

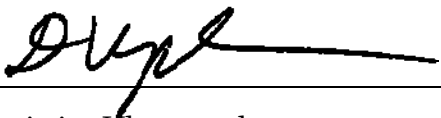
EXPERT REPORT of DIMITRIOS VLASSOPOULOS

Pakootas, et al. v. Teck Cominco Metals, Ltd.
Case No. CV-04-0256-LRS United States District
Court for Eastern District of Washington

Prepared for

The Confederated Tribes of the Colville Reservation
and the State of Washington

Prepared by



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1 INTRODUCTION

1.1 Retention and Assignment

I have been retained jointly by the State of Washington and the Confederated Tribes of the Colville Reservation (CCT) to render expert opinions in this case with regard to the release of toxic constituents from Teck Cominco's Trail Operations, located approximately 10 miles upstream from the United States-Canada border in Trail, British Columbia, Canada, to the Upper Columbia River (UCR) site in northeastern Washington state. Specifically, I was asked to give my opinions on the occurrence and release of toxic elements associated with wastes originating at the Trail smelter that have been discharged into the Columbia River in Canada and subsequently transported into the United States, where they have accumulated in the river sediments upstream of the Grand Coulee Dam.

The opinions presented herein are based on review of pertinent reports, data, publications, and other documents, as well as results of additional field and laboratory investigations conducted in support of my evaluations.

1.2 Qualifications

I am a Senior Associate with Anchor QEA, LLC, a privately owned environmental science and engineering consulting firm with corporate headquarters in Seattle, Washington. I am located in the firm's Portland, Oregon, office and my primary area of expertise is in geochemistry. In this capacity, I conduct scientific investigations for various clients and provide expert consultant services. Prior to joining Anchor QEA in July 2010, I was an Associate with S.S. Papadopoulos and Associates, Inc. (SSPA), a water-resources and environmental consulting firm. I was continuously employed at SSPA since first joining the firm in 1992, and managed the firm's Portland, Oregon, office between 2006 and June 2010.

My education and experience encompasses the fields of geochemistry, geology, and hydrogeology. I hold a Ph.D. in Environmental Sciences with a specialty in geochemistry from the University of Virginia, a M.S. in Geochemistry from the California Institute of Technology, a M.Sc. in Geological Sciences from McGill University, and a B.Sc. in Geology (with Honors) from Concordia University. Additional details of my credentials, professional

experience, publication record, and previous depositions and testimony given can be found in my resume, which is provided as Appendix A.

1.3 Compensation

Anchor QEA is being compensated at my standard billing rate of \$183 per hour for office work and \$274.50 for deposition and trial testimony.

2 STATEMENT OF OPINIONS

2.1 Opinion 1

Slag and liquid wastes generated at Teck Cominco's Trail Operations have been historically discharged into the Columbia River at Trail, British Columbia. These materials have been transported by the river into the United States, where they have accumulated within and contaminated the sediments of the Upper Columbia River and Lake Roosevelt, between the U.S.-Canada border and the Grand Coulee Dam.

2.2 Opinion 2

Slag discharged from the Teck Cominco smelter is a predominantly glassy material. Once released into the aquatic environment, it slowly but irreversibly breaks down to more stable weathering products by physical and chemical processes. Through the action of these processes, heavy metals and other potentially toxic constituents present in the slag including arsenic, antimony, barium, cadmium, copper, lead, and zinc are released over time from the slag to the sediment porewater and the aquatic environment.

2.3 Opinion 3

Metals associated with sewer effluents from the Trail smelter (including arsenic, cadmium, copper, mercury, lead, and zinc) have been discharged in both dissolved and particulate forms. Particulate-bound metals are carried downriver and eventually settle out of the water column as fine-grained sediment in depositional areas. Part of the dissolved metals load released to the river system will adsorb onto suspended particulate matter and is also carried downriver and eventually deposited as sediment. Biogeochemical processes occurring within these sediments result in the remobilization of sediment-bound metals, and their release into sediment porewater and the aquatic environment. The rate and extent of metals release is a function of biogeochemical redox conditions within the sediments, which are expected to vary across the Upper Columbia River site, depending in part on factors such as sediment grain size, organic matter content, metal concentrations, and burial depth.

2.4 Opinion 4

The smelter slag and liquid effluent-related metals present in the sediments of the Upper Columbia River represent continuing, long-term sources of potentially toxic metal

contaminants. Slag weathering processes and subsurface sediment biogeochemical processes drive the release of metals stored in the contaminated sediments, facilitating their transfer to the aquatic environment, and ultimately leading to environmental exposure.

3 BASES OF OPINIONS

3.1 Opinion 1

Slag and liquid wastes generated at Teck Cominco's Trail Operations have been historically discharged into the Columbia River at Trail, British Columbia. These materials have been transported by the river into the United States, where they have accumulated within and contaminated the sediments of the Upper Columbia River and Lake Roosevelt, between the U.S.-Canada border and the Grand Coulee Dam.

The Teck Cominco smelter located at Trail, British Columbia, has been in operation since 1896. Since at least 1930, water-granulated slag generated from the lead smelting operations was discharged to the Columbia River. This practice continued until 1995 when slag disposal to the river was eventually discontinued. Over this period of time, it is estimated that on the order of 13 million tons of granulated slag were produced and ultimately discharged to the Columbia River (USEPA 2006; Queneau 2010). In addition to slag, wastewater effluents from the smelter and the nearby fertilizer plant, which has been in operation since 1930, have also been discharged to the river through sewers. The British Columbia Ministry of the Environment Phase I Kootenay Air and Water Quality Study estimated total effluent volumes from all sewers was 55 to 60 million gallons per day in 1974 and 1975 (BC MoE 1977, p.31). Both slag and wastewater effluents carry significant concentrations of potentially toxic metals.

In formulating this opinion, I reviewed information on the nature, chemical composition, and quantities of the wastes generated by Teck Cominco's facilities. I also reviewed and analyzed an extensive sediment chemistry database for the UCR site, which includes data on metals concentrations compiled from previous studies, as well as new sampling conducted in support of my evaluation. I relied on two independent approaches to identify unique fingerprints of the metal-bearing wastes discharged from Trail. Using these fingerprints, I was able to establish a link between the metals in the sediments and the metals historically discharged from Trail. The approaches I used are based on two types of fingerprinting: 1) geochemical fingerprinting; and 2) lead isotope fingerprinting.

The chemical composition of slag is unique and dominates the geochemical signature of the river sediments for a significant distance downstream of Trail and into the United States.

The sediment geochemical evaluation included factor analysis of the sediment data to identify factors (i.e., geochemical signatures) that explain the observed variations in metals concentrations. By comparing these geochemical signatures with the chemical profiles of discharges from the Trail facility, I was able to recognize two of the signatures as being associated with specific sources from Trail, including slag and liquid wastes. The identification of the smelter as the source of the slag geochemical signature in UCR sediments was confirmed by its spatial distribution. Strong slag signatures are observed in sediments between Kettle Falls and Trail, but are absent upstream of Trail.

The results of the geochemical analysis were independently corroborated by collecting and analyzing sediment samples for lead isotopes. The isotope data clearly show the pervasive impact of historic discharges from the Teck Cominco smelter on sediments of the UCR from the U.S.-Canada border to Kettle Falls. From the lead isotope evaluation, I was also able to identify a number of sediment samples with little or no smelter-derived metals inputs. The metals concentrations in these samples are from one to more than two orders of magnitude lower than in overlying contaminated sediments, and clearly document the magnitude of sediment quality impacts from smelter-derived metals in this part of the river system.

The physical and chemical characteristics of Trail slag and liquid effluents, respectively, are briefly summarized in the two following subsections. This is followed by a description of the sediment chemistry database and associated data analysis, and concludes with a discussion of the lead isotope data.

3.1.1 Granulated Slag

Granulated slag is the primary solid phase byproduct of the smelting furnaces at the Trail facility that was discharged directly to the Columbia River. Slag from lead smelting is granulated using water to result in a relatively uniform grain size, which facilitates transport of the byproduct. Since the 1930s, granulated slag has been fumed to recover a portion of the residual zinc. The fuming process is also efficient at reducing the residual levels of lead in the slag. The granulated fumed slag consists predominantly of sand-sized, glassy iron-rich granules that contain various amounts of residual metals. Previous studies conducted by Cominco and others provide information on the bulk chemistry, grain size distribution, and physical properties of water-granulated fumed slag produced at Trail. As summarized in

CH2M Hill (2004b) and Queneau (2010), the bulk chemical composition of water-granulated fumed slag consists of iron (31.5 to 49.1 percent by weight as Fe₂O₃), silica (21.5 to 29.4 percent as SiO₂), and calcium (9 to 17 percent as CaO). In addition, the metals concentrations shown in Table 1 have been reported from analyses of bulk samples.

The chemical composition of slag is very distinctive compared to the typical ranges of natural soils and sediments (San Juan 1994; Mason and Dragun 1996; Reimann and de Caritat 1998). Slag is highly enriched in iron, zinc, copper, and manganese. Enrichment in antimony, barium, cadmium, chromium, cobalt, and lead may also be significant.

Table 1
Reported Metals Concentrations in Trail Smelter Slag

Metal	Concentration
Antimony	<25 (below detection limits) to 326 milligrams per kilogram (mg/kg)
Arsenic	Generally <100 mg/kg (below detection limits)
Barium	683 to 2,100 mg/kg
Cadmium	<1 (below detection limits) to 300 mg/kg
Chromium	210 to 311 mg/kg
Cobalt	37.6 to 333 mg/kg
Copper	1,800 to 11,900 mg/kg
Iron	279,000 to 339,000 mg/kg
Lead	14 to 6,650 mg/kg
Manganese	5,330 to 11,500 mg/kg
Mercury	<0.005 mg/kg (below detection limits)
Nickel	17.2 to 41.1 mg/kg
Selenium	<50 mg/kg (below detection limits)
Vanadium	56.6 to 76.6 mg/kg
Zinc	19,900 to 48,200 mg/kg

3.1.2 Liquid Effluents

Historically, wastewater effluent from the Cominco facility has been discharged to the Columbia River through several sewer outfalls including the fertilizer operation, the metallurgical plants, and the slag launder system. These sewers discharge significant quantities of metals to the river. For example, between 1980 and 1996, average discharges for dissolved metals were as high as 18 kilograms per day (kg/d) of arsenic, 62 kg/d of

cadmium, 200 kg/d of lead, and 7,400 kg/d of zinc (Cominco 1997b). Total metals discharges were generally higher than these estimates, however, because a significant portion of the metals are discharged as solid particulates. Additionally, up to 4 kg/d of total mercury and 350 kg/d of dissolved zinc were discharged from fertilizer plant operations (Cominco 1997b).

Queneau (2010) estimated the cumulative non-slag metals discharges (i.e., liquid effluents) to the Columbia River from the Trail facility between 1921 and 2005. These estimates are reproduced in Table 2. For comparison, cumulative discharges for slag-associated metals for the same time period estimated by Queneau are also provided.

Table 2
Estimated Cumulative Discharges from the Trail Facility to the Columbia River (1921-2005)

Metal	Liquid Effluents (tons)	Slag (tons)
Arsenic	677	2,838
Cadmium	972	193
Lead	22,298	45,735
Mercury	227	--
Zinc	284,222	511,870

As can be seen from Table 2, about twice as much lead and zinc was discharged to the Columbia River in the form of slag as was discharged in the form of liquid effluents, while most of the cadmium and essentially all of the mercury have come from liquid waste effluents.

These estimates do not include additional discharges of metals to the river from numerous reported spills that have occurred at the facility (MacDonald 1997), and that still occur to the present day (Duncan 2008a, 2008b).

3.1.3 Geochemical Signatures of Metals Discharges from the Trail Facility in Upper Columbia River Sediments

The historical impact of the metals discharged from the Trail facility on sediment quality in the UCR is recorded in the sediment chemistry. Metals associated with slag and liquid effluents from Trail that have been introduced into the UCR and have been deposited with other sedimentary materials will impart distinctive geochemical signatures on the sediment

deposits. The characteristically unnatural chemical composition of slag will result in higher sediment metals concentrations for the metals present in high concentrations in slag relative to naturally derived sediment components (i.e., strong enrichment in iron, zinc, copper, and manganese). Similarly, sediments impacted by liquid effluents will also be characterized by enrichment in zinc and other metals, but will be distinguishable from slag-impacted sediments notably due to the relative enrichment in mercury and cadmium. These geochemical signatures were used to identify sediments contaminated by Trail slag and liquid effluents and map their distribution within the Upper Columbia River.

3.1.3.1 UCR Sediment Chemistry Database

In conducting the evaluation of geochemical signatures, I used an extensive sediment chemistry database developed for the UCR site by the plaintiffs. This electronic database includes a compilation of sediment data obtained from the U.S. Environmental Protection Agency's RI/FS database for the UCR Site (version dated October 23, 2009), the Washington State Department of Ecology's EIMS, and the U.S. Geological Survey's NWIS and NURE databases. The database includes sediment samples from locations within the Columbia River as well as from tributary streams. I reviewed the contents of the database and consider it to be a reliable source of information for conducting the geochemical evaluations described below. The database is being provided with this report.

The database was subsequently augmented with data from: 1) sediment sampling conducted in April 2010 by Northwest Hydraulic Consultants (NHC) at several locations on the Columbia River in Canada between the Hugh Keenleyside Dam in British Columbia and the International Border (NHC 2010); and 2) sample data from a sediment coring study conducted by the CCT in May 2010 at in-river locations between the U.S.-Canada border and Northport, Washington. The Sampling and Quality Assurance Plan for the sediment coring study, sample locations, analytical laboratory reports, and an analytical data validation report performed by Anchor QEA are included in Appendix B. This additional data is being provided with this report.

I reviewed the methodology, sampling locations, and results of the NHC and sediment coring studies and consider these data to be reliable.

3.1.3.2 *Exploratory Data Analysis*

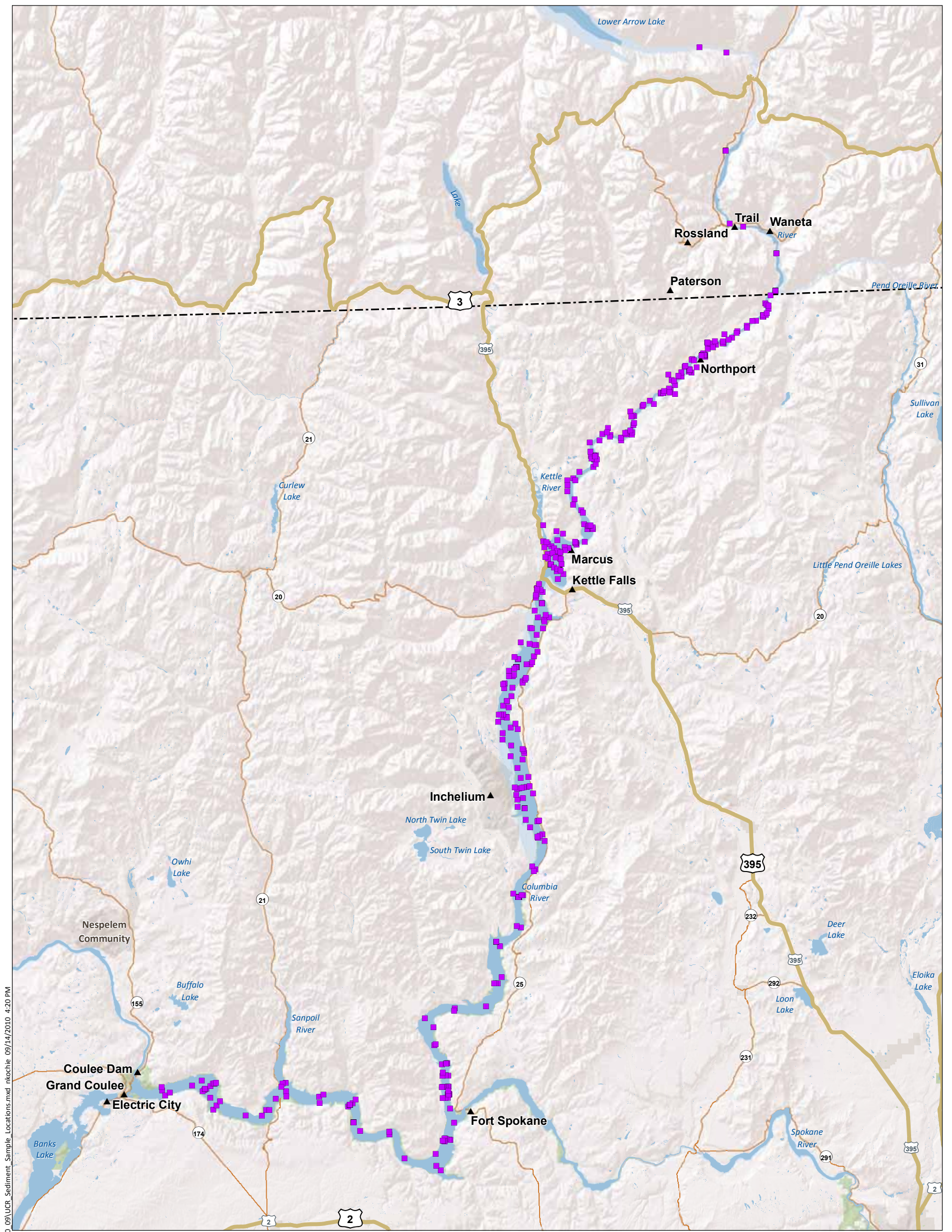
Exploratory data analysis (EDA) methods, specifically principal component analysis (PCA) and factor analysis (FA), were used to evaluate geochemical signatures of metals in UCR sediments. In general, PCA and FA are common statistical procedures used to combine the information provided by a large number of measured variables, such as the concentrations of a suite of metals in sediment samples, into a smaller number of variables that are combinations of the original variables. These new variables are referred to as components (for PCA) or factors (for FA). The first component explains as much variability in the samples as possible, with each subsequent component accounting for less and less of the remaining variability (Reimann et al. 2008).

The relative contribution of each original variable to each component or factor is typically referred to as the 'loading of variable x to Factor A'. The loading of the individual metals to each factor serves as a geochemical signature. For example, a factor indicative of high slag content would have a high loading in metals found in slag. A specific sediment sample with a high 'score' or value for this slag factor can then be interpreted as having a high slag input.

The factor scores in the samples can be mapped to examine spatial distributions of the signatures. If the score of a factor increases toward the location of a potential source, and the signature of that factor is consistent with the known chemical signature of the potential source, the obvious conclusion is that the potential source is the actual source. The power of these methods is that they rely on the multidimensional patterns in the data to identify sources, with few underlying assumptions. These methods are widely used in environmental forensic investigations for identification of contaminant sources and apportionment (Johnson et al. 2008).

A subset of the full database was initially selected for analysis based on sample locations. All sediment samples located within the Columbia River main stem were included. In addition, sediment samples in tributary streams located within one mile upstream of their confluence with the river were also included to represent the background sediment chemistry. For this sample subset, concentrations of aluminum, antimony, arsenic, barium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, sodium, vanadium, and zinc were tabulated. Sample results from the coring study that were flagged as "rejected" after quality assurance/quality control (QA/QC) review were removed,

and a small number of additional samples were removed due to inconsistencies in their records. Non-detect results were either substituted with zeros if the reported detection limit for an analysis was less than 1/100th of the maximum detected value for that analyte, or otherwise removed, and results for duplicate samples were averaged. Inspection of cross-plots identified eight samples with outliers in one or more metals (where the analyte result was at least twice as high as the next highest value), and these were also removed. The resulting dataset contains 1,386 samples. The distribution of the sample locations is shown in Figure 1.



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- Sediment Sample Locations
- ▲ Cities
- Highways
- Water Bodies
- Canadian Border



Figure 1
Sediment Sample Locations Used in Factor Analysis

Prior to analysis, the concentration data were transformed by scaling the values for each metal to the maximum concentration reported for that metal, in order to homogenize the variance of major, minor, and trace metals. PCA and FA were performed for the full suite of nineteen metals, as well as for several subsets of these metals, to evaluate the effect of including or excluding specific metals. Sodium was excluded from some subsets because its distribution appeared to be dependent on analytical method. Antimony was excluded from some subsets because it was rarely detected downstream of the confluence with the Spokane River. Finally, the common rock-forming elements aluminum, calcium, magnesium, sodium, and potassium were excluded. PCA was performed first to determine the number of significant factors. In general, the results of the PCA showed that three components account for at least 93 percent of the variance and additional components beyond these individually accounted for less than 2 percent of the variance. This was followed by extraction of the three factors using both orthogonal (varimax) and oblique (quartmin) rotation. Orthogonal factor rotation assumes the factors are not correlated, while oblique rotation allows for some correlation between factors, which is generally a more realistic assumption. The results of these analyses are provided in Appendix C.

The analysis of different subsets of metals by the two factor extraction methods described above generally produced factors that showed similar overall geochemical patterns. However, the following discussion is focused on results for the analysis that included the metals arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, vanadium, and zinc. Of the 1,386 samples in the sediment dataset, FA was performed on 604 samples that had analytical results for all thirteen of these metals.

The loadings of the metals on the three factors extracted by oblique rotation are summarized graphically in Figure 2. Factor 1 has highest loadings (in decreasing order) for iron, zinc, copper, and manganese. Factor 1 also has very low loadings for cadmium, mercury, nickel, and vanadium. These metal associations are consistent with the chemical composition of slag as described earlier in Section 3.1.1 and shown on Table 1, and Factor 1 therefore represents addition of metals to UCR sediments in proportions similar to those found in slag.

The interpretation of Factor 1 as a signature of Teck Cominco slag is confirmed by the spatial distribution of the factor scores. Figure 3 shows the distribution pattern for Factor 1 scores.

Tracing the sample scores upstream from the Grand Coulee Dam, sample scores for Factor 1 are low but abruptly increase at Kettle Falls. From Kettle Falls to Trail, the scores are variable but generally high in the river. Upstream of Trail, Factor 1 scores drop to near 0, indicating it is absent upstream of the smelter. The spatial distribution of Factor 1 scores appears to reflect the distribution of slag in the UCR at the sediment sampling locations included in the analysis. The downstream limit of the Factor 1 slag signature in the river sediments is also consistent with direct observations of slag particles in bed sediment samples by Cox et al. (2005). Based on these observations, I interpret the Factor 1 metals signature to be due to slag discharged from Trail.

Factor 2 has highest loadings for nickel and vanadium, metals that are not enriched in slag. When the major rock-forming elements were included in the analysis, aluminum and magnesium also had very high loadings on Factor 2 (not shown). The strong association with aluminum and magnesium indicates that Factor 2 most likely represents natural geologic variations in the sources of sediment components.

Factor 3 has highest loadings for cadmium, mercury, and lead. Cadmium and mercury are the two metals that were predominantly associated with the liquid effluents discharged from the Trail facility (see Table 2) and lead is also a significant component of liquid effluents. When major rock-forming elements are included in the factor analysis, magnesium also has a high loading on Factor 3 (not shown), indicating a possible association with silicate minerals. I interpret these associations as being indicative of metals originally introduced in liquid effluents that are attached to sediment particles in the river.

The interpretation of Factor 3 as a signature of Teck Cominco liquid effluents is also confirmed by the spatial distribution of the sample scores. Figure 4 shows the distribution pattern for Factor 3 scores. As occurred for Factor 1, the signal for Factor 3 abruptly decreases upstream of Trail. The highest score is found at Trail, and samples with high scores are observed throughout the UCR site downstream from Trail. These observations point to liquid effluents from Trail as the source of the Factor 3 metals signature.

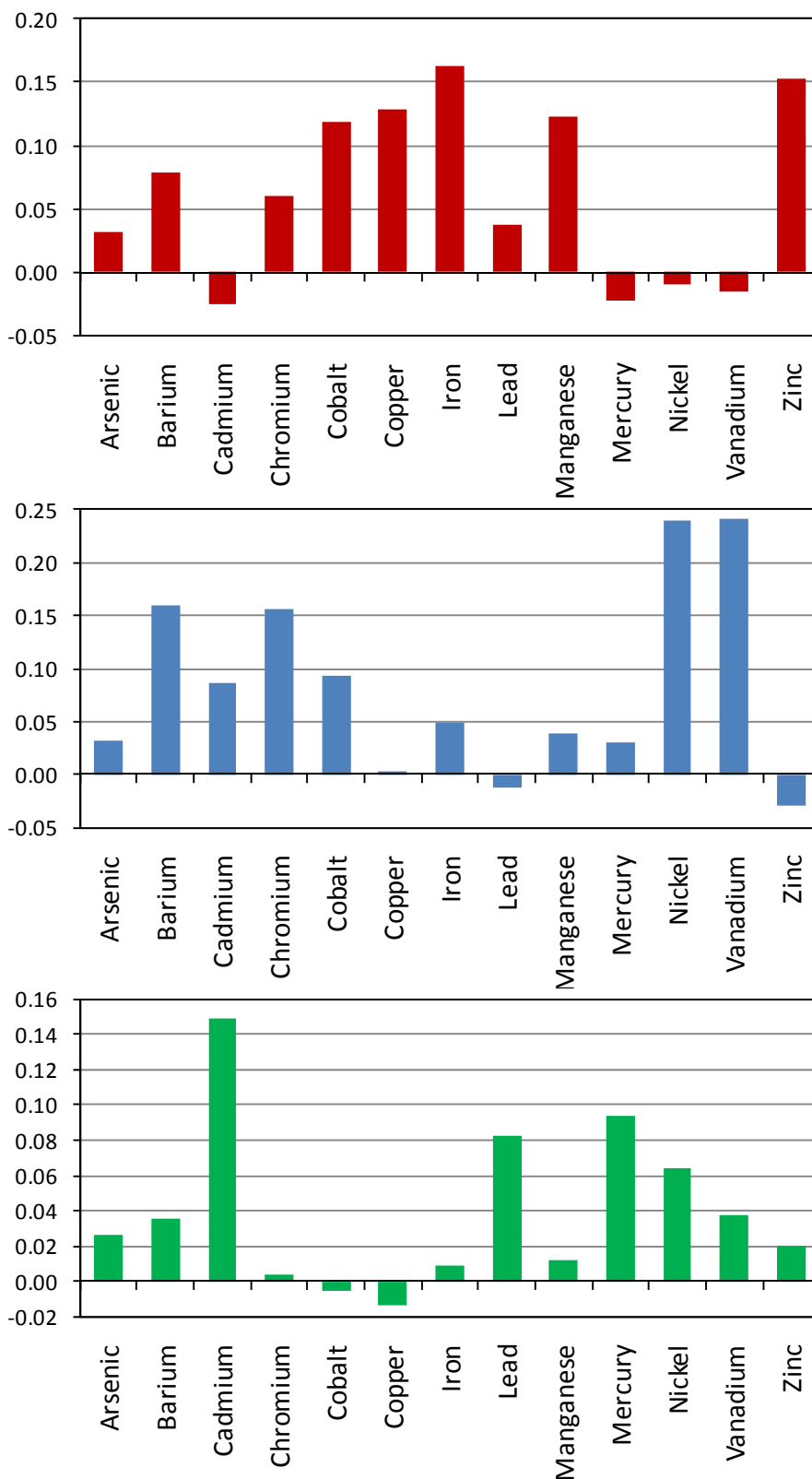
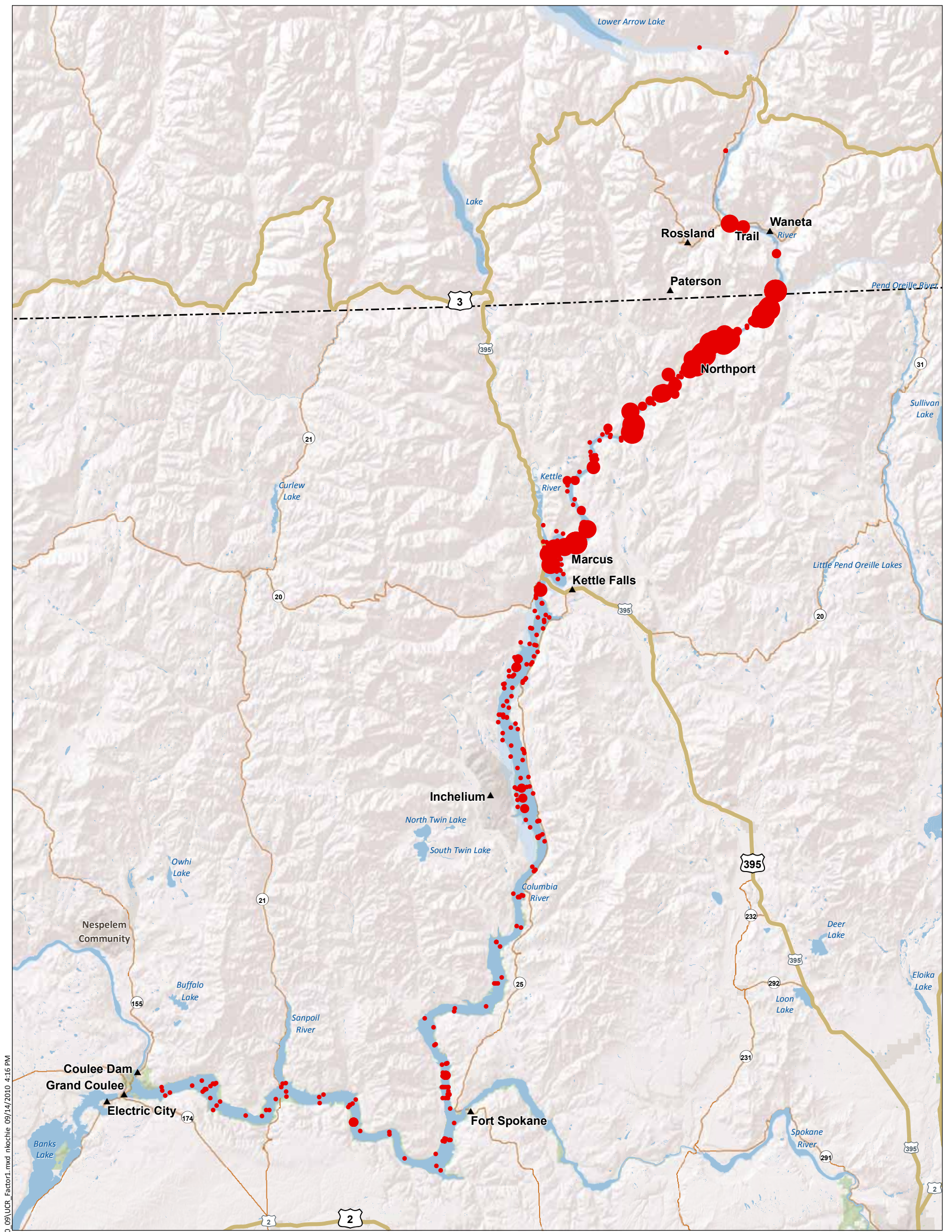



Figure 2
Metals loadings on Factor 1 (top), Factor 2 (middle), and Factor 3 (bottom)

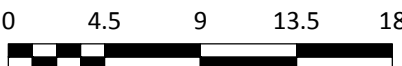


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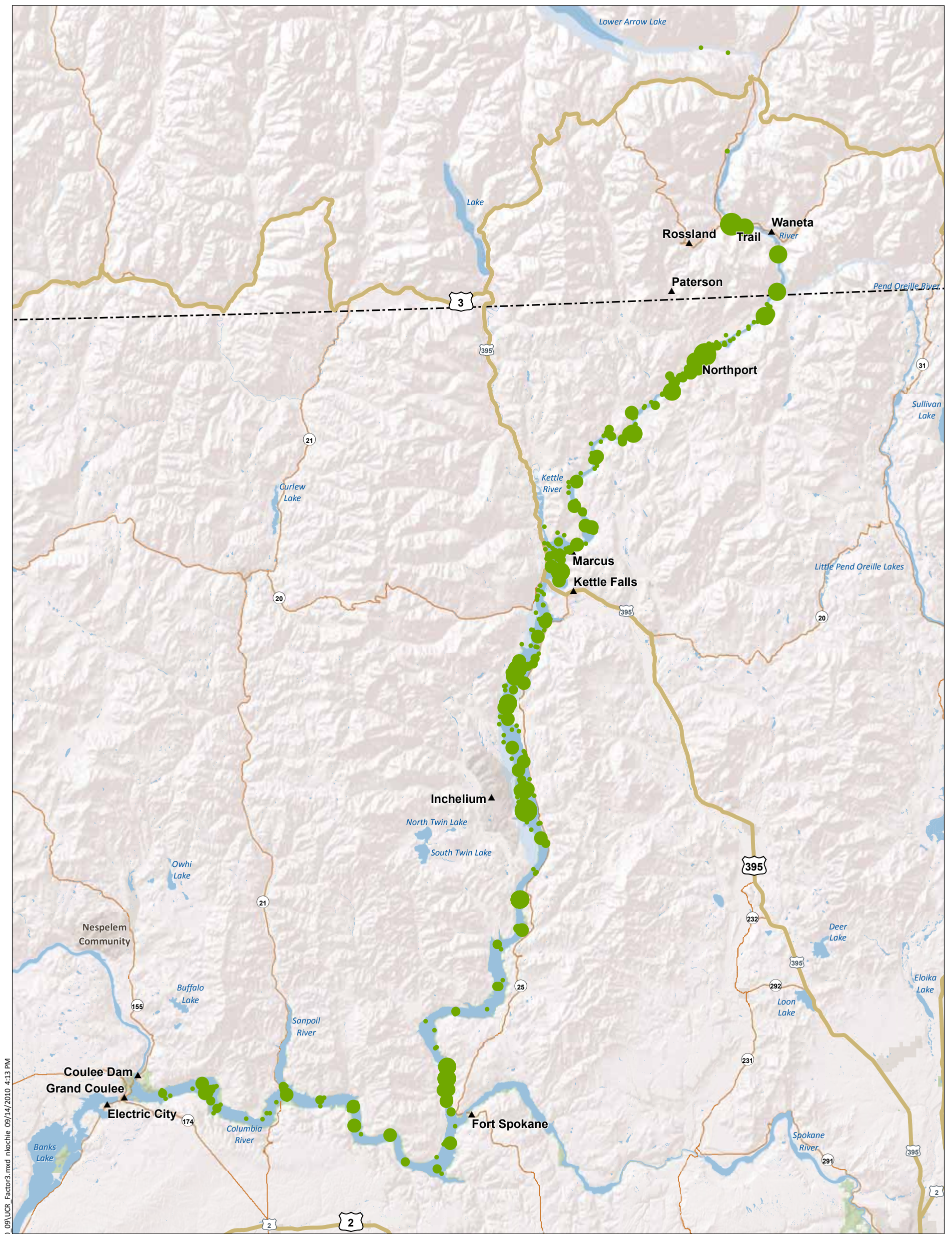
Rotated Factor 1	▲ Cities
● < 0.37	— Highways
● 0.37 - 0.74	■ Water Bodies
● 0.74 - 1.48	⋯ Canadian Border
● 1.48 - 2.96	
● > 2.96	



Miles




0 4.5 9 13.5 18



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Rotated Factor 3		▲ Cities
● < 0.45	— Highways	■ Water Bodies
● 0.45 - 0.9	— Canadian Border	
● 0.9 - 1.8		
● 1.8 - 3.6		
● > 3.6		



Miles



3.1.4 Lead Isotope Tracing of Metals Sources in Upper Columbia River Sediments

While the chemical composition of slag is unique and dominates the geochemical signature of the river sediments for a significant distance downstream of Trail and into the United States, the question of whether and to what extent other natural or anthropogenic sources of metals from tributary watersheds also contribute to the observed elevated metals concentrations is not as easily addressed by this approach. This question is particularly relevant to the UCR site in view of the long history of precious and base metal mining and processing activities in northeastern Washington and south-central British Columbia, which date back to the 1880s, and include the Metaline mining district in Pend Oreille County, the Northport mining district in Stevens County, the Republic district in Ferry County, and others (E&E 2000; Hurst 2000; USEPA 2002, 2003; G.G Booth & Associates 2008). In addition to potential impacts from historic lead-zinc and copper mining and mineral processing operations within mineralized tributary watersheds of the UCR (which were generally of much smaller scale and shorter in duration than the Trail smelter), natural weathering and erosion of mineralized rocks in these watersheds may also contribute to locally elevated loadings of metal-enriched sediments to the river.

To evaluate the potential significance of local metals sources other than Trail on UCR sediment chemistry, I used lead isotope signatures. Lead is known to exhibit significant natural variations in the proportions of its isotopes, and this feature provides a powerful means of discriminating between different sources of lead in the environment. When sources have different signatures, lead isotopic discrimination is definitive.

Selected samples from the CCT sediment coring study, as well as archived samples from Dowling (2007) were submitted to Professor Bruce Nelson at the University of Washington for lead isotope analysis. The lead isotope laboratory report is provided in Appendix D.

I identified a signature uniquely associated with lead discharged from Trail. This was based on a review of published data on the lead isotope signatures of two entities: 1) ore concentrates processed at Trail; and 2) ore deposits located within the tributary watersheds of the UCR site. Lead isotope data for UCR sediment samples were compared to these source signatures. The origin of the elevated lead concentrations (and other associated metals by

proxy) in the sediments is unequivocally attributed to discharges from the Trail facility. The Trail lead signature completely swamps the background (natural or derived from local mining activities) lead isotope signatures of UCR sediments sampled between the U.S.-Canada border and Kettle Falls.

3.1.4.1 *Stable Lead Isotopes*

Individual atoms of the same element can have different masses depending on the number of neutrons. These different possible versions of each element are called isotopes. Isotopes can be stable or unstable (radioactive). Naturally occurring lead has four stable isotopes: Pb-204, Pb-206, Pb-207, and Pb-208. The latter three are called “radiogenic” because they are produced by the radioactive decay of uranium (U-238 and U-235) and thorium (Th-232), respectively. Pb-204 is not radiogenic and is considered to be a stable reference isotope. The three radioactive parent elements, U-238, U-235, and Th-232, decay at different rates, with half lives of 4.468 billion years, 704 million years, and 14.01 billion years, respectively (Dickin 1995; Faure and Mensing 2005).

The isotopic composition of lead is commonly expressed in terms of isotope ratios (e.g., normalized to Pb-204) and is widely used in geology for various purposes, including geochronology (age dating of rocks) and mineral exploration. The isotope ratios of lead are unaltered by smelting and other manufacturing processes (Flegal and Smith 1995; Shiel et al. 2010), and therefore retain the isotope ratios of the ore from which the lead was derived.

The isotopic composition of lead in an ore deposit depends on a number of factors, but in simplest terms can be understood in terms of the geologic age of the ore deposit. The isotope ratios of Pb-206/Pb-204, Pb-207/Pb-204, and Pb-208/Pb-204 in the Earth have been steadily increasing over the Earth’s history due to radioactive decay of uranium and thorium. Because of the chemical differences between these elements, lead is effectively separated from uranium and thorium during the formation of a lead ore mineral such as galena (lead sulfide), and the isotopic ratios of lead in the galena are frozen in at the time of its formation. Geologically older lead ores tend to have lower lead isotope ratios (less radiogenic lead) than more recently formed ores. Different lead deposits therefore can have distinctive lead isotopic compositions, and lead isotope signatures can be used as tracers to identify the

different natural and industrial contributions of lead in the environment (Sangster et al. 2000).

3.1.4.2 *Isotope Signatures of Lead Sources in the UCR*

Lead isotope data for the main ores historically processed at the Trail smelter (Sullivan Mine, Red Dog, and Pine Point), as well as from various mining districts in northeast Washington and south-central British Columbia, were compiled from published literature sources (Ayuso et al. 2004; Beaudoin 1997; Church 2010; Cumming et al. 1990; Godwin and Sinclair 1982; Godwin et al. 1982, 1988; Shiel et al. 2010; Small 1973). The data compiled from these sources is included in Appendix D.

Figures 5 and 6 are scatter plots of Pb-206/Pb-204 versus Pb-208/Pb-204 and Pb-207/Pb-204 versus Pb-208/Pb-204 ratios for lead from the Trail smelter and local geologic sources (mineral deposits located in tributary watersheds of the UCR site). As can be seen, the Trail lead signature is distinct from local geologic sources with only a minor degree of overlap between Red Dog ores and three samples, which include two duplicate analyses of galena from the Bonanza Mine and a sample from a nearby prospect, which have the least radiogenic lead ores in the area (Church 2010).

Queneau (2010) provides information on the major ore concentrates historically processed at Trail. Between 1921 and 1992, 85 percent of the lead concentrates came from the Sullivan Mine. From 1993 to 2001, close to 50 percent came from Sullivan and almost 40 percent came from the Red Dog Mine. Sullivan supplied almost 90 percent of the zinc concentrates until 1962. From 1963, about half of the zinc feeds came from Pine Point Mine until it was shut down in 1989, with about 35 percent coming from Sullivan. Between 1990 and 2001, Red Dog accounted for 55 percent of zinc feed and Sullivan for 40 percent. Since 2001, Red Dog has been the main source of both lead and zinc concentrates. These ores were imported from other regions (Sullivan is located in southeastern British Columbia, Red Dog is located in Alaska, and Pine Point is located in the Northwest Territories), and the lead from these deposits is generally isotopically distinct from local lead sources within the UCR site. The Sullivan ores, for example, which were formed approximately 1.5 billion years ago, are much older than any of the rocks exposed within the UCR site, and their exotic lead isotope signature is easily distinguished from local sources.

The fields marked by dashed lines in Figures 5 and 6 represent possible compositions of mixtures of concentrates from the Sullivan, Red Dog, and Pine Point mines used as ore feed for the Trail smelter. Slag produced from these feeds would have the same isotopic composition. Early slag produced from feeds with a higher proportion of Sullivan ore would be less radiogenic (i.e., lower isotope ratios) than later slag with a higher percentage of Red Dog or Pine Point ore in the feed. While changes in the proportions of different ore sources used in the smelter feed would produce variations in slag isotope ratios over time, these would all fall within the range delineated by the three main ore sources. Similarly, in the river sediments, mixtures of early slag with later slag would also fall within the range defined by the ore concentrates.

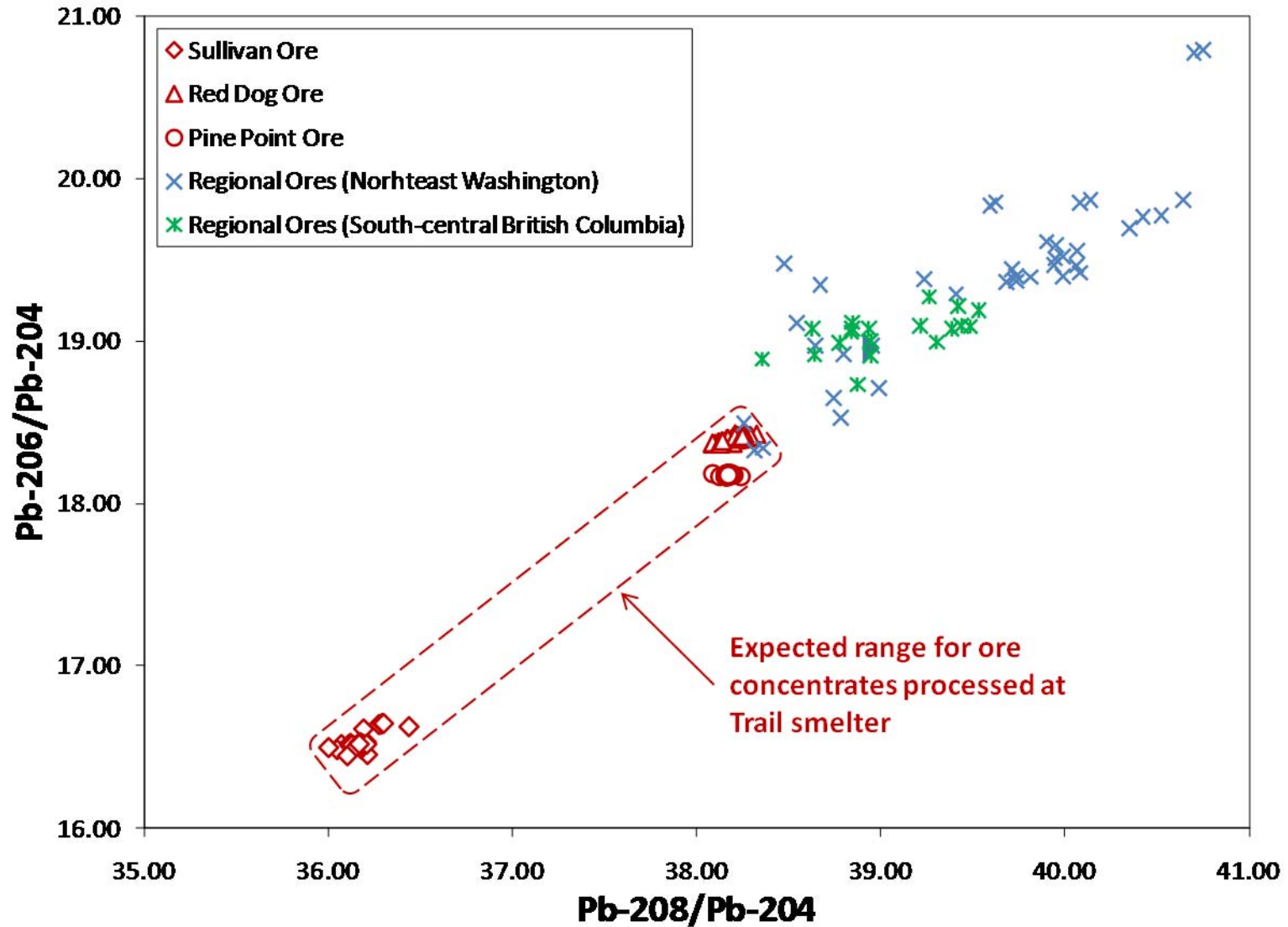


Figure 5

Pb-206/Pb-204 versus Pb-208/Pb-204 isotope ratio plot showing signatures of regional and smelter-derived lead sources

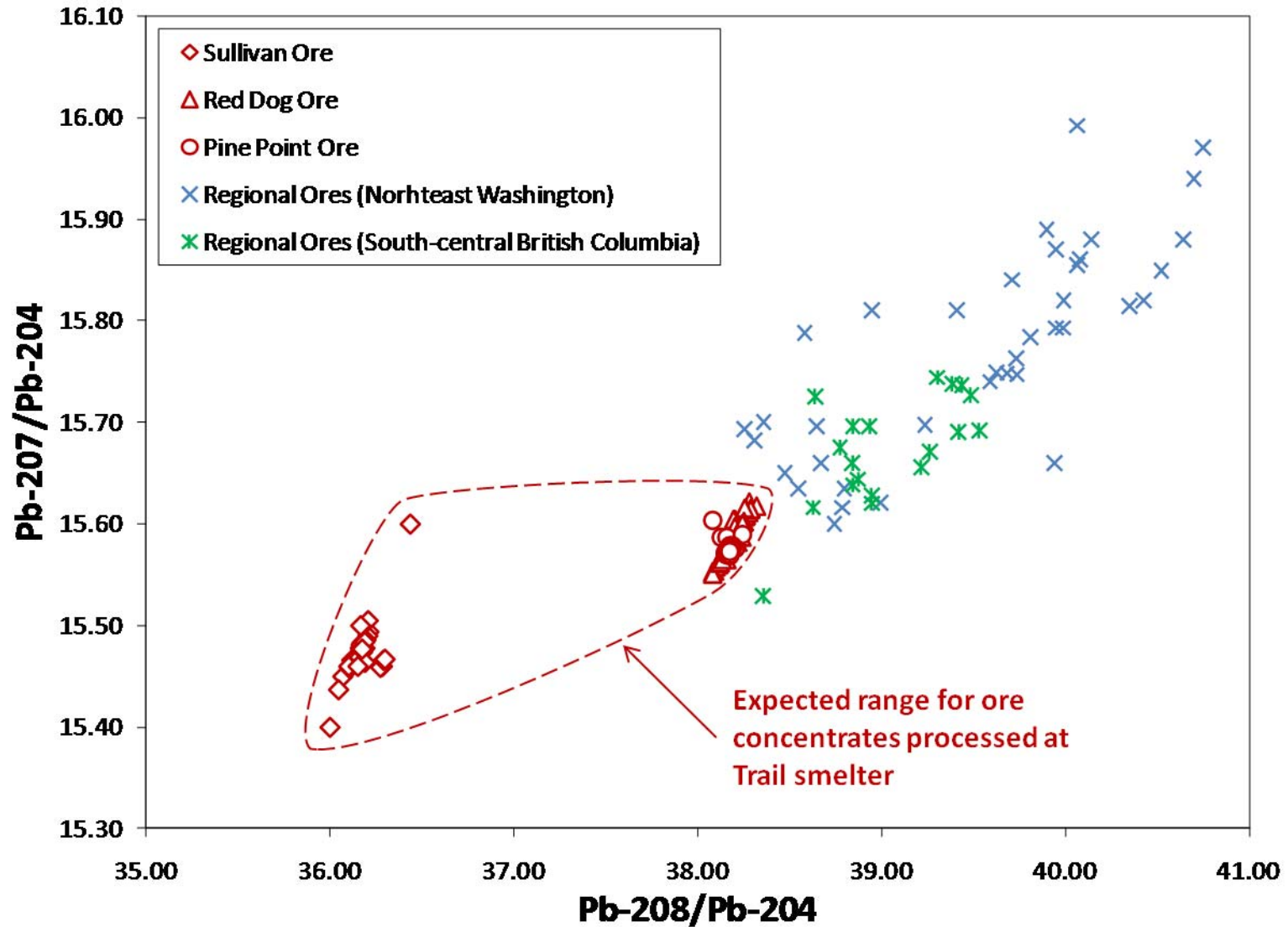


Figure 6

Pb-207/Pb-204 versus Pb-208/Pb-204 isotope ratio plot showing signatures of regional and smelter-derived lead sources

3.1.4.3 *Lead Isotope Signatures in UCR Sediments*

Lead isotopic compositions of selected UCR sediment samples from the CCT sediment coring study (31 samples collected from several locations between the International Border and Northport, Washington) and Dowling (2007) (8 samples collected from several locations between Deadman's Eddy and Kettle Falls) are plotted in Figures 7 and 8. The isotopic compositions of slag material separated from five of the sediment samples are also plotted. All of the slag samples and most of the whole sediment samples plot entirely within the Trail smelter field, unequivocally proving the smelter as the source of lead in these samples.

The slag content of the 8 archived samples from Dowling (2007) was also estimated at the University of Washington. Figure 9 shows slag content versus Pb-206/Pb-204 ratio in these samples. Trail lead is characterized by Pb-206/Pb-204 ratios less than 18.5 while local lead sources have Pb-206/Pb-204 ratios greater than 18.3. Samples with little or no slag present still have isotope ratios indicating that all of the lead in these samples is from Trail. This is either evidence that these samples contain Trail lead from non-slag sources (i.e., liquid effluents) or that slag may have been present originally and has dissolved over time, releasing lead and other metals to the sediment. Cox et al. (2004) documented the occurrence of extensive dissolution and weathering features on slag particles recovered from UCR sediments.

Figure 10 plots Pb-206/Pb-204 ratio versus river mile (RM). With the exception of six samples (encircled on the plot), all the samples have Pb-206/Pb-204 ratios less than 18.5, indicating that the Trail facility is the dominant source of lead in the UCR at least as far downriver as Kettle Falls. The significance of the six samples with Pb-206/Pb-204 ratios greater than 18.5 located at river miles 738 (Deadman's Eddy area) and 743 (Black Sand Beach area) becomes clear on Figure 11, which is a scatter plot of Pb-206/Pb-204 ratio versus lead concentration. These six samples appear to contain no lead from the Trail smelter and have total lead concentrations between 5 and 15 mg/kg. These samples are from the lower sections of cores BSB4A, BSB6A (located near the west bank across the river from Black Sand Beach), and DE#14A. Figure 12 shows the concentration profiles of lead, zinc, and copper in these cores. Elevated metals concentrations are present nearest the surface, and lower concentrations are found at depth, coinciding with the disappearance of the Trail smelter lead isotope signature. I conclude that the deeper samples in these cores represent pre-

smelter sediment, and the metals concentrations in these samples are representative of background sediment quality at these locations. Pre-smelter sediment was encountered in these three cores because the slag-impacted sediment layer was relatively thin, ranging from approximately 1.3 feet at location DE#14A to 3.5 feet at location BSB4A. Slag was present to much greater depths at all the other coring locations. The metals concentrations in these six samples are summarized in Table 3.

Two of the samples on Figure 10 (at RM 738 and 745) that plot within the narrow zone of overlap between Trail lead and locally derived lead (Pb-206/Pb-204 between 18.3 and 18.5) are also notable. Their lead concentrations are also intermediate between the pre-smelter sediment and the contaminated sediments, which indicates that these samples either contain slag from smelting of Sullivan-poor ore, or a relatively low slag content.

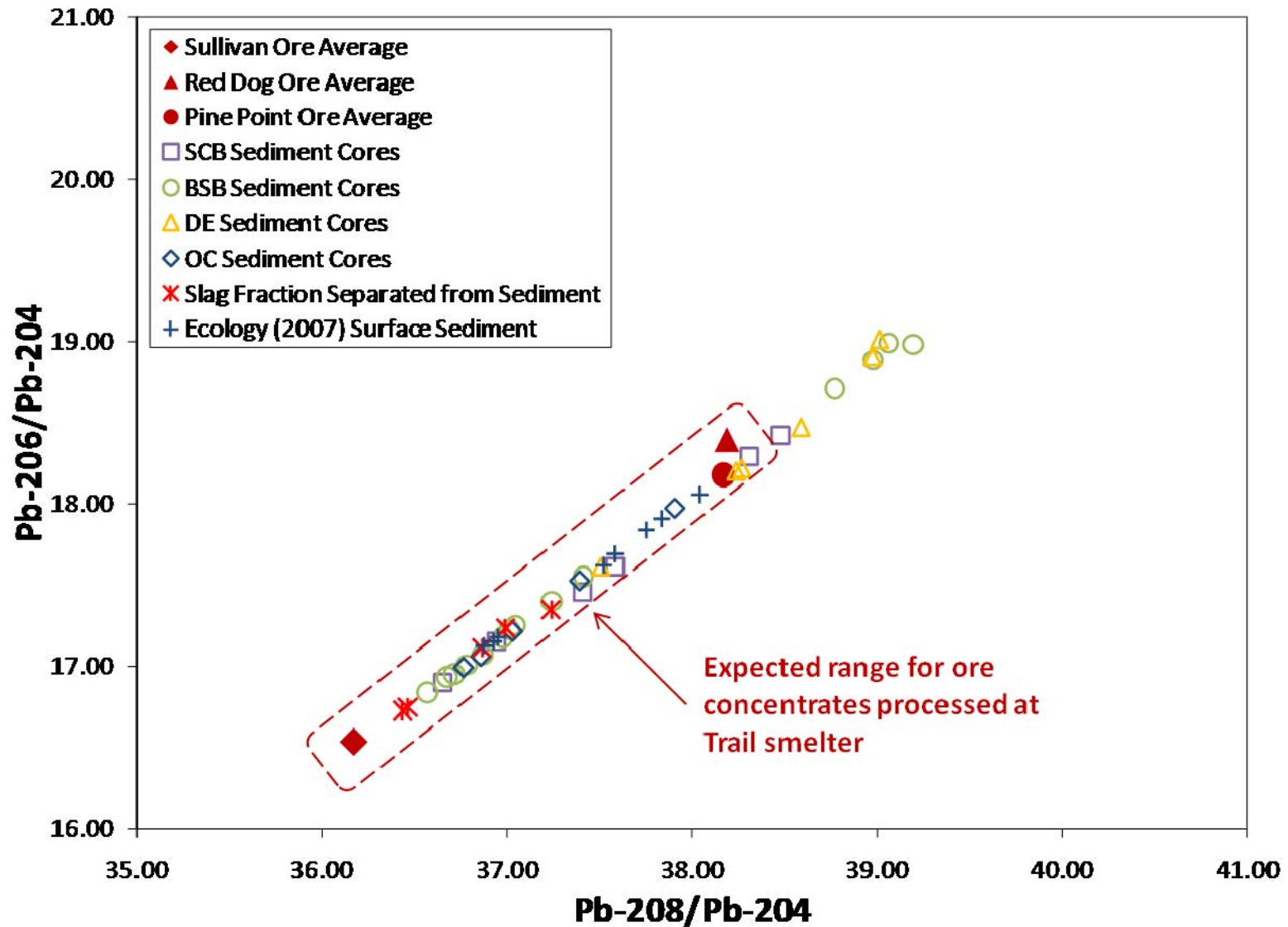


Figure 7
 Pb-206/Pb-204 versus Pb-208/Pb-204 isotope ratio plot for UCR sediment samples

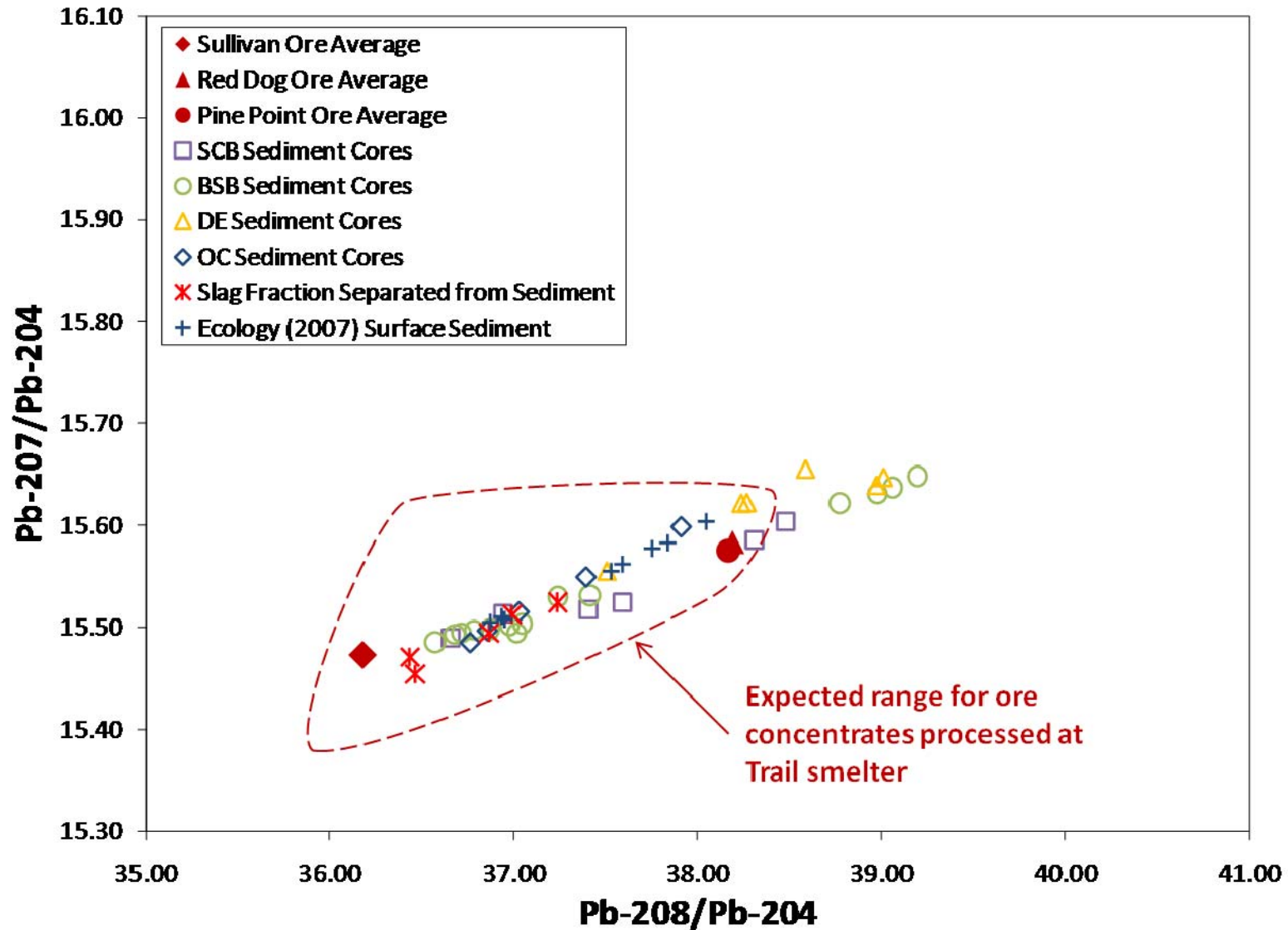


Figure 8

Pb-207/Pb-204 versus Pb-208/Pb-204 isotope ratio plot for UCR sediment samples

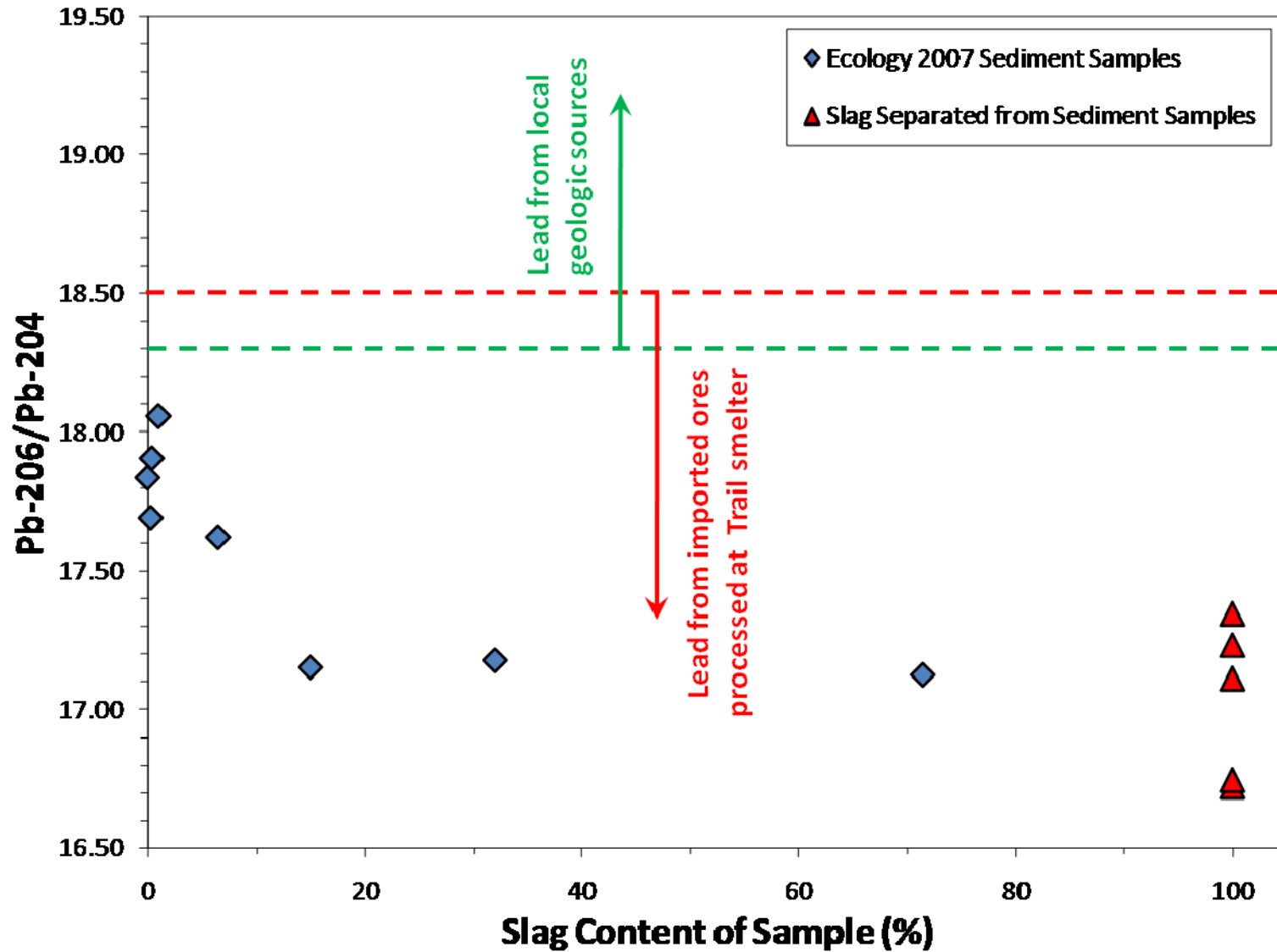


Figure 9

Pb-206/Pb-204 isotope ratio versus slag content of UCR sediment samples and slag separates

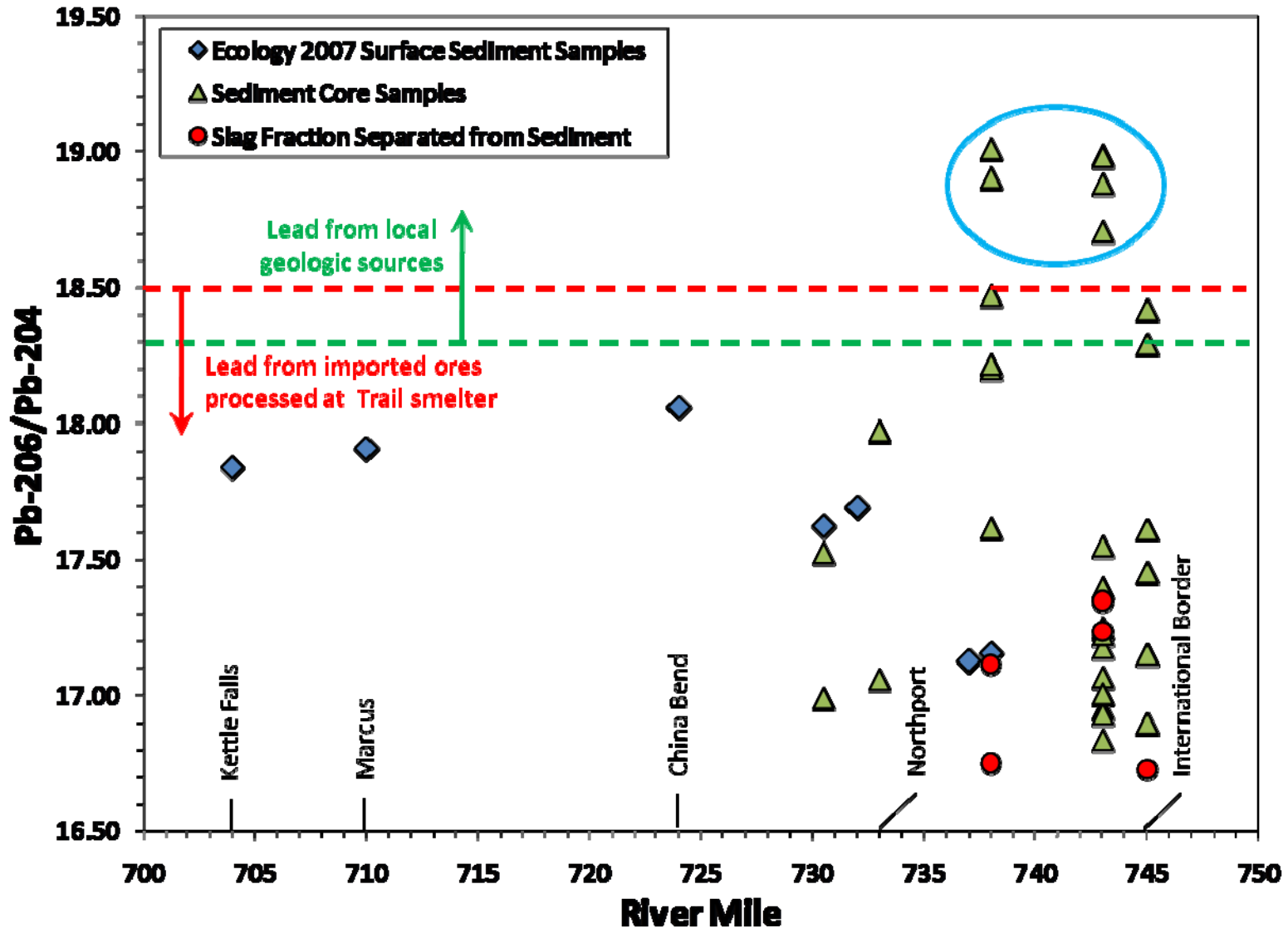


Figure 10
 Pb-206/Pb-204 isotope ratio versus River Mile for UCR sediment samples and slag separates

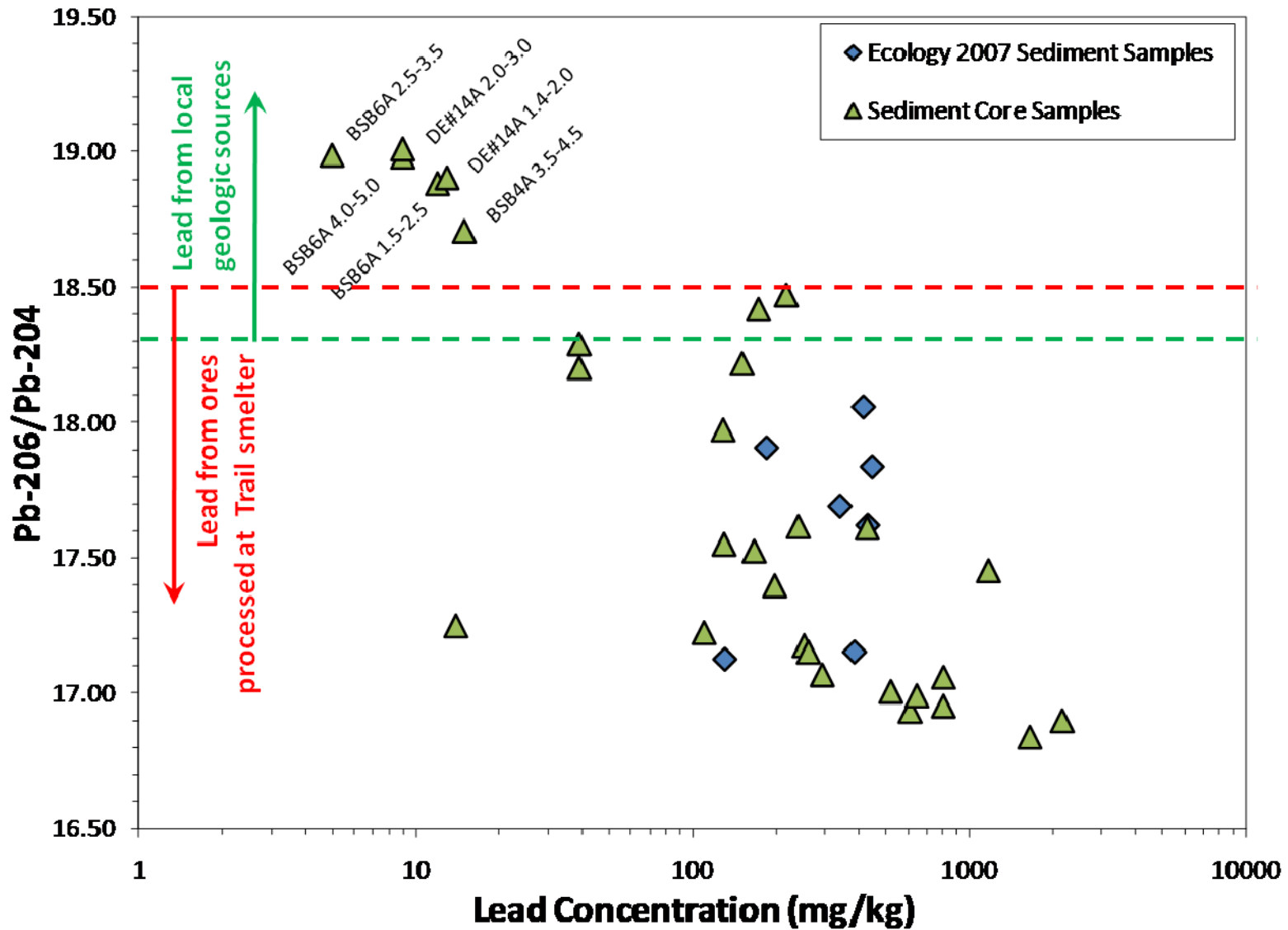


Figure 11
 Pb-206/Pb-204 isotope ratio versus lead concentration of UCR sediment samples

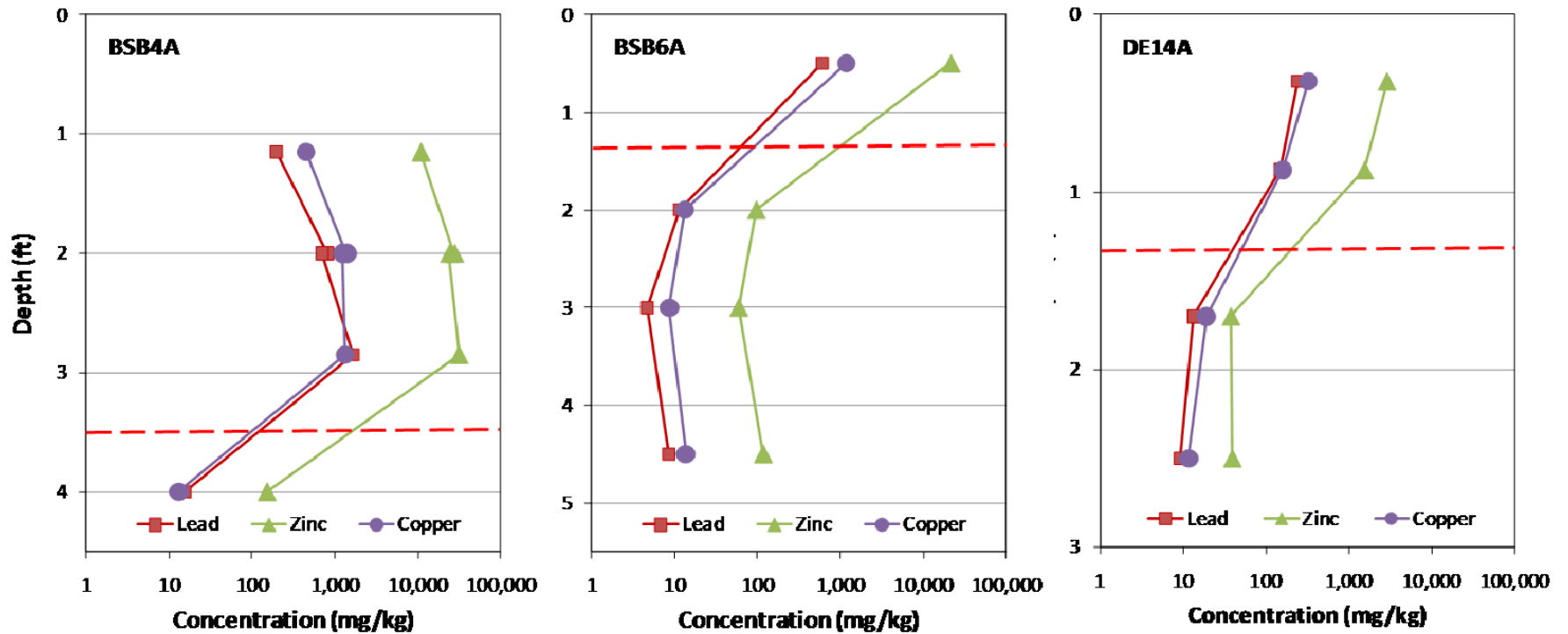


Figure 12

Concentration profiles of lead, zinc, and copper in three UCR sediment cores in which pre-smelter sediment was encountered. The horizontal dashed line represents the top of the pre-smelter horizon at these locations

Table 3
Metals Concentrations in Pre-smelter Sediment and Maximum Detected in Core Samples

Metal	Mean Pre-Smelter (mg/kg)	Maximum Pre-Smelter (mg/kg)	Maximum Detected (mg/kg)
Arsenic	2.1	2.5	45.6
Antimony	0.1	0.2	1,040
Barium	49	58	996
Beryllium	0.38	0.7	1.3
Cadmium	0.25	0.30	15.4
Chromium	9.3	12.7	81.8
Cobalt	3.0	3.6	40.6
Copper	13.3	19.1	1,870
Iron	9,790	12,300	245,000
Lead	10.5	15.3	2,160
Manganese	364	546	8,480
Mercury	<0.05	<0.05	6.4
Nickel	8.1	10.7	16.0
Silver	0.05	0.05	2.8
Thallium	0.14	0.25	13.9
Zinc	83	151	31,300

Figures 13 through 16 present scatter plots of metals concentrations versus Pb-206/Pb-204 ratio of sediment samples. Samples that are contaminated with Trail smelter lead, as indicated by Pb-206/Pb-204 ratios less than 18.5, also exhibit elevated concentrations of antimony, arsenic, barium, cadmium, chromium, cobalt, copper, iron, manganese, mercury, silver, thallium, and zinc relative to the background samples. Maximum detected concentrations are also given in Table 3. Metals concentrations in the contaminated sediments are up to two orders of magnitude higher than background values.

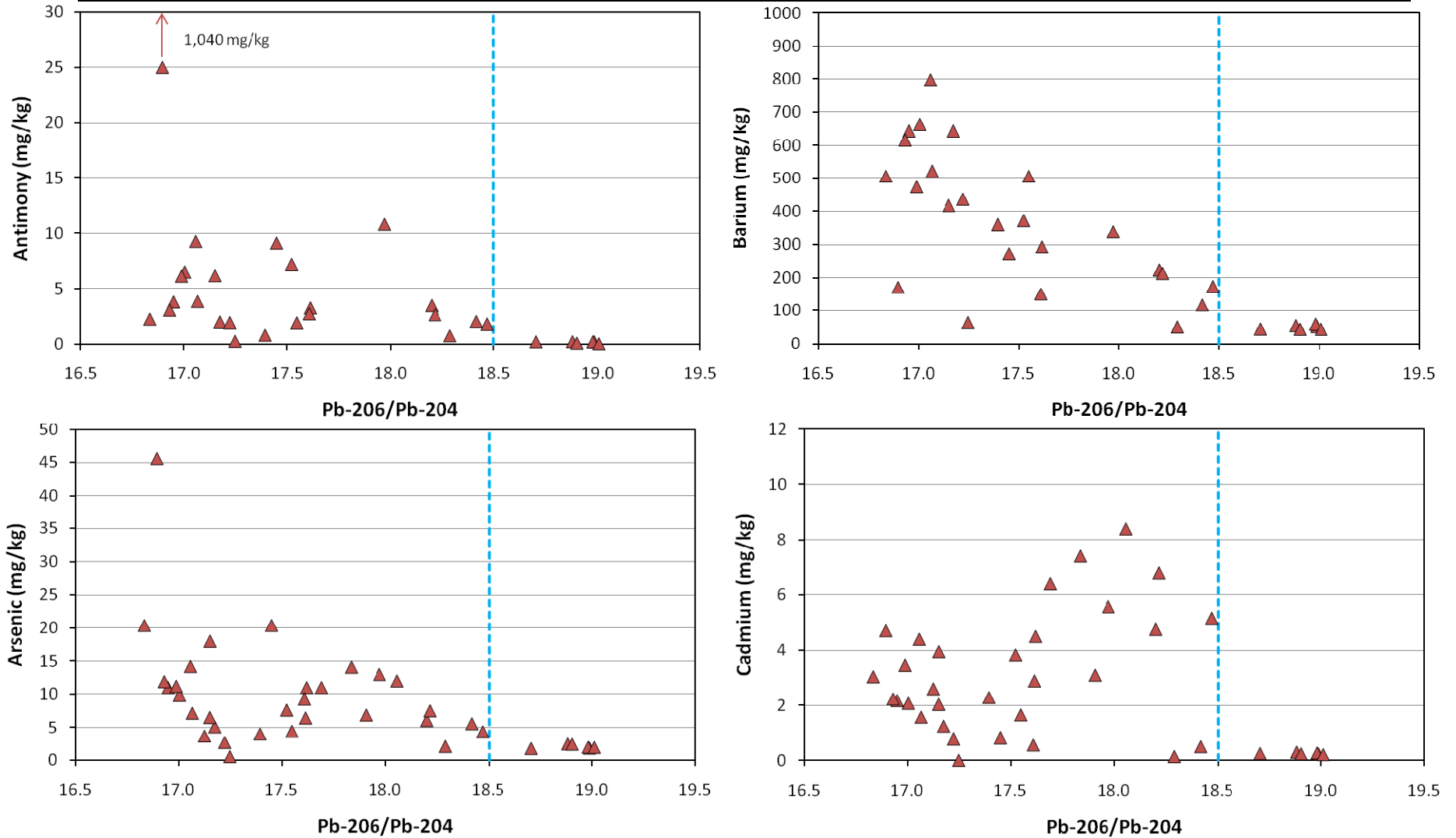


Figure 13

Antimony, arsenic, barium, and cadmium concentrations of UCR sediment samples versus Pb-206/Pb-204 isotope ratio. Vertical dashed line indicates upper limit for Pb-206/Pb-204 of Trail smelter lead

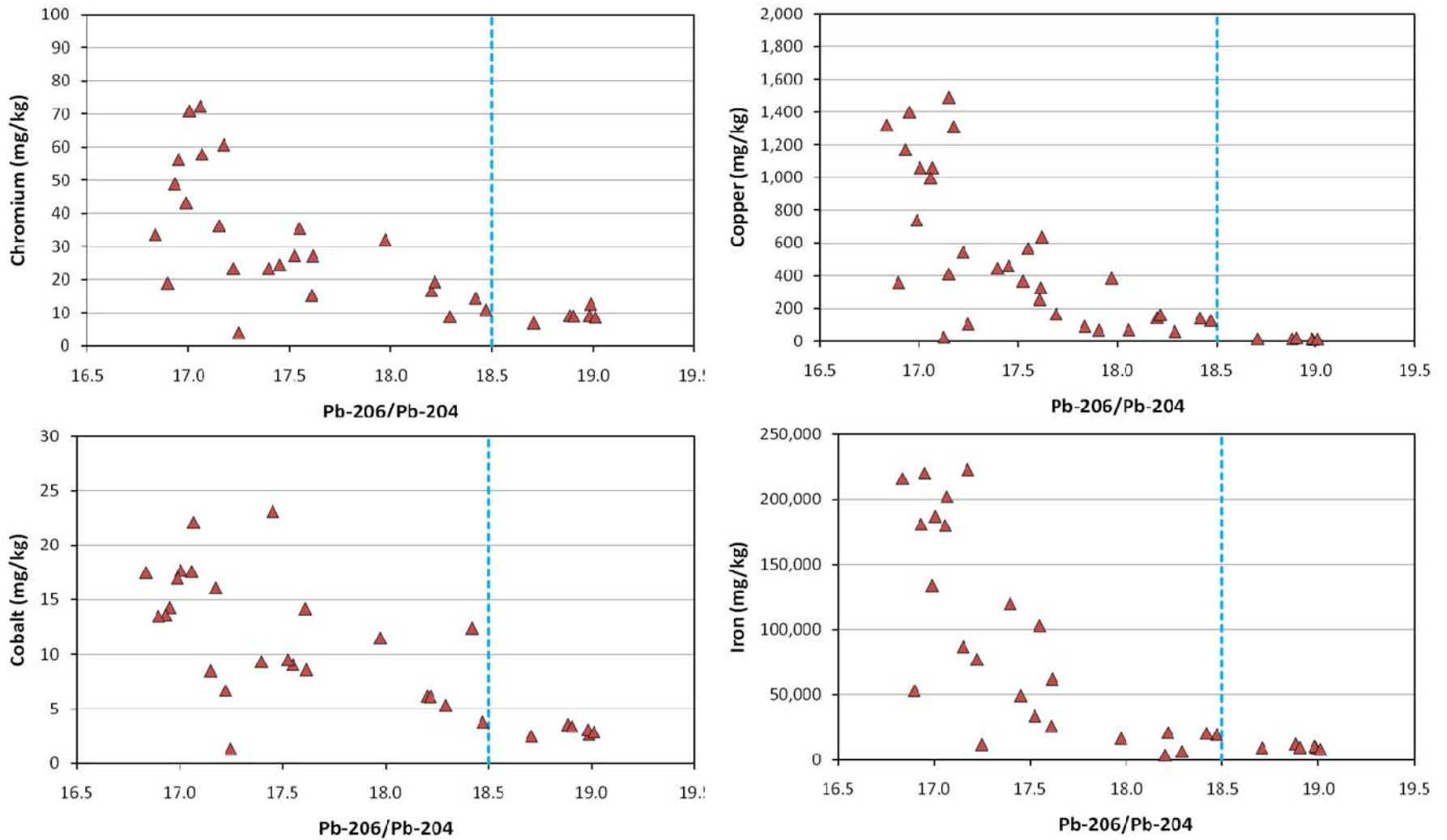


Figure 14
Chromium, cobalt, copper, and iron concentrations of UCR sediment samples versus Pb-206/Pb-204 isotope ratio. Vertical dashed line indicates upper limit for Pb-206/Pb-204 of Trail smelter lead

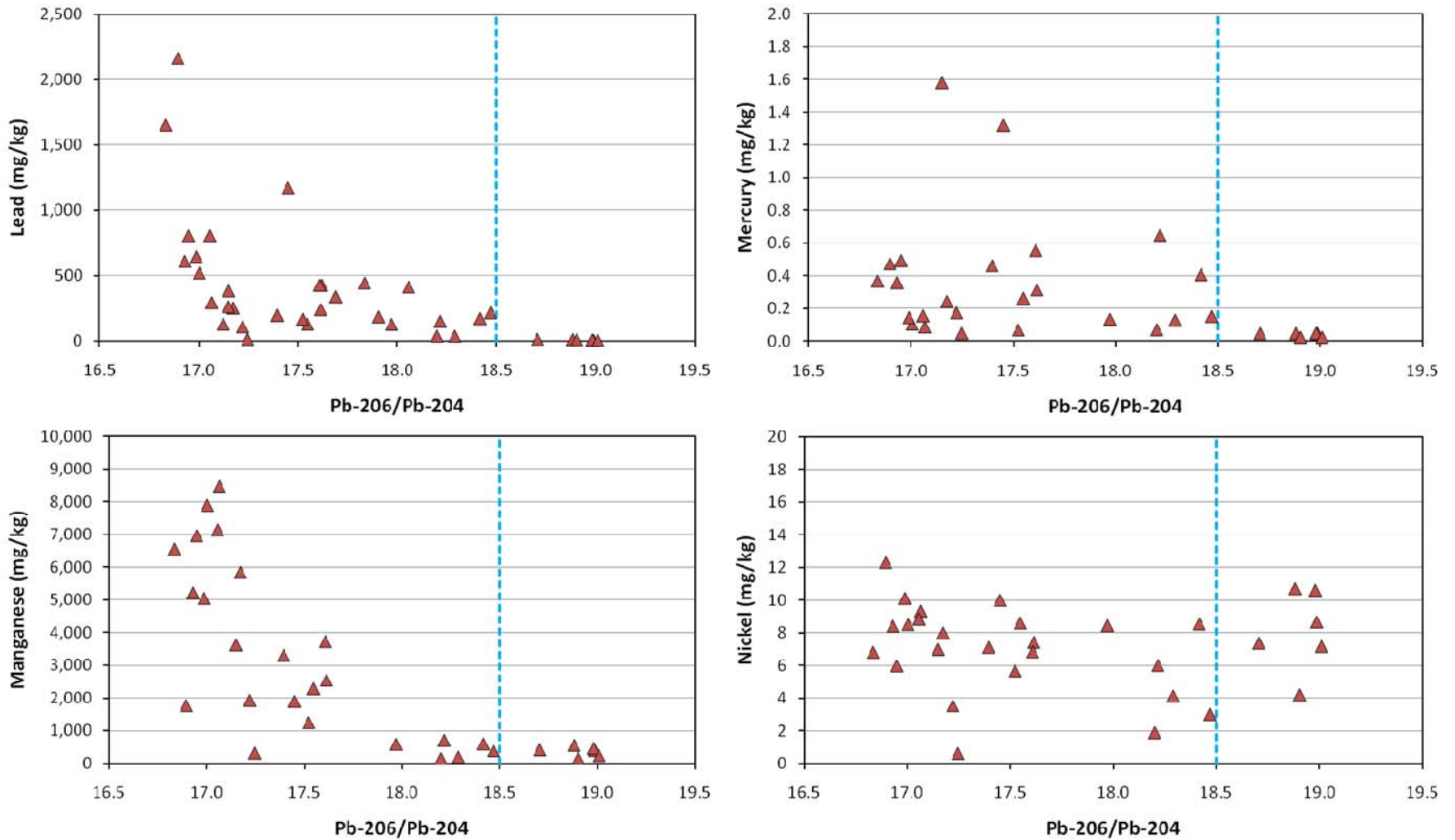


Figure 15
Lead, manganese, mercury, and nickel concentrations of UCR sediment samples versus Pb-206/Pb-204 isotope ratio. Vertical dashed line indicates upper limit for Pb-206/Pb-204 of Trail smelter lead

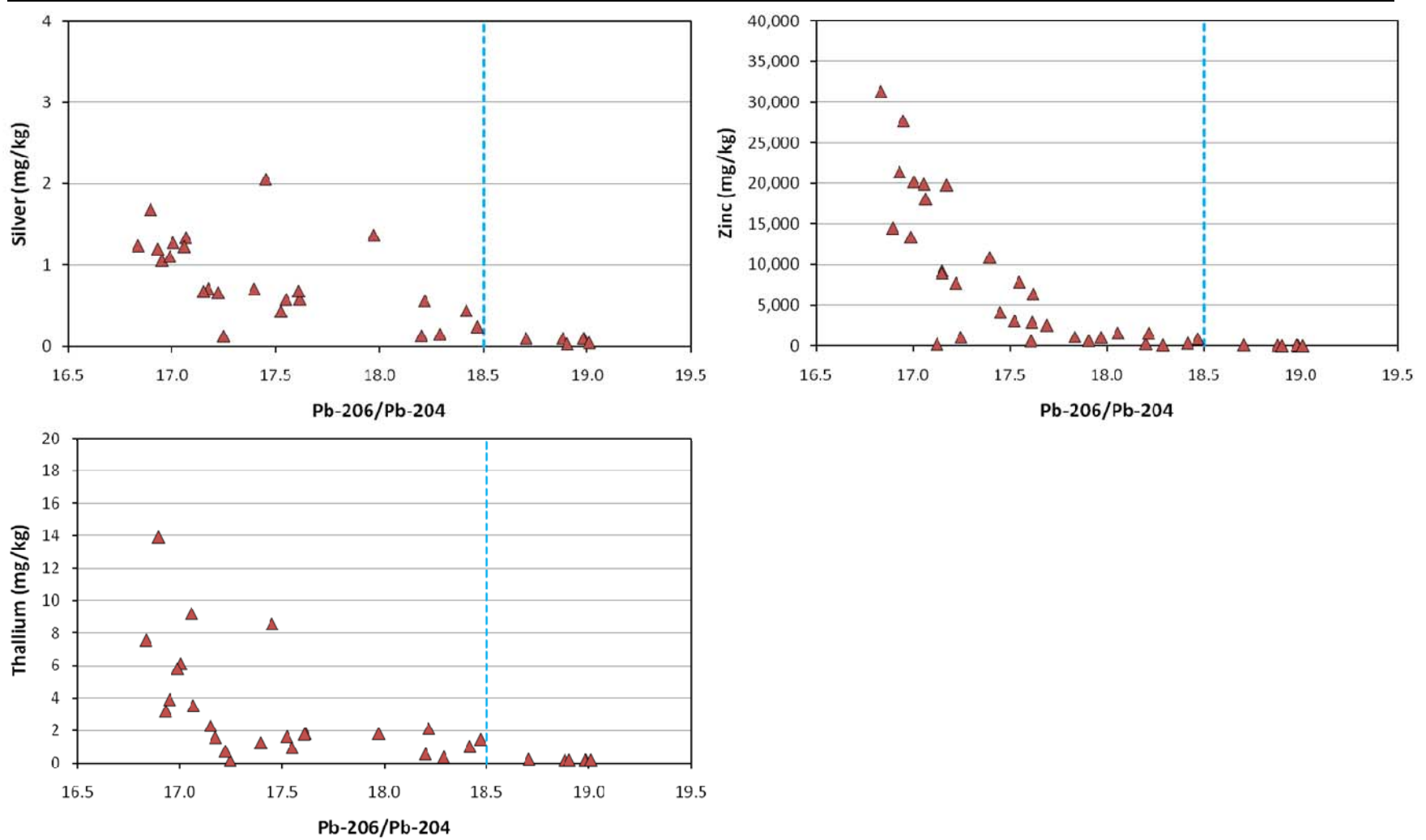


Figure 16
Concentration profiles of lead, zinc, and copper in three UCR sediment cores in which pre-smelter sediment was encountered.
The horizontal dashed line represents the top of the pre-smelter horizon at these locations

3.2 Opinion 2

Slag discharged from the Teck Cominco smelter is a predominantly glassy material. Once released into the aquatic environment, it slowly but irreversibly breaks down to more stable weathering products by physical and chemical processes. Through the action of these processes, heavy metals and other potentially toxic constituents present in the slag including arsenic, antimony, barium, cadmium, copper, lead, and zinc, are released over time to the sediment porewater and the aquatic environment.

The rate and magnitude of metals release from slag to water depends on its mineralogical composition. Trail smelter slag is a mostly glassy material, due to the rapid quenching of the molten slag during the granulation process. It also contains small inclusions of metals and sulfide phases. Glasses are thermodynamically unstable materials. When placed in contact with water, they spontaneously and continuously dissolve. As this process continues, the glass is converted to more stable weathering products such as clay minerals, and releases some of its constituents to water. The metal and sulfide inclusions are reactive when exposed to the aquatic environment and will also release their constituents to water.

Two lines of evidence demonstrate that these processes are occurring in the slag-impacted sediments of the UCR, and result in the release of metals from slag. First, the release of metals from slag is documented under laboratory conditions. This is based on 1) slag leaching studies conducted by Cominco, and 2) a study of metals release from slag separated from UCR sediments conducted for the present evaluation. This line of evidence demonstrates that slag leaches metals to water under a variety of laboratory conditions representative of the range of conditions in which slag-bearing sediments are found within the UCR. Second, metals concentrations were determined in sediment porewater from areas known to contain Trail slag. Of the heavy metals, zinc, antimony and copper were detected at the highest concentrations in porewater samples. These three metals, which are enriched in slag, also show the highest concentrations in the laboratory release experiments. These independent yet complementary lines of field and laboratory evidence lead to the conclusion that slag present in UCR sediments releases metals to porewater.

The following sections start with a brief review of the mineral composition of Trail slag to provide context on its reactivity. This is followed by an evaluation of metals release from

Trail slag based on previous as well as the current laboratory studies, and concludes with a summary of the findings of the porewater study.

3.2.1 Mineral Composition and Reactivity of Trail Slag

Trail smelter slag is composed almost entirely of amorphous glass, according to a report on the mineralogy of Canadian non-ferrous smelter slags (CANMET 1995). The report also identifies metal-rich inclusions containing copper antimonide (with traces of iron, nickel, and arsenic) and copper-iron sulfide within the glass matrix. It was shown that essentially all the zinc (3.4 percent by weight) in the slag occurs in the glass phase. These findings on the mineralogy of Trail slag were also confirmed in a later study by Microlab Northwest (2001). In addition to the copper-antimony and iron copper sulfide phases, this study also identified a separate lead-rich phase. These studies establish that the Trail slag consists mainly of an iron calcium silicate glass matrix with metallic and sulfide inclusions. Most of the zinc content is found in the glass, while copper, antimony, and arsenic are found in the metal/sulfide inclusions.

Glasses are metastable materials that slowly but spontaneously break down in the environment to produce more stable products (White, 1984). In water environments, dissolution and leaching of the glass preferentially releases the more soluble constituents. As these elements are released, they may eventually precipitate to form more stable phases such as clay minerals. Chemical constituents that do not fit into these newly formed mineral structures will accumulate in the water and/or be transported away. In this way, certain elements present in glassy materials will be continually released in contact with water.

Metal sulfides and antimonides are more reactive in the surficial environment than glasses. This is because they are readily decomposed by reaction with the oxygen present in water. A well known example is the oxidation of iron sulfide in mining wastes to produce acidic mine drainage. The inclusions in slag, when exposed to water, will also undergo oxidation reactions and release dissolved metals.

3.2.2 Release of Metals from Trail Slag

3.2.2.1 Slag Leaching Studies by Cominco

Since the 1970s, Cominco has conducted a number of studies to evaluate the leaching of slag constituents. Of particular relevance are a series of studies conducted in the 1980s and early 1990s to evaluate leaching of metals from slag under various conditions. The results of these studies are presented in a series of reports and memoranda (Cominco 1989, 1991a, 1991b, 1991c, 1991d, 1992a, 1992b, 1992c, 1992d, 1993). One series of tests involved percolation of simulated rain water through columns packed with slag. These column tests were carried out for at least 80 weeks (Cominco, 1993). In these tests, zinc and copper leachability was found to increase dramatically after 16-19 weeks. Lead and cadmium were also detected in the leachate solutions. Zinc and copper concentrations in the water exiting the columns remained at levels far exceeding 10,000 micrograms per liter ($\mu\text{g/L}$) from week 48 on [TECK_0289192, TECK_0164509-10].

A more recent slag column leaching study (Cominco 2001a, 2001b) showed similar results, noting that “the leachate metals concentration levels were several orders of magnitude higher than limits set for freshwater streams” [TECK 0165857]. The maximum concentrations reported in the column leaching solutions were 300 $\mu\text{g/L}$ for copper, 500 $\mu\text{g/L}$ for cadmium, 900 $\mu\text{g/L}$ for nickel, 1700 $\mu\text{g/L}$ for lead, and up to 50,000 $\mu\text{g/L}$ for zinc.

3.2.2.2 Metals Release from Slag Separated from UCR Sediments

The Cominco leaching studies demonstrate the release of metals from Trail slag by reaction with water. However, these studies were designed to evaluate metals leaching from stockpiled slag and used simulated rain water as the leaching solution, which is more acidic than Columbia River water. In order to obtain data more representative of slag present in the river, a study of metals release from slag was undertaken under my direction. The study evaluated the release of elements from slag to Columbia River water under laboratory conditions. The laboratory work was performed by Professor Joseph Ryan at the University of Colorado, Boulder. The report is provided in Appendix E.

Slag was isolated from sediment cores from near the International Boundary (SCB12A), Black Sand Beach (BSB5A), and Deadman’s Eddy (DE#8C) by heavy liquid separation. The release

of a suite of major and trace elements from the three slag fractions were measured in a series of short-term (3 day) experiments and a long-term (28 day) experiment. The short-term release experiments were conducted to examine the effects of agitation rate, oxic versus near-anoxic conditions, crushing of slag, and pH on element release. The long-term release experiment was conducted under nitrogen-purged near-anoxic conditions with crushed slag fractions in Columbia River water at near-neutral pH.

The results of the short-term experiments show that near-anoxic conditions increased the release of arsenic and aluminum, and decreased the release of zinc, but had no effect on the release of other elements relative to oxic conditions. The experiment with crushed slag was intended to assess the effect of slag transport and abrasion on metals release. Crushing increased the slag surface area and the release of iron, arsenic, aluminum, cobalt, lead and manganese, but had little effect on the release of other elements. The effect of acidic pH (5.4) was to increase the release of some elements (iron, zinc, barium, cobalt, manganese, and strontium) and decrease the release of other elements (arsenic, chromium, antimony), while basic pH (10) had the opposite effect.

The 28 day experiment established that most of the metals present in the slag in measurable concentrations were released to the river water at concentrations greater than those initially present in the river water. Relatively high concentrations were observed for the release of iron, aluminum, barium, copper (especially for slag fraction DE#8C), lead (especially for slag fraction SCB12A), zinc, and arsenic. Antimony and selenium were released at relatively high levels by slag fraction DE#8C. Maximum released concentrations were 17 µg/L for arsenic, 152 µg/L for antimony, 47 µg/L for copper, 20 µg/L for lead, 6 µg/L for selenium, and 84 µg/L for zinc.

3.2.2.3 *Metals Concentrations in Porewater of Slag-Bearing Sediment*

As part of my evaluation, I also conducted sediment porewater (interstitial water) sampling to document dissolved metals concentrations in sediments known to contain Trail slag. Porewater sampling of slag-containing sediment deposits exposed on the banks of the UCR was conducted at four locations including the mid-stream bar near the U.S.-Canada border, Black Sand Beach, and Deadman's Eddy (two locations). The porewater sampling plan, field

sampling data, laboratory analytical results, and a data validation report are provided in Appendix F.

At each location, porewater samples were collected at two sites from approximately 6 feet below the sediment surface. Site locations were selected to evaluate potential changes in porewater chemistry from upstream to downstream within sediment features. Samples were collected at high and low river water levels to evaluate the effect of water-level induced fluctuations on porewater chemistry. The samples were analyzed for total and dissolved metals, as well as major ions, alkalinity, and total organic carbon. The results are summarized in Table 4.

Maximum dissolved concentrations detected for selected metals were 2.16 µg/L for arsenic, 352 µg/L for antimony, 0.635 µg/L for cadmium, 14.5 µg/L for copper, 3.36 µg/L for lead, and 155 µg/L for zinc. In general, the three metals detected at highest concentrations in porewater (i.e. antimony, zinc, and copper) were also found to release the highest concentrations from slag. This observation is not surprising, since it is exactly what would be expected if the slag were the source of these metals in porewater.

No systematic changes in porewater concentrations were found between samples collected during daily high and low river levels. Samples collected at upstream versus downstream sites at a given location also generally did not show systematic changes in porewater concentrations. One exception was at Black Sand Beach, where the metals concentrations at site BSB1, located approximately 100 feet upland from site BSB2, were consistently higher than at site BSB1 located at the shoreline (Table 4). Differences in metals concentrations between sampling locations also appear to be related to differences in metal release patterns of the slag present at different locations in the river. For example, the highest concentrations of antimony and copper were detected at location DE2 (Deadman's Eddy). As mentioned earlier, slag from this part of the river (isolated from core DE#8C) also released the highest concentrations of antimony and copper.

The similarities between the metals detected in the porewaters of slag-bearing sediments and the metals release patterns of slag isolated from these sediments is strong evidence that the metals in porewater are being released from slag particles.

Table 4
Summary of Porewater Chemistry Data

Analyte	Units	MRL	MSB 1 PW AM	MSB 1 PW PM	MSB 2 PW AM	MSB 2 PW PM	BSB1 PW AM	BSB1 PW PM	BSB 2 PW AM	BSB 2 PW PM	UDE-PW-01 AM	UDE-1 PW PM	UDE-PW-02 PM	UDE-PW-02 AM	DE1 PW AM	DE1 PW PM	DE2 PW AM	DE2 PW PM
Aluminum, dissolved	µg/L	55	nd	301	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	128
Antimony, dissolved	µg/L	0.2	11.4	13.8	11.9	9.33	71.1	83.9	14.9	8.18	2.13	2.6	1.66	1.46	16	9.58	352	282
Arsenic, dissolved	µg/L	1	2.16	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.48	nd
Barium, dissolved	µg/L	0.3	30	61.6	55.3	36.8	113	150	71.7	54.8	23.9	23.3	95.4	100	164	103	112	193
Beryllium, dissolved	µg/L	0.2	1.28	nd	nd	1.34	1.33	nd	nd	0.335	9.59	0.785	2.00	1.54	nd	0.852	0.491	nd
Cadmium, dissolved	µg/L	0.2	nd	nd	nd	nd	0.442	0.635	nd	nd	nd	nd	nd	nd	0.364	nd	nd	0.264
Calcium, dissolved	µg/L	100	23000 J	27200	30700	29100 J	34500 J	34000	18500	17400 J	25300 J	27700 J	28500 J	28900 J	60000	52800 J	46800 J	65400
Chromium, dissolved	µg/L	0.6	2.27 U	4.89	4.92	2.45 U	3.47 U	1.22	3.77	2.14 U	2.59 U	2.83 U	3.42 U	2.52 U	5.05	3.79 U	2.56 U	4.61
Cobalt, dissolved	µg/L	0.3	nd	0.5	nd	nd	0.375	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Copper, dissolved	µg/L	0.4	3.47	4.24	2.72	1.62	10.7	4.44	1.92	6.17	5.46	6.60	4.00	4.88	3.94	7.35	12.9	14.5
Iron, dissolved	µg/L	100	nd	381	nd	nd	116	nd	nd	nd	nd	nd	nd	nd	nd	134	nd	220
Lead, dissolved	µg/L	0.2	3.36	0.596	nd	2.65	2.96	nd	nd	2.35	2.37	2.9	2.54	2.65	nd	2.69	2.62	nd
Magnesium, dissolved	µg/L	100	5550 J	6510	4670	4870 J	4590 J	4900	3790	4100 J	6140 J	6300 J	7960 J	8440 J	7470	9210 J	6360 J	8010
Manganese, dissolved	µg/L	1	0.605 J	13.2	1.3	nd	8.48	14.7	1.78	nd	nd	nd	nd	nd	nd	nd	nd	7.64
Mercury, dissolved	µg/L	0.00005	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Nickel, dissolved	µg/L	0.5	nd	nd	0.588	nd	0.748	nd	nd	nd	nd	nd	nd	nd	1.91	nd	nd	nd
Potassium, dissolved	µg/L	500	8420 J	1550	2470	3880 J	3050 J	2240	1550	3420 J	4330 J	2740 J	7190 J	3760 J	1258	5490 J	6440 J	2980
Selenium, dissolved	µg/L	1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Silver, dissolved	µg/L	0.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sodium, dissolved	µg/L	100	1770 J	5850	2160	1520 J	2290 J	5180	1460	320 J	383 J	378 J	1770 J	361 J	1920	2040 J	2040 J	3161
Thallium, dissolved	µg/L	0.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Vanadium, dissolved	µg/L	0.5	0.993	1.45	0.707	0.54	1.92	nd	nd	nd	1.04	1.06	1.03	0.874	1.74	1.41	1.2	0.797
Zinc, dissolved	µg/L	1.5	27.7	39.9	82.4	76.6	155	126	29.1	21.9	3.78	6.63	43.7	46.7	46.6	79.8	58.8	74.2
Silica	mg/L		4370	5810	5270	4910	3850	4470	3050	2280	2960	3540	8910	7300	6980	7770	4190	5940
Bromide	mg/L	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chloride	mg/L	0.1	0.825	0.879	0.833	0.890	1.36	1.31	0.880	0.817	0.760	0.823	0.787	0.793	0.590	0.706	0.917	0.903
Fluoride	mg/L	0.1	0.533	0.525	0.545	0.502	0.352	0.414	0.234	0.175	0.313	0.246	0.308	0.250	0.439	0.395	0.456	0.412
Nitrate	mg/L	0.1	0.318 J	0.348 J	1.19 J	0.551 J	0.208 J	0.294 J	0.211 J	0.284 J	0.222 J	0.212 J	0.1 U J	0.176 J	2.03 J	1.27 J	1.73 J	2.47 J
Nitrite	mg/L	0.1	0.1 UJ	R	0.1 UJ	R	R	R	R	R	0.1 UJ	0.1 UJ	0.1 UJ	0.1 UJ	0.1 UJ	R	0.1 UJ	R
Phosphate	mg/L	0.1	0.1 UJ	R	0.1 UJ	R	R	R	R	R	0.1 UJ	0.1 UJ	0.1 UJ	0.1 UJ	0.1 UJ	R	0.1 UJ	R
Sulfate	mg/L	0.1	12.2	13.1	20.6	17.2	19.8	19.3	9.60	9.30	13.4	12.4	12.5	12.6	41.8	46.9	46.3	101
Total Organic Carbon	mg/L	0.5	0.742	0.810	0.691	0.678	1.05	0.968	0.906	0.884	0.856	0.919	1.07	1.07	1.17	0.827	1.05	0.937
Total Alkalinity	mg/L CaCO3	5.0	75.0	86.0	80.0	62.0	89.0	92.0	60.0	58.0	82.0	84.0	96.0	100	112	128	104	110

Notes:
 U - not detected
 J - estimated val Ue
 R - data rejected
 UJ - non-detect, estimated reporting limit

3.3 Opinion 3

Metals associated with sewer effluents from the Trail smelter (including arsenic, cadmium, copper, mercury, lead, and zinc) have been discharged in both dissolved and particulate forms. Particulate-bound metals are carried downriver and eventually settle out of the water column as fine-grained sediment in depositional areas. Part of the dissolved metals load released to the river system will adsorb onto suspended particulate matter and is also carried downriver and eventually deposited as sediment.

Biogeochemical processes occurring within these sediments result in the remobilization of sediment-bound metals, and their release into sediment porewater and the aquatic environment. The rate and extent of metals release is a function of biogeochemical redox conditions within the sediments, which are expected to vary across the Upper Columbia River site, depending in part on factors such as sediment grain size, organic matter content, metal concentrations, and burial depth.

3.3.1 Fate of Liquid Effluents in the Upper Columbia River

Metals in Teck Cominco's liquid effluents, including arsenic, cadmium, copper, lead, mercury, and zinc have a strong affinity to become attached to particle surfaces in the river, especially iron oxide particles (Hart 1982; Gaillardet et al. 2003). This process, called adsorption, regulates the partitioning of the metals between dissolved and particulate forms. While dissolved metals are transported with the river water, suspended particles are subject to sedimentation. Larger, denser particles and grains will settle out before finer, less dense particles. Due to their grain size and density, most of the slag particles will settle out of the water quickly and are transported primarily along the river bed at a much slower rate than the water. Metals associated with finer suspended particles will be carried further downstream before being deposited. As discussed in section 3.1.3, this expected difference in spatial distribution of slag-related versus effluent-related metals is recorded in the sediment geochemical signatures that show slag-related metals appear to extend downriver from Trail as far as Kettle Falls, while liquid effluents-related metals occur throughout the UCR site.

3.3.2 Metals Release from Sediment

The geochemical behavior of metals in contaminated sediments is the result of complex physical, chemical and biological processes (Santschi et al. 1990). Remobilization of

contaminant metals from sediments occurs through biogeochemical reactions driven by the decomposition of organic matter accumulated in the sediment. Oxygen dissolved in porewater is used by bacteria to metabolize the organic matter. In fine-grained sediments, the resupply of oxygen from overlying water is limited, and oxygen within the sediment becomes depleted, leading to anoxic conditions. Once oxygen is depleted, bacteria turn to alternate sources of oxygen to continue decomposing the organic matter. Iron oxides are usually the most important alternate source in freshwater sediments. As bacteria use iron oxide to metabolize the organic matter, the iron oxide is dissolved. This releases iron and metals adsorbed to the iron oxide to the porewater.

The extent of these processes and their effect on porewater metals concentrations have not been adequately characterized at the UCR site to date. However, it is my opinion that these processes are definitely occurring in at least some parts of the UCR site. Lake Coeur d'Alene, Idaho, where sediments have been contaminated by more than a century of mining, provides a relevant example. The Lake Coeur d'Alene sediments are rich in iron oxides, making them efficient scavengers for metal sorption (Tonkin et al. 2002; Balistrieri et al. 1999). Iron oxide reduction has also been shown to be an important process in the sediments (Cummings et al. 2000; Toevs et al. 2006). Porewater concentrations up to 910 µg/L for arsenic, 46 µg/L for lead, and 1,000 µg/L for zinc have been measured (Balistrieri et al. 2000).

The greatest potential for remobilization of metals from sediments by biogeochemical processes is therefore in areas of fine-grained sediment accumulations. Such conditions exist in the mid-channel of the UCR along the approximately 100 mile reach between Kettle Falls and the Grand Coulee Dam (USEPA 2006, Figure 5-8). Total organic carbon in these sediments is also generally greater than 5,000 mg/kg (USEPA 2006, Figures 5-18 and 5-19). Therefore, contaminated sediments along a substantial length of Lake Roosevelt have the potential for metals remobilization.

3.4 Opinion 4

The smelter slag and liquid effluent-related metals present in the sediments of the Upper Columbia River represent continuing, long-term sources of potentially toxic metal contaminants. Slag weathering processes and subsurface sediment biogeochemical processes drive the release of metals stored in the contaminated sediments, facilitating

their transfer to the aquatic environment, and ultimately leading to environmental exposure.

Opinions 2 and 3 provide the technical basis and evidence for the release of metals from sediments in the UCR contaminated by metals discharged from the Trail facility. Metals are continually released from slag as a result of dissolution of the glass and oxidation of metallic and sulfide inclusions. Porewater concentrations may be partly regulated by formation of secondary reactive mineral phases such as iron oxides which can take up the released metals. However, these phases have a finite adsorption capacity and, depending on the rate of release of a trace metal relative to the rate of formation of secondary phases, porewater concentrations of slag-related metals may either increase, decrease, or fluctuate with time, similar to what is observed in the slag release experiments.

Similarly, biogeochemical reactions involving reduction and dissolution of sedimentary iron oxides will also result in increasing concentrations of metals in porewater due to the release of adsorbed metals, either originally introduced into the sediments as particulate-associated metals from Trail liquid effluents, or as metals previously released by dissolution of slag and adsorbed onto sedimentary iron oxides.

As metals concentrations in sediment porewater increase, due either to dissolution of slag particles or biogeochemical reduction of iron oxides and release of adsorbed metals, a concentration gradient is established between porewater and the overlying water column. This gradient is the driving force for the movement of metals from porewater to surface water by diffusion. Because of their elevated metals concentrations, sediments contaminated by discharges from the Trail smelter are a long-term source of dissolved metals to the aquatic environment of the Upper Columbia River and Lake Roosevelt.

4 ADVISORY USE OF ADDITIONAL INFORMATION

I reserve the right to amend and modify my analyses and opinions based on continued study of the case materials and analysis of new information. I may additionally change the format of the information depicted in this report and its attachments, use additional information drawn from the materials considered in forming my opinions, and/or use additional exhibits at trial.

5 REFERENCES CITED AND ADDITIONAL MATERIALS REVIEWED AND RELIED UPON

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A repository of additional materials I reviewed and relied upon can be accessed via FTP at: <ftp://ftp.anchorqea.com/documents> (username: data@dimitri, password: f0rest)

APPENDIX A

RESUME

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

EDUCATION

University of Virginia, PhD, Environmental Sciences, 2000

California Institute of Technology, MS, Geochemistry, 1993

McGill University, MS, Geological Sciences, 1989

Concordia University, BS, Geology (Honors), 1986

EXPERIENCE SUMMARY

Mr. Vlassopoulos has over 20 years experience in environmental geochemistry with focus on evaluating natural and anthropogenic effects on soil, sediment, and water quality, biogeochemical and reactive transport modeling, isotope hydrology, environmental forensics, and in-situ monitoring and treatment technologies.

REPRESENTATIVE PROJECT EXPERIENCE

Port of Seattle, Washington

Conducted geochemical evaluations of arsenic and mercury exceedances in groundwater, and demonstrated a natural background origin influenced by seasonal redox fluctuations in the vicinity of subsurface peat deposits.

Des Moines Creek Basin Commission, King County, Washington

Provided technical oversight and guidance to mitigate potential environmental impacts from arsenic-bearing soils at a stormwater detention facility construction site. Services included development of sampling and monitoring plans, evaluation of arsenic mobility data, development and treatability testing of in-situ process for soil amendment to mitigate arsenic mobility during construction and subsequent operation of the facility.

Barbee Mill, Renton, Washington

Provided technical guidance and remedial design assistance for arsenic-contaminated groundwater at a former industrial site undergoing restoration for residential redevelopment. Evaluation of site conditions and remedial alternatives including in situ redox manipulation and permeable reactive barriers to ensure restoration within the client's required timeframe.

Sherwin Williams, Emeryville, California

Retained to provide technical guidance and peer-review of remedial feasibility investigations at a former lead arsenate pesticide manufacturing facility.

Rhone-Poulenc Inc., California and New Jersey

Evaluated former industrial sites contaminated with arsenic. Activities included demonstration of natural attenuation of groundwater arsenic plume, in-situ arsenic fixation of soil by chemical treatment, and design and pilot testing of an in-situ groundwater treatment system using zero-valent iron.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

Seattle-Tacoma International Airport

Conducted a vadose zone fate and transport modeling analysis to evaluate potential water quality impacts from fill materials used for construction of the third runway embankment, in support of permit applications and PCHB hearings.

Port of Vancouver, Washington

Retained as expert witness in environmental remediation cost recovery litigation. Evaluated role of surface water on the groundwater flow system and groundwater contamination from multiple chlorinated solvent sources using compound-specific stable isotope signatures to allocate commingled groundwater plume. The case was settled to the satisfaction of the client.

Noveon, Kalama, Washington

Conducted an evaluation of natural and enhanced attenuation for diphenyl ether and other chemicals in groundwater at an operating chemical plant, and developed an in situ bioremediation scheme to shorten cleanup timeframe. A Cleanup Action Plan was submitted and approved. The project is currently in design phase.

Oregon Steel Mill, Portland, Oregon

Conducted a geochemical evaluation of impacts from slag fill on shallow groundwater quality and demonstrated to ODEQ that offsite migration of dissolved metals was being mitigated by natural attenuation.

Electric Power Research Institute

Developed a geochemical reaction database for modeling adsorption of oxyanion-forming elements (antimony, arsenic, boron, chromium, molybdenum, selenium, sulfate, vanadium) on iron hydroxides.

Mamm Creek Hydrogeologic Evaluation

Conducted a critical review of a Garfield County consultant report on groundwater quality impacts related to gas drilling and production activities on behalf of the COGCC. The review evaluated the report's conclusions by analyzing an updated groundwater quality database for the study area provided by COGCC to assess whether dissolved methane and chloride concentrations showed statistically significant time trends. Findings were presented before the Commission.

Columbia Basin Ground Water Management Area, Washington

Evaluation of regional and locally enhanced groundwater recharge to basalt aquifers through multivariate statistical analysis of regional hydrochemistry data, collection, and interpretation of ambient geochemical and isotope tracer data, and groundwater age dating.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

Columbia Basin Ground Water Management Area, Washington

Evaluated seasonal, geologic and hydrologic controls on nitrate concentration trends in domestic wells completed in the suprabasalt sediment aquifers in the Pasco and Quincy Basins, demonstrating the importance of recharge from unlined canals in mitigating nitrate levels in some areas within the Columbia Basin Irrigation Project.

Confederated Tribes of the Colville Reservation, Washington

As part of a groundwater resource areas study, conducted a geochemical evaluation of sources and controls on arsenic concentrations in groundwater on the Colville Indian Reservation. Developed site selection guidelines to minimize potential risk of arsenic exceedances in future supply wells.

Gilliam and Morrow Counties, Oregon

For a confidential client, evaluated source and origin of dissolved hydrocarbon gases in the Columbia River Basalt aquifers based on gas geochemistry, stable isotope signatures, and age dating methods.

Western Snake River Plain Malheur County, Oregon

For a confidential client, evaluated source and origin of dissolved hydrocarbon gases and their relationship to the groundwater system using stable isotopes, noble gases, and age dating methods.

Colorado Oil and Gas Conservation Commission, Garfield County, Colorado

Conducted geochemical evaluations of groundwater and recharge sources in the Piceance Basin as part of a baseline water quality study prior to start of coalbed methane production in a 30-square-mile study area.

Higgins Farm Superfund Site, New Jersey

Retained to support remedial systems takeover and scope of work negotiations with USEPA on behalf of an industrial client. The project involved compilation and scrubbing of a multiyear groundwater quality database including data collected by multiple entities, and development and application of an automated process for evaluating and reporting robust trend statistics for constituent concentrations in many wells over time. The results of this analysis provided the basis for optimizing long-term monitoring efforts at the site.

Mexicali Valley Aquifer

Evaluated geochemical relationships between ground water and surface water in a regional aquifer. The effect of surface water recharge on regional groundwater quality was investigated by examining geospatial distributions of groundwater chemistry, using multivariate statistical methods to identify sources of water and solutes, and geochemical modeling to understand chemical evolution in the regional flow system.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

City of Portland Bureau of Water Works, Portland, Oregon

Evaluated occurrence, origin, and treatment options for manganese in the city's well field.

Soda Lake, Casper, Wyoming

Developed a biogeochemical fate and transport model for selenium in an artificially maintained playa lake to predict future ecological impacts for use in decision analysis of management options.

Agrico, Pensacola, Florida

Provided technical support for litigation involving groundwater contamination from a former fertilizer production plant. Reconstructed historical fluoride concentrations in wastewater through geochemical modeling and used radioisotope data to evaluate sources of radium in groundwater.

Union Pacific Railroad, Eugene, Oregon

Evaluated potential for CVOC exposure through soil vapor intrusion pathway in homes adjacent to a rail yard and successfully demonstrated to ODEQ that CVOCs in ambient air, and not groundwater, were responsible for the majority of the contamination detected in crawl space air samples.

Orion Safety Products

Conducted a state-wide evaluation of potential for stormwater quality impacts from perchlorate present in safety flares used on California highways.

Wah Chang Superfund Site, Albany, Oregon

Evaluated effectiveness of natural attenuation in meeting ROD-required cleanup time frame for chlorinated solvents in groundwater. The analysis was accepted by EPA Region 10.

General Electric, Rome, Georgia

Developed and applied a laboratory soil-water partitioning procedure for PCB contaminated soils to determine site-specific risk-based soil cleanup levels for groundwater protection.

Interstate Technology Regulatory Council

Developed and co-authored the regulatory guidance document *A Systematic Approach to In Situ Bioremediation, Including Nitrate, Carbon Tetrachloride and Perchlorate*. Served as instructor for training class based on this document.

City of Tigard, Oregon

Conducted water quality/compatibility evaluation for operating aquifer storage recovery (ASR) system.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

Sunrise Water Authority, Oregon

Conducted water quality compatibility evaluation for ASR pilot study.

City of Salem, Oregon

Evaluated disinfection byproduct formation potential during storage phase in an operating ASR system.

Baker City, Oregon

Evaluated water quality compatibility for ASR project, using geochemical modeling to predict potential effects of subsurface mixing of source water with native groundwater

U.S. Environmental Protection Agency

Developed framework for characterizing and assessing risks of exposure and environmental effects risk associated with geologic carbon sequestration, in support of regulatory guidance development.

Nestlé Waters America

Conducted water quality evaluations related to development and production quality control of spring water bottling operations.

Town of Poolesville, Maryland

Investigated causes of elevated gross alpha radioactivity in several of the community's water supply wells, and developed a monitoring and treatment plan to ensure compliance with federal drinking water regulations.

Palermo Wellfield Superfund Site, Tumwater, Washington

Evaluated source of groundwater contamination by chlorinated solvents using compound-specific stable isotope analysis for cost recovery case. Testified in Federal Court.

Crompton, Elmira, Ontario

Retained as expert witness in liability allocation of a commingled groundwater ammonia. Allocated ammonia between two sources based on stable nitrogen isotope signatures. The case was settled to the satisfaction of the client.

U.S. Department of Justice

Served as expert for environmental torts claims related to groundwater contamination by chlorinated solvents at military installations and other government facilities.

Photographic Imaging Manufacturers Association

Conducted an independent review of the USEPA's human exposure risk assessment for silver-bearing wastes.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

Pier 64, San Francisco, California

Evaluated the biodegradation of petroleum hydrocarbons and origin of methane in groundwater along the shore of San Francisco Bay. Study involved dissolved gas sampling and use of compound-specific isotope signatures to identify sources and degradation pathways and rates.

Berkeley Pit, Butte, Montana

Provided technical support in litigation over allocation of liability for cleanup costs between PRPs. Evaluated the impact of historical and ongoing operations on pit-lake water quality and cleanup costs based on field, laboratory, and geochemical modeling studies.

Atlantic Richfield Company, Clark Fork River, Montana

Provided technical support for natural resource damage litigation at historical mining and smelting operations. Evaluations included field sampling, characterization and modeling studies of metals attenuation in groundwater, estimation of background (pre-mining) groundwater quality in the Butte mining district, and identification and separation of mining-waste-related sulfate from natural geothermal sulfate loading to the Clark Fork River using stable isotope signatures.

U.S. National Park Service, Kentucky

Designed and implemented an extensive field investigation at a historic coal mining district to identify and characterize multiple mine drainage sources discharging to a designated Wild and Scenic River. The project included evaluation of pollutant loadings through long-term and storm-event monitoring, and prioritizing point sources for remediation. Isotope tracers were used to estimate seepage rates from coal spoil piles.

Numerous Sites and Clients

Evaluated nature, sources and reconstructed release histories at several sites affected by petroleum hydrocarbons using hydrocarbon fingerprinting techniques, stable isotopes, and simulation modeling.

Transco, Eastern United States

Provided technical support for development of remedial investigation plan for a large number of natural gas transport facilities across the eastern United States. Project involved the definition of risk-based action levels, based on a detailed compositional fate and transport model for petroleum hydrocarbon fractions.

ChemDyne Superfund Site

Evaluated contaminant mass removal by a pump-and-treat system operating for 15 years and estimated subsurface contaminant distribution for use in transport modeling. Prepared a report that was submitted and approved by USEPA.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

Panhandle Eastern Pipeline Company

Developed a protocol for evaluating subsurface natural attenuation of PCBs and petroleum hydrocarbons at multiple sites along a major pipeline system. Developed a specialized field filtration technique for sampling PCBs in groundwater.

PUBLICATIONS

Book

O'Day, P., D. Vlassopoulos, X. Meng, and L.G. Benning, editors. 2005. *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation*. ACS Symposium Series Vol. 915. Washington, DC: American Chemical Society/Oxford University Press. 450 p.

Articles

Vlassopoulos, D., B. Bessinger, and P. O'Day. 2010. Aqueous solubility of As_2S_3 and thermodynamic stability of thioarsenites. In *Water-Rock Interaction*. Birkle, P., and I.S. Torres-Alvarado, editors. Boca Raton: CRC Press. 823-826.

Root, R.A, D. Vlassopoulos, N.A. Rivera, M.T. Rafferty, C. Andrews, and P.A. O'Day. 2009. Speciation and Natural Attenuation of Arsenic and Iron in a Tidally Influenced Shallow Aquifer. *Geochimica et Cosmochimica Acta*. 73: 5528-5553.

Serrano, S., P.A. O'Day, D. Vlassopoulos, M.T. Garcia-Gonzalez, and F. Garrido. 2009. A Surface Complexation and Ion Exchange Model of Pb and Cd Competitive Sorption on Natural Soils: *Geochimica et Cosmochimica Acta*. 73: 543-558.

Adams, D.J., B. Faris, and D. Vlassopoulos. 2006. Evaluating In Situ Bioremediation for Groundwater Cleanup: *Chemical Engineering Progress*. 102, no. 2: 20-28.

Vlassopoulos, D., N. Rivera, P.A. O'Day, M.T. Rafferty, and C.B. Andrews. 2005. Arsenic Removal by Zerovalent Iron: A Field Study of Rates, Mechanisms, and Long-Term Performance. In *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation*. O'Day, P.A., D. Vlassopoulos, X. Meng, and L.G. Benning, editors. ACS Symposium Series Vol. 915. Washington, DC: American Chemical Society. 344-360.

O'Day, P.A., D. Vlassopoulos, R. Root, and N. Rivera. 2004. The Influence of Sulfur and Iron on Dissolved Arsenic Concentrations in the Shallow Subsurface Under Changing Redox Conditions: *Proceedings of the National Academy of Sciences of the United States of America*. 101: 13703-13708.

Faris, B., and D. Vlassopoulos. 2003. A Systematic Approach to In Situ Bioremediation in Groundwater: *Remediation*. 13: 27-52.

Raffensperger, J.P., and D. Vlassopoulos. 1999. The Potential for Free and Mixed Convection in Sedimentary Basins: *Hydrogeology Journal*. 7: 505-520.

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- Wood, S.A., C.D. Tait, D. Vlassopoulos, and D.R. Janecky. 1994. Solubility and Spectroscopic Studies of the Interaction of Palladium with Simple Carboxylic Acids and Fulvic Acid at Low Temperature: *Geochimica et Cosmochimica Acta*. 58: 625-637.
- Vlassopoulos, D., G.R. Rossman, and S.E. Haggerty. 1993. Coupled Substitution of H and Minor Elements in Rutile and Implications of High OH Contents in Nb- and Cr-Rich Rutile from the Upper Mantle: *American Mineralogist*. 78: 1181-1191.
- St-Seymour, K., and D. Vlassopoulos. 1992. The Importance of Magma Mixing at Nisyros Volcano, Greece, as Inferred from Incompatible Trace Element Systematics: *Journal of Volcanology and Geothermal Research*. 50: 273-299.
- St-Seymour, K., D. Vlassopoulos, T.H. Pearce, and C. Rice. 1990. The Record of Magma Chamber Processes in Plagioclase Phenocrysts at Thera Volcano, Aegean Volcanic Arc, Greece: *Contributions to Mineralogy and Petrology*. 104: 73-84.
- Vlassopoulos, D., and S.A. Wood. 1990. Gold Speciation in Natural Waters I. Solubility and Hydrolysis Reactions of Gold in Aqueous Solution: *Geochimica et Cosmochimica Acta*. 54: 3-12.
- Vlassopoulos, D., S.A. Wood, and A. Mucci. 1990. Gold Speciation in Natural Waters II. The Importance of Organic Complexing - Experiments with Some Simple Model Ligands: *Geochimica et Cosmochimica Acta*. 54: 1575-1586.
- Wood, S.A., and D. Vlassopoulos. 1990. The Dispersion of Pt, Pd, and Au in Surficial Media about Two PGE-Cu-Ni Prospects in Quebec: *Canadian Mineralogist*. 28: 649-663.
- Wood, S.A., D. Vlassopoulos, and A. Mucci. 1990. Effects of Concentrated Matrices on the Determination of Trace Levels of Palladium and Gold in Aqueous Samples Using Solvent Extraction-Zeeman Effect Graphite Furnace Atomic Absorption Spectrometry and Inductively Coupled Plasma-Mass Spectrometry: *Analytica Chimica Acta*. 229: 227-318.
- St-Seymour, K., and D. Vlassopoulos. 1989. The Potential for Future Explosive Volcanism Associated with Dome Growth at Nisyros, Aegean Volcanic Arc, Greece: *Journal of Volcanology and Geothermal Research*. 37: 351-364.
- Wood, S.A., and D. Vlassopoulos. 1989. Experimental Determination of the Hydrothermal Solubility and Speciation of Tungsten at 500° C and 1 kbar: *Geochimica et Cosmochimica Acta*. 53: 303-312.
- St-Seymour, K., S. Kumarapeli, and D. Vlassopoulos. 1988. Petrotectonics of Achaean Yasinski Metabasalts, Superior Province, Canada: Implications for Genesis of Achaean Greenstone Belts: *Neues Jahrbuch für Geologie und Paläontologie, Abhandlungen*. 177: 165-183.

Theses

- Vlassopoulos, D. 2000. The Origins of Molecular Nitrogen in the Subsurface: Thermodynamic, Kinetic and Isotopic Constraints. PhD dissertation. University of Virginia.
- Vlassopoulos, D. 1989. Some Experimental Studies Bearing on the Solubility and Speciation of Gold in Natural Waters. MS thesis. McGill University.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

Selected Conference Presentations

- Vlassopoulos, D., J. Goin, M. Zeff, K. Lindsey, T. Tolan, and V. Johnson. 2009. Regional Groundwater Geochemistry of the Columbia River Basalt Aquifer System, South-Central Washington. GSA Annual Meeting, Portland, Oregon, October 18-21.
- Vlassopoulos, D., M. Karanovic, V. Johnson, C.A. Gazis, T. Tolan, and K. Lindsey. 2009. Groundwater Recharge and Residence Times in the Columbia River Basalt Aquifer System, Washington. GSA Annual Meeting, Portland, Oregon, October 18-21.
- Goin, J., D. Vlassopoulos, and M. Nielson. 2009. Factors Influencing Nitrate Distribution in Groundwater of the Columbia Basin Ground Water Management Area. GSA Annual Meeting, Portland, Oregon, October 18-21.
- Serrano, S., P.A. O'Day, B. Bessinger, and D. Vlassopoulos. 2009. Immobilization of Mercury(II) by Ettringite-Type Phases: Modeling and Experiments. GSA Annual Meeting, Portland, Oregon, October 18-21.
- Vlassopoulos, D., B. Bessinger, V. Illera and P. O'Day. 2009. Lithologic, Hydrologic, and Biogeochemical Influences on Spatio-Temporal Variability of As and Hg Concentrations in Groundwater. *Geochimica et Cosmochimica Acta*, vol 73, p. A1389. Goldschmidt 2009, Davos, Switzerland.
- O'Day, P.A., S. Serrano, B. Bessinger, V. Illera and D. Vlassopoulos. 2009. Sediment Remediation of Metal and Metalloid Contaminants with Reactive Amendments. *Geochimica et Cosmochimica Acta*, vol 73, p. A959. Goldschmidt 2009, Davos, Switzerland.
- Vlassopoulos, D., J. Goin, C. Gazis, and V. Johnson. 2009. Environmental Isotope and Age Tracer Studies in the Columbia Basin Ground Water Management Area. Presentation at the 7th Washington Hydrogeology Symposium, Tacoma, Washington, April 27-30.
- Bessinger, B., and D. Vlassopoulos. 2009. A Geochemical Reactive Transport Model of Arsenic and Trihalomethanes in Aquifer Storage & Recovery Systems. Presentation at the 7th Washington Hydrogeology Symposium, Tacoma, Washington, April 27-30.
- Goin, J.C., and D. Vlassopoulos. 2009. Distribution and Seasonal Trends of Nitrate in Unconfined Aquifers of the Pasco and Quincy Basins, Washington. Presentation at the 7th Annual Washington Hydrogeology Symposium, Tacoma, Washington, April 27-30.
- Vlassopoulos, D. 2009. The Age of Groundwater in Columbia River Basalt Aquifers, East-Central Washington. Invited Presentation at the Oregon Ground Water Association Spring Technical Meeting, Silverton, Oregon, March 7.
- Bessinger, B., D. Vlassopoulos, S. Serrano, and P. O'Day. 2009. Reactive Transport Modeling of Arsenic and Mercury in a Chemically Amended Sediment Cap. Presentation at the Fifth International Conference on Remediation of Contaminated Sediments. Jacksonville, Florida, February 2-5, 2009.
- Vlassopoulos, D., S. Serrano, D.G. Kinniburgh, and D.L. Parkhurst. 2008. A CD-MUSIC Surface Complexation Database for Modeling Oxyanion Sorption on Iron Oxyhydroxides. *Geochimica*

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

- et *Cosmochimica Acta*, vol 72, p. A986. Goldschmidt 2008, Vancouver, BC.
- Root, R. A., P.A. O'Day, J. Hering, K.M. Campbell, and D. Vlassopoulos. 2008. Predicting arsenic behavior in high iron subsurface environments. *Geochimica et Cosmochimica Acta*, vol 72, p. A805. Goldschmidt 2008, Vancouver, BC.
- Vlassopoulos, D. 2008. Application of Stable Isotopes to Site Characterization: CVOC Sources, Commingled Plumes, and Groundwater-Surface Water Interactions. Invited Presentation at the U.S. Environmental Protection Agency Ground water Forum, Portland Oregon, July 8-10.
- Vlassopoulos, D., M. Conrad, M.J. Riley, T. Belunes, and P. Boyden. 2007. Environmental and Compound-Specific Stable Isotopes: Geochemical Forensic Tools with Application to Site Characterization in a Complex Hydrogeologic Situation. Oral presentation at the 6th Washington Hydrogeology Symposium, May 1-3, Tacoma, Washington.
- Vlassopoulos, D., M.J. Riley, J. Strunk, and P. Agid. 2007. Biogeochemical Controls on Spatial and Temporal Variability of Arsenic Concentrations in Shallow Groundwater, Seattle-Tacoma International Airport. Oral presentation at the 6th Washington Hydrogeology Symposium, May 1-3, Tacoma, Washington.
- Vlassopoulos, D., M. Conrad, and M.J. Riley. 2007. Source Identification and Allocation of Chlorinated Solvent Contamination Among Multiple Sources: Use and Limitations of Compound-Specific Isotope Analysis. Abstract and Oral Presentation at the Groundwater Resources Association Symposium on Applications of Isotope Tools to Groundwater Studies, March 28-29, Concord, California. Concord, CA. March 23-29.
- Serrano, S., P.A. O'Day, D. Vlassopoulos, F. Garrido, and T. García-González. 2006. Surface Complexation Modeling of Competitive Adsorption of Pb and Cd on Soils. Abstract and Oral Presentation at the 232nd American Chemical Society National Meeting, September 10-14, San Francisco, California. San Francisco, California
- Illera, V., P.A. O'Day, S. Cho, N.A. Rivera, R. Root, M. Rafferty, and D. Vlassopoulos. 2006. Immobilization of Arsenic in a Contaminated Soil Using Ferrous Sulfate and Type V Portland Cement. Poster presentation at the 232nd American Chemical Society National Meeting, September 10-14, San Francisco, California. San Francisco, California.
- Vlassopoulos, D., D. Sorel, T. Luong, M. Karanovic, M. Tonkin, K. Chiang, M. Rafferty, and M. Riley. 2006. Assessment of Potential Perchlorate Impacts from Use of Safety Flares Along California Roadways. Presented at the Groundwater Resources Association (GRA) 16th Symposium in the Contaminants in Groundwater Series--Perchlorate 2006: Progress Toward Understanding and Cleanup, January 26, 2006, Santa Clara, California.
- Illera, V., P.A. O'Day, N. Rivera, R. Root, M.T. Rafferty, and D. Vlassopoulos. 2005. Soil Remediation of an Arsenic-Contaminated Site With Ferrous Sulfate and Type V Portland Cement: EOS Transactions American Geophysical Union. 86, no. 52, Fall Meeting Supplement: Abstract B31A-0954.
- O'Day, P.A., and D. Vlassopoulos. 2004. Biogeochemical Controls on Speciation, Fate, and Cycling of Arsenic in Subsurface Environments. Presented at the GRA Symposium on Arsenic in Groundwater: Impacts on a Critical Resource, October 18-19, 2004, Fresno, California.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

- Rivera, N., P.A. O'Day, R. Root, and D. Vlassopoulos. 2004. Arsenic Removal by Zero Valent Iron. Presented at the GRA Symposium on Arsenic in Groundwater: Impacts on a Critical Resource, October 18-19, 2004, Fresno, California.
- Root, R., P.A. O'Day, N. Rivera, V. Illera, and D. Vlassopoulos. 2004. Redox-Controlled Natural Attenuation of Arsenic in a Tidally Influenced Shallow Aquifer. Presented at the GRA Symposium on Arsenic in Groundwater: Impacts on a Critical Resource, October 18-19, 2004, Fresno, California.
- O'Day, P.A., and D. Vlassopoulos. 2003. A General Biogeochemical Model for Arsenic Cycling in Shallow Aquifers. Presented at the 226th American Chemical Society National Meeting, September 7-11, 2003, New York, New York.
- Rafferty, M.T., C.B. Andrews, D. Vlassopoulos, D. Sorel, and K.M. Binard. 2003. Remediation of an Arsenic Contaminated Site. Presented at the 226th American Chemical Society National Meeting, September 7-11, 2003, New York City, New York.
- Rivera Jr., N.A., P.A. O'Day, D. Vlassopoulos, and R. Root. 2003. Mechanisms of Arsenic Removal by Zero Valent Iron Reactive Barriers. Presented at the 226th American Chemical Society National Meeting, September 7-11, 2003, New York, New York.
- Root, R., P.A. O'Day, N.A. Rivera Jr., and D. Vlassopoulos. 2003. Natural Attenuation of Arsenic Under Fluctuating Redox Conditions in Contaminated Estuary Sediments. Presented at the 226th American Chemical Society National Meeting, September 7-11, 2003, New York, New York.
- Vlassopoulos, D., C.B. Andrews, M. Rafferty, P.A. O'Day, and N.A. Rivera Jr. 2003. In Situ Arsenic Removal by Zero Valent Iron: An Accelerated Pilot Test Simulating Long-Term Permeable Reactive Barrier Performance. Presented at the 226th American Chemical Society National Meeting, September 7-11, 2003, New York City, New York.
- O'Day, P.A., and D. Vlassopoulos. 2002. Applications of Synchrotron X-ray Absorption Spectroscopy to Biogeochemical Speciation, Fate, and Remediation of Metal and Metalloid Contaminants in Natural Settings. Presented at the American Geophysical Union Fall Meeting, San Francisco, California. (invited speaker). In *Eos*. 83.
- Vlassopoulos, D., J. Pochatila, A. Lundquist, C.B. Andrews, M.T. Rafferty, K. Chiang, D. Sorel, and N.P. Nikolaidis. 2002. An Elemental Iron Reactor for Arsenic Removal from Groundwater. In *Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, May 20-23, 2002, Monterey, California. Gavaskar, A.R., and A.S.C. Chen, editors. Battelle Press.
- O'Day, P.A., D. Vlassopoulos, and R. Root. 2001. Direct Determination of Arsenic and Iron Speciation In Sediments and Groundwater Using X-Ray Absorption Spectroscopy: A Tidal Marsh Case Study. Presented at the Geological Society of America Annual Meeting, Boston, Massachusetts. In *Abstracts with Programs*, Geological Society of America. A117.
- Andrews, C.B., and D. Vlassopoulos. 2000. Modeling the Migration of Arsenic in Groundwater, Understanding the Processes. Geological Society of America, Annual Meeting, October, 2000, Reno, Nevada. In *Abstracts with Programs*, Geological Society of America. A406-7.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

- Vlassopoulos, D., and C.B. Andrews. 2000. The Intertwined Fate of Iron and Arsenic in Contaminated Groundwater Entering a Tidal Marsh, San Francisco Bay. National Ground Water Association Theis 2000 Conference on Iron in Groundwater, September 15-18, 2000, Jackson Hole, Wyoming. (invited speaker).
- Vlassopoulos, D., C. Andrews, R. Hennem, and S. Macko. 1999. Natural Immobilization of Arsenic in the Shallow Groundwater of a Tidal Marsh, San Francisco Bay. Presented at the The American Geophysical Union 1999 Spring Meeting, May 31-June 4, Boston, Massachusetts.
- Vlassopoulos, D., S.A. Macko, M. Schoell, and Y. Tang. 1999. Origin of Molecular Nitrogen in the Subsurface: Thermodynamic and Kinetic Pathways and Associated Isotopic Fractionations. Presented at the American Association of Petroleum Geologists Hedberg Research Conference on Natural Gas Formation and Occurrence, Durango, Colorado.
- Vlassopoulos, D., S.A. Macko, M. Schoell, Y. Tang, and E. Zhang. 1998. Generation of Nitrogen Gas During Thermal Evolution of Sedimentary Basins: An Experimental Investigation of Isotopic Fractionation. Presented at the Geological Society of America Annual Meeting, San Diego, California. In GSA Abstracts w. Programs. A214.
- Lolcama, J.L., D. Vlassopoulos, and S. Bakaletz. 1997. Field Implementation of a Novel Hydrochemistry Approach for Abandoned Mine Land Characterization. HazWaste World/Superfund XVIII Conference and Exhibition, December 1-4, 1997, Washington, DC. In Proceedings of the HazWaste World/Superfund XVIII Conference. 237-246.
- Vlassopoulos, D. 1997. Subsurface Fluid Reservoirs on Mars: A Possible Explanation for the Fate of an Early Greenhouse Atmosphere. Presented at the Lunar and Planetary Institute Conference on Early Mars, Houston, Texas.
- Vlassopoulos, D., P. Lichtner, W. Guo, and R. Hennem. 1995. Long-Term Controls on Attenuation of Mine-Waste Related Contamination in Alluvial Aquifers: The Role of Aluminosilicate Clay Minerals. Proceedings of the American Geophysical Union, 1995 Spring Meeting, Baltimore, Maryland, May 30-June 2. In Eos Supplement. 76, no. 17. S150.
- Wood, S.A., C.D. Tait, D. Janecky, and D. Vlassopoulos. 1991. The Interaction of Pd with Fulvic Acid and Simple Organic Acids - Solubility and Spectroscopic Studies. Presented at the Geological Society of America, 1991 Annual Meeting, San Diego, California, United States, October 21-24, 1991. In Eos. 71. 626. Also presented at the Geological Society of America, 1991 Annual Meeting. Abstracts with Programs - Geological Society of America. 23, no. 5: 214.
- Vlassopoulos, D., G.R. Rossman, and S.E. Haggerty. 1990. Hydrogen in Natural and Synthetic Rutile (TiO₂): Distribution and Possible Controls on its Incorporation. Presented at the American Geophysical Union Spring Meeting, May 29-June 1, 1990, Baltimore, Maryland. In Eos. 71, no. 17. 626. April 24. Also presented at the American Chemical Society National Meeting, Dallas, Texas.
- Vlassopoulos, D., and S.A. Wood. 1989. The Speciation of Au in Natural Waters: The Importance of Hydrolysis Reactions and Dissolved Organic Ligands. Presented at the GAC-MAC Joint Annual Meeting, Montreal, Quebec. In GAC-MAC Program with Abstracts. 14. A94.

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

- Vlassopoulos, D., S.A. Wood, and A. Mucci. 1989. Contents of Pt, Pd, and Au in Lake and Ground Waters Associated with Two Pt-Pd Showings in Mafic Rocks in Quebec. Presented at the Geological and Mineralogical Associations of Canada (GAC-MAC) Joint Annual Meeting, Montreal, Quebec. In GAC-MAC Program with Abstracts. 14. A71.
- Wood, S.A., D. Vlassopoulos, and P. Kranidiotis. 1989. The Volatility of High Technology (Li, Be, Ga, Ge, REE, Nb, Ta) and Related Metals in Magmatic Systems: Applications to Ore Formation. Presented at the Geological and Mineralogical Associations of Canada (GAC-MAC) Annual Meeting, Montreal, Quebec. In GAC-MAC Program with Abstracts. 14. A32.
- Vlassopoulos, D., and S.A. Wood. 1988. Comparison of Extraction Techniques for Au and Pt in Concentrated Aqueous Solutions and Applications to Graphite Furnace Atomic Absorption Spectrometry. Presented at the American Geophysical Union Spring Meeting, Baltimore, Maryland. In Eos. 69.
- Vlassopoulos, D., S.A. Wood, and A. Mucci. 1988. The Solubility and Speciation of Gold in Aqueous Solutions Containing Organic Ligands at 25°C. Presented at the Goldschmidt Conference, The Geochemical Society Meeting, Baltimore, Maryland, May 11-13.
- Wood, S.A., and D. Vlassopoulos. 1988. The Hydrothermal Solubility of Tungsten Oxides at 500° C and 1 kbar in HCl, NaCl, NaOH and Pure Water Solutions. Presented at the Goldschmidt Conference, The Geochemical Society Meeting, Baltimore, Maryland, May 11-13.

EXPERT WITNESS DEPOSITIONS AND TESTIMONY

Depositions

- Abarca, Raul Valencia, et al., v. Merck & Co., Inc., et al. U.S. District Court for the Eastern District of California, Fresno Division. Case No. 1 :07-CV-0388 OWW DLB.
- United States v. Washington State Department of Transportation, et al. U.S. District Court for the Western District of Washington at Tacoma. Case No. 05-5447RJB. June 29, 2006
- Port of Vancouver vs. Cadet Manufacturing Company. U.S. Bankruptcy Court for the Western District of Washington at Tacoma. Case No. 99-30304T. June 15, 2005
- Port of Vancouver vs. Cadet Manufacturing Company. U.S. Bankruptcy Court for the Western District of Washington at Tacoma. Case No. 99-30304T. December 7, 2004
- Domingo Aragon and Eva Aragon et al. v. Department of the Air Force, ex rel United States of America et al. U.S. District Court for the District of New Mexico. Case No. CIV 94-592 JP/LCS. July 25, 1995

Testimony

- United States v. Washington State Department of Transportation, et al. U.S. District Court for the Western District of Washington at Tacoma. Case No. 05-5447RJB. January 10, 2007

DIMITRIOS VLASSOPOULOS, PhD

Senior Managing Scientist

Awards and Honors

Research Grant: Sequestration and Immobilization of Metal and Metalloid Contaminants in Sediments. NIH Grant R01 ES016201 (Superfund Research Program), 2007-2010 (co-PI)

Pegau Geology Award, University of Virginia, 1997

Dupont Fellowship, University of Virginia, 1996-1998

University of Virginia President's Fellowship, 1995-1998

Reinhardt Research Fellowship, McGill University, 1986-1987

Professional Societies

American Geophysical Union

Geochemical Society

Geological Society of America

International Association of Geochemistry

National Ground Water Association

APPENDIX B
SEDIMENT CORE STUDY

APPENDIX C

EXPLORATORY DATA ANALYSIS

APPENDIX D
LEAD ISOTOPE DATA REPORT

APPENDIX E
SLAG METALS RELEASE STUDY

APPENDIX F
IN SITU POREWATER SAMPLING STUDY
