Viburnum Trend Lead Mining District Transition Zone Assessment Study Report

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Southeast Missouri Lead Mining District

Natural Resource Damage Assessment and Restoration

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LIST OF ACRONYMS

ALAD	Delta-Aminolevulinic Acid Dehydratase
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
COC	Chain of Custody
CV	Coefficient of Variation
DI	Deionized Water
DOI	Department of the Interior
Eco-SSL	Ecological Soil Screening Level
GIS	Geographic Information System
GPS	Global Positioning System
ICS	Incremental Composite Sampling
ITRC	Interstate Technology & Regulatory Council
LOAEL	Lowest Observable Adverse Effect Level
MDNR	Missouri Department of Natural Resources
NRDAR	Natural Resources Damage Assessment and Restoration
OPA	Oil Pollution Act
RSD	Relative Standard Deviation
SA	Sampling Area
SAP	Sampling and Analysis Plan
SD	Standard Deviation
SEMOLMD	Southeast Missouri Lead Mining District
SU	Sampling Unit
TRV	Toxicity Reference Value
UCL	Upper Confidence Limit
USEPA	United States Environmental Protection Agency
USFS	United States Forest Service
USFWS	United States Fish and Wildlife Service
VTLMD	Viburnum Trend Lead Mining District
XRF	X-ray Fluorescence

1.0 Introduction

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), as amended, and the Oil Pollution Act (OPA) provide for the restoration of natural resources lost or injured by hazardous substance releases (§107(f)) and discharges of oil (§1006). Under these Acts, designated state and federal officials act on behalf of the public for natural resources and their services. The Missouri Department of Natural Resources (MDNR) together with the U.S. Department of the Interior (DOI) represented by the U.S. Fish and Wildlife Service (USFWS) and the U.S. Department of Agriculture represented by United States Forest Service (USFS), acting as Trustees, are conducting Natural Resource Damage Assessment and Restoration (NRDAR) activities in the Viburnum Trend Lead Mining District (VTLMD) in Southeast Missouri. The purpose of conducting NRDAR is to identify and document the extent of injuries to natural resources, quantify the injuries and all associated losses to the public and select restoration projects. This study is part of the assessment process as outlined in the Final Phase 1 Damage Assessment Plan for Southeast Missouri Lead Mining District published by the Trustees (MDNR and USFWS 2009).

2.0 Site Information

2.1 Location

The VTLMD, also known as the New Lead Belt of Southeast Missouri primarily consists of a string of mines and related facilities oriented north-south across parts of Washington, Crawford, Iron, Reynolds, and Shannon Counties in southeast Missouri (Figure 1). Seven tailings impoundments within the VTLMD were assessed as part of this investigation; Brushy Creek, Buick, Fletcher, New Viburnum, Old Viburnum, Sweetwater, and West Fork. Areas around the Buick smelter, in Iron County, were also assessed.

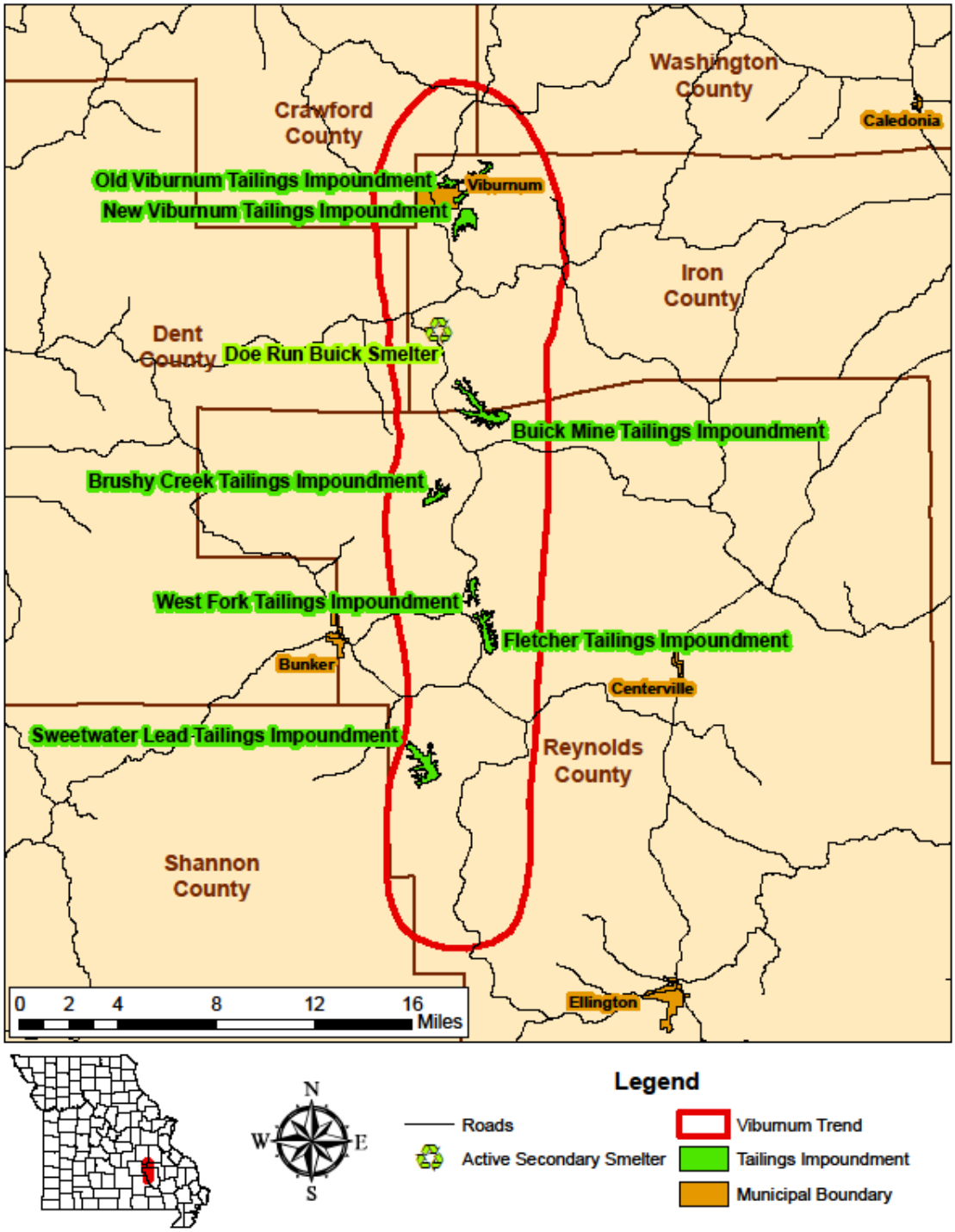

Figure 1. Map of the Viburnum Trend Lead Mining District, Missouri.

2.2 Description

The VTLMD is an active lead (Pb) and zinc (Zn) mining district within the Southeast Missouri Lead Mining District (SEMOLMD). Topography in the New Lead Belt is characterized by rolling hills dissected by narrow floodplain, creek, and river valleys. Hills and ridges are generally steep sided with flat tops consisting of thin mantles of clayey soils. The major physical features of the area are the St. Francois Mountains in the east, and the dissected topography of the Salem Plateau in the northern and central portions. The principal drainage systems for the VTLMD are the north flowing Courtois and Huzzah Creeks and their tributaries and the east and south flowing Black River and its tributaries.

Mining in the VTLMD is ongoing, and the district remains a major producer of metals: Missouri's mines have yielded much of the United States' national production of lead, and since 1997, all the lead produced in Missouri originated in Viburnum Trend mines. In addition to lead, the mines produce substantial amounts of zinc and lesser quantities of copper and silver (Seeger 2008). Mining operations within the VTLMD have been conducted at a number of facilities including Buick, Fletcher, Magmont, West Fork, Brushy Creek, Sweetwater, and the Central Mill in Viburnum (Seeger 2008). Tailings impoundments associated with each of these areas are shown in Figure 1.

Mining in the Viburnum Trend has consisted entirely of the room and pillar method along the ore trend (Seeger 2008). Ore is first crushed within the mine, and then removed to the surface for beneficiation, including further crushing. Following the crushing, the slurried fine material is sent to flotation cells and separated into mineral concentrates through circuits specific to each metal (lead and zinc at all mills, copper as well at all except Sweetwater and West Fork). The mineral concentrates are settled and dewatered before further action (transport to a buyer). The resultant waste is collected in tailings ponds along with process water. Unlike earlier operations in the SEMOLMD, the VTLMD operations never used density separation methods, which result in chat piles (Seeger 2008).

Historically, some of the material mined in the VTLMD was processed at the Buick smelter, located 2 miles northwest of Buick mine and mill, which operated as a primary smelting facility intermittently until being converted to a secondary resource recycling facility in 1991 (Seeger 2008). The facility was renamed the Buick Resource Recovery Facility and has continued operations since.

2.3 History/Contaminants of Concern

Releases of heavy metals from the tailings impoundments, mines, and smelter in the VTLMD have been documented by previous investigations (Wixson 1977, USFS 2012). Elevated levels of cadmium, copper, lead, nickel, and zinc have been measured in surface and shallow subsurface soil at facilities within the VTLMD. A comprehensive study of lead in the environment of the VTLMD found contamination in soils, leaf litter, vegetation, and streams in the area (Wixson 1977). Much of the investigations focused on the areas near Buick smelter where lead concentrations as high as 130,000 milligrams/kilograms (mg/kg) were found in decomposed leaf litter at a distance of 0.25 miles, and concentrations above the background were detected up to 30 miles away (Butherus 1975). Jackson and Watson (1977) found that arthropod biomass and leaf litter decomposition rates were significantly reduced within 0.8 kilometer (km) of Buick smelter as a result of lead contamination. More recent sampling conducted on Mark Twain National Forest lands in 2011 found lead and zinc levels across a wide area to be elevated above the Ecological Soil Screening Levels (Eco-SSL, USEPA 2005) identified by the U.S. Environmental Protection Agency (USEPA) (USFS 2012). Lead concentrations greater than 120 mg/kg were detected up to 7 miles away from Buick smelter and up to 1000 feet from West Fork and Fletcher tailings impoundments (USFS 2012). According to the PLUTO database maintained by the U.S. Geological Survey (USGS 2001) which contains a compilation of data from several historic soil surveys, average naturally occurring lead concentrations are approximately 33 mg/kg in Iron County and 36 mg/kg in Reynolds County. Zinc concentrations found in the database are approximately 61 mg/kg in Iron County and 72 mg/kg in Reynolds County.

Based on a review of existing available data and comparisons of the concentrations measured relative to common screening benchmarks, the primary contaminants of concern identified for this NRDAR were lead and zinc. The Missouri Trustees for Natural Resource Damage Assessment and Restoration (Trustees) are investigating potential injuries to natural resources in parts of Reynolds and Iron Counties, Missouri resulting from releases of hazardous substances from the VTLMD (USFWS 2008, 2009). Consequently, the Trustees jointly designed this study to investigate the extent of the potential release of heavy metals from the smelter and tailings impoundments in the VTLMD.

3.0 Methods

3.1 Study Goals

The primary study goal is to develop an estimate of the area surrounding each VTLMD tailings impoundment within which the lead concentration exceeds pre-determined benchmarks established based on resource injury. The benchmarks represent lead and zinc concentrations above which detrimental effects have been observed in various organisms. An additional study goal is to determine the impact of contamination from airborne emissions from Buick smelter.

3.2 Ecological Benchmarks

Exposure risk to wildlife from lead is often assessed on a dosage basis rather than an associated concentration in soils. Edens et al. (1976) identified the lowest dose at which adverse reproductive effects were observed (Lowest Observable Adverse Effect Level or LOAEL) as 11.3 mg/kg body weight (bw)/day. Based on bioavailability data and exposure models described in the Ecological Risk Assessment of the Big River Mine Tailings Superfund Site (USEPA 2006), and accounting for site specific bioavailability data and ingestion rate information from Hansen et al. (2011), an American Robin (*Turdus migratorius*) which spends 75% of its time in a contaminated area would be expected to experience injury (defined here as exceeding a

biochemical LOAEL toxicity reference value (TRV)) at a soil concentration of 147 mg/kg Pb in the soil. The biochemical LOAEL TRV was chosen because it represents exposure that causes greater than 50% inhibition of the delta-aminolevulinic acid dehydratase (ALAD) enzyme. This specific enzymatic inhibition is defined within CERCLA DOI NRDAR regulations as injury. Sample et al. (2011) observed 490 mg/kg Pb as the lowest soil Pb concentration at which songbirds began to experience adverse effects due to lead poisoning. The effects of zinc on wildlife are difficult to assess because, unlike lead, zinc is a necessary nutrient in the right concentrations, and the ability of organisms to regulate zinc levels in the body is highly variable (Eisler 1993). However, multiple criteria have been identified with respect to vegetation. The USEPA has identified an Eco-SSL for zinc of 160 mg/kg for plants (USEPA 2007). Struckoff et al. (2013) observed a 10 percent reduction in the average floristic quality of plant communities at soil Zn levels of 448 mg/kg. In this investigation, lead concentrations of 147 mg/kg and zinc concentrations of 160 mg/kg were used as the lower benchmarks which represent the lowest point at which injury to wildlife and plants, respectively, may potentially occur. Lead concentrations of 490 mg/kg and zinc concentrations of 448 mg/kg were used as higher benchmarks which represent a point at which injury to wildlife or plants has been observed.

3.3 Sampling Area Selection

In-situ X-Ray Fluorescence (XRF) was used within 20-meter wide rectangular sampling areas (SAs) to identify in real-time the distance at which lead and zinc concentrations approached each target benchmark, and then incremental composite soil samples were collected from sampling units (SUs) within the SAs defined by the in-situ data.

A 2-day pilot study was conducted on October 1-2, 2012 during which sampling was conducted at the Buick impoundment. Other full-scale sampling events were conducted on December 3-6, 2012, April 8-9, and May 12-14, 2013. Areas around the Buick smelter were sampled on July 11-12, 2013.

A number of proposed sampling area locations for each impoundment were selected using Geographic Information Systems (GIS) tools prior to traveling to the site. Once in the field, the sampling team selected from the proposed SAs based on a number factors including lead concentrations observed from in-situ XRF analysis, orientation relative to predominant wind direction, topographic features, and proximity to tailings dams. Each SA was established as a rectangular area 20 meters wide beginning at the impoundment edge and extending away perpendicularly as far as necessary to encompass the target concentration. The number of SAs established at each impoundment varied based on sequence of sampling (more SAs were established at impoundments visited early during the December 2012 sampling event), and findings from in-situ XRF analysis. Table 1 provides a summary of the number of SAs established at each impoundment. The locations of each sampled SA are shown in Figures A-8 through A-13. After selecting each SA, in-situ XRF analyses were used to establish the boundaries of the SUs as described in Section 3.4.

Table 1. Number of Sampling Areas assessed at each tailings impoundment and around Buick smelter.

Impoundment	Number of Sampling Areas Assessed
Brushy Creek	3
Buick	6
Fletcher	5
New Viburnum	5
Old Viburnum	4
Sweetwater	4
West Fork	4
Buick Smelter	6

3.4 In-Situ XRF Analysis

All XRF instruments were calibrated at the beginning and end of each day using standard reference materials containing known concentrations of lead and zinc in soil at various levels (41

mg Pb/kg to 5532 mg Pb/kg and 104 mg Zn/kg to 6952 mg Zn/kg). The XRF operation and calibration procedures are discussed in more detail in the Sampling and Analysis Plan (MDNR 2012). Once per day, during each sampling event, field precision checks were conducted with each XRF analyzer. Each analyzer was positioned on bare soil, as described above, and 7 consecutive readings were taken without moving the analyzer.

The center of each SA at the tailings impoundment edge was located using Global Positioning System (GPS). Five or six 30-second in-situ XRF readings were collected along a line parallel with the tailings impoundment at distances of approximately 5 feet apart. At each location, the duff layer and/or any vegetation were removed with a stainless steel trowel until the interface between the duff and soil layer was visible (Photograph 1). The surface of the soil was then loosened using the trowel; rocks, sticks and other larger particle debris were manually removed, and the analyzer was placed directly on the soil for analysis. The individual XRF results and their averages were recorded on a field sheet (Appendix D), and a locational data point was collected. GPS was used to navigate to points further away from the edge of the tailings impoundment, and a new set of XRF readings were collected in a similar manner. Locational data points were collected using the GPS at each SA. This process was repeated at a number of distance intervals away from the impoundment within the SA until the approximate distance was identified at which the average lead concentration approached 490 mg/kg. This distance was marked on the field sheet and in the field using flagging. The team proceeded collecting XRF data at additional distance intervals until the approximate distance was identified at which the average lead concentration approached 147 mg/kg. Lead was chosen as the primary ecological benchmark because concentrations were typically higher than those of zinc at these sites.

During the October and December sampling events, the in-situ XRF data was used to identify the boundaries of two variable-size SUs within each SA. The area within the SA from the edge of

the tailings to the distance where the lead level reached 490 mg/kg was designated as SU1, while the area within the SA formed by the outer edge of SU1 and the distance where the lead level reached 147 mg/kg was designated as SU2. In cases where no average lead levels above 490 mg/kg were detected at any of the distance intervals, the area within the SA from the tailings impoundment edge to the distance where the lead levels reached 147 mg/kg was identified as SU1 (i.e. in those SAs there was no SU2; see Table 4). A total of 23 variable-size SUs were established within the 19 SAs sampled during those events.

Data from the October and December sampling events demonstrated that estimates of average lead concentration within SUs using in-situ XRF analyses are comparable (R^2 = 0.81) to estimates made from incremental composite samples (ICS) which were collected from the same SUs, processed, and analyzed in the laboratory, as described in the following section. When field analytical methods provide results comparable to fixed lab methods, field analytics are preferable due to the ability to collect such a larger density of data in a given unit of time. Based on the observed agreement between in-situ and ICS results (Figure 5-B), subsequent sampling events in April and May 2013 focused primarily on obtaining a high density of in-situ XRF readings within each SA (MDNR 2013a). During these later events ICS were collected from a single distance interval as described below, but only as a continuing check on the in-situ data. A total of 19 fixed-distance SUs were established within the 12 SAs sampled during the April and May events.

During the July sampling events around Buick smelter, the procedure used was similar to that described above for April and May events (MDNR 2013b). In-situ data was collected at various distances along transects oriented approximately perpendicular to the smelter at various distances. Sampling began at the end of the transect closest to the smelter and moved outward from there, away from the smelter. Each sampling location was uniquely identified by the distance from the beginning of the transect. Six transects were sampled out of the 12 potential transects identified prior to sampling (see figure A-15). Within each transect, one incremental

composite sample was collected from one sampling location in the manner described above for the fixed-distance SUs (MDNR 2013b).

3.5 Sample Collection for Laboratory Analysis

During the October and December sampling events, incremental composite soil samples were collected from within 14 of the 23 variable-size SUs. Each ICS consisted of 30 equal-mass increments of soil collected from locations equally-spaced across the SU. Increment spacing varied and was based on the size of the SU to ensure even distribution within the SU. At each increment location, a stainless steel trowel was used to remove the duff layer, any vegetation, sticks or rocks, and loosen the top inch of soil. The Sampling and Analysis Plan (SAP) described the use of incremental sampling core tools to collect each increment (MDNR 2012). However, the presence of rocks and roots in the shallow soil prevented the use of these tools. Instead, following loosening of the surface soil and removal of rocks and non-soil debris, a small flat-bottom aluminum scoop was used to collect an increment of soil of approximately 30 grams which was placed into a thick-walled resealable plastic bag (Photographs 1 and 2 in Appendix B). The distance between increments was measured by pacing off using an average distance of 2.5 feet/step. The process was repeated at each increment location resulting in a single plastic bag containing 30 soil increments for each SU.

The sampling design used at the Buick impoundment during the October 2012 pilot study specified use of a variable number of increments (30-100) per ICS depending on the size of the SU sampled (MDNR 2012). However, replicate ICS data from the pilot study showed a high level of overall sampling and analysis precision. The percent relative standard deviation among replicate 50-increment ICS was below 4%. Based on this finding, the planning team concluded that ICS consisting of fewer increments could be collected without significantly reducing data quality. Therefore, all ICS collected during the December 2012 sampling event consisted of 30 increments rather than the original variable amount described in the SAP (MDNR 2012).

During the April, May and July sampling events ICS were collected from fixed distance SUs of approximately 30'x10' from individual distance increments within each SA, encompassing the locations of the in-situ readings (MDNR 2013a, 2013b). ICS collection was conducted at a frequency of 10% of the distance intervals assessed or about 1-2 per SA. Distance intervals for ICS sampling were selected to represent the range of concentrations observed across the SAs with emphasis placed on distance intervals where the lead concentration is near a benchmark. A 30-increment composite sample was collected from each fixed-distance SU as described above for the variable size SUs. ICS samples were collected in triplicate from one SU within each SA to assess the precision of laboratory methods.

The duff layer in the New Viburnum impoundment SAs appeared be far thicker and contain a greater presence of fine light grey dust than at the other impoundments. This dust was also present on the surfaces of trees and shrubs within the New Viburnum impoundment SAs. In-situ analyses and ICS sample collection was conducted of both the duff layer and mineral soil layer at this impoundment. In SA3, in-situ XRF analyses were conducted on both the duff material and top of the soil at each distance interval within the SA. In SA1/SU1, an ICS was collected from both the duff material and soil.

Replicate ICS were collected from 9 of the 14 SUs sampled to assess the precision of the overall sampling and analysis procedure. In these SUs, three independent ICS were collected as described above with the locations of the 30 increments comprising each sample offset from each other spatially within the SU as much as possible.

At each impoundment, a sample was collected of the tailings material itself in the area adjacent to most of the SAs during the October and December sampling events. A disposable stainless steel spoon was used to collect a 10-aliquot composite sample from the top 2 inches of tailings across an area of approximately 100ft^2. All soil and tailings samples were stored at ambient

outdoor temperatures during the sampling events until being transported to the MDNR laboratory for conditioning and analysis.

The stainless steel trowels and sampling scoops were decontaminated between SUs by removing soil adhering to the tools with a nylon bristle brush, washing the tools with Simple Green® cleanser, rinsing with deionized water and drying with paper towels. A rinsate blank was collected by each sampling team following the decontamination procedure once during each sampling event. Deionized water was rinsed over the tools and collected into a 100 ml HDPE bottle. The rinsate was preserved to pH < 2 with nitric acid and submitted to the MDNR analytical laboratory for analysis of lead, cadmium, copper, nickel and zinc.

3.6 Sample Conditioning

Soil and tailings samples were returned to the laboratory, spread out on paper-lined aluminum trays and placed in vertical drying racks. The samples were allowed to air dry at ambient temperatures for five days and then each was placed into a 2mm[1] mesh stainless steel sieve. The sieves were processed for 2 minutes in a motorized sieve-shaker apparatus, and the fraction of soil that passed through the sieve was placed in a thin-walled 1-gallon resealable plastic baggie[2]. Sieves were decontaminated between samples by scrubbing with a nylon bristle brush, spraying with deionized water, and wiping down with paper towels. The size fraction retained by the sieve was discarded. The sample conditioning process is shown in photographs 3, 4, and 5 in Appendix B. The discarded material consisted primarily of small rocks. Rocks of this size present a much smaller exposure risk to plants and wildlife relative to the matrix of sand, silt, and clay sized particles.

[1] Samples collected at the Buick impoundment during the October 2012 pilot study were processed using a 0.25 mm sieve.
[2] Some tailings samples were analyzed by XRF both prior to and after sieving.

3.7 Sample Analysis

Prior to initiating XRF analysis each day, periodically throughout the day, and again at the end of the day, several standard reference materials containing known lead concentrations in soil were analyzed. The results were plotted on control charts and verified to be within control limits of +/- 2SD prior to proceeding with sample analysis.

Sieved soil samples were analyzed by XRF directly through the baggie. Each sample was analyzed by XRF four times with manual mixing of the sample between analyses. The results of these analyses are reported as average concentrations. Once per day per analyzer, a precision check was performed by analyzing a selected soil sample 7 consecutive times without moving the baggie between analyses. Following XRF analysis, fourteen of the ICS samples and one tailings sample from each impoundment were submitted to the MDNR analytical laboratory for confirmatory analysis of lead, cadmium, copper, nickel and zinc.

3.8 Data Analysis

3.8.1 Estimating Transition Zone Acreages

The width of the transition zone is determined by soil lead and zinc concentrations as a function of distance from the tailings impoundment. Linear regression models were used to quantify the relationship between concentrations of metals in the soil and distance from the impoundments within each SA. The resulting regression equations were used to predict the distance from the impoundment at which each of the benchmark concentrations would occur at each Sampling Area. The average distance to each of the benchmark contaminant concentrations was calculated for each tailings impoundment separately. GIS software was used to generate a buffer around each impoundment bounded by the average target contaminant concentration distance estimates, resulting in an estimate of the acres of land around each impoundment contaminated above each of the ecological benchmarks.

3.8.2 Estimating Average Lead Concentrations

Estimates of the average lead concentration within the SUs were calculated as 95% upper confidence limits (UCLs). Separate UCL estimates were calculated for each SU using the in-situ XRF data and the ICS data (Table 4). In-situ data was grouped by SU and data from each SU was plotted as a histogram. ProUCL® statistical software was used to conduct goodness-of- fit analysis and calculate UCLs. In-situ XRF data from approximately half the SUs conformed to a normal distribution, and for those data UCLs were calculated using the Student's *t* method. Some SU data followed a gamma distribution and some a lognormal distribution, while SU data for a few SUs followed no discernible distribution. UCLs for these SUs were calculated in ProUCL® using the calculation method appropriate for the distribution. The in-situ data from the April and May sampling events was grouped into Variable Size SUs according to metal concentrations and UCLs were calculated for those similar to data from the earlier sampling events.

For SUs in which field replicate ICS were collected, 95% UCLs were calculated using the three replicate results and the Student's *t* approach described in Interstate Technical Regulatory Council (ITRC) Incremental Sampling Methodology Guidance Document (ITRC 2012). For SUs in which no replicates were collected, the coefficient of variation (CV) was extrapolated from another SU in which replicates were collected. The extrapolated CV was then used in calculating a UCL. Extrapolation of the CV between SUs is most valid when the degree of dispersion in lead or zinc concentrations within the SUs is similar. The in-situ XRF data support this extrapolation. Although, as shown by the goodness-of-fit analyses, the lead concentration between SUs follows different distributions, the degree of skewness is low for all SUs; the CV for 22 of the 23 SUs examined was below 1.0 which is considered low dispersion (ITRC 2012).

4.0 Results

4.1 Transition Zone Soil

During this study, 31 separate impoundment Sampling Areas were investigated. Concentrations of lead greater than 147 mg/kg were measured at 27 different SAs (87%) while concentrations greater than 490 mg/kg were measured at 15 different SAs (48%). Zinc concentrations greater than 160 mg/kg were measured at 24 different SAs (77%) while concentrations greater than 448 mg/kg were measured at 11 different SAs (35%). In most cases, those SAs which contained elevated concentrations of zinc, also contained elevated levels of lead, with the exception of two SAs at West Fork. Table C-1, provides a summary of mean lead and zinc concentrations with distance from the impoundment for each SA as measured by in-situ XRF. Table 4 shows the results of in-situ XRF analysis for variable size SUs from each impoundment. Average lead concentrations ranged from 1238 mg/kg to 131 mg/kg while average zinc ranged from 694 mg/kg to 54 mg/kg.

4.2 Tailings

Fourteen tailings samples were collected from the impoundments during the October and December sampling events. The composition of tailings samples was highly variable, with lead concentrations ranging from 293 mg/kg to 6975 mg/kg.

Table **2** provides a comparison of metals composition in the samples of tailings collected at each impoundment, and Figure 2 presents this data graphically. Analysis for lead was conducted prior to and after sieving for 12 of the tailings samples to assess the distribution of metals in different particle size fractions. Table 3 is a summary of lead concentrations in the bulk tailings samples vs. the <0.25 mm particle size fraction. The lead concentration is higher in the bulk tailings than in the fine particle size fraction for slightly over half of the samples analyzed, but for the majority of samples the difference in concentration was less than 10%. The trend was less clear with respect to zinc. Zinc concentrations were higher in the fine fraction of half of the samples and higher in the bulk sample for half of the samples with percent differences ranging from 39%

to less than 1%. Pb:Zn ratios of the bulk tailings and fine particle size fraction were in relatively close agreement in all samples (Table 3).

Table 2. Metallic composition of mine tailings from impoundments in the Viburnum Trend. ND indicates a value below the detection limit.

Impoundment	Tailings Concentration, mg/kg (analyzed by XRF)					
	Lead	Zinc	Copper	Nickel	Arsenic	Cadmium
Brushy Creek SA1	685	1375	257	97	ND	52
Buick SA1[1]	6975	1427	395	219	130	56
Buick SA2[1]	743	602	308	97	34	49
Fletcher SA2	3114	1263	215	101	65	ND
Fletcher SA4	313	400	166	ND	ND	ND
Fletcher SA5	808	614	93	56	ND	41
New Viburnum SA1	748	934	817	92	ND	47
New Viburnum SA2	868	806	1004	112	33	ND
Old Viburnum SA2	293	1015	199	74	ND	46
Sweetwater SA1	354	587	340	65	ND	ND
Sweetwater SA2	1381	2369	157	116	46	49
West Fork SA1	2345	2157	83	126	40	40
West Fork SA2	1289	2944	73	61	ND	84
West Fork SA3	1530	1058	ND	173	ND	ND

[1] Samples sieved to <0.25mm; all other samples sieved to <2mm.

Table 3. Lead and zinc concentrations of bulk tailings samples and the fine (< 0.25 mm) particle fraction.

Impoundment	Sampling Area	Lead, mg/kg		Zinc, mg/kg		Pb:Zn Ratio	
		Bulk Tailings	< 0.25 mm Particle Size	Bulk Tailings	< 0.25 mm Particle Size	Bulk Tailings	< 0.25 mm Particle Size
Brushy Creek	1	680	685	1626	1375	0.42	0.50
Fletcher	2	3152	3114	1162	1263	2.71	2.47
Fletcher	4	307	313	472	400	0.65	0.78
Fletcher	5	721	808	540	614	1.34	1.32
New Viburnum	1	821	748	933	934	0.88	0.80
New Viburnum	2	882	868	757	806	1.17	1.08
Old Viburnum	2	329	293	1086	1015	0.30	0.29
Sweetwater	1	366	354	458	587	0.80	0.60
Sweetwater	2	1520	1381	2380	2369	0.64	0.58
West Fork	1	2673	2345	2390	2157	1.12	1.09
West Fork	2	584	1289	1984	2943	0.29	0.44
West Fork	3	1825	1530	1177	1058	1.55	1.45

4.3 Incremental Composite Samples

Incremental composite samples were collected from 21 variable-size sampling units during the October and December sampling events. Table and C-6 provide a summary of estimates of mean lead and zinc concentrations respectively, in each variable size SUs using both the in-situ data and the ICS data. During the April and May sampling events, ICS samples were collected from 19 fixed distance SUs. Tables C-7 and C-8 show in-situ and ICS data for lead and zinc respectively, from fixed-distance SUs.

Table 4. Results from in-situ X-Ray Fluorescence (XRF) analysis of soils in variable-size sampling units near tailings impoundments in the Viburnum Tend Mining District.

Tailings Impoundment	Sampling Area	Sampling Unit	Distance (ft) from Tailings	Date of Sampling	Lead (mg/kg)			Zinc (mg/kg)		
					Average	Standard Deviation	95% UCL	Average	Standard Deviation	95% UCL
Brushy Creek	SA1	SU1	0 - 170	12/6/2012	654	274	813	531	235	667
		SU2	170 -500		296	87	323	221	73	243
	SA2	SU1	0 - 500	5/14/2013	265	134	303	164	88	189
	SA3	SU1	0 - 320	4/9/2013	786	391	888	652	438	950
		SU2	320 - 720		233	148	272	177	114	206
Buick	SA1	SU1	0 - 525	10/1/2012	1241	705	1478	459	282	553
		SU2	525 - 2700	10/2/2012	532	412	630	153	112	179
	SA2	SU1	0 - 330	10/2/2012	792	455	1037	491	285	621
		SU2	330 - 800		366	198	488	171	103	202
	SA4	SU1	0 - 250	12/4/2012	195	84	221	54	21	61
	SA5	SU1	0 - 90	5/13/2013	677	459	856	288	204	368
		SU2	90 - 2900		279	172	312	90	63	123
	SA7	SU1	0 - 90	5/14/2013	714	500	877	295	251	374
		SU2	90 - 1760		330	188	383	109	73	130
Fletcher	SA1	SU1	0 - 20	12/3/2012	483	390	633	438	364	602
		SU2	20 - 1100		131	46	142	63	28	77
	SA2	SU1	0 - 700	12/3/2012	259	137	288	146	84	*
	SA3	SU1	0 - 300	12/3/2012	144	98	179	97	72	120
	SA4	SU1	0 - 270	12/3/2012	225	122	278	165	83	201
	SA5	SU1	0 - 600	12/4/2012	250	235	306	128	58	150
New Viburnum	SA1	SU1	0 - 500	12/5/2012	1361	539	1520	694	302	783
		SU1	500 - 2860	4/9/2013	913	540	1025	363	237	423
	SA2	SU1	0 - 330	12/5/2012	1248	372	1353	637	196	692
		SU2	330 - 1300	5/12/2012	397	276	476	201	145	*
	SA3	SU1	0 - 300	12/6/2012	727	419	904	406	338	595
		SU2	300 - 450		431	211	553	127	74	177
		SU2	450 - 1500	4/8/2013	288	177	349	103	52	119
	SA4	SU1	0 - 550	4/8/2013	1193	499	1322	531	303	609
		SU2	550 - 3700		325	168	358	123	60	135
	SA5	SU1	0 - 900	4/8/2013	823	431	918	356	206	474
		SU2	900 - 2300		248	143	279	105	61	118

* Data for these areas did not follow any discernible distribution and UCLs could not be reliably calculated.

Table 4 cont. Results from in-situ X-Ray Fluorescence (XRF) analysis of soils in variable-size sampling units near tailings impoundments in the Viburnum Tend Mining District.

Tailings Impoundment	Sampling Area	Sampling Unit	Distance (ft) from Tailings	Date of Sampling	Lead (mg/kg)			Zinc (mg/kg)		
					Average	Standard Deviation	95% UCL	Average	Standard Deviation	95% UCL
Old Viburnum	SA2	SU1	0 - 450	12/6/2012	283	128	302	92	23	103
		SU1	450 - 2000	4/9/2013	284	129	312	83	32	90
	SA3	SU1	0 - 500	4/9/2013	521	209	564	261	203	293
		SU2	500 - 1400		576	329	655	123	53	136
	SA4	SU1	0 - 170	4/9/2013	194	171	*	164	234	*
Sweetwater	SA1	SU1	0 - 100	12/5/2012	209	91	251	250	179	332
	SA2	SU1	0 - 700	12/5/2012	349	347	463	313	342	424
	SA3	SU1	0 - 150	4/9/2013	546	206	610	1176	410	1303
		SU2	150 - 2370		233	92	253	269	231	*
West Fork	SA1	SU1	0 - 170	12/4/2012	292	324	534	446	857	*
	SA2	SU1	0 - 320	12/4/2012	202	142	249	270	254	395
	SA3	SU1	0 - 200	12/4/2012	133	31	143	99	27	110
	SA4	SU1	0 - 600	12/4/2012	187	106	218	104	149	213

* Data for these areas did not follow any discernible distribution and UCLs could not be reliably calculated.

4.4 Smelter Sampling Areas

Six smelter sampling areas were investigated. Average Pb and Zn concentrations in each location are reported in Table C-2. Lead concentrations greater than 490 mg/kg Pb were observed at all six of the Buick smelter transects (Table C-2). Average lead concentrations ranged from 130.6 mg/kg to 2449.8 mg/kg. Average zinc concentrations ranged from 23.4 mg/kg to 198.9 mg/kg.

4.5 Sampling and Analysis Precision

Overall sampling and analysis precision was assessed by examining the percent relative standard deviation (%RSD) in Pb and Zn concentrations between replicate field ICS samples collected within a portion of the SUs. The %RSD between replicate ICS lead concentrations varied between 1.8 and 26.5, with most results falling below 6.0 (Table 5). Zinc concentrations %RSD ranged from 1.7 to 16.2 although the average %RSD was 18% higher than that of lead. This is a high overall precision and indicates that sampling design and analytical processes are reproducible and representative. Lead concentrations in the ICS samples measured using the

XRF were in very close agreement with the results of laboratory analysis. A comparison between the two methods is shown in Figure 6.

Agreement between ICS results and in-situ XRF results was variable for both lead and zinc. Percent difference between ICS and in-situ lead concentrations ranged from 53% to 9% in the variable-size SUs and from 77% to 6% in the fixed-distance SUs. Agreement was slightly greater between ICS and in-situ zinc concentrations ranging from 46% to 1% in the variable-size SUs and from 56% to 1% in the fixed distance SUs.

Table 5. Overall Sampling and Analysis Precision.

Impoundment	Sampling Area	Sampling Unit (Distance)	% RSD Between Field Replicate ICS		Mean Pb (mg/kg)	Mean Zn (mg/kg)
			Lead (Pb)	Zinc (Zn)		
Brushy Creek	SA1	SU1	1.8	4.1	654	447
Brushy Creek	SA1	SU2	10	8.1	296	273
Brushy Creek	SA2	(30’)	8.6	12.2	453	247
Brushy Creek	SA3	(50’)	1.5	10.2	1326	1534
Buick	SA2	SU1*	2.9	5.8	792	285
Buick	SA2	SU2*	3.8	1.7	366	103
Buick	SA5	(90’)	12.9	16	631	229
Buick	SA7	(1760’)	2.9	6.5	554	133
New Viburnum	SA1	(2210’)	8	5.1	2606	912
New Viburnum	SA2	SU1	5.2	11.8	1248	1023
New Viburnum	SA3	(800’)	7.3	11.04	893	218
New Viburnum	SA4	(550’)	10.9	9	1038	356
New Viburnum	SA5	(750’)	1.4	5.2	769	286
Old Viburnum	SA2	SU1	5.5	6.2	283	125
Old Viburnum	SA2	(1000’)	7.1	4.1	312	74
Old Viburnum	SA3	(600’)	3.9	4.4	491	131
Old Viburnum	SA4	(20’)	6	10.2	334	232
Sweetwater	SA1	SU1	4.3	10.4	209	169
Sweetwater	SA3	(2170’)	9.1	9.7	212	132
West Fork	SA2	SU1	8.5	12.2	202	201
West Fork	SA4	SU1	26.5	16.2	187	77

* Replicate ICS contained 50 increments; all others contained 30 increments.

Laboratory results for the rinsate blanks are included in Table . Zinc was detected in all of the rinsate samples at concentrations ranging from 0.74 micrograms/liter (ug/l) to 2.61 ug/l. Lead was measured in two of the blanks at 2.03 ug/l and 0.51 ug/l and was not detected (<0.50 ug/l) in the others. Cadmium, copper, and nickel were not detected in any of the samples.

Table 6. Laboratory results of rinsate blanks collected from sampling equipment. All results are reported in ug/l.

Sample Date	Cadmium	Copper	Lead	Nickel	Zinc
10/2/2012	< 0.1	< 0.5	0.51	< 0.5	1.57
12/3/2012	< 0.1	< 0.5	2.03	< 0.5	2.61
12/4/2012	< 0.1	< 0.5	< 0.5	< 0.5	1.74
4/8/2013	< 0.1	< 0.5	< 0.5	< 0.5	1.00
4/9/2013	< 0.1	< 0.5	< 0.5	< 0.5	0.74
5/13/2013	< 0.1	< 0.5	< 0.5	< 0.5	1.96
7/12/2013	< 0.1	< 0.5	< 0.5	< 0.5	1.16

4.6 Transition Zone Size

The results of regression analysis show that lead concentrations at 17 of the 31 SAs (55%) were significantly ($p < 0.05$) linearly related to distance from the impoundments. These regression equations are listed in Table C-3. The relationship between metals concentrations and distance varied considerably between impoundments. Significant concentration-distance relationships were observed in all of the SAs at both Brushy Creek and Sweetwater, while there were no significant relationships detected at Old Viburnum or West Fork. Buick and New Viburnum impoundments each contained one SA with a non-significant concentration-distance relationship while Fletcher contained two (Table C-3). Due to the finding of no statistical significance in some of the regression equations, all of the derived transition zone distances should be

considered estimates. Regression analysis results of zinc concentrations show a similar pattern to that of lead (Table C-4). Regression analysis of in-situ data from the smelter transects shows a significant negative relationship between both Pb and Zn concentrations and distance from the smelter (Figure A-14).

The predicted distances for the 147 mg/kg and 490 mg/kg lead benchmark concentrations in each SA are listed in Table C-3. Predicted distances for the zinc benchmark values are listed in Table C-4. Average distances from each impoundment are listed in Table 7. The predicted distances to the benchmark values varied considerably both between impoundments and between separate SAs within each impoundment. Lead concentrations above 490 mg/kg were not measured at West Fork, thus no high-lead transition zone was predicted around that impoundment. In contrast, the predicted 490 mg/kg Pb distance from SAs at New Viburnum ranged from 695 to 1901 feet with an average distance of 1,143 feet. Average distances of the 147 mg/kg Pb benchmark ranged from 265 feet at West Fork to 1,927 feet at New Viburnum. Zinc transition zones were smaller than the corresponding lead transition zones at each impoundment with the exception of the 448 mg/kg zones at Sweetwater and West Fork, which were 280 feet and 49 feet wider respectively than the 490 mg/kg Pb zone at those impoundments (Table 7). Acreage for the zinc transition zones is not reported in instances where the corresponding lead zone was larger. The 448 mg/kg Zn transition zones at Sweetwater and West Fork were 417 acres and 35 acres respectively.

Table 7 provides a summary of the number of acres around each impoundment that contain lead and zinc concentrations above each of the ecological benchmarks. The area of the high-lead transition zones ranged from 1 acre around Fletcher to 829 acres around Buick. The area of the low-lead (Pb > 147 mg/kg) transition zones ranged from 182 acres around West Fork to 1760 acres around Buick. When the area of the high-lead zones are subtracted from the low-lead zones the largest resulting intermediate zone (490 mg/kg > Pb > 147 mg/kg) is 1,607 acres around Old Viburnum. Because of the close proximity of Old and New Viburnum impoundments, the low-

lead transition zones overlap. When the transition zones from both impoundments are combined to remove the overlap, the resulting area is 2,863 acres in the entire low-lead zone and 2,020 acres in the intermediate zone. The overlap of low-zinc (>160 mg/kg) transition zones between Old and New Viburnum was less than one half of an acre.

Table 7. Estimated average width and area of transition zones around tailings impoundments. Estimations derived from regression equations in Tables C-3 and C4.

	Width (ft) of Transition Zone				Estimated Acres of Contaminated Soil			
Impoundment	**Pb >147 mg/kg**	**Zn >160 mg/kg**	**Pb >490 mg/kg**	**Zn >448 mg/kg**	**Pb >147 mg/kg**	**Pb >490 mg/kg**	**Zn >160 mg/kg**	**Zn >448 mg/kg**
Brushy Creek	580	445	205	165	401	166	325	135
Buick	1220	551	452	35	1760	829	961	78
Fletcher	399	55	1	2	409	1	72	3
New Viburnum	1927	1383	1143	208	1293	748	907	167
Old Viburnum	1418	122	63	0	1702	95	181	0
Sweetwater	701	574	6	286	889	9	757	417
West Fork	265	163	0	49	182	0	115	35
Old and New Viburnum Combined*					2863			

*Due to the proximity of the Old and New Viburnum impoundments the 147 mg/kg Pb transition zones overlap. The combined area removes this overlap.

5.0 Discussion

5.1 Transition Zone Soil

Overall, 87% of the sampling areas investigated contained Pb concentrations in the soil above 147 mg/kg, while almost half of the SAs (48%) contained Pb concentrations above 490 mg/kg. Likewise, 77% of the sampling areas contained Zn concentrations above 160 mg/kg and 35% contained Zn concentrations higher than 448 mg/kg. These results indicate the potential for

ecological injury to occur in the areas adjacent to the tailings impoundments. Regression analysis indicates that metal concentrations in the soils increase significantly with proximity to at least 5 of the 7 impoundments investigated in this study.

5.2 Tailings

The composition of tailings samples, in terms of individual elemental concentrations and the ratio of Pb to Zn, varied considerably between impoundments, and between samples collected from the same impoundment. Figure 2 shows the metallic composition of tailings samples collected from each impoundment. Differences between elemental concentrations in the bulk tailings and fine particle fraction were slight. Additionally, the Pb:Zn ratio of bulk samples was in close agreement with that of the fine particle fraction (Table 3).

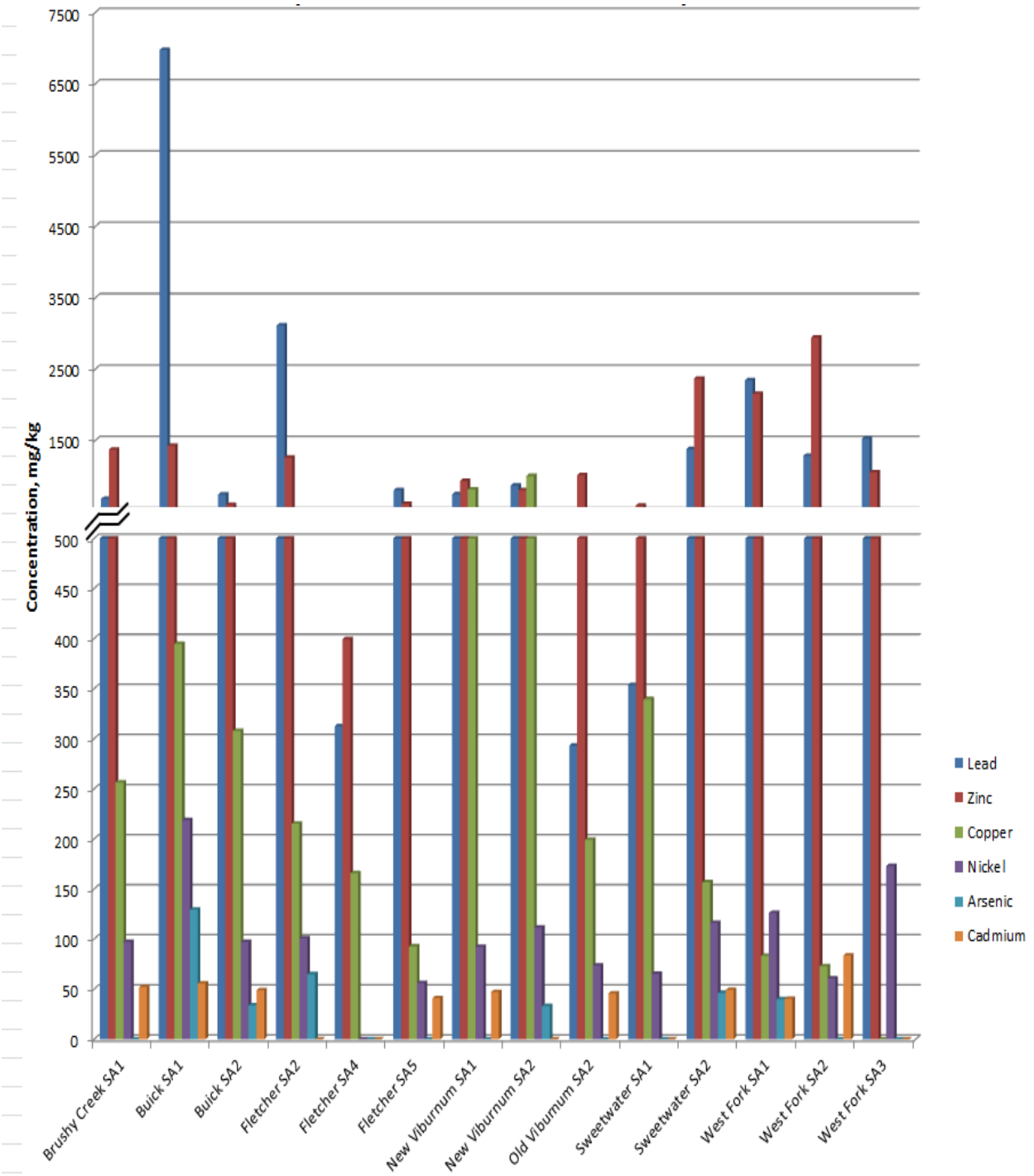

Figure 2. Comparison of tailings composition between impoundments. (Note vertical scale is broken.)

5.3 Pb:Zn Ratio

The ratio of Pb to Zn is noticeably higher in soils surrounding most of the impoundments than it is in the tailings samples collected from the impoundments themselves. These results are shown in Table 8. The only exception to this trend is seen at Buick, where the ratios were nearly equal. These disparities between tailings and soils may be a result of differences in the weathering or leaching of the two elements. Zinc may leach from the topsoil faster, leaving a greater proportion of lead at the surface. The solubility and leaching ability of metals is dependent on the chemical species of the compounds, which was not investigated in this study. In a study of soils near a tailings impoundment in St. Francois County, Missouri, Aide (2009) found that, relative to lead, a greater percentage of total zinc was in an easily leachable form. The similarity in composition of the bulk tailings and fine particle fractions suggests that differences in the Pb:Zn ratio are not a result of differences in mobility of various fractions of the source material. The Pb:Zn ratio in soils around Buick smelter is considerably higher than that of the tailings or soil around the impoundments. This suggests that deposition from smelter emissions is disproportionately higher in Pb compared to windblown dust from tailings impoundments. Lead products and historically lead ore concentrate are the primary minerals processed and smelted at the Buick facility, rather than zinc, which likely explains the differences in the Pb:Zn ratio between smelter deposition and windblown tailings deposition.

Table 8. Average Pb:Zn concentration ratios of mine tailings and of the surrounding soils.

Average Pb:Zn Ratios		
Impoundment	**Tailings**	**Soil**
Brushy Creek	0.42	1.43
Buick	3.06	2.97
Fletcher	1.57	1.91
New Viburnum	1.02	2.44
Old Viburnum	0.30	3.03
Sweetwater	0.72	1.03
West Fork	0.99	1.47
Near Buick Smelter	NA	6.99

5.4 Duff vs. Mineral Soil

The majority of in-situ XRF measurements were collected on the surface of the soil at the interface between the soil and the duff material, and the ICS were collected from the top 1 inch of soil. However, differences in lead concentrations within the duff material above the soil was also of interest, particularly at the New Viburnum impoundment where the duff layer was observed to be significantly thicker than at the other impoundments and where dust the same color as tailings was observed coating the duff. The sampling team conducting in-situ readings within both the duff and the mineral soil in SA3 and collected an ICS of both the duff and mineral soil in SA1 at New Viburnum. The average lead concentration in SU1 is 2,390 mg/kg in the duff layer compared with 1,520 mg/kg in the underlying soil based on the ICS sample results. Figure 3 provides a comparison of lead concentrations in the duff vs. the soil at various distances from the New Viburnum impoundment in SA3 as measured by in-situ XRF.

With a few exceptions, the lead concentrations are generally higher in the duff than in the soil at all distances from the impoundment as measured by in-situ XRF, but the ratio of duff Pb:soil Pb is highly variable with no clear trend with distance. This difference between concentrations between duff and the underlying mineral soil suggests that the source of contamination is material deposited at the ground surface or on foliage prior to leaf fall, consistent with wind-blown material or smelter emissions. Lead has been found to absorb strongly to organic matter (Svendsen et al 2007), which limits its mobility through the soil profile. In a study of tailings contaminated soil in St. Francois County, Missouri, Aide (2009) found that a relatively small proportion of the metallic contaminants were in a water-soluble form, suggesting that percolation rates are limited.

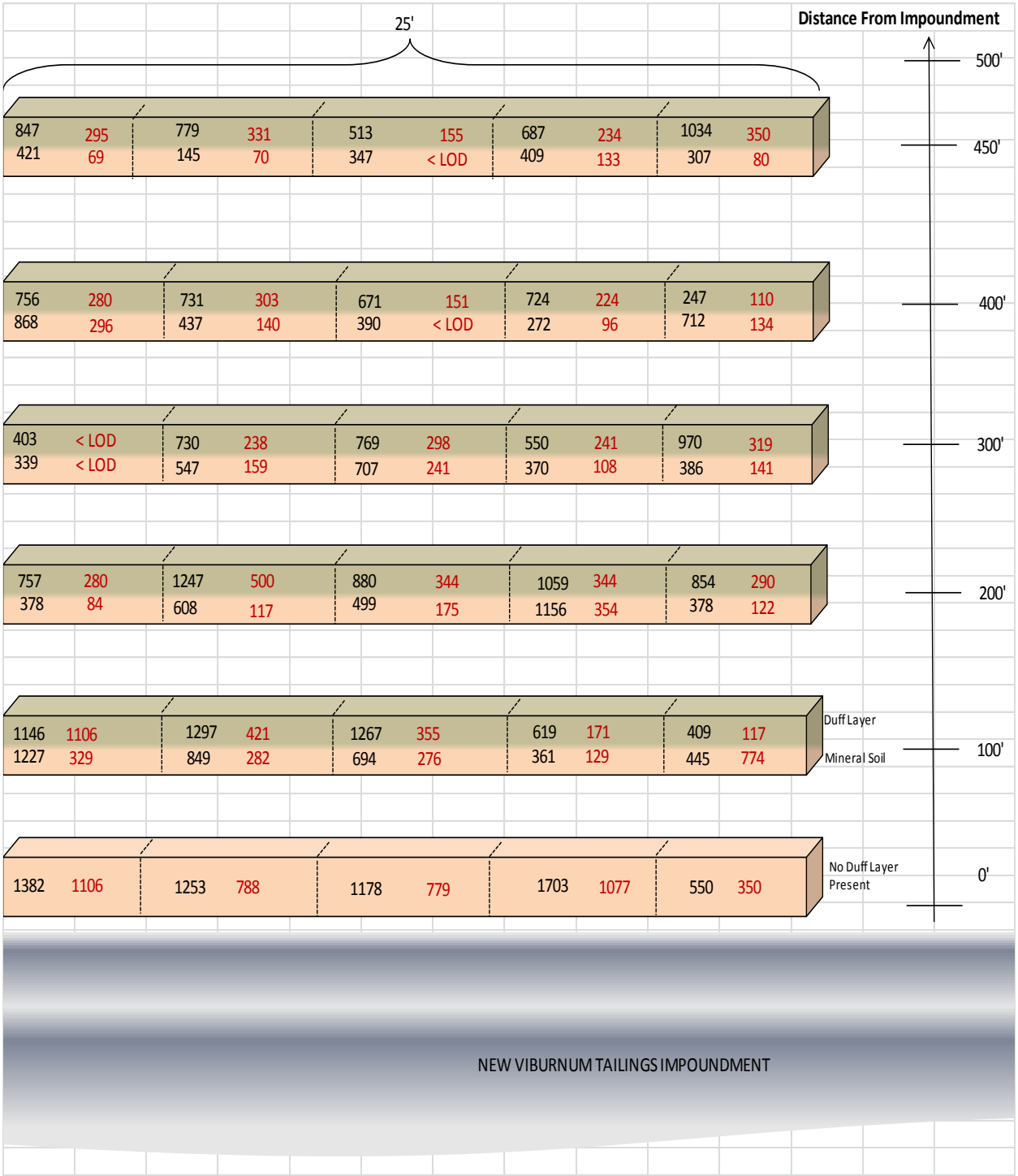

Figure 3. Lead (shown in black) and zinc (in red) concentrations (mg/kg) in Duff vs. Soil at SA3 in the New Viburnum Impoundment.

5.5 Impact of Buick Smelter

The results of sampling near Buick smelter are similar to those of earlier studies, that lead concentrations in these areas are highly elevated (Butherus 1975, Jackson and Watson 1977, Bornstein 1989, USFS 2012). Deposition of fallout from Buick smelter may contribute to the elevated lead levels around Old and New Viburnum and Buick impoundments. These impoundments had the largest predicted transition zones of any of the impoundments. Buick impoundment SA 1, only 2.8 miles southeast of the smelter, exhibited a highly variable, non-linear pattern of lead concentrations (Figure A-2) which may be explained by the influence of smelter fallout. None of the SAs around Old Viburnum displayed a statistically significant correlation with distance from the impoundment with respect to lead (Table C-3), which suggests contamination around that impoundment may be largely influenced by fallout from Buick smelter, approximately 6 miles away. The proximity of the tailings impoundments to Buick smelter are listed in Table 9. Previous investigations in this area found concentrations of lead exceeding 120 mg/kg up to 7 miles from Buick smelter (Butherus 1975). Studies of smelter fallout in other regions have found that contamination can extend up to 24 miles away (Buchauer 1973, Cartwright et al 1975).

Table 9. Distances of tailings impoundments from Buick smelter in the Viburnum Trend Lead Mining District, Missouri.

Impoundment	Distance from Buick Smelter (miles)
Brushy Creek	6.2 to 7.0
Buick	2.2 to 4.2
Fletcher	11.6 to 13.4
New Viburnum	4.0 to 5.1
Old Viburnum	5.4 to 7.1
Sweetwater	17.0 to 18.6
West Fork	10.0 to 11.1

5.6 Vegetation and Topography

A comparison between Old and New Viburnum impoundments suggests that differences in the vegetation covering the tailings may explain some of the variability observed between impoundments and SAs. The Old and New Viburnum impoundments are located in very close proximity to each other but have noticeable differences in the pattern of metal contamination in their surrounding soils. A lack of vegetation is noticeable in aerial imagery of New Viburnum (Figure A-11). By contrast Old Viburnum, which has not been used since 1975, has noticeably more vegetation covering the tailings and also has much lower metallic concentrations in the surrounding soils. Both impoundments have relatively wide low-Pb transition zones, but New Viburnum has a much larger high-Pb transition zone (Figure A-11).

Variation in topography affects the deposition pattern of windblown material (Goosens 1996) and may explain some of the spatial variability of lead concentrations observed in this study. Deposition rates of windblown dust particles tend to be higher on the windward side of hills (Goosens 1996). This type of pattern was observed in SAs at various impoundments, and was particularly noticeable where the SA was long and crossed a ridge or valley, such as SA 5 at New Viburnum impoundment, shown in Figure 4. Another example can be seen in the difference between SA 3 and SA 4 at Buick impoundment. Although these sampling areas were only 280 feet apart (Figure A-9), Pb concentrations at 0 and 50 feet from the impoundment were 31% and 54% higher respectively in SA 4 than SA 3 (Table C-1). SA 3 is in a valley while SA 4 follows a ridge.

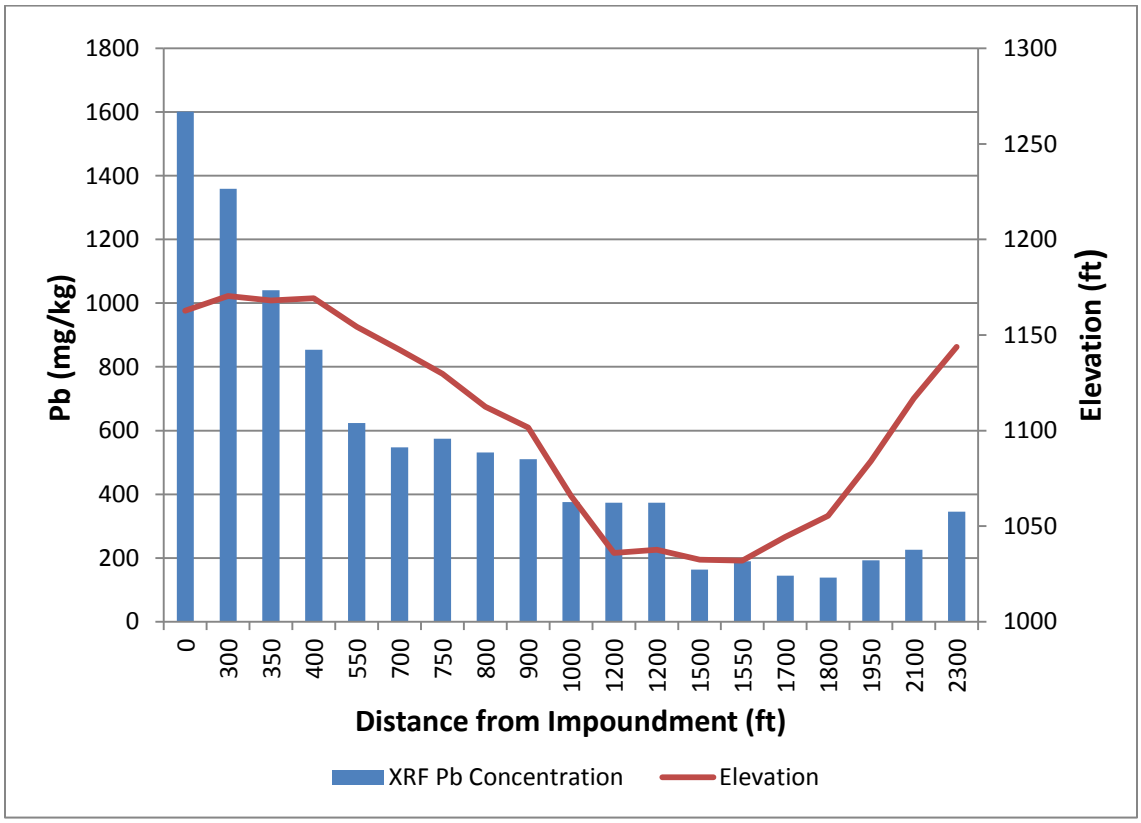

Figure 4. Elevation and lead (Pb) concentrations in soils of Sampling Area 5 near New Viburnum tailings impoundment.

5.7 Sampling Accuracy and Precision

The results of the laboratory XRF analysis of ICS samples were in close agreement with in-situ XRF results. Concentrations in ICS samples were generally slightly higher than the corresponding in-situ measurements, which is likely due to the fact that the ICS were sieved and measurements were conducted on only the fraction of particles less than 2 mm. Previous studies have found that metallic contaminants tend to be more concentrated in the finer portions of soil samples (Kalnicky et al 1998). ICS results from the fixed-distance SUs employed in April and May indicate that the in-situ results tended to slightly underestimate metal concentrations (Figure 5, Plates C and D) more than the variable-size SU samples collected in October and December

(Figure 5, Plates A and B). It is difficult to determine if this is due to differences in the collection methodology between the two types of SUs, or if there were differences in soil conditions, such as moisture content, between the two sets of sampling events. Soils may have been drier when the variable size SUs were employed in October and December compared to April and May, when the fixed-distance SUs were employed. Increased soil moisture can result in underestimation of metal concentrations measured using XRF instruments (Kalnicky et al. 1998). Samples measured in the lab were dried prior to analysis and thus the XRF results would not be affected by moisture content. Overall, the level of agreement between ICS and in-situ measurements demonstrates the accuracy of the in-situ sampling methods and supports the validity of the results.

As shown in Figure 6, comparisons between XRF and laboratory analysis results for Pb indicate that XRF analysis of ICS samples consistently yield accurate results across a wide range of concentrations. These results serve to increase confidence in the methods employed in this study. In general, soil samples gave very similar results using the two methods (R^2 = 0.99, Figure 6, Plate B) while tailings samples were slightly less consistent (R^2 = 0.93, Figure 6, Plate D).

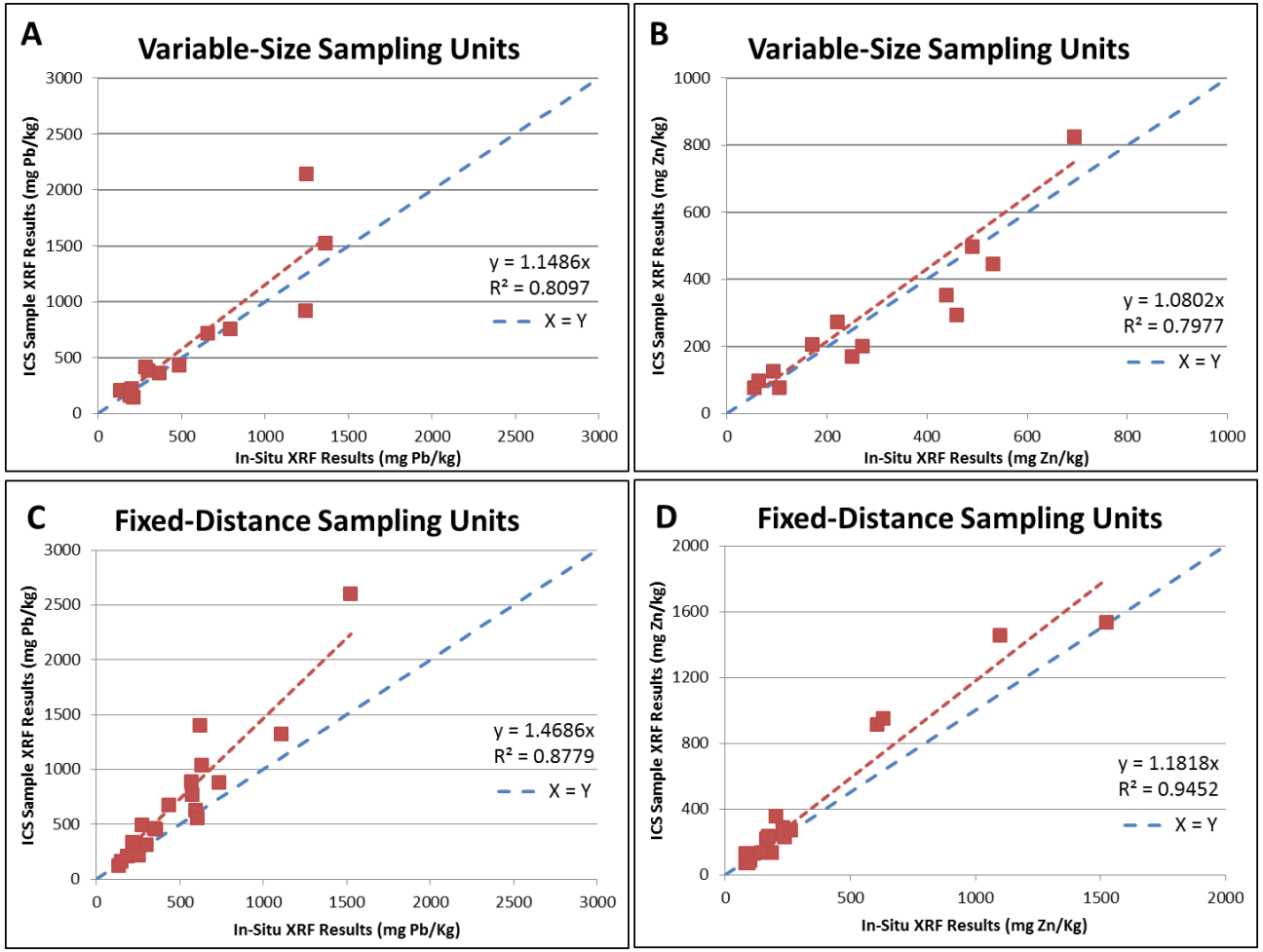

Figure 5. Comparison between In-Situ and Incremental Composite Sample XRF results for lead (Pb, panels A and C) and zinc (Zn, panels B and D). All units are in mg/kg.

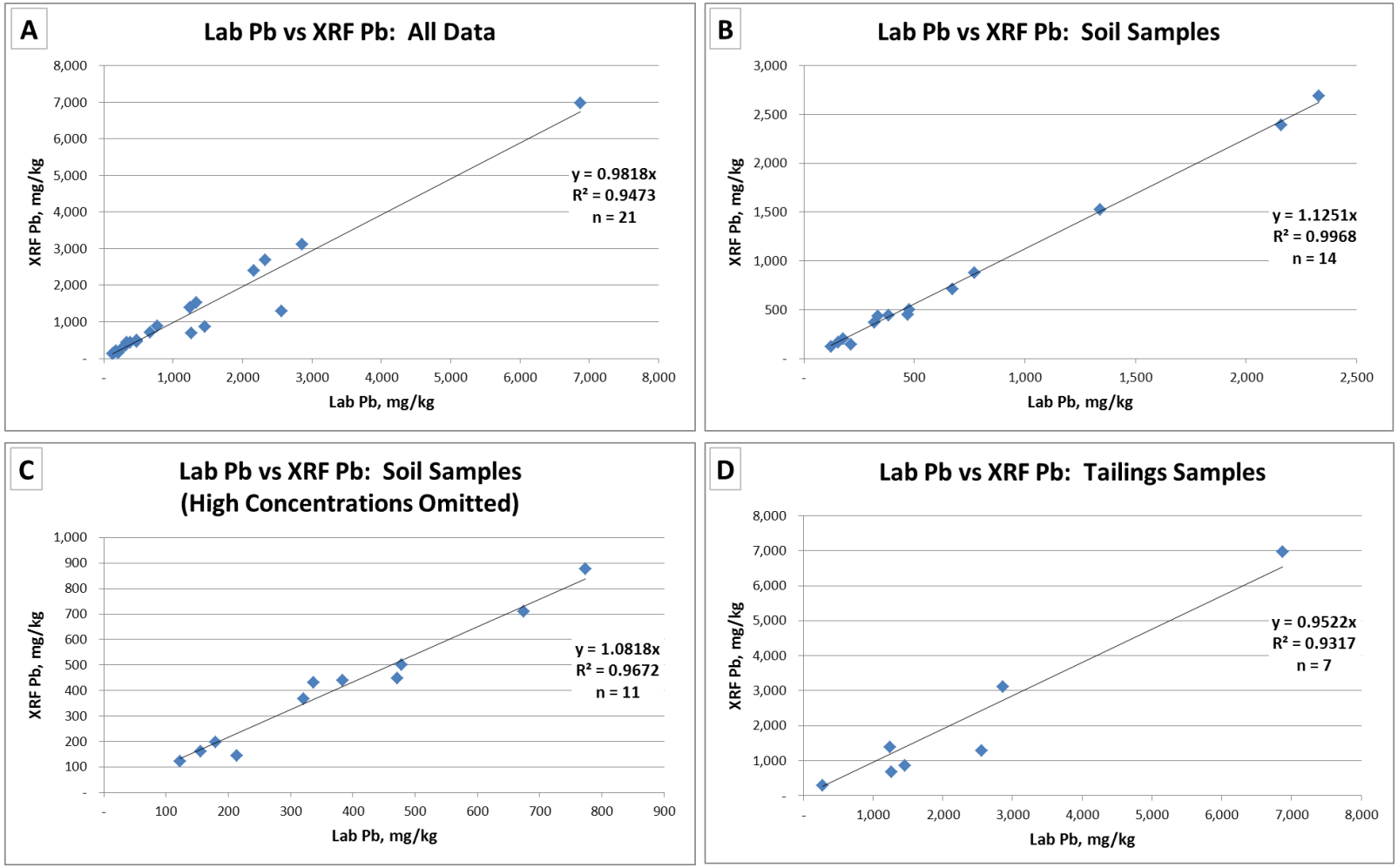

Figure 6. Comparison between XRF and laboratory analysis results for lead (Pb) concentrations.

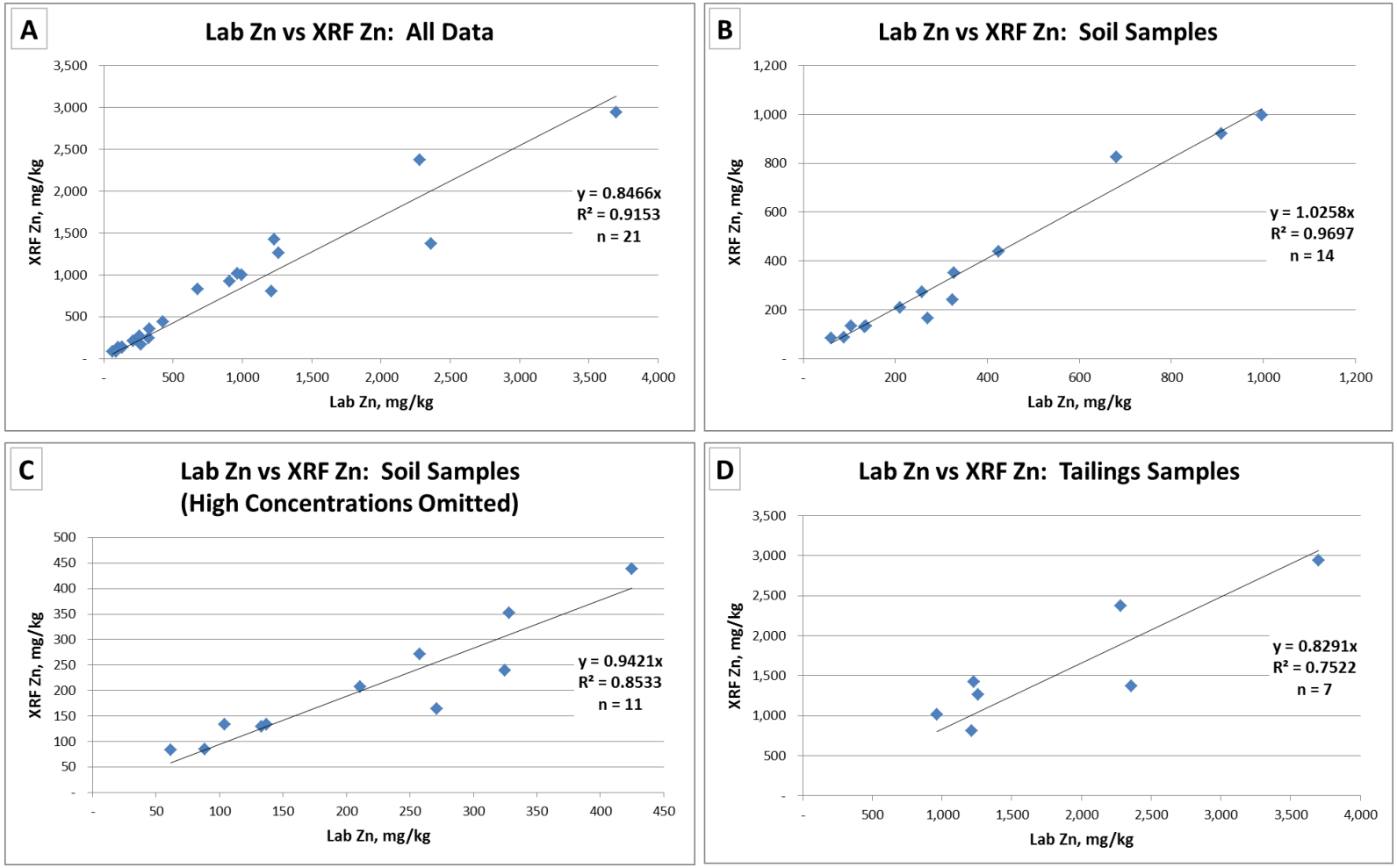

Figure 7. Comparison between XRF and laboratory analysis results for zinc (Zn) concentrations.

Low concentrations of lead and zinc were measured in the equipment rinsate blanks indicating there may be some carry-over of these metals on the sampling tools between SUs even following decontamination. Approximately 2 ug/l lead was measured in one of the rinsate blanks (Table 6). The rinsate volume used was 100 ml. Therefore approximately 0.2 ug of lead may remain on the sampling tools after decontamination. If this 0.2 ug of lead were carried over into a soil sample, the resulting concentration attributable to cross-contamination would be 4 orders of magnitude below the detection level for lead in soil. This indicates that the decontamination procedures used were adequate to prevent cross-contamination between SU samples at levels that could interfere with decision making.

6.0 Conclusions

Lead concentrations above 490 mg/kg were detected in 45% of tailings impoundment sampling areas and 100% of smelter sampling areas. Concentrations above 147 mg/kg were detected at 90% of impoundment sampling areas. The total predicted area of transition zone land with lead concentrations greater than 490 mg/kg and 147 mg/kg is 1848 acres and 6504 acres respectively. There were statistically significant relationships between soil lead concentrations and distance from the impoundments at 17 of the 31 tailings impoundment sampling areas investigated during this study. These linear relationships indicate that tailings are being released from the impoundments and contributing to the contamination of the surrounding soils. In many cases, these soils contained concentrations of lead greater than 490 mg/kg, which indicates that wildlife in the area are being exposed to harmful levels of lead. Additionally, elevated levels of lead were detected in soils beyond the expected influence from impoundments, between approximately 1 and 4 miles away from Buick smelter. Lead concentrations in those soils increased significantly with increasing proximity to the smelter facility. These data suggest that fallout from Buick smelter is also contributing to injury to vegetation and wildlife.

Zinc concentrations greater than 448 mg/kg were detected in 35% of impoundment sampling areas but were not detected above this level in any of the smelter sampling areas. Concentrations above 160 mg/kg were detected at 77% of impoundment sampling areas and 17% of smelter sampling areas. The total predicted area of transition zone land with zinc concentrations greater than 448 mg/kg and 160 mg/kg is 835 acres and 3318 acres respectively. In general, transition zones for lead were larger than those of zinc. Zinc concentrations were significantly related to distance from the impoundments at 18 of the areas sampled.

Although the results of this study find that lead concentrations decreased significantly with distance from the impoundments, it was difficult to confidently estimate the average widths of the transition zones due to the high level of variability among sampling areas. While some impoundments such as Brushy Creek and New Viburnum show strong correlations between Pb and distance, these variables were not significantly related at others, such as Old Viburnum and West Fork (Tables C-3 and C-4). However, even at impoundments with weak Pb-distance correlations, Pb concentrations above 147 mg/kg were detected indicating that contamination is present. Increased sampling density may be needed in future investigations to address to high degree of variability.

The results of this investigation demonstrate that soils around tailings impoundments in the Viburnum Trend Lead Mining District contain levels of lead and zinc which exceed ecological benchmarks. The observed contamination levels are sufficient to cause injury to vegetation and wildlife. Areas around the smelter are similarly contaminated with elevated levels of lead, however only the area closest to the smelter was found to have elevated levels of zinc.

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Date: 8/15/2014

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APPENDIX A

Additional Figures

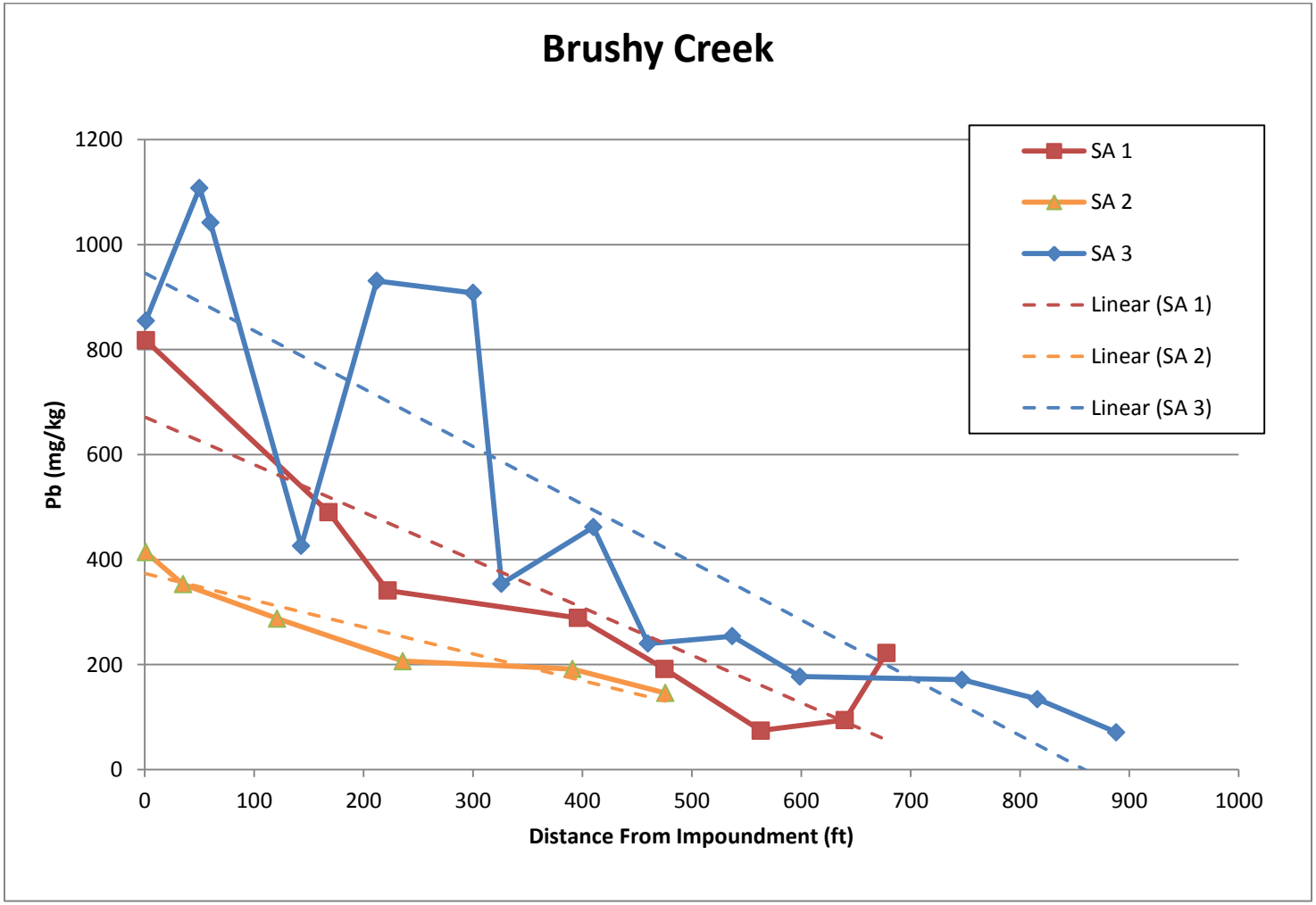

Figure A-1. Lead (Pb) concentration with distance at 3 sampling areas around Brushy Creek tailings impoundment.

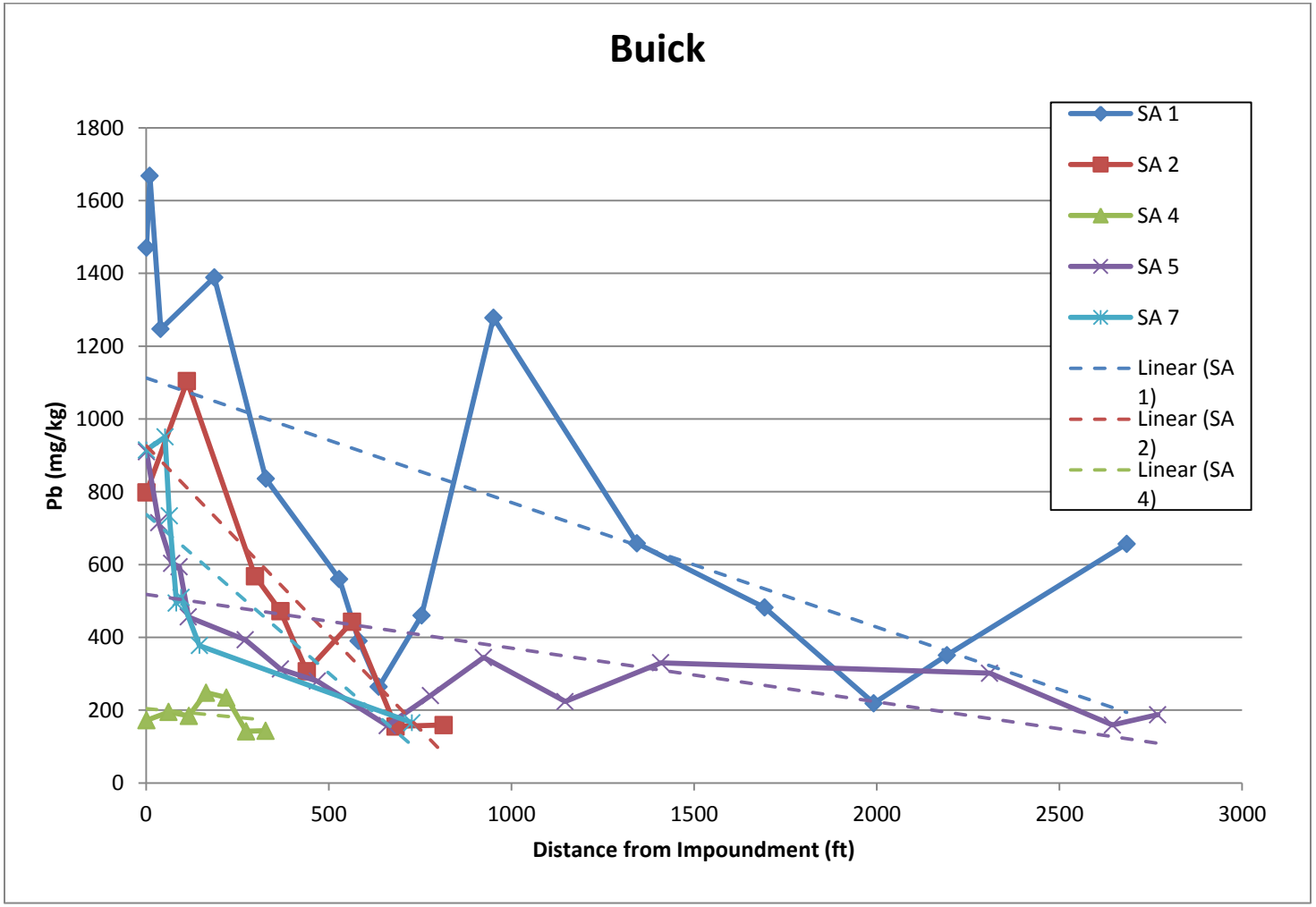

Figure A-2. Lead (Pb) concentration with distance at 5 sampling areas around Buick tailings impoundment.

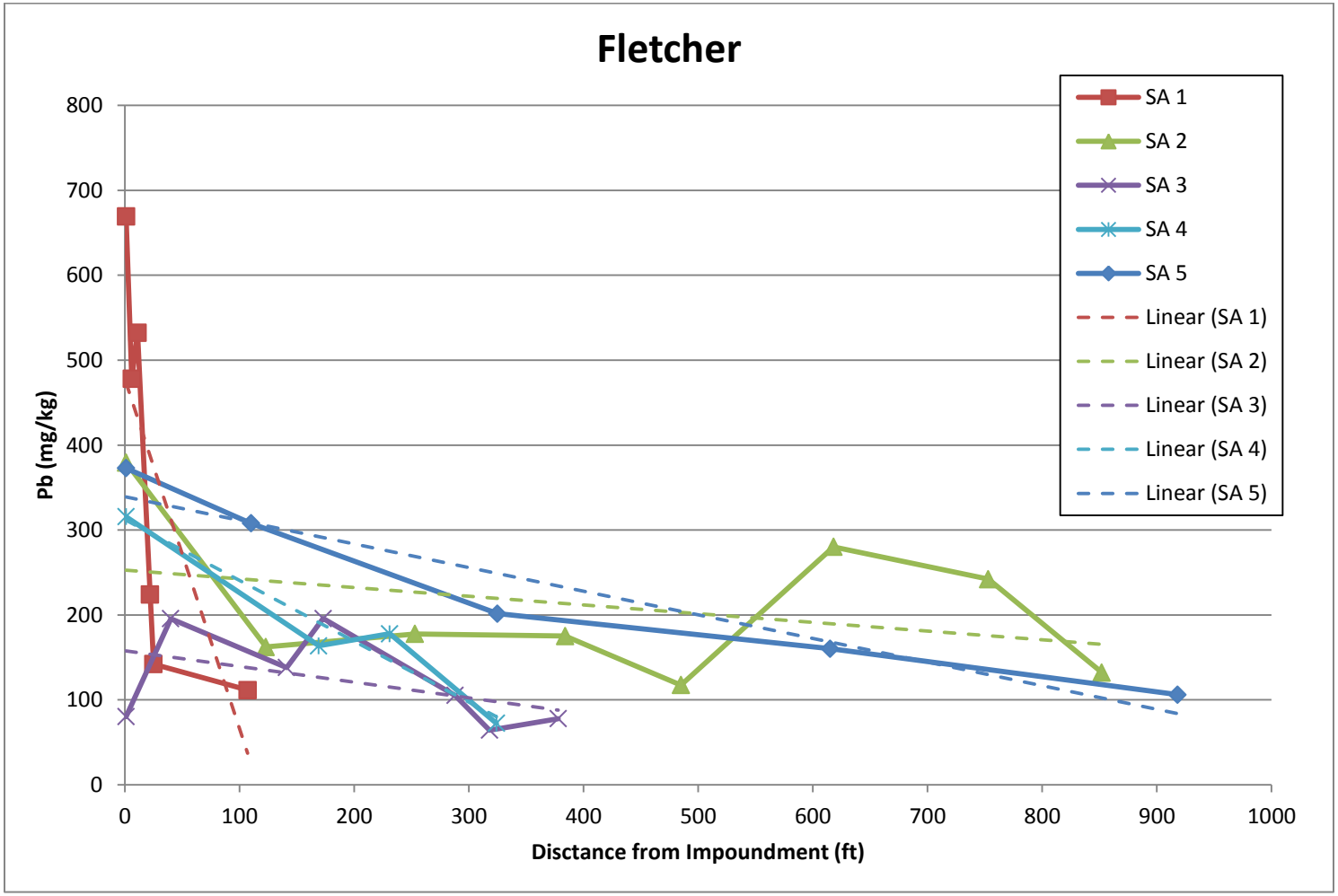

Figure A-3. Lead (Pb) concentration with distance at 5 sampling areas around Fletcher tailings impoundment.

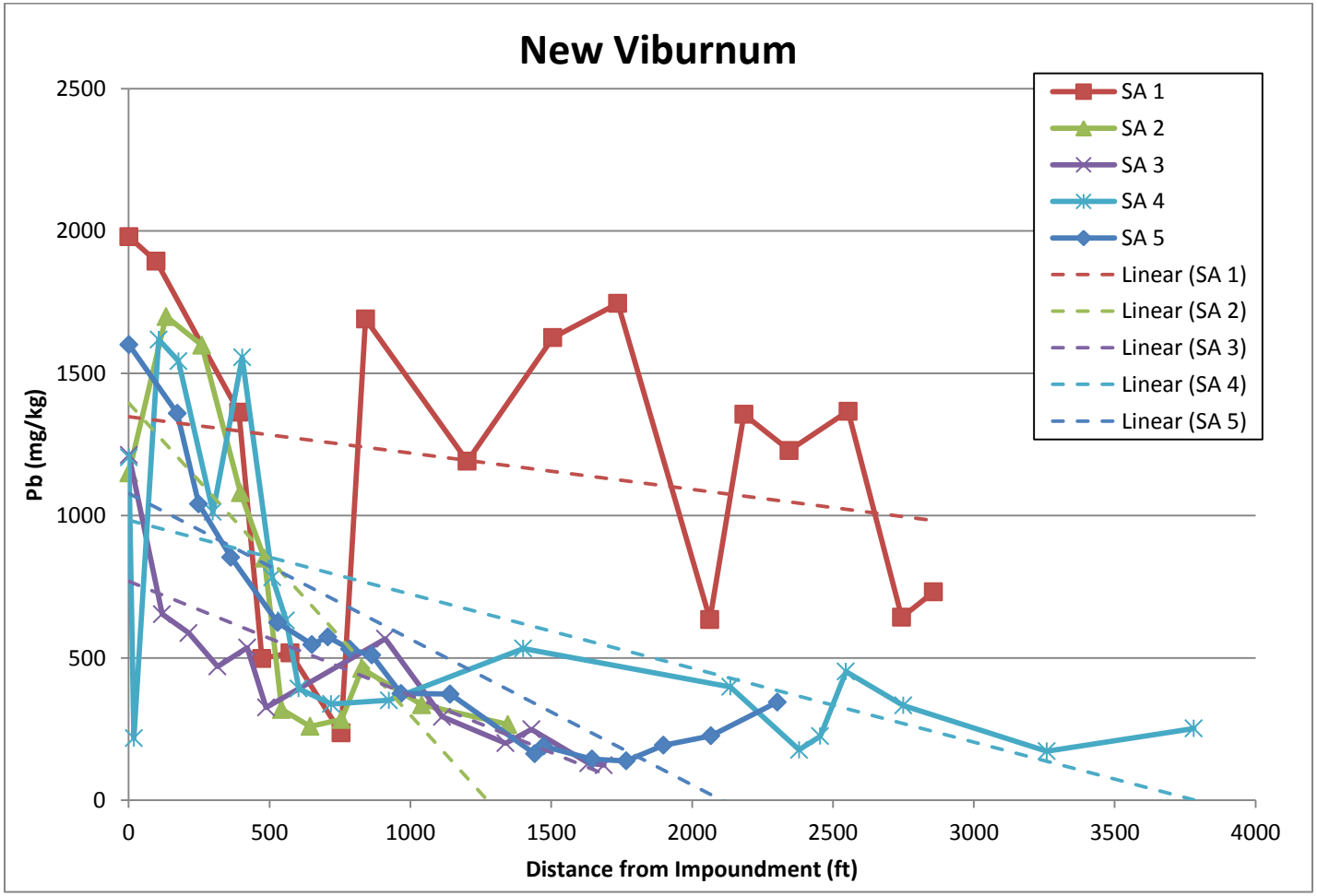

Figure A-4. Lead (Pb) concentration with distance at 5 sampling areas around New Viburnum tailings impoundment.

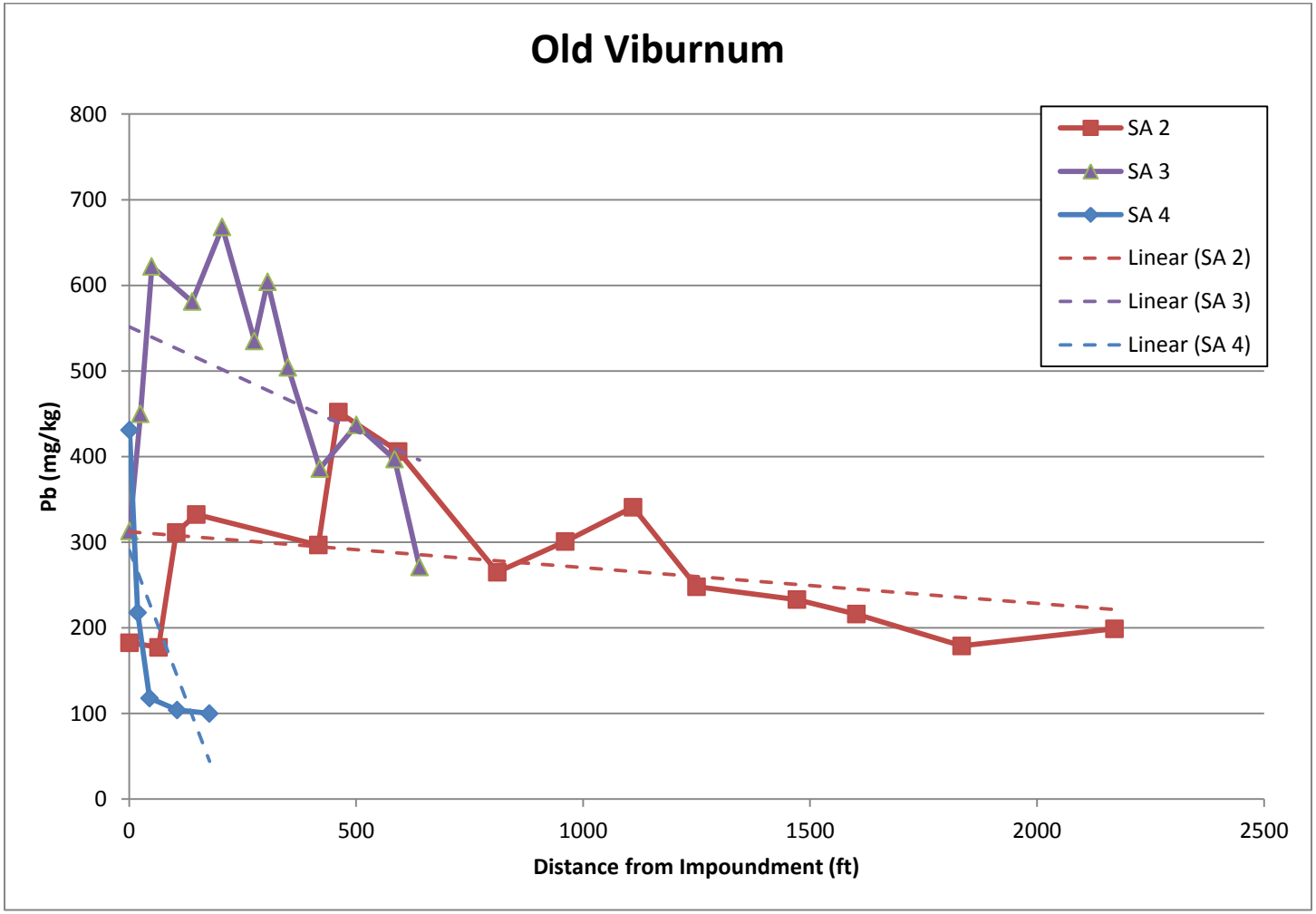

Figure A-5. Lead (Pb) concentration with distance at 3 sampling areas around Old Viburnum tailings impoundment.

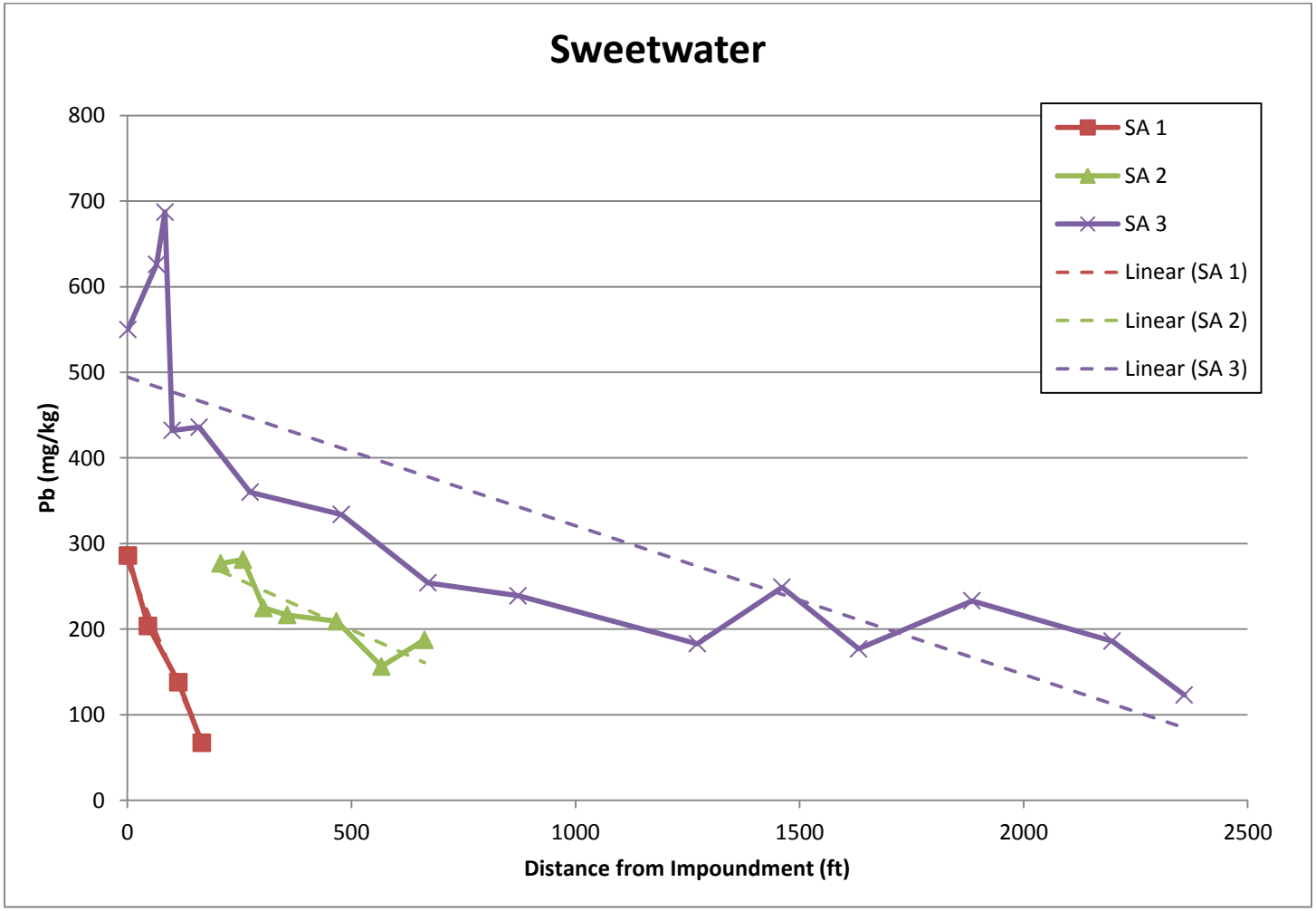

Figure A-6. Lead (Pb) concentration with distance at 3 sampling areas around Sweetwater tailings impoundment.

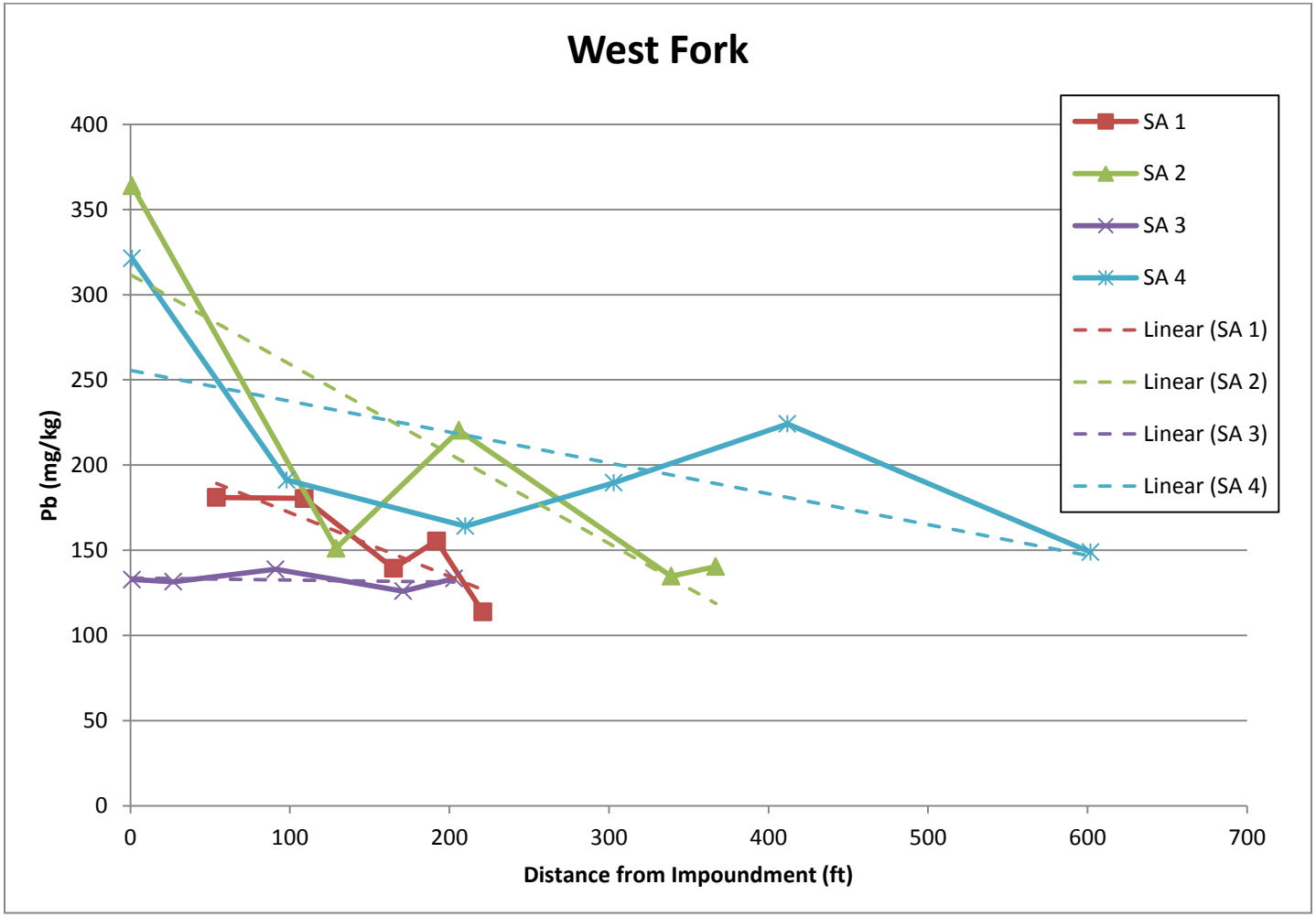

Figure A-7. Lead (Pb) concentration with distance at 4 sampling areas around West Fork tailings impoundment.

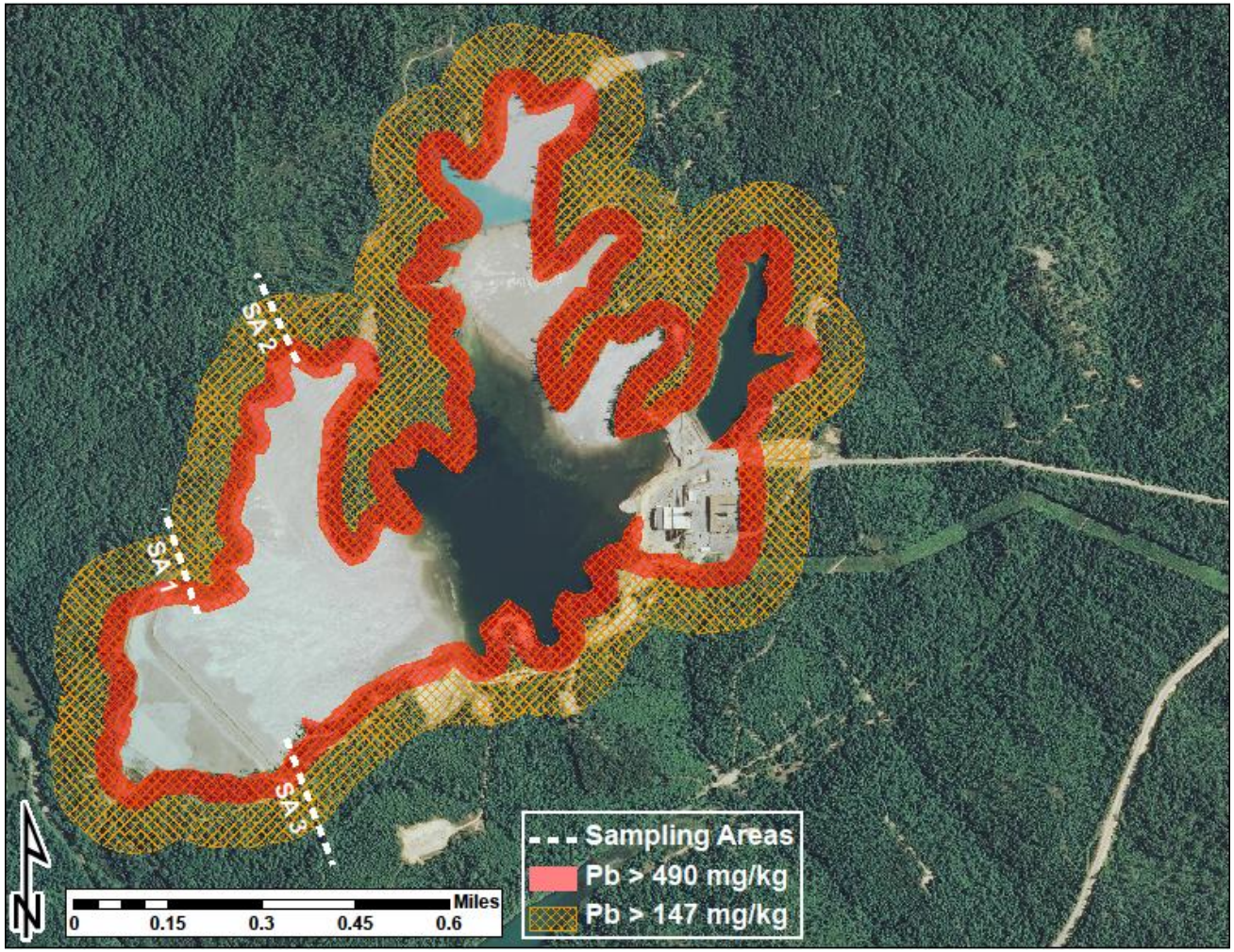

Figure A-8. Transition zones and Sampling Areas around Brushy Creek Impoundment, Viburnum Trend Mining District, Missouri.

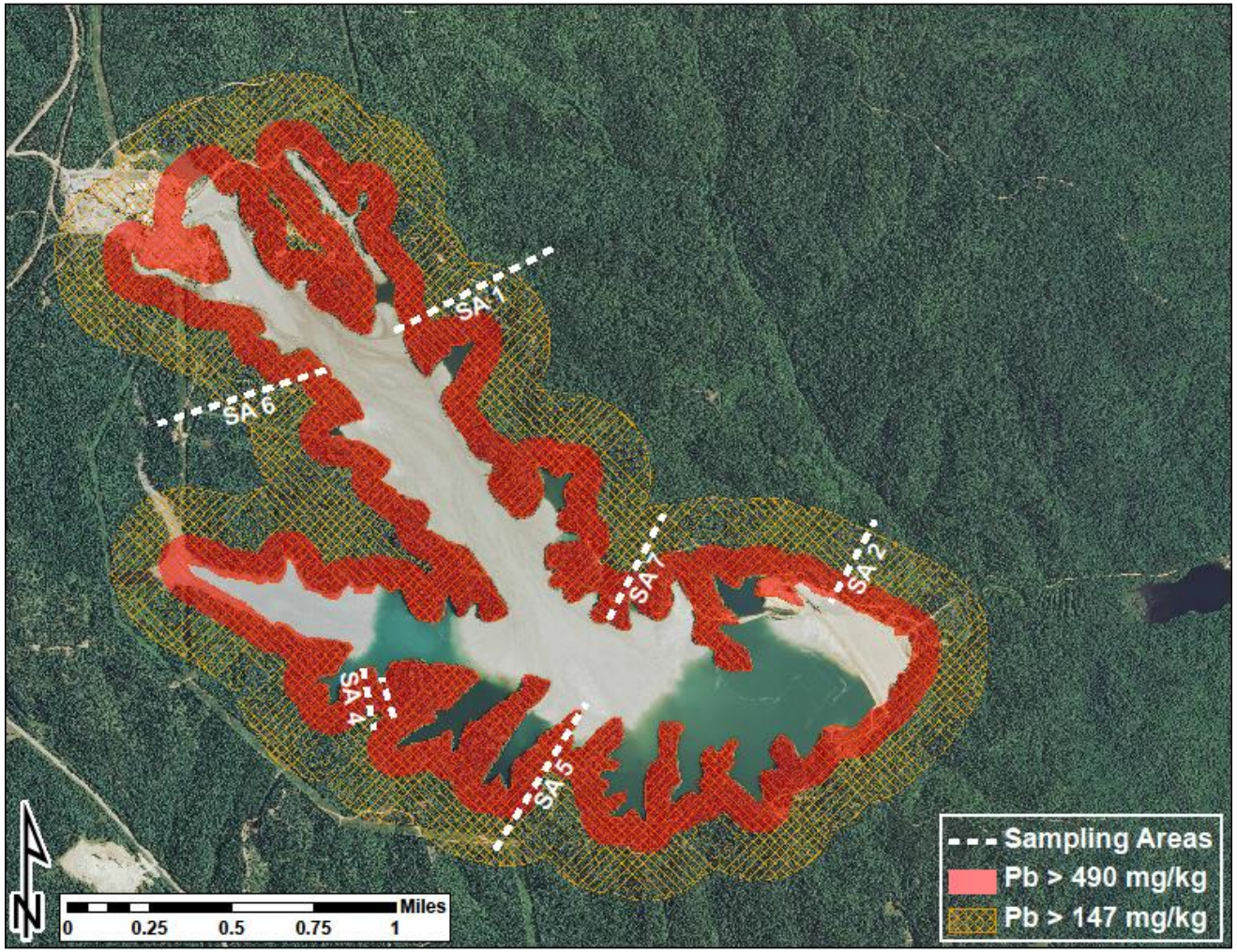

Figure A-9. Transition zones and Samplng Areas around Buick impoundment, Viburnum Trend, Missouri.

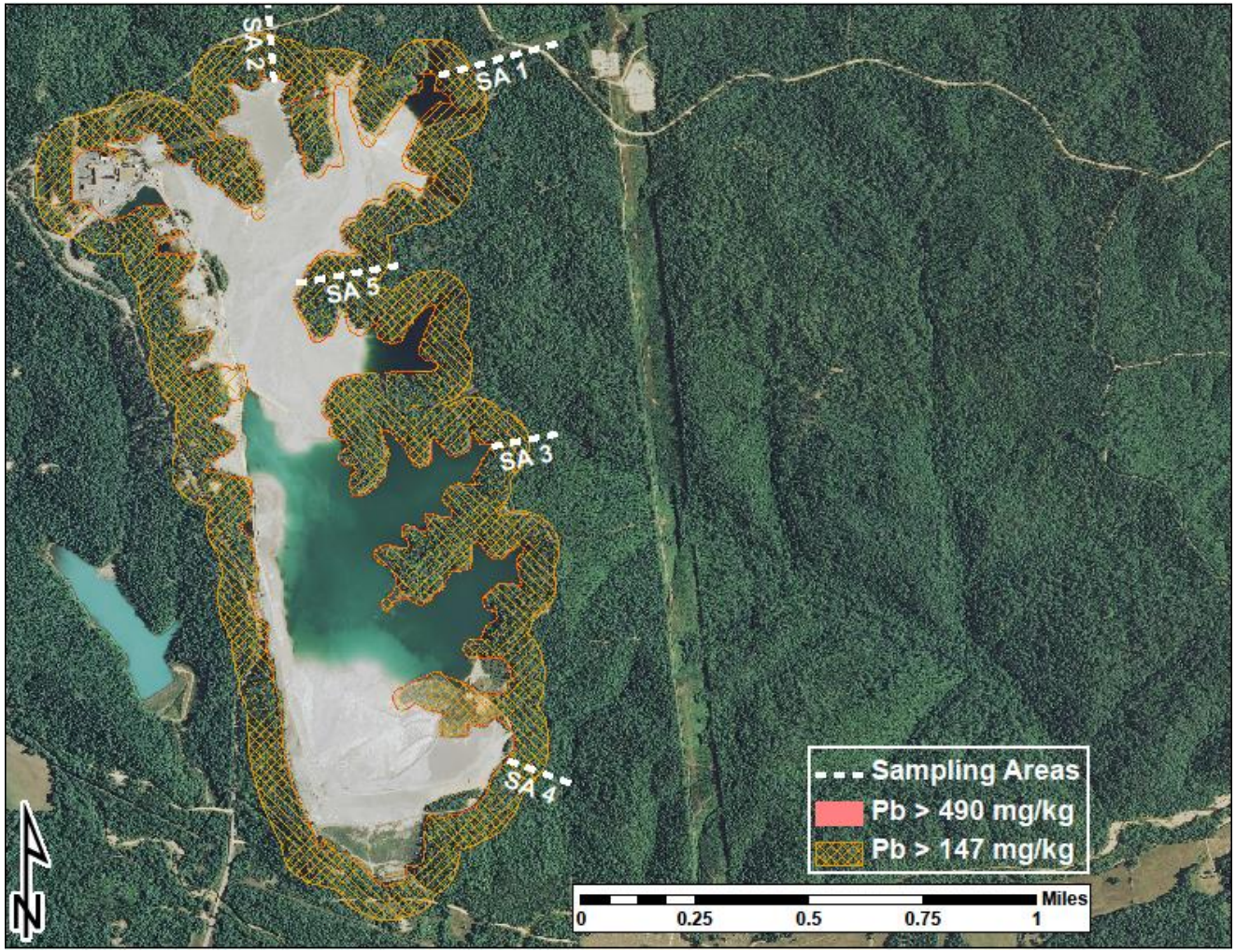

Figure A-10. Transition zones and Sampling Areas around Fletcher impoundment, Viburnum Trend Mining District, Missouri.

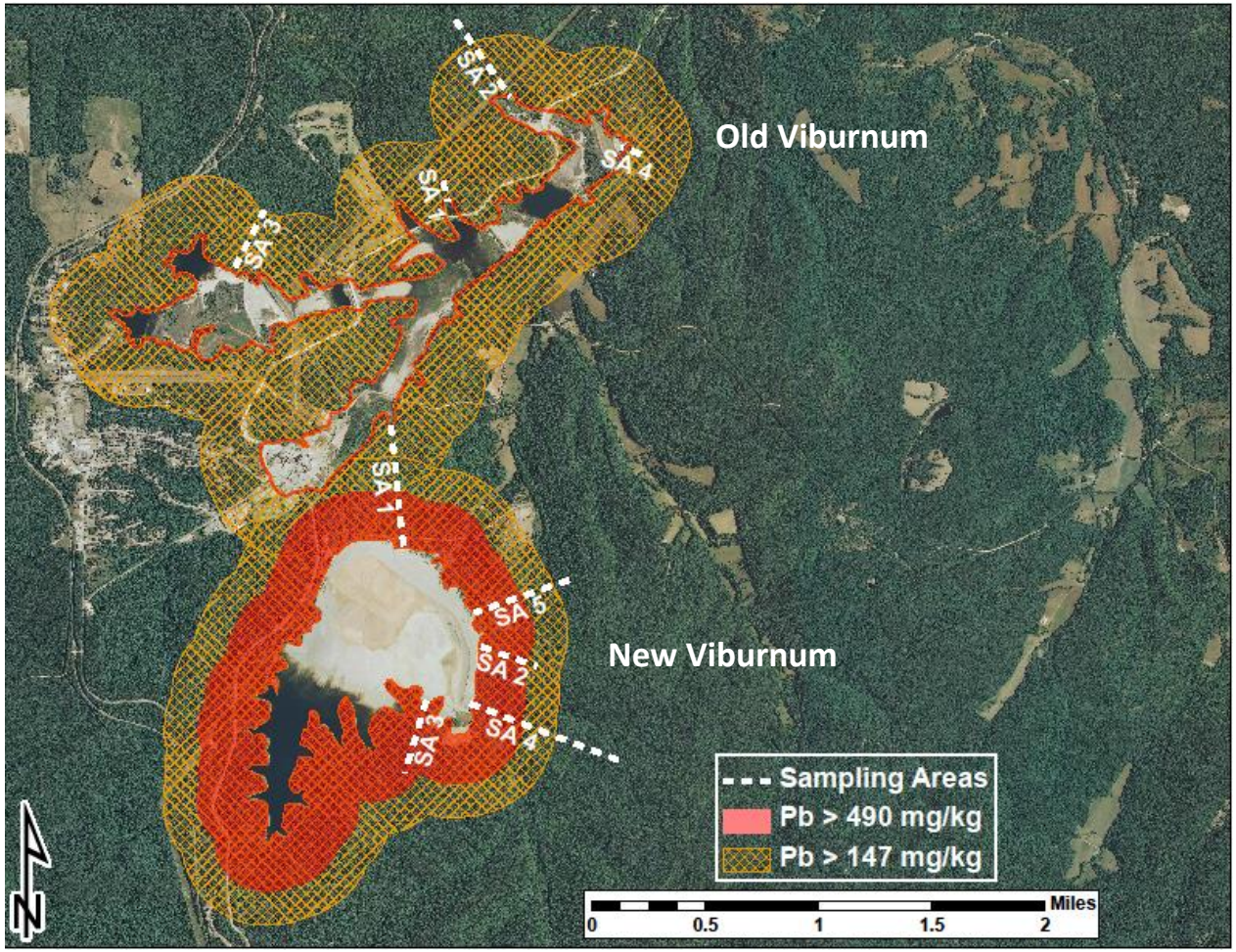

Figure A-11. Transition zones and Sampling Areas around Old and New Viburnum impoundments, Viburnum Trend Mining District, Missouri.

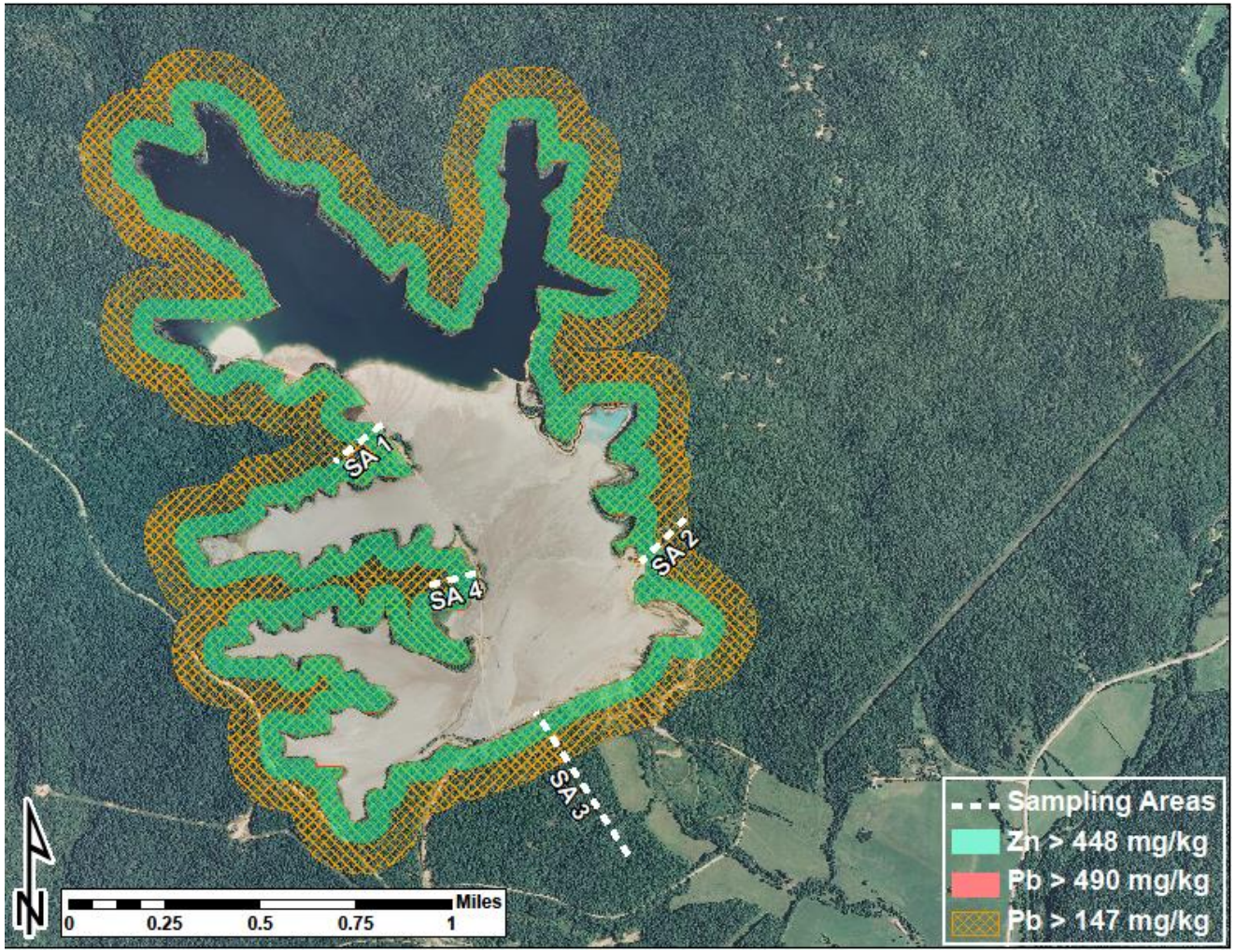

Figure A-12. Transition zones and Sampling Areas around Sweetwater impoundment, Viburnum Trend Mining District, Missouri.

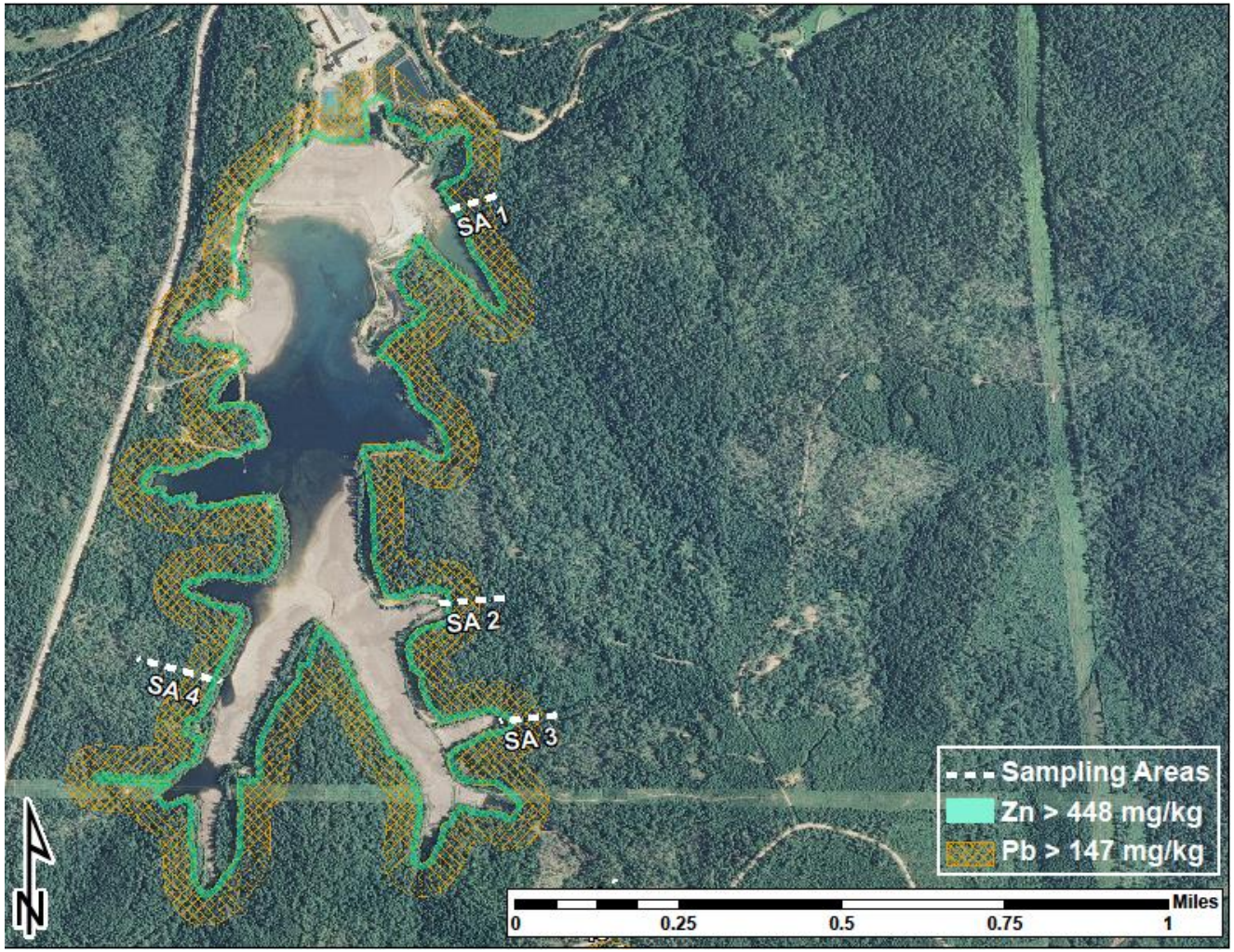

Figure A-13. Transition zone and Sampling Areas around West Fork impoundment, Viburnum Trend Mining District, Missouri.

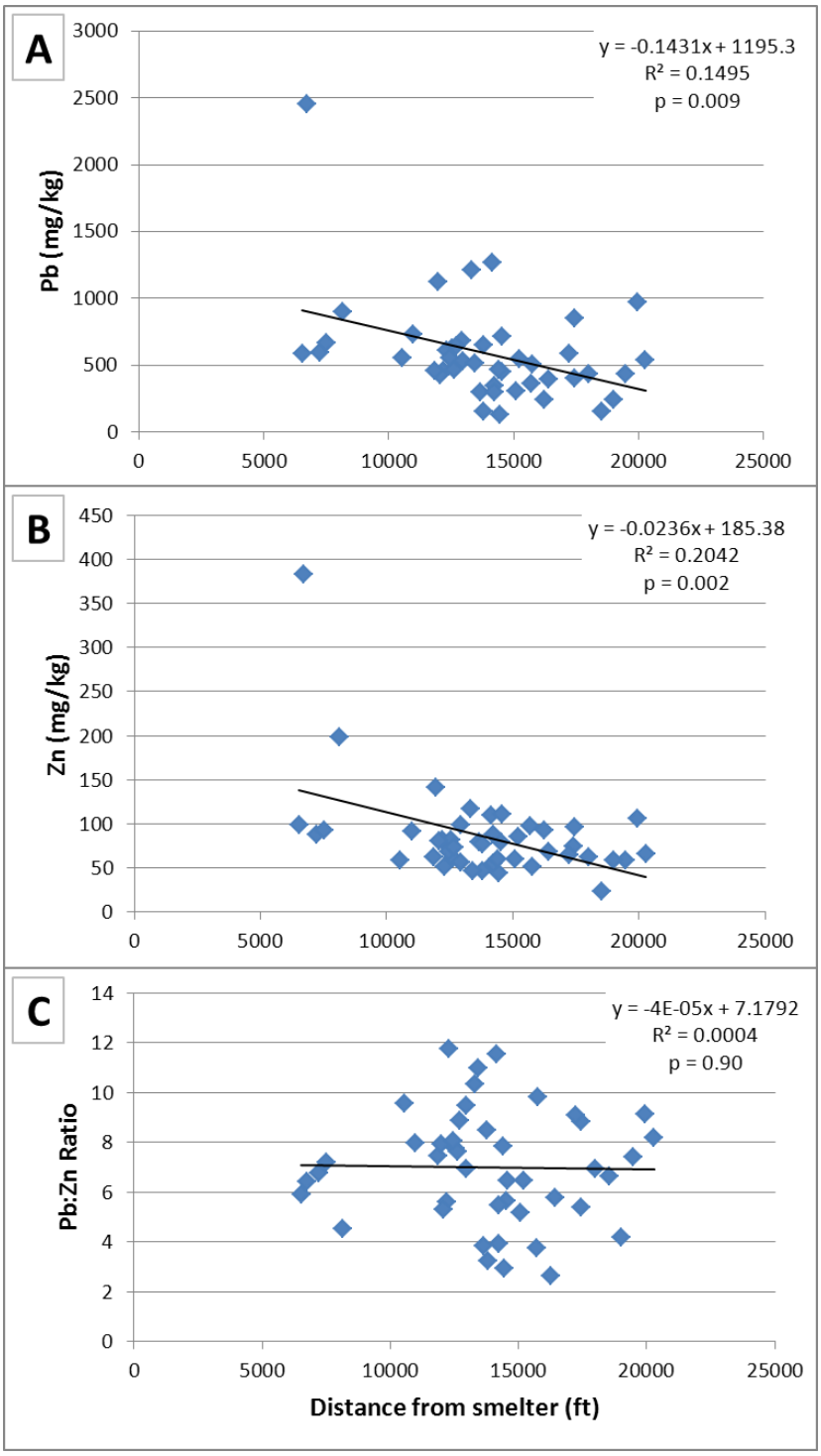

Figure A-14. Results of regressions between distance from Buick smelter, and lead (Pb), zinc (Zn), and the ratio of lead to zinc (Pb:Zn).

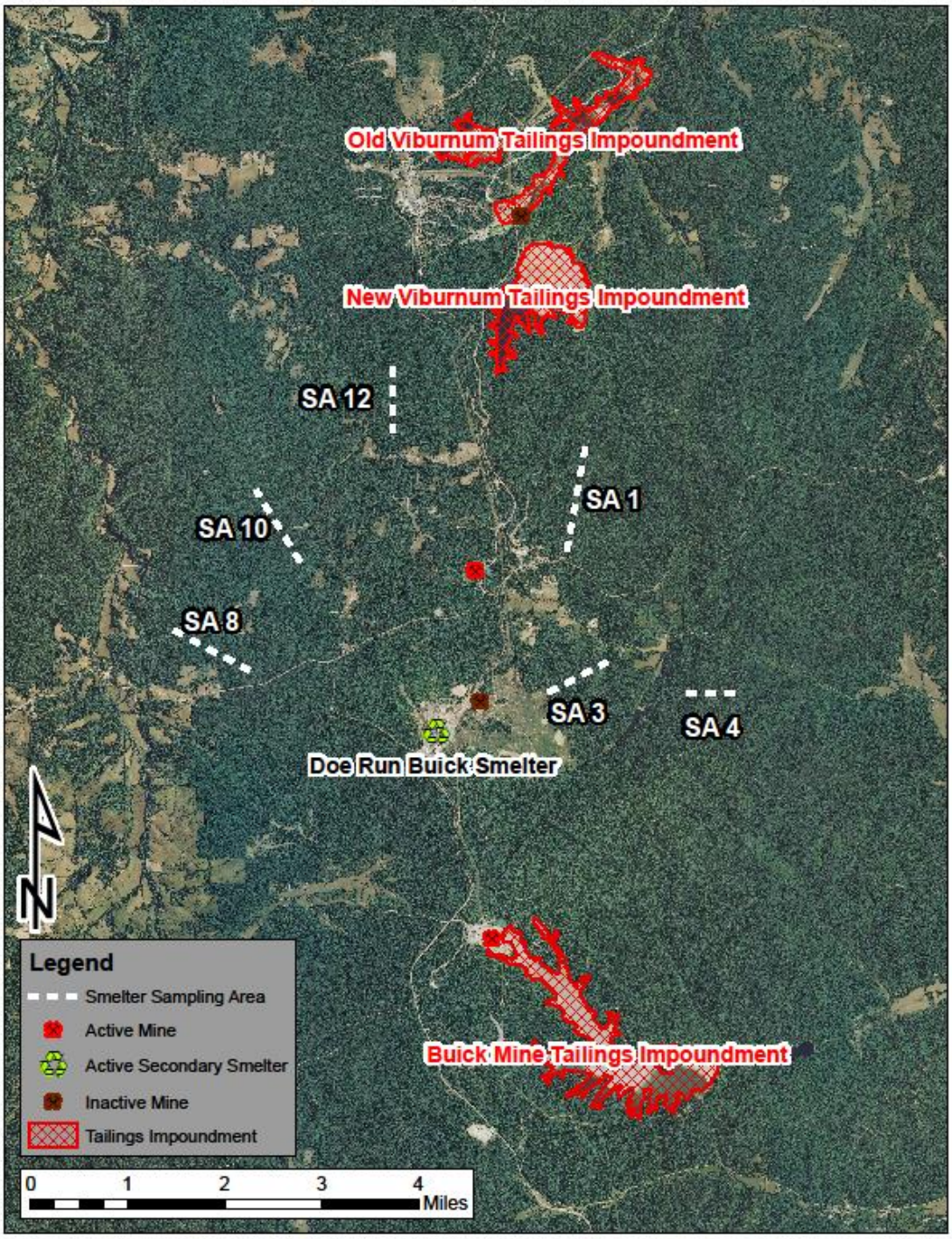

Figure A-15. Map of Buick smelter Sampling Areas and nearby tailings impoundments in the Viburnum Trend Mining District, Missouri.

APPENDIX B

Photographs

Photograph 1. Triplicate Incremental Composite Samples (ICS) being collected during an April 2013 sampling event.

Photograph 2. Small stainless steel scoop being used to measure one increment of soil of an ICS collected during an April 2013 sampling event.

Photograph 3. ICS samples being spread onto pans and large rocks and organic material being removed following an October 2012 sampling event.

Photograph 4. ICS samples spread out to dry on a rack following an October 2012 sampling event.

Photograph 5. Mechanical sieve shaker used to process soil samples.

APPENDIX C
Additional Tables

Table C-1. Mean lead and zinc concentrations in tailings impoundment sampling areas measured using in-situ handheld XRF devices.

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
Brushy Creek	1	0	818	186	23	5	705	182	26	5	1.16
		170	490	260	53	5	356	122	34	5	1.38
		220	341	48	14	17	263	45	17	17	1.30
		330	289	40	14	5	210	30	14	5	1.38
		500	192	99	52	7	125	62	50	7	1.54
		570	74	18	24	3	54	5	9	2	1.38
		650	94	25	26	5	52	13	24	5	1.80
	2	0	414	151	36	6	279	79	28	6	1.49
		30	353	79	22	6	229	52	23	6	1.54
		100	288	102	35	6	159	54	34	6	1.81
		200	206	72	35	6	121	50	41	6	1.71
		400	192	61	32	6	119	47	39	6	1.61
		500	146	64	44	6	79	26	32	6	1.85
	3	0	855	564	66	6	446	201	45	6	1.92
		50	1108	240	22	6	1522	388	26	6	0.73
		100	941	330	35	5	698	226	32	5	1.35
		150	426	233	55	6	394	210	53	6	1.08
		200	931	192	21	6	650	237	36	6	1.43
		300	354	163	46	6	326	118	36	6	1.09
		320	908	255	28	6	537	75	14	6	1.69
		350	403	264	65	7	370	173	47	6	1.09
		400	240	132	55	6	187	68	36	6	1.28
		450	253	78	31	6	172	53	31	6	1.48
		500	177	74	42	6	120	56	47	6	1.47
		600	222	93	42	6	147	68	46	6	1.50
		680	171	32	19	6	141	39	27	6	1.21
		720	134	42	31	6	100	25	25	6	1.34
		800	71	33	47	6	47	30	63	6	1.51
Buick	1	0	1471	838	57	4	501	209	42	4	2.94
		10	1668	1003	60	6	697	362	52	6	2.39

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
Buick	1	50	1247	647	52	5	514	326	64	5	2.43
		100	1480	685	46	5	556	340	61	5	2.66
		200	1389	389	28	5	450	67	15	5	3.09
		300	836	336	40	5	260	74	28	5	3.22
		500	560	268	48	5	193	76	39	5	2.89
		550	390	114	29	5	145	46	32	5	2.69
		600	264	151	57	5	102	51	50	5	2.59
		750	460	146	32	5	137	40	29	5	3.35
		900	1278	731	57	5	365	212	58	5	3.50
		1300	658	319	49	6	141	62	44	6	4.68
		1700	482	129	27	5	129	51	39	5	3.75
		2000	219	49	23	5	72	17	23	5	3.02
		2200	351	110	31	5	118	23	20	5	2.97
		2700	657	362	55	5	171	102	60	5	3.84
	2	0	798	411	51	3	555	268	48	3	1.44
		125	1104	581	53	5	679	311	46	5	1.63
		300	568	248	44	7	330	200	61	7	1.72
		370	472	156	33	24	267	102	38	24	1.77
		450	307	124	40	8	185	72	39	8	1.66
		600	443	270	61	6	253	128	50	6	1.75
		700	155	54	35	7	93	55	59	7	1.66
		800	159	65	41	5	85	42	49	5	1.88
	3	0	119	25	21	3	39	8	21	2	3.05
		50	89	28	31	3	32	10	31	3	2.78
	4	0	172	87	51	6	38	20	54	3	4.55
		50	195	80	41	4	45	21	46	4	4.32
		100	184	58	31	5	48	19	39	4	3.87
		150	248	79	32	5	57	15	27	4	4.37
		200	234	115	49	5	45	26	58	5	5.21
		250	142	62	43	5	58	18	30	5	2.42
		300	143	49	34	5	74	30	40	3	1.95
	5	0	910	723	79	7	425	306	72	7	2.14
		30	715	215	30	6	312	94	30	6	2.29

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
Buick	5	60	603	227	38	6	219	85	39	6	2.76
		90	594	184	31	6	237	72	30	6	2.51
		135	456	185	41	6	164	71	43	6	2.77
		295	393	210	53	6	162	84	52	6	2.43
		395	313	205	65	6	125	79	63	6	2.49
		500	280	107	38	6	83	36	44	6	3.39
		700	158	46	29	6	54	7	13	6	2.90
		820	240	164	68	6	90	56	62	6	2.66
		965	345	203	59	6	95	54	57	6	3.63
		1200	224	120	54	6	61	34	55	6	3.65
		1460	330	98	30	6	78	25	32	6	4.26
		2360	301	89	30	6	80	23	29	6	3.78
		2760	159	111	70	8	42	12	30	8	3.82
		2900	187	108	58	6	50	15	29	6	3.76
	6	2250	1202	614	51	6	266	120	45	6	4.53
		2580	936	195	21	6	239	46	19	6	3.91
	7	0	915	493	54	7	374	258	69	7	2.44
		25	951	693	73	6	480	396	83	6	1.98
		50	734	432	59	8	260	142	55	8	2.82
		70	494	317	64	8	202	117	58	8	2.44
		90	510	243	48	6	187	105	56	6	2.72
		140	377	173	46	6	153	84	55	6	2.47
		730	165	49	29	6	62	26	43	6	2.67
		850	249	89	36	6	78	31	40	6	3.19
		1000	236	46	19	6	83	15	18	6	2.83
		1330	348	89	25	6	91	23	25	6	3.83
		1760	605	188	31	6	187	96	51	6	3.24
Fletcher	1	0	669	484	72	6	716	384	54	5	0.93
		5	478	343	72	12	434	304	70	12	1.10
		10	532	509	96	5	671	450	67	4	0.79
		20	224	108	48	5	140	53	38	3	1.60
		30	142	22	15	5	59	26	44	3	2.40
		100	111	76	68	2	32	18	56	2	3.45

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
Fletcher	1	150	119	91	77	5	79	55	69	4	1.52
		200	128	15	12	5	71	19	27	2	1.79
		350	135	46	34	23	45	19	41	16	2.98
		600	107	24	22	5	26	8	32	2	4.11
		900	146	48	33	5	67	28	41	3	2.20
		1250	61	34	56	5	22	1	6	3	2.82
	2	0	379	119	31	24	310	365	118	23	1.22
		100	162	54	33	5	66	26	39	4	2.47
		200	178	89	50	5	71	32	45	5	2.49
		300	175	44	25	5	75	32	43	4	2.35
		400	117	13	11	6	65	16	24	6	1.81
		500	280	84	30	5	114	35	31	4	2.46
		600	242	39	16	5	115	11	10	4	2.10
		700	132	74	56	6	88	22	25	5	1.51
	3	0	80	47	59	5	173	113	66	5	0.46
		50	196	145	74	5	109	61	56	4	1.79
		150	138	74	53	5	51	24	48	5	2.69
		200	196	86	44	8	101	59	58	7	1.93
		300	105	90	85	8	62	51	82	6	1.70
		350	64	19	30	6	47	14	30	5	1.36
		400	78	29	37	5	49	18	36	4	1.58
	4	0	316	133	42	7	243	85	35	5	1.30
		150	164	37	23	5	130	31	24	5	1.26
		200	178	105	59	7	136	77	57	7	1.31
		300	73	22	31	5	71	14	20	5	1.02
	5	0	373	92	25	5	169	42	25	5	2.21
		100	308	104	34	5	186	71	38	4	1.66
		300	201	48	24	5	83	2	2	3	2.42
		600	160	94	59	5	83	22	27	4	1.94
		900	107	24	22	5	49	10	21	4	2.18
New Viburnum	1	0	1980	262	13	4	1012	381	38	4	1.96
		100	1894	355	19	5	975	138	14	5	1.94
		400	1363	253	19	18	699	148	21	18	1.95

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
New Viburnum	1	500	498	116	23	6	245	74	30	6	2.03
		600	518	518	100	6	252	232	92	6	2.05
		750	236	158	67	7	123	74	60	7	1.92
		840	1691		0	1	1125		0	1	1.50
		1200	1191	164	14	5	540	54	10	5	2.21
		1500	1626	452	28	3	647	127	20	3	2.51
		1700	1746		0	1	707		0	1	2.47
		2210	1523	266	17	6	608	137	23	6	2.50
		2360	1029	477	46	12	350	205	59	12	2.94
		2560	1367	439	32	6	467	152	33	6	2.93
		2760	642	237	37	6	268	79	29	6	2.40
		2860	716	99	14	6	217	29	14	6	3.29
	2	0	1150	459	40	5	597	291	49	5	1.93
		100	1699	276	16	5	776	153	20	5	2.19
		200	1599	266	17	5	734	120	16	5	2.18
		300	1081	238	22	21	584	184	31	20	1.85
		450	850	508	60	5	390	239	61	5	2.18
		500	319	71	22	5	162	34	21	4	1.97
		600	259	22	8	5	124	12	9	3	2.10
		700	284	97	34	5	131	20	16	3	2.17
		850	462	157	34	5	243	50	20	3	1.90
		1000	335	92	27	5	148	26	18	3	2.27
		1300	266	80	30	5	122	41	33	4	2.19
	3	0	1213	422	35	5	820	305	37	5	1.48
		100	653	344	53	6	322	236	73	6	2.03
		200	587	339	58	5	171	108	63	5	3.45
		300	470	155	33	5	162	56	35	4	2.90
		400	536	246	46	5	167	89	53	4	3.22
		450	326	111	34	5	88	30	35	4	3.70
		800	567	167	29	6	163	49	30	6	3.47
		1000	293	87	30	6	109	41	38	6	2.70
		1200	201	73	36	6	83	33	40	6	2.43
		1300	249	78	31	6	108	47	43	6	2.31

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
New Viburnum	3	1500	130	37	28	6	51	16	32	6	2.54
		1550	123	22	18	6	54	23	42	6	2.26
	3 (duff)	100	948	407	43	5	307	155	51	5	3.09
		200	1010	182	18	4	369	91	25	4	2.73
		300	685	217	32	5	274	41	15	4	2.50
		400	626	214	34	5	214	82	39	5	2.93
		450	772	193	25	5	273	80	29	5	2.83
	4	0	1205	473	39	6	772	506	66	6	1.56
		100	1619	175	11	6	735	244	33	6	2.20
		200	1542	308	20	6	616	137	22	6	2.50
		300	1013	434	43	6	433	160	37	6	2.34
		400	1556	436	28	6	644	172	27	6	2.42
		500	783	374	48	6	315	144	46	6	2.49
		550	632	175	28	6	201	43	22	6	3.15
		600	384	233	61	24	150	74	49	24	2.56
		700	338	38	11	6	158	29	18	6	2.15
		900	351	67	19	6	163	28	17	6	2.15
		1360	533	185	35	6	200	71	35	6	2.66
		2000	398	133	33	6	144	58	41	6	2.77
		2250	170	61	36	10	75	25	33	10	2.25
		2400	225	111	49	6	89	28	32	6	2.53
		2500	512	133	26	6	174	34	20	6	2.95
		2700	333	121	36	6	111	42	37	6	2.99
		3200	172	56	32	6	56	14	25	6	3.04
		3700	252	146	58	6	82	55	68	6	3.07
	5	0	1601	259	16	6	715	85	12	6	2.24
		300	1359	336	25	6	633	122	19	6	2.15
		350	1042	327	31	6	496	164	33	6	2.10
		400	854	208	24	6	358	85	24	6	2.39
		550	624	161	26	6	243	52	22	6	2.56
		700	548	49	9	25	217	19	9	25	2.52
		750	574	92	16	6	232	48	20	6	2.47
		800	472	82	17	9	182	32	18	9	2.59

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
New Viburnum	5	900	510	129	25	6	203	50	24	6	2.52
		1000	375	100	27	6	143	43	30	6	2.63
		1200	373	63	17	6	152	28	18	6	2.44
		1500	163	28	17	6	69	19	27	6	2.36
		1550	185	45	24	6	140	133	95	6	1.32
		1700	149	33	22	6	112	33	29	6	1.33
		1800	138	17	12	6	59	11	18	6	2.36
		1950	193	29	15	6	75	10	13	6	2.57
		2100	226	27	12	6	76	17	23	6	2.99
		2300	345	238	69	11	112	64	57	11	3.09
Old Viburnum	1	0	146	41	28	5	57	6	11	2	2.58
		25	234	111	48	4	278	325	117	3	0.84
		50	113	16	14	2	63	11	17	2	1.80
	2	0	183	47	26	4	96	0	0	2	1.91
		50	177	13	7	5	58	12	20	3	3.04
		100	311	101	33	23	95	10	11	16	3.27
		150	332	233	70	4	112	30	26	3	2.96
		450	297	173	58	6	78	42	54	4	3.79
		450	452	157	35	6	108	17	16	6	4.19
		600	406	118	29	6	108	18	17	6	3.77
		850	265	103	39	6	90	32	36	6	2.95
		1000	301	59	19	6	91	20	22	6	3.30
		1100	341	125	37	6	96	37	39	6	3.53
		1250	248	99	40	6	87	41	47	6	2.84
		1450	233	76	32	6	75	24	32	6	3.10
		1550	216	79	36	6	77	31	40	6	2.81
		1800	179	82	46	6	50	21	43	6	3.54
		2000	199	100	50	6	51	22	44	6	3.92
	3	0	313	31	10	6	402	52	13	6	0.78
		50	450	104	23	6	395	49	12	6	1.14
		100	622	273	44	6	631	462	73	6	0.99
		150	580	151	26	6	221	51	23	6	2.63
		200	668	247	37	9	232	63	27	9	2.88

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
Old Viburnum	3	250	535	182	34	6	183	63	34	6	2.93
		300	604	252	42	9	191	74	39	9	3.16
		350	504	215	43	6	159	48	31	6	3.18
		400	386	71	18	6	119	17	14	6	3.23
		500	437	133	30	6	122	33	27	6	3.59
		550	397	199	50	6	112	56	50	6	3.54
		600	271	81	30	6	82	25	31	6	3.31
		700	416	130	31	6	105	35	34	6	3.96
		800	626	162	26	25	139	32	23	25	4.50
		900	440	105	24	6	100	28	28	6	4.42
		1000	517	116	22	6	115	25	22	6	4.49
		1200	553	230	42	6	108	46	42	6	5.13
		1300	756	334	44	6	139	48	34	6	5.45
		1400	1275	191	15	6	226	26	11	6	5.63
	4	0	431	263	61	6	490	359	73	6	0.88
		20	218	68	31	6	173	123	71	6	1.26
		50	118	34	29	6	63	21	33	6	1.88
		100	104	7	7	6	51	14	27	6	2.05
		170	100	9	9	6	43	9	21	6	2.30
Sweet-water	1	0	286	82	29	5	466	129	28	5	0.61
		50	204	57	28	5	168	46	27	5	1.22
		100	138	71	52	5	117	66	56	5	1.18
		150	67	47	70	5	52	44	85	5	1.29
	2	0	974	461	47	6	935	400	43	6	1.04
		200	277	220	79	5	208	87	42	5	1.33
		250	281	193	69	10	188	111	59	10	1.50
		300	225	94	42	4	141	24	17	2	1.60
		350	217	186	86	2	4097	5420	132	2	0.05
		450	209	83	40	4	176	49	28	3	1.19
		600	156	35	23	3	113	19	17	3	1.38
		700	188	176	94	5	175	150	86	4	1.07
	3	0	549	212	39	6	1300	726	56	6	0.42
		60	626	180	29	6	1108	201	18	6	0.57

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
Sweet-water	3	75	687	317	46	6	1352	448	33	6	0.51
		100	432	31	7	6	1097	256	23	6	0.39
		150	436	72	17	6	1022	206	20	6	0.43
		250	359	76	21	6	785	153	20	6	0.46
		450	334	55	16	6	550	90	16	6	0.61
		650	253	90	36	6	362	116	32	6	0.70
		850	239	104	43	6	212	81	38	6	1.12
		1250	183	42	23	6	129	30	23	6	1.41
		1450	248	54	22	6	150	52	34	6	1.65
		1600	177	39	22	6	118	32	27	6	1.49
		1850	233	85	37	6	145	39	27	6	1.61
		2170	186	34	18	6	145	26	18	6	1.28
		2370	122	19	15	6	91	21	23	6	1.34
	4	0	121	45	37	6	92	37	40	6	1.31
		75	104	30	29	6	97	29	30	6	1.07
West Fork	1	0	1210	368	30	5	2436	899	37	5	0.50
		50	181	103	57	5	180	89	49	4	1.00
		100	180	89	50	22	910	3047	335	17	0.20
		150	139	49	35	5	123	42	34	4	1.13
		170	155	65	42	6	98	48	48	5	1.58
		200	114	55	48	5	79	49	62	5	1.44
	2	0	364	213	59	5	631	255	40	5	0.58
		100	151	69	45	5	190	113	59	4	0.79
		150	220	132	60	5	196	52	27	3	1.13
		300	135	26	20	5	107	32	30	4	1.26
		320	140	74	53	5	116	83	71	4	1.20
	3	0	133	30	23	5	104	22	21	3	1.28
		20	132	28	21	4	115	37	32	4	1.14
		60	139	45	32	5	283	404	143	5	0.49
		100	126	19	15	5	73	18	25	4	1.73
		200	133	40	30	5	103	20	19	4	1.30
	4	0	321	121	38	5	409	215	53	5	0.79
		100	191	135	71	5	91	92	101	5	2.10

Impound-ment	Sampling Area	Distance ft	Lead				Zinc				Ratio
			Mean, mg/kg	SD	%RSD	n	Mean, mg/kg	SD	%RSD	n	Pb:Zn
West Fork	4	200	164	48	29	5	78	4	5	3	2.12
		300	190	56	29	5	57	10	17	3	3.32
		400	224	80	36	5	85	6	7	4	2.65
		600	149	98	66	21	32	10	31	16	4.67

Table C-2. Mean lead and zinc concentrations from sampling areas near Buick smelter, in the Viburnum Trend Mining District, measured in-situ using a handheld XRF device.

Sampling Area	Distance from Start of Transect (ft)	Distance from Smelter (ft)	Lead (Pb)				Zinc (Zn)			
			Mean (mg/kg)	Standard Deviation	% RSD	n	Mean (mg/kg)	Standard Deviation	% RSD	n
1	0	12214	455.7	240.6	52.8	7	81.8	43.3	53.0	7
	350	12546	630.9	178.6	28.3	6	81.4	17.7	21.8	6
	790	12953	681.2	303.0	44.5	6	98.4	41.5	42.2	6
	1200	13323	1208.1	452.5	37.5	6	117.1	34.1	29.1	6
	1590	13660	302.6	154.7	51.1	6	78.9	33.5	42.4	6
	2130	14144	1264.0	480.0	38.0	6	109.8	17.7	16.1	6
	2570	14547	447.1	152.2	34.0	6	79.6	35.6	44.7	6
	4870	17430	400.3	141.1	35.3	6	74.3	30.2	40.7	6
3	0	6537	585.6	187.5	32.0	6	99.1	20.9	21.1	6
	530	6727	2449.8	593.2	24.2	6	382.5	163.0	42.6	6
	1050	7232	591.3	439.2	74.3	6	87.3	40.8	46.7	6
	1350	7521	664.5	350.6	52.8	6	92.7	66.3	71.5	6
	2050	8155	897.4	268.0	29.9	6	198.8	76.2	38.3	6
4	0	13810	150.7	56.3	37.4	6	46.9	16.5	35.2	6
	430	14253	346.7	120.9	34.9	6	88.4	51.7	58.5	6
	750	14557	713.7	369.3	51.7	6	110.6	44.7	40.4	6
	1400	15217	547.0	232.9	42.6	6	84.9	21.9	25.8	6
	1990	15705	361.6	140.7	38.9	6	97.1	52.8	54.3	6
	2440	16249	243.1	47.2	19.4	6	93.2	26.4	28.4	6
8	0	10550	558.2	147.7	26.5	6	58.6	15.7	26.7	6
	450	10996	728.1	316.6	43.5	6	91.3	29.7	32.6	6
	1700	12073	428.6	174.7	40.8	6	80.7	35.0	43.4	6
	2250	12623	470.1	161.8	34.4	6	61.7	21.1	34.2	6
	4100	14461	130.6	36.6	28.0	6	44.7	26.9	60.2	6
	4710	15093	309.8	159.0	51.3	6	60.1	23.6	39.2	6
10	0	11854	460.2	142.8	31.0	6	61.8	28.9	46.8	6
	145	11978	1123.2	381.0	33.9	6	141.6	81.3	57.4	6
	310	12304	607.7	91.7	15.1	6	51.6	15.6	30.3	6
	465	12462	552.0	185.6	33.6	6	68.4	19.1	27.9	6
	680	12700	642.7	225.6	35.1	6	72.7	44.2	60.8	6
	880	12959	532.2	261.4	49.1	6	56.3	11.9	21.2	6

Sampling Area	Distance from Start of Transect (ft)	Distance from Smelter (ft)	Lead (Pb)				Zinc (Zn)			
			Mean (mg/kg)	Standard Deviation	% RSD	n	Mean (mg/kg)	Standard Deviation	% RSD	n
10	1330	13438	513.1	273.1	53.2	6	46.8	25.2	53.8	6
	1680	13785	651.4	212.6	32.6	6	77.0	28.7	37.2	6
	2120	14217	298.4	166.9	55.9	6	54.5	18.9	34.6	6
	2320	14389	467.7	175.2	37.5	6	59.6	31.2	52.3	6
	4970	15759	506.4	133.3	26.3	6	51.6	11.4	22.1	6
	5120	16423	395.3	232.3	58.8	6	68.7	42.2	61.5	6
12	0	20284	542.2	339.6	62.6	7	66.4	32.3	48.6	7
	300	19958	968.8	415.0	42.8	6	106.3	47.0	44.2	6
	760	19494	438.7	192.8	43.9	6	59.2	27.3	46.0	6
	1280	19005	243.8	68.2	28.0	6	58.7	21.2	36.2	6
	1780	18532	155.3	56.7	36.5	6	23.4	11.6	49.6	6
	2330	17995	435.2	203.2	46.7	6	62.7	15.4	24.6	6
	2890	17461	853.0	188.4	22.1	6	96.7	48.6	50.2	6
	3130	17225	587.9	233.1	39.6	6	64.9	26.2	40.4	6

Table C-3. Regression equations derived from in-situ XRF data for lead. Italicized P-values are not statistically significant (P > 0.05)

Impoundment	Sampling Area	Equation	R^2	p value	Predicted Distance (ft)	
					Pb = 490 mg/kg	Pb = 147 mg/kg
Brushy Creek	1	y = -0.9063x + 671.03	0.82	0.002	199.7	576.0
	2	y = -0.5099x + 373.43	0.91	0.003	0.0	440.1
	3	y = -1.1009x + 945.78	0.74	< 0.001	414.0	723.8
Buick	1	y = -0.3424x + 1113.2	0.37	0.016	1820.1	2816.0
	2	y = -1.0395x + 926.93	0.79	0.003	420.3	748.4
	3	No T-Zone	NA	NA	0.0	0.0
	4	y = -0.0952x + 204.19	0.07	*0.561*	0.0	579.7
	5	y = -0.1476x + 517.74	0.42	0.007	187.9	2498.2
	7	y = -0.8722x + 737.82	0.58	0.047	284.1	675.1
Fletcher	1	y = -17.53x + 615.11	0.26	0.007	7.1	26.6
	2	y = -0.1029x + 252.85	0.12	*0.391*	0.0	1009.2
	3	y = -0.1834x + 157.43	0.22	*0.283*	0.0	46.0
	4	y = -0.7137x + 311.57	0.94	0.030	0.0	227.8
	5	y = -0.278x + 339.04	0.92	0.010	0.0	683.6
New Viburnum	1	y = -0.1658x + 1364.7	0.08	*0.401*	5275.6	7332.3
	2	y = -1.096x + 1395.6	0.62	0.003	826.3	1137.4
	3	y = -0.4016x + 769.19	0.67	0.001	695.2	1544.3
	4	y = -0.2601x + 984.31	0.41	0.003	1900.5	3211.5
	5	y = -0.5124x + 1078.5	0.70	< 0.001	1148.5	1814.0
Old Viburnum	1	No T-Zone	NA	NA	0.0	0.0
	2	y = -0.0418x + 312.27	0.12	*0.206*	0.0	3906.0
	3	y = -0.2425x + 551.31	0.17	*0.177*	252.8	1659.0
	4	y = -1.5662x + 316.68	0.55	*0.258*	0.0	107.1
Sweetwater	1	y = -1.2649x + 276.89	0.99	0.006	0.0	101.1
	2	y = -0.2349x + 316.56	0.77	0.010	0.0	713.3
	3	y = -0.1736x + 494.3	0.69	< 0.001	24.8	1989.1
	4	No T-Zone	NA	NA	0.0	0.0
West Fork	1	y = -0.3731x + 209.31	0.77	*0.052*	0.0	161.6
	2	y = -0.5255x + 311.56	0.68	*0.087*	0.0	309.3
	3	No T-Zone	NA	NA	0.0	0.0
	4	y = -0.1812x + 255.64	0.41	*0.173*	0.0	588.5

Table C-4. Regression equations derived from in-situ XRF data for zinc. Italicized P-values are not statistically significant (P > 0.05)

Impoundment	Sampling Area	Equation	R^2	p value	Predicted Distance (ft)	
					Zn = 448 mg/kg	Zn = 160 mg/kg
Brushy Creek	1	y = -0.9307x + 579.98	0.8801	0.002	141.8	451.3
	2	y = -0.3528x + 239.37	0.8388	0.01	0.0	225.0
	3	y = -0.9485x + 784.23	0.5434	0.002	354.5	658.1
Buick	1	y = -0.1603x + 425.03	0.4777	0.003	0.0	1653.3
	2	y = -0.6997x + 592.93	0.8306	0.002	207.1	618.7
	3	No T-Zone	NA	NA	0.0	0.0
	4	No T-Zone	NA	NA	0.0	0.0
	5	y = -0.0752x + 208.4	0.4313	0.006	0.0	643.6
	7	y = -0.3781x + 308.63	0.4539	*0.097*	0.0	393.1
Fletcher	1	y = -26.068x + 742.84	0.8011	0.04	11.3	22.4
	2	y = -0.1157x + 163.05	0.1795	*0.296*	0.0	26.4
	3	No T-Zone	NA	NA	0.0	0.0
	4	y = -0.5153x + 238.4	0.9507	0.025	0.0	152.1
	5	y = -0.1434x + 170.34	0.8113	0.037	0.0	72.1
New Viburnum	1	y = -0.1376x + 734.79	0.1894	*0.105*	2084.2	4177.3
	2	y = -0.5355x + 677.52	0.6618	0.002	428.6	966.4
	3	y =-0.2147x + 364.43	0.3952	0.029	0.0	952.2
	4	y = -0.147x + 488.48	0.5393	< 0.001	275.4	2234.6
	5	y = -0.2298x + 477.14	0.6742	< 0.001	126.8	1380.1
Old Viburnum	1	No T-Zone	NA	NA	0.0	0.0
	2	No T-Zone	NA	NA	0.0	0.0
	3	y = -0.6133x + 416.12	0.6804	< 0.001	0.0	417.6
	4	y = -1.8047x + 289.56	0.468	*0.203*	0.0	71.8
Sweetwater	1	y = -2.225x + 382.81	0.7837	*0.115*	0.0	100.1
	2	y = -0.088x + 202.96	0.2209	*0.347*	0.0	488.2
	3	y = -0.5092x + 1029.9	0.7668	< 0.001	1142.8	1708.4
	4	No T-Zone	NA	NA	0.0	0.0
West Fork	1	y = -8.4842x + 1686.9	0.5906	*0.074*	146.3	180.3
	2	y = -1.2462x + 507.89	0.7472	*0.058*	48.1	279.2
	3	No T-Zone	NA	NA	0.0	0.0
	4	y = -0.45x + 247.17	0.4842	*0.124*	0.0	193.7

Table C-5. Comparison of In-Situ and Incremental Composite Sample (ICS) results for lead concentrations (mg/kg) from variable size Sampling Units (SU).

Tailings Impoundment	Sampling Area	Sampling Unit (length)	SU Size (ft^2)	ICS Replicate	ICS Results	Average of In-Situ Readings (# of readings)	Average of ICS Results	Standard Deviation of In-Situ Results	Standard Deviation of ICS Results	Percent Difference of ICS vs. In-Situ	95% UCL of ICS Results
Brushy Creek	SA1	SU1 (0-170')	10200	1	710	654 (n=10)	721	274	12.8	10%	743
				2	718						
				3	735						
		SU2 (170-500')	19800	1	360	296 (n=29)	387	87	39	27%	453
				2	432						
				3	370						
Buick	SA1	SU1 (0'-525')*	31500	--	918	1241 (n=35)	918	705	26**	30%	983
	SA2	SU1 (0'-330')*	19800	1	771	792 (n=14)	758	455	22	4%	813
				2	770						
				3	732						
		SU2 (330'-800')*	28200	1	346	366 (n=31)	363	198	14	1%	399
				2	368						
				3	374						
	SA4	SU1 (0-250')*	1500	--	213	195 (n=30)	213	84	8.1**	9%	233
Fletcher	SA1	SU1 (0-20')	1200	--	430	483 (n=28)	430	390	43**	12%	538
		SU2 (20-1100')	64800	--	206	131 (n=50)	206	46	8.1**	45%	226
	SA2	SU1 (0-700')	42000	--	--	259 (n=61)	--	137	--	--	--
	SA3	SU1 (0-300')	18000	--	--	144 (n=31)	--	98	--	--	--
	SA4	SU1 (0-270')	16200	--	--	225 (n=19)	--	122	--	--	--
	SA5	SU1 (0-600')	36000	--	--	250 (n=20)	--	235	--	--	--
New Viburnum	SA1	SU1 (0'-500')	30000	--	1524	1361 (n=33)	1524	539	112**	11%	1814
	SA2	SU1 (0'-330')	19800	1	2043	1248 (n=36)	2146	372	112	53%	2334
				2	2129						
				3	2265						
	SA3	SU1 (0'-300')	18000	--	--	727 (n=21)	--	419	--	--	--
		SU2 (300'-450')	9000	--	--	431 (n=10)	--	211	--	--	--
Old Viburnum	SA2	SU1 (0-450')	27000	1	395	283 (n=42)	416	128	23	38%	455
				2	412						
				3	441						
Sweetwater	SA1	SU1 (0-100')	6000	1	155	209 (n=15)	148	91	6.4	34%	159
				2	143						
				3	145						
	SA2	SU1 (0-700')	42000	--	--	349 (n=39)	--	347	--	--	--
West Fork	SA1	SU1 (0-170')	10200	--	--	292 (n=38)	--	324	--	--	--
	SA2	SU1 (0'-320')	19200	1	273	202 (n=25)	226	412	19.4	11%	300
				2	219						
				3	186						
	SA3	SU1 (0-200')	12000	--	--	133 (n=24)	--	31	--		--
	SA4	SU1 (0'-600')	36000	1	198	187 (n=46)	164	106	43.5	13%	237
				2	179						
				3	115						

*ICS results on 50-increment composite samples; soil sieved to 0.25 mm. All other ICS results are on 30-increment samples sieved to 2mm.

**No replicates collected in this SU. For purposed of calculating a UCL, the SD was borrowed from an SU in which replicates were collected.

Table C-6. Comparison of In-Situ and Incremental Composite Sample (ICS) results for zinc concentrations (mg/kg) from variable size Sampling Units (SU).

Tailings Impoundment	Sampling Area	Sampling Unit (length)	SU Size (ft²)	ICS Replicate	ICS Results	Average of In-Situ Readings (# of readings)	Average of ICS Results	Standard Deviation of In-Situ Results	Standard Deviation of ICS Results	95% UCL of In-Situ Readings	95% UCL of ICS Results
Brushy Creek	SA1	SU1 (0-170')	10200	1	439	531 (n=10)	447	235	18.4	17%	478
				2	468						
				3	434						
		SU2 (170-500')	19800	1	267	221 (n=31)	273	73	22.1	21%	310
				2	297						
				3	254						
Buick	SA1	SU1 (0'-525')*	31500	--	294	459 (n=35)	294	282	22**	44%	331
	SA2	SU1 (0'-330')*	19800	1	497	491 (n=15)	498	285	29.0	1%	547
				2	528						
				3	470						
		SU2 (330'-800')*	28200	1	201	171 (n=32)	205	103	3.5	18%	211
				2	208						
				3	205						
	SA4	SU1 (0-250')*	1500	--	77	54 (n=30)	77	21	12.5**	35%	98
Fletcher	SA1	SU1 (0-20')	1200	--	352	438 (n=28)	352	364	18.4**	22%	383
		SU2 (20-1100')	64800	--	98	63 (n=53)	98	28	7.8**	43%	111
	SA2	SU1 (0-700')	42000	--	--	146 (n=61)	--	84	--	--	--
	SA3	SU1 (0-300')	18000	--	--	97 (n=29)	--	72	--	--	--
	SA4	SU1 (0-270')	16200	--	--	165 (n=17)	--	83	--	--	--
	SA5	SU1 (0-600')	36000	--	--	128 (n=20)	--	58	--	--	--
New Viburnum	SA1	SU1 (0'-500')	30000	--	826	694 (n=33)	826	302	120.5**	17%	1029
	SA2	SU1 (0'-330')	19800	1	987	637 (n=37)	1023	196	120.5	46%	1226
				2	924						
				3	1157						
	SA3	SU1 (0'-300')	18000	--	--	406 (n=18)	--	338	--	--	--
		SU2 (300'-450')	9000	--	--	127 (n=10)	--	74	--	--	--
Old Viburnum	SA2	SU1 (0-450')	27000	1	120	92 (n=30)	125	23	7.8	30%	138
				2	121						
				3	134						
Sweetwater	SA1	SU1 (0-100')	6000	1	188	250 (n=15)	169	179	17.5	39%	198
				2	154						
				3	164						
	SA2	SU1 (0-700')	42000	--	--	313 (n=34)	--	342	--	--	--
West Fork	SA1	SU1 (0-170')	10200	--	--	446 (n=34)	--	857	--	--	--
	SA2	SU1 (0'-320')	19200	1	201	270 (n=20)	201	254	24.5	29%	242
				2	225						
				3	176						
	SA3	SU1 (0-200')	12000	--	--	99 (n=18)	--	27	--		--
	SA4	SU1 (0'-600')	36000	1	83	104 (n=36)	77	149	12.5	29%	98
				2	86						
				3	63						

*ICS results on 50-increment composite samples; soil sieved to 0.25 mm. All other ICS results are on 30-increment samples sieved to 2mm.

**No replicates collected in this SU. For purposed of calculating a UCL, the SD was borrowed from an SU in which replicates were collected.

Table C-7. Comparison of in-situ and incremental composite sample (ICS) results for lead concentrations (mg/kg) from fixed-distance Sampling Units (SUs).

Tailings Impoundment	Sampling Area	Distance From Tailings (ft)	ICS Replicate	ICS Results	Average of In-Situ Readings	Average of ICS Results	Standard Deviation of In-Situ	Standard Deviation of ICS	Percent Difference of ICS vs. In-Situ	95% UCL of ICS Results
Brushy Creek	2	30	1	449	353	453	79	38.7	25%	519.0
			2	494						
			3	417						
	3	50	1	1349	1108	1326	240	20.4	18%	136.0
			2	1310						
			3	1319						
		720	--	123	134	123	42	--	9%	--
Buick	5	90	1	639	594	631	184	58.0	6%	728.0
			2	684						
			3	569						
		965	--	460	345	460	203	--	29%	--
	7	50	--	878	734	878	432	--	18%	--
		1760	1	569	605	554	188	16.1	9%	581.0
			2	556						
			3	537						
New Viburnum	1	2210	Duff 1	2369	1523	2606	266	209.4	52%	2959.0
			Duff 2	2685						
			Duff 3	2765						
			Mineral	509	--	509	--	--	--	--
	3	800	1	821	567	893	167	65.2	45%	1003.0
			2	910						
			3	948						
	4	550	1	997	632	1038	175	112.8	49%	1229.0
			2	1166						
			3	952						
		3700	--	214	252	214	146	--	16%	--
	5	750	1	776	574	769	92	11.0	29%	787.0
			2	774						
			3	756						
		1700	--	162	149	162	33	--	8%	--
Old Viburnum	2	1000	1	311	301	312	59	22.0	4%	349.0
			2	335						
			3	291						
	3	100	--	1399	622	1399	273	--	77%	--
		600	1	469	271	491	81	19.2	58%	523.0
			2	500						
			3	504						
	4	20	1	311	218	334	68	20.0	42%	368.0
			2	347						
			3	344						
Sweetwater	3	100	--	679	432	679	31	--	44%	--
		2170	1	201	186	212	34	19.3	13%	244.0
			2	200						
			3	234						

Table C-8. Comparison of in-situ and incremental composite sample (ICS) results for zinc concentrations (mg/kg) from fixed-distance Sampling Units (SUs).

Tailings Impoundment	Sampling Area	Distance From Tailings (ft)	ICS Replicate	ICS Results	Average of In-Situ Readings	Average of ICS Results	Standard Deviation of In-Situ	Standard Deviation of ICS	Percent Difference of ICS vs. In-Situ	95% UCL of ICS Results
Brushy Creek	2	30	1	240	229	247	52	30.1	8%	3
			2	280						
			3	221						
	3	50	1	1624	1522	1534	388	157.0	1%	18
			2	1626						
			3	1353						
		720	--	85	100	85	25	--	16%	--
Buick	5	90	1	243	237	229	72	36.7	4%	290
			2	256						
			3	187						
		965	--	104	95	104	54	--	9%	--
	7	50	--	271	260	271	142	--	4%	--
		1760	1	143	187	133	96	8.7	34%	148
			2	128						
			3	128						
New Viburnum	1	2210	Duff 1	862	608	912	137	46.6	40%	991
			Duff 2	921						
			Duff 3	954						
			Mineral	108	--	108	--	--	--	--
	3	800	1	193	163	218	49	24.1	29%	259
			2	221						
			3	241						
	4	550	1	350	201	356	43	32.0	56%	410
			2	391						
			3	328						
		3700	--	72	82	72	55	--	13%	--
	5	750	1	273	232	286	48	14.8	21%	311
			2	282						
			3	302						
		1700	--	129	112	129	33	--	14%	--
Old Viburnum	2	1000	1	73	91	74	21	3.1	21%	79
			2	77						
			3	71						
	3	100	--	950	631	950	462	--	40%	--
		600	1	124	82	131	25	5.8	46%	140
			2	134						
			3	134						
	4	20	1	206	173	232	123	23.6	29%	272
			2	252						
			3	238						
Sweetwater	3	100	--	1457	1097	1457	256	--	28%	--
		2170	1	123	145	132	26	12.9	9%	154
			2	127						
			3	147						

APPENDIX D
Sampling Documentation

Contents:

- Field Data Sheets
- Soil Sample Log Sheets
- Chain of Custody Sheets
- Laboratory Reports

APPENDIX E
Sampling and Analysis Plans

Contents:

- Sampling and Analysis Plan for the Viburnum Trend Lead Mining District Transition Zone Assessment Study.
- Sampling Design Modifications for Field Work Conducted the Week of April 8, 2013
- Buick Smelter Sampling and Analysis Plan