0.719		0.12				
190	149		5.19		0.357				0.714
191	94.3		1.52		0.136				0.356
192			0.507		0.1				
193			4.65		0.416				
194			3.96		0.35				
195			0.668		0.0972				
196			0.293		0.0697				
197	13.7	U	0.257		0.053				0.14
198			0.2		0.0506				
199			0.238		0.056				
200	9.11		0.228	U	0.05	U			0.118
201			0.173		0.122				
202	5.16	U	0.1	U	0.05	U			0.0393
203			0.1	U	0.05	U			
204	19.1		0.436		0.0516				0.449

	T	U	V	W	X	Y	Z	AA	AB
205			0.1	U	0.05	U			
206			0.1	U	0.05	U			
207			0.1	U	0.05	U			
208			0.547		0.0752				
209			0.21		0.0523				
210			0.1	U	0.05	U			
211			8.09		0.816				
212			0.524		0.0841				
213			10.7		0.694				
214	110		3.86		0.321				0.529
215			0.234		0.0556				
216			3.62		0.235				
217			1.54		0.157				
218			0.103		0.05	U			
219			0.157		0.05	U			
220			0.141		0.05	U			
221			0.394		0.0671				
222			0.648		0.0637				
223			0.897		0.12				
224			1.07		0.127				
225			6.09		0.61				
226	66		5.57		0.538				1.2
227			1.08		0.148				
228			1.34		0.158				
229			0.21		0.0668				
230			4.62		0.335				
231			3.53		0.337				
232			0.115		0.05	U			
233			4.79		0.391				
234	98.8		3.06		0.311				0.355
235			0.1	U	0.05	U			
236			1.77		0.182				
237			0.362		0.0619				
238			0.452		0.0643				
239			0.462		0.0654				
240			0.834		0.106				
241	65.3		1.76		0.181				0.388
242			1.47		0.153				
243			0.1	U	0.05	U			
244			1.92		0.173				
245	44.9		1.24		0.142				0.298
246			0.124		0.0588				
247			0.731		0.0792				
248			0.915		0.105				
249			0.176		0.0617				
250			0.1	U	0.05	U			
251	122		4.64		0.409				0.576
252			3.01		0.29				
253			0.156		0.0639				
254									
255	14.3		0.276		0.0562		16		0.063

	T	U	V	W	X	Y	Z	AA	AB
256	16.5		0.294		0.0574		20.3		0.066
257	198		18.7		1.5		681		2.57
258	238		3.61		0.427		201		0.636
259	71.9		3.85		0.272		164		0.767
260	187		5.78		0.58		297		0.867
261	99		14.2		1.07		462		1.81
262	148		2.63		0.32		142		0.422
263	187		11.3		1.05		652		0.917
264	60.3		1.04		0.134		43		0.17
265	40.7		0.623		0.0954		27.1		0.105

	AC	AD	AE
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10			
11	**Flag**	**Silver**	**Flag**
12			
13			
14			
15			
16		0.321	UJ
17		0.413	J
18		0.265	J
19		0.465	J
20		0.217	J
21		0.147	J
22		0.184	
23		0.169	
24		0.339	J
25		0.147	J
26		0.102	UJ
27		0.159	UJ
28		0.171	UJ
29		0.231	UJ
30		0.379	J
31		0.448	J
32		0.138	UJ
33		0.13	UJ
34		0.55	J
35		0.849	J
36		0.432	J
37		0.205	UJ
38		1.51	J
39		0.233	UJ
40		0.258	UJ
41		0.31	UJ
42		0.468	J
43		0.345	UJ
44		0.182	J
45		0.166	J
46		0.242	J
47		0.127	J
48		0.713	
49		0.469	
50		0.254	
51		0.469	

	AC	AD	AE
52		0.307	
53		0.248	
54		0.381	
55		0.346	
56		0.195	
57		0.386	
58		0.409	
59		0.126	
60		0.103	
61		0.15	UJ
62		0.226	UJ
63		0.162	
64		0.193	
65		0.162	
66		0.209	J
67		0.43	J
68		0.226	
69		0.716	
70		0.0879	J
71		0.049	UJ
72		0.162	J
73		0.118	J
74			
75	J	0.31	
76	J	0.651	
77	J	0.844	
78	J	0.337	
79	J	1.21	
80	J	0.186	
81	J	0.164	
82	J	0.211	
83	J	0.306	
84	J	0.542	
85			
86	UJ	0.0528	
87	UJ	0.0635	
88	J	0.0554	
89	J	0.0533	
90	J	0.099	
91	J	0.093	
92	J	0.082	
93	J	0.077	
94			
95			
96			
97			
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99	UJ		
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	AC	AD	AE
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130	UJ		
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134	J		
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138	UJ		
139	UJ		
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190	J		
191	J		
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196			
197	J		
198			
199			
200	UJ		
201			
202	UJ		
203			
204	J		

	AC	AD	AE
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214	J		
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223			
224			
225			
226	J		
227			
228			
229			
230			
231			
232			
233			
234	J		
235			
236			
237			
238			
239			
240			
241	J		
242			
243			
244			
245	J		
246			
247			
248			
249			
250			
251	J		
252			
253			
254			
255	J	0.0891	J

	AC	AD	AE
256	J	0.117	J
257	J	1.69	J
258	J	0.551	J
259	J	0.452	J
260	J	0.785	J
261	J	1.07	J
262	J	0.462	J
263	J	0.753	J
264	J	0.165	J
265	J		

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	**Attachment C**															
2																
3	**Tacoma Smelter Plume Site**															
4																
5	**Trace Element Analyses:**															
6	**Maximum Concentrations by Boring**															
7																
8																
9																
10		**Location:**					**Sample Code:**				**Maximum concentration (in ppm, dry weight):**					
11	**Study**	**Type**		**Direction**	**Distance**		**Location**	**DU**	**Boring**		**Arsenic**	**Lead**	**Antimony**	**Bismuth**	**Indium**	**Silver**
12				**(degrees)**	**(miles)**											
13																
14	King County	undisturbed		39.25	21.62		2	1	2		49	300	5.91	3.48	0.255	0.413
15	Mainland	undisturbed		38.45	22.01		3	1	1		35	170	2.49	1.81	0.136	0.465
16		undisturbed		36.19	24.99		11	1	3		25	94	1.08	0.749	0.0576	0.217
17		undisturbed		60.82	15.92		21	1	1		11	57	1.21	0.357	0.05	0.184
18		undisturbed		59.17	18.85		30	1	3		51	200	2.69	1.47	0.107	0.339
19		undisturbed		51.04	19.24		31	1	2		9.6	32	0.724	0.42	0.05	0.159
20		undisturbed		57.99	19.20		34	1	2		47	81	3.27	1.08	0.0953	0.231
21		undisturbed		19.56	16.87		36	1	1		79	220	11.7	3.52	0.29	0.448
22		undisturbed		16.16	19.79		37	1	2		86	530	20.7	4.66	0.585	0.651
23		undisturbed		20.98	19.10		38	1	1		30	130	3.11	0.632	0.0643	0.138
24		undisturbed		22.15	16.43		46	1	2		60	180	16.8	3.86	0.321	0.844
25		undisturbed		30.49	14.74		55	1	1		81	280	4.5	4.96	0.441	0.849
26		undisturbed		38.69	16.50		57	1	3		30	200	7.19	2.36	0.208	0.432
27		undisturbed		37.09	12.92		58	1	2		36	64	2.9	0.93	0.105	1.51
28		undisturbed		42.48	12.47		60	1	2		140	580	27.7	9.05	0.916	1.21
29		undisturbed		49.93	12.59		62	1	3		48	100	5.09	1.65	0.161	0.31
30		undisturbed		56.54	11.07		65	1	1		69	100	6.12	1.95	0.268	0.468
31		undisturbed		91.41	7.73		70	1	1		29	110	2.26	1.18	0.141	0.182
32		undisturbed		86.28	8.85		74	1	1		17	49	4.1	0.813	0.121	0.211
33		undisturbed		82.08	11.64		77	1	3		41	130	2.88	1.46	0.135	0.242
34		undisturbed		76.52	11.05		79	1	1		62	410	21.2	3.55	0.382	0.542
35		undisturbed		67.50	11.15		84	1	3		180	400	6.03	5.3	0.468	0.713
36		undisturbed		65.79	11.67		85	1	3		63	170	6.1	2.47	0.263	0.469
37		undisturbed		37.14	13.62		89	1	1		29	170	6.72	2.47	0.165	0.381
38		undisturbed		31.82	14.31		97	1	3		71	270	4.24	3.38	0.246	0.346
39		undisturbed		63.91	9.89		101	1	2		50	67	2.55	1.11	0.104	0.409
40		undisturbed		67.61	19.19		229	1	2		20	85	2.35	0.886	0.0783	0.126
41		undisturbed		44.12	22.61		408	1	1		31	56	1.27	0.473	0.0588	0.226
42		undisturbed		70.52	16.78		503	1	3		30	619	21.9	2.14	0.106	0.193

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
43		undisturbed		90.37	7.28		504	1	1		21	220	2.96	2.23	0.312	0.43
44		undisturbed		49.48	23.28		505	1	3		44	190	2.21	3.27	0.211	0.716
45		undisturbed		23.07	17.53		507	1	1		17	37	1.6	0.331	0.05	0.0879
46		undisturbed		47.77	21.79		512	1	3		47	84	1.27	1.22	0.109	0.162
47																
48																
49	Vashon-Maury	disturbed		17.88	6.64		2	1	7		23	61	2.23	0.595	0.0986	
50	Island	disturbed		21.31	8.89		4	1	4		13	45	2.3	0.623	0.0951	
51		disturbed		13.64	9.28		5	1	2		23	49	2.23	0.494	0.0805	
52		disturbed		16.7	9.38		6	2	6		64	86	6.9	1.82	0.178	
53		disturbed		16.7	9.38		6	3	2		11	150	1.7	0.446	0.0691	
54		undisturbed		16.7	9.38		6	4	1		61	430	43.3	13.4	0.924	
55		undisturbed		16.7	9.38		6	4	3		38	100	6.42	2.33	0.209	
56		undisturbed		16.7	9.38		6	4	4		23	250	5.75	0.687	0.091	
57		disturbed		16.7	9.38		6	5	1		70	240	13.4	3.9	0.274	
58		disturbed		16.7	9.38		6	5	3		50	230	11	3.62	0.327	
59		disturbed		16.93	9.31		7	2	2		8.7	290	2.83	0.683	0.0839	
60		disturbed		15.72	7.29		11	1	5		19	36	2.23	0.525	0.082	
61		disturbed		15.72	7.29		11	1	6		56	66	4.01	1.35	0.151	
62		disturbed		35.95	6.45		13	1	4		19	30	2.36	0.627	0.0763	
63		disturbed		35.95	6.45		13	1	5		110	69	7.98	1.64	0.17	
64		disturbed		12.98	11.07		19	1	3		33	54	2.91	0.81	0.0784	
65		disturbed		9.49	7.72		20	1	4		27	54	3.93	1.28	0.126	
66		disturbed		22.27	9.37		21	1	1		130	440	29.7	7.61	0.709	
67		disturbed		22.27	9.37		21	1	2		120	320	17.4	6.11	0.488	
68		disturbed		22.27	9.37		21	1	5		20	22	2.4	0.3	0.0541	
69		disturbed		22.27	9.37		21	1	8		66	270	17.3	4.34	0.326	
70		disturbed		21.28	8.55		22	1	1		110	240	14.4	5.41	0.432	
71		disturbed		13.15	11.55		26	2	3		27	65	4.47	0.912	0.105	
72		disturbed		-2.92	4.67		27	1	1		69	300	25.3	7.81	0.518	
73		disturbed		-2.92	4.67		27	1	2		67	150	7.66	2.44	0.209	
74		disturbed		-2.92	4.67		27	1	7		4.4	8	1	0.175	0.0962	
75		disturbed		-2.92	4.67		27	2	1		37	380	9.07	0.504	0.114	
76		disturbed		-2.92	4.67		27	3	2		74	300	16.5	5.65	0.519	
77		disturbed		-2.92	4.67		27	7	1		11	14	1.29	0.372	0.0603	
78		disturbed		24.52	6.55		28	1	1		70	130	10.1	3.25	0.32	
79		disturbed		24.52	6.55		28	1	3		62	120	4.57	1.34	0.146	
80		disturbed		24.52	6.55		28	1	6		71	79	8.08	1.89	0.206	
81		disturbed		24.52	6.55		28	2	5		130	580	15.5	5.19	0.357	
82		disturbed		24.52	6.55		28	2	6		100	190	14.8	4.65	0.416	
83		disturbed		10.04	13.96		30	1	3		17	900	1.45	0.293	0.0697	
84		disturbed		2.89	10.47		33	2	3		26	11	1.05	0.238	0.122	

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
85		disturbed		-3.53	7.51		35	2	1		4.5	310	2.29	0.436	0.0516	
86		disturbed		-3.53	7.51		35	2	6		9.5	120	1.57	0.1	0.05	
87		disturbed		15.53	7.37		37	1	8		18	28	1.83	0.547	0.0752	
88		undisturbed		23.78	6.95		38	3	1		130	360	27.9	8.09	0.816	
89		undisturbed		23.78	6.95		38	3	2		140	390	43.7	10.7	0.694	
90		undisturbed		23.78	6.95		38	3	3		130	220	14.6	3.62	0.235	
91		disturbed		28.62	5.63		39	1	1		13	22	2.19	0.394	0.0671	
92		disturbed		28.62	5.63		39	1	3		58	46	5.93	1.07	0.127	
93		disturbed		28.62	5.63		39	1	4		86	360	16.8	6.09	0.61	
94		undisturbed		28.62	5.63		39	6	2		150	220	16.2	4.62	0.337	
95		undisturbed		28.62	5.63		39	6	3		100	240	16.4	4.79	0.391	
96		undisturbed		28.62	5.63		39	6	4		94	100	6.91	1.77	0.182	
97		disturbed		45.39	8.78		42	2	2		16	16	1.48	0.294	0.0574	0.117
98		disturbed		45.39	8.78		42	2	5		36	61	5.51	0.834	0.106	
99		undisturbed		45.39	8.78		42	3	1		59	84	7.2	1.76	0.181	
100		undisturbed		45.39	8.78		42	3	2		59	99	7.41	1.92	0.173	
101		disturbed		7.62	9.53		43	1	2		37	73	5.08	0.915	0.105	
102		disturbed		43.61	8.26		45	1	1		14	19	1.89	0.176	0.0617	
103		disturbed		43.61	8.26		45	1	6		110	200	16.1	4.64	0.409	
104		undisturbed		41.36	7.56		84	1	1		230	681	68.1	18.7	1.5	1.69
105		undisturbed		28.62	5.63		101	1	2		160	297	17.9	5.78	0.58	0.785
106		undisturbed		-7.04	3.03		1065	1	1		120	462	50.5	14.2	1.07	1.07
107		undisturbed		30.99	5.69		1100	1	1		180	652	27	11.3	1.05	0.753
108																
109																
110		NOTES:														
111		Directions are in degrees (clockwise) measured from smelter tall stack.														
112		Distances are in miles measured from smelter tall stack.														
113		All not detected values assigned their detection limits.														

	A	B	C	D	E	F	G	H	I	J	K	L
1	**Attachment D1**											
2												
3	**Tacoma Smelter Plume Site**											
4												
5	**Analytical Results, Extended Trace Eelements List**											
6	**Initial Sample Group, Vashon-Maury Island**											
7												
8												
9	**BATTELLE MARINE SCIENCES LABORATORIES**											
10	1529 West Sequim Bay Road											
11	Sequim, Washington											
12	(360) 681-3604											
13												
14						Concentrations in µg/g dry wt - not blank corrected						
15		**SPONSOR ID**					**Hg**	**Ag**	**V**	**Cr**	**Co**	**Ni**
16	MSL					Percent	CVAA	GFAA	ICP-MS	ICP-MS	ICP-MS	ICP-MS
17	Code	Dash	Sample ID	Comments	Sample Date	Dry Wt	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap
18												
19	1600-1	21	1-42-2-2-1	Lt Brown Sandy	8/28/2000	93.9	0.063	0.0891	98.3	113	11.8	48.6
20	1600-6	6	1-42-2-2-2	Lt Brown Sandy	8/28/2000	91.2	0.066	0.117	113	101	20.7	57.6
21												
22	1600-2	1	1-1065-1-1-1	Dark Brown Loa	11/8/2000	43.3	1.81	1.07	52.8	64.0	22.8	37.8
23	1600-3	2	1-1065-1-1-2	Med Brown Loa	11/8/2000	77.0	0.422	0.462	99.4	88.6	14.8	42.5
24												
25	1600-11	10	1-1100-1-1-1	Dark Brown Lig	11/8/2000	58.5	0.917	0.753	68.4	50.1	10	29.9
26	1600-4 r1	11	1-1100-1-1-2		11/8/2000	92.2	0.170	0.165	94.5	130	11.9	57.4
27	1600-4 r2	11	1-1100-1-1-2		11/8/2000	92.2	0.233	0.199	88.6	86.2	11.3	58.9
28	1600-5	12	1-1100-1-1-3		11/8/2000	91.8	0.105	NA	90.9	83.5	11.5	58.2
29												
30	1600-7	4	1-101-1-2-1	Med Brown Org	10/11/2000	57.7	0.767	0.452	18.1	52.5	2.19	18.1
31	1600-8	5	1-101-1-2-2	Med Brown Org	10/11/2000	78.3	0.867	0.785	68.4	64.9	8.05	38.4
32												
33	1600-9	10	1-84-1-1-1	Med Brown Org	10/9/2000	68.6	2.57	1.69	63.6	55.4	14.7	36.2
34	1600-10	11	1-84-1-1-2	Lt Brown Sandy	10/9/2000	86.1	0.636	0.551	80.9	102	13.0	40.7
35												
36												

	A	B	C	M	N	O	P	Q	R	S	T	U	V
1	**Attachment D1**												
2													
3	**Tacoma Smelter Plume Site**												
4													
5	**Analytical Results, Extended Trac**												
6	**Initial Sample Group, Vashon-Mau**												
7													
8													
9	**BATTELLE MARINE SCIENCES LA**												
10	1529 West Sequim Bay Road												
11	Sequim, Washington												
12	(360) 681-3604												
13													
14					Concentrations in µg/g dry wt - not blank corrected					Wet Wt			Concent
15				**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Br**	**Mo**	**Ru**
16	MSL			ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
17	Code	Dash	Sample ID	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Boric Acid	Boric Acid	Sed Evap	Sed Evap
18													
19	1600-1	21	1-42-2-2-1	30.7	70.3	14.0	1.39	14.3	0.0871	6770	7210	1.45	0.0165
20	1600-6	6	1-42-2-2-2	31.7	82.7	15.7	1.55	16.5	0.841	6430	7050	0.748	0.0153
21													
22	1600-2	1	1-1065-1-1-1	767	294	7.17	0.948	99.0	2.96	7380	17044	1.61	0.0446
23	1600-3	2	1-1065-1-1-2	179	134	14.4	1.63	148	0.549	11500	14935	0.507	0.0185
24													
25	1600-11	10	1-1100-1-1-1	355	135	11.5	1.34	187	1.20	NA		0.982	0.0244
26	1600-4 r1	11	1-1100-1-1-2	51.2	85.5	15.5	1.56	60.3	0	6070	6584	0.522	0.00895
27	1600-4 r2	11	1-1100-1-1-2	62.2	111	14.9	1.67	66.6	0.299	7460	8091	0.500	0.0209
28	1600-5	12	1-1100-1-1-3	37.1	75.9	14.8	1.59	40.7	0	3500	3813	0.549	0.022
29													
30	1600-7	4	1-101-1-2-1	154	78.3	2.89	0.406	71.9	1.50	6250	10832	0.652	0.0185
31	1600-8	5	1-101-1-2-2	240	107	11.3	1.44	187	1.52	8760	11188	0.547	0.0201
32													
33	1600-9	10	1-84-1-1-1	487	174	10.0	1.25	198	2.98	6200	9038	2.21	0.0200
34	1600-10	11	1-84-1-1-2	163	133	14.4	1.55	238	0.979	2610	3031	0.587	0.0240
35													
36													

	A	B	C	W	X	Y	Z	AA	AB	AC	AD	AE	AF
1	**Attachment D1**												
2													
3	**Tacoma Smelter Plume Site**												
4													
5	**Analytical Results, Extended Trac**												
6	**Initial Sample Group, Vashon-Mau**												
7													
8													
9	**BATTELLE MARINE SCIENCES LA**												
10	1529 West Sequim Bay Road												
11	Sequim, Washington												
12	(360) 681-3604												
13													
14				rations in µg/g dry wt - not blank corrected							Wet Wt		Wet Wt
15				**Rh**	**Pd**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**I**	**Cs**
16	MSL			ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
17	Code	Dash	Sample ID	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Boric Acid	Boric Acid	Boric Acid
18													
19	1600-1	21	1-42-2-2-1	0.00640	0.382	0.304	0.0562	1.41	1.36	0.00697	61.9	65.9	1.57
20	1600-6	6	1-42-2-2-2	0.0121	0.258	0.344	0.0574	1.35	1.48	0.0378	25.2	27.6	1.48
21													
22	1600-2	1	1-1065-1-1-1	0.0459	0.904	8.38	1.07	9.92	50.5	1.44	272	628	0.317
23	1600-3	2	1-1065-1-1-2	0.0144	0.421	2.83	0.320	4.17	10.1	0.470	141	183	1.10
24													
25	1600-11	10	1-1100-1-1-1	0.0321	0.287	3.12	1.05	15.5	27.0	1.09	NA	NA	NA
26	1600-4 r1	11	1-1100-1-1-2	0.00967	0.476	1.69	0.134	1.87	5.98	0.236	60.1	65.2	1.55
27	1600-4 r2	11	1-1100-1-1-2	0.0127	0.116	2.22	0.143	1.97	6.15	0.322	59	64.0	1.60
28	1600-5	12	1-1100-1-1-3	0.0134	0.174	0.684	0.0954	1.49	4.81	0.254	15.7	17.1	1.45
29													
30	1600-7	4	1-101-1-2-1	0.0157	0.147	0.795	0.272	4.15	14.9	0.209	243	421	0.155
31	1600-8	5	1-101-1-2-2	0.0196	0.404	1.67	0.580	7.15	17.9	0.685	88.1	113	0.980
32													
33	1600-9	10	1-84-1-1-1	0.0295	0.381	5.80	1.50	16.2	68.1	0.958	165	241	0.911
34	1600-10	11	1-84-1-1-2	0.0120	0.210	3.63	0.427	5.30	18.8	0.668	48.3	56.1	1.72
35													
36													

	A	B	C	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP
1	**Attachment D1**												
2													
3	**Tacoma Smelter Plume Site**												
4													
5	**Analytical Results, Extended Trac**												
6	**Initial Sample Group, Vashon-Mau**												
7													
8													
9	**BATTELLE MARINE SCIENCES LA**												
10	1529 West Sequim Bay Road												
11	Sequim, Washington												
12	(360) 681-3604												
13													
14				g/g dry wt -	Wet Wt		Wet Wt				Concentrations in µg/g dry wt -		
15				**Cs**	**La**	**La**	**Ce**	**Ce**	**Sm**	**Yb**	**W**	**Pt**	**Au**
16	MSL			ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
17	Code	Dash	Sample ID	Boric Acid	Boric Acid	Boric Acid	Boric Acid	Boric Acid	Sed Evap	Sed Evap	Sed Evap	Sed Evap	Sed Evap
18													
19	1600-1	21	1-42-2-2-1	1.67	12.3	13.1	26.1	27.8	10.8	1.00	0.691	0.0309	0.0442
20	1600-6	6	1-42-2-2-2	1.62	10.7	11.7	23.6	25.9	10.1	0.996	0.772	0.0263	0.0792
21													
22	1600-2	1	1-1065-1-1-1	0.732	2.45	5.66	4.64	10.7	6.99	0.711	0.453	0	0.113
23	1600-3	2	1-1065-1-1-2	1.43	7.81	10.1	15.7	20.4	8.95	1.12	0.537	0.0324	0.0600
24													
25	1600-11	10	1-1100-1-1-1	NA	NA	NA	NA	NA	11.1	0.937	1.53	0.0223	0.0811
26	1600-4 r1	11	1-1100-1-1-2	1.68	9.74	10.6	19.3	20.9	9.56	0.97	0.552	0.0142	0.0494
27	1600-4 r2	11	1-1100-1-1-2	1.74	9.35	10.1	19.5	21.1	6.38	0.677	0.614	0.0409	0.0448
28	1600-5	12	1-1100-1-1-3	1.58	10.3	11.2	23.1	25.2	8.36	0.813	0.645	0.0311	0.101
29													
30	1600-7	4	1-101-1-2-1	0.269	1.37	2.37	2.55	4.42	3.55	0.373	0.200	0.0184	0.148
31	1600-8	5	1-101-1-2-2	1.25	7.62	9.73	15.7	20.1	10.3	0.972	0.463	0.0265	0.112
32													
33	1600-9	10	1-84-1-1-1	1.33	8.23	12.0	15.0	21.9	10.6	0.929	0.665	0.0239	0.116
34	1600-10	11	1-84-1-1-2	2.00	16.9	19.6	29.2	33.9	10.1	0.936	0.611	0.0255	0.0814
35													
36													

	A	B	C	AQ	AR	AS	AT
1	**Attachment D1**						
2							
3	**Tacoma Smelter Plume Site**						
4							
5	**Analytical Results, Extended Trac**						
6	**Initial Sample Group, Vashon-Mau**						
7							
8							
9	**BATTELLE MARINE SCIENCES LA**						
10	1529 West Sequim Bay Road						
11	Sequim, Washington						
12	(360) 681-3604						
13							
14				not blank corrected			
15				**Tl**	**Pb**	**Bi**	**Po**
16	MSL			ICP-MS	ICP-MS	ICP-MS	ICP-MS
17	Code	Dash	Sample ID	Sed Evap	Sed Evap	Sed Evap	Sed Evap
18							
19	1600-1	21	1-42-2-2-1	0.259	16.0	0.276	0
20	1600-6	6	1-42-2-2-2	0.250	20.3	0.294	0
21							
22	1600-2	1	1-1065-1-1-1	0.489	462	14.2	0
23	1600-3	2	1-1065-1-1-2	0.297	142	2.63	0
24							
25	1600-11	10	1-1100-1-1-1	0.53	652	11.3	0
26	1600-4 r1	11	1-1100-1-1-2	0.239	43.0	1.04	13.1
27	1600-4 r2	11	1-1100-1-1-2	0.253	47.5	0.990	0
28	1600-5	12	1-1100-1-1-3	0.199	27.1	0.623	0
29							
30	1600-7	4	1-101-1-2-1	0.0814	164	3.85	7.14
31	1600-8	5	1-101-1-2-2	0.270	297	5.78	0
32							
33	1600-9	10	1-84-1-1-1	0.420	681	18.7	0
34	1600-10	11	1-84-1-1-2	0.359	201	3.61	12.1
35							
36							

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**Attachment D2**												
2													
3	**Tacoma Smelter Plume Site**												
4													
5	**Analytical Results, Extended Trace Elements List**												
6	**Initial Sample Group, King County Mainland**												
7													
8													
9	***BATTELLE MARINE SCIENCE LABORATORIES***												
10	1529 West Sequim Bay Road										**KING COUNTY - ONSITE EN**		
11	Sequim, Washington 98382-9099										METALS IN SOILS SCREE		
12	360/681-3604											(Samples Received	
13													
14			**Percent**									(concentrations in µg	
15	**MSL Code**	**Sponsor ID**	**Dry Wt.**		Ag		Hg		V		Cr		Co
16					GFAA		CVAA		ICP-MS		ICP-MS		ICP-MS
17													
18	1664-1	ORCHARD-	74.1		0.0528		0.0115		124		39.4		17.5
19	1664-2	ORCHARD-	80.9		0.0635		0.0106		128		41.3		18.2
20	1664-3	ORCHARD-	82.5		0.0554		0.0158		117		41.5		17.5
21	1664-4	ORCHARD-	83.6		0.0533		0.0165		118		47.0		18.4
22	1664-5	ORCHARD-	87.6		0.0990		0.0483		135		57.5		18.9
23	1664-6	ORCHARD-	87.2		0.0930		0.0400		150		55.0		20.0
24	1664-7	ORCHARD-	81.9		0.0820		0.0396		130		53.8		18.3
25	1664-8	ORCHARD-	84.7		0.0770		0.0238		127		49.3		18.0
26													
27	1664-9	1-60-1-2-1	59.7		1.21		1.04		61.7		62.9		8.76
28	1664-10	1-60-1-2-2	87.7		0.186		0.130		94.4		75.3		10.7
29	1664-11	1-79-1-1-1	49.6		0.306		1.26		20.4		17.1		2.06
30	1664-12	1-79-1-1-2	56.3		0.542		1.47		26.6		19.8		2.85
31	1664-13	1-74-1-1-1	61.8		0.164		0.227		37.4		26.6		3.75
32	1664-14	1-74-1-1-2	73.0		0.211		0.223		67.6		40.7		8.37
33	1664-15	1-37-1-2-1	48.2		0.310		0.628		21.9		19.3		1.77
34	1664-16	1-37-1-2-2	78.4		0.651		1.56		47.6		36.1		3.14
35	1664-17	1-46-1-2-1	45.4		0.844		1.23		31.1		29.5		2.77
36	1664-18	1-46-1-2-2	71.5		0.337		0.361		73.5		72.1		5.99

	N	O	P	Q	R	S	T	U	V	W	X	Y	Z
1													
2													
3													
4													
5													
6													
7													
8													
9													
10	**NVIRONMENTAL**												
11	ENING STUDY												
12	6/1/01)												
13													
14	/g dry wt)												
15		Ni		Cu		Zn		Ga		Ge		As	
16		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS	
17													
18		22.3		27.2		106		19.7		1.36		16.7	
19		23.8		26.7		101		20.7		1.48		21.3	
20		22.4		25.5		112		20.3		1.33		15.2	
21		23.5		27.8		114		21.3		1.56		26.9	
22		31.7		33.4		134		20.6		1.74		47.0	
23		29.6		32.5		122		19.8		1.77		40.2	
24		27.3		30.5		97.9		20.4		1.68		76.2	
25		26.2		29.6		91.8		19.4		1.70		77.8	
26													
27		30.3		205		152		9.04		1.06		146	
28		48.5		32.8		86.6		14.9		1.39		26.8	
29		17.8		70.9		99.3		2.75		0.267		40.8	
30		22.1		103		113		3.38		0.385		61.7	
31		19.5		33.1		56.6		6.21		0.585		10.8	
32		23.4		33.3		60.4		11.5		1.18		28.6	
33		14.3		66.6		74.5		2.67		0.320		24.4	
34		32.5		165		146		4.92		1.12		86.6	
35		22.2		93.4		101		4.34		0.606		70.6	
36		28.3		44.8		47.3		11.0		1.29		67.2	

	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15	Se		Br		Y		Mo		Ru		Rh		Pd
16	ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS
17													
18	0.261		2320		2400		0.712		0.00		0.0124		0.396
19	0.665		2760		2430		0.638		0.00699		0.0172		0.463
20	0.723		3440		2400		0.743		0.00156		0.0127		0.385
21	0.581		4370		3750		0.765		0.00		0.0179		0.528
22	0.487		4120		4890		0.817		0.00555		0.0151		0.500
23	1.07		3720		4040		0.806		0.00		0.0130		0.357
24	0.707		4820		4990		0.857		0.00		0.0176		0.436
25	0.694		4930		3800		0.802		0.00671		0.0166		0.444
26													
27	1.79		12000		1780		1.86		0.00		0.0239		0.218
28	0.895		11300		2670		0.574		0.00351		0.00711		0.194
29	0.549		14800		968		1.92		0.00		0.0107		0.0
30	1.06		19700		874		1.76		0.00		0.0153		0.142
31	0		6390		1320		0.857		0.00		0.00736		0.129
32	0.705		11900		2280		0.612		0.000166		0.00813		0.182
33	0.589		9070		803		1.37		0.00		0.00747		0.0794
34	1.96		14500		1440		1.07		0.00		0.0184		0.0873
35	1.26		9290		1440		1.38		0.00		0.00925		0.213
36	0.964		8330		2170		0.498		0.00		0.00949		0.214

	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15		Cd		In		Sn		Sb		I		Te	
16		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS	
17													
18		0.379		0.0469		1.50		0.528		0.00		1.93	
19		0.225		0.0500		1.57		0.588		0.00		1.57	
20		0.341		0.0456		1.45		0.526		0.00		2.55	
21		0.226		0.0480		1.61		0.713		6.44		0.821	
22		0.313		0.0631		2.37		1.19		0.00		2.59	
23		0.296		0.0693		2.03		1.16		0.00		3.57	
24		0.251		0.0559		1.76		0.850		0.00		4.97	
25		0.204		0.0574		1.72		0.910		0.00		4.14	
26													
27		3.48		0.916		15.4		27.7		0.00		51.3	
28		0.606		0.0771		1.61		3.14		0.00		14.9	
29		0.875		0.151		3.59		11.5		0.00		13.1	
30		1.43		0.382		6.82		21.2		0.00		24.6	
31		0.221		0.036		1.94		2.64		0.00		3.97	
32		1.17		0.121		2.60		4.10		27.8		8.99	
33		0.395		0.105		8.74		6.84		0.00		8.15	
34		0.616		0.585		14.2		20.7		0.00		40.8	
35		0.715		0.321		7.71		16.8		0.00		42.2	
36		0.579		0.163		2.95		6.19		89.2		18.0	

	BA	BB	BC	BD	BE	BF	BG	BH	BI	BJ	BK	BL	BM
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15	Cs		La		Ce		Sm		Yb		W		Pt
16	ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS
17													
18	0.572		11.8		26.0		49700		0.912		1.88		0.0472
19	0.582		13.0		30.9		48500		0.894		2.00		0.0456
20	0.587		10.3		24.7		44300		0.796		1.88		0.0620
21	1.14		15.9		35.9		61900		1.31		2.42		0.0521
22	2.23		19.3		45.4		78800		1.88		4.03		0.0519
23	1.57		16.1		37.0		66300		1.57		3.10		0.0478
24	1.88		17.1		40.6		72500		1.57		3.48		0.0651
25	1.39		15.3		35.8		63500		1.41		3.56		0.0543
26													
27	0.747		7.06		13.1		20300		0.551		2.05		0.0233
28	1.29		9.72		22.8		31500		0.802		1.65		0.0399
29	0.254		2.46		4.22		7730		0.198		1.98		0.00951
30	0.300		3.06		5.57		9950		0.268		1.67		0.00878
31	0.529		4.31		8.85		14100		0.432		1.19		0.0156
32	0.965		8.37		18.3		28000		0.765		1.46		0.0181
33	0.255		2.38		4.10		6600		0.241		1.31		0.00869
34	0.412		3.09		7.58		12400		0.398		1.30		0.0122
35	0.425		5.25		9.15		15000		0.330		1.31		0.0128
36	0.646		9.54		20.5		31500		0.746		1.10		0.0193

	BN	BO	BP	BQ	BR	BS	BT	BU	BV	BW
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15		Au		Tl		Pb		Po 210.98		Bi
16		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS
17										
18		1.41		0.352		110		16.7		0.242
19		1.22		0.341		112		3.31		0.241
20		1.65		0.355		129		4.29		0.248
21		1.38		0.445		193		0.0		0.318
22		1.79		0.543		241		1.64		0.330
23		1.95		0.442		206		16.6		0.279
24		1.45		0.576		364		0.0		0.347
25		1.45		0.573		361		0.0		0.330
26										
27		2.75		0.680		705		0.0		9.05
28		0.998		0.226		27.5		0.0		0.433
29		0.531		0.268		355		0.0		2.06
30		0.608		0.359		482		0.0		3.55
31		0.729		0.124		61.9		0.0		0.362
32		0.697		0.259		81.4		10.3		0.813
33		0.642		0.155		200		8.25		1.27
34		1.88		0.369		533		0.00		4.66
35		1.67		0.232		265		0.00		3.86
36		1.05		0.230		135		5.63		1.95