

Preliminary Review and Evaluation of Available Air Quality Monitoring Data and Consideration of Potential Present-Day Health Risks

Upper Columbia River Valley, near Northport, Washington



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Upper Columbia River Valley, near Northport, Washington

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Abstract

Air quality conditions in the upper Columbia River valley of northeast Washington State were evaluated using existing air monitoring data obtained from two monitoring stations near Trail, British Columbia, and one monitoring station near Northport, Washington. These stations are located approximately 1.3, 11.8, and 32.5 kilometers down-valley from a large metals smelting facility in Trail that has operated for over 100 years. The positions of these monitors within the Columbia River valley permit air pollutant concentration gradients to be evaluated at varying distances from the smelter. This evaluation focuses on the elements arsenic, cadmium, and lead in airborne particulate matter 10-µm and smaller in aerodynamic diameter (PM10).

Based on the availability and completeness of the records, air monitoring data collected from approximately 1993 to 2009 near Northport, as well as through 2014 in British Columbia, were used. Concurrent air monitoring at all three stations occurred during an extended interval in this period. Regression analyses of the concentrations data from the three monitors were done to estimate or best predict concentration gradients between stations. Potential particulate element concentrations between the international border and Northport were estimated by interpolation along the concentration gradients.

Results of these analyses suggest PM10 arsenic and cadmium concentrations may have exceeded State of Washington Acceptable Source Impact Levels (ASILs) in the upper Columbia River valley from Northport to the international border at least through 2014. Estimates of mean PM10 arsenic, cadmium, and lead concentrations also were evaluated with cancer unit risk factors and non-cancer health risk concentration screening thresholds.

Results of the health risks evaluations suggest further evaluations are needed to more confidently assess community health risks, including potential increased chance of developing cancer due to long-term inhalation. Additional air monitoring is recommended to directly quantify current concentrations of particulate matter toxic metals and metalloids in the upper Columbia River valley.

History of Air Quality Monitoring in Northeast Washington

Residents of the greater Northport-area community have expressed concerns to the Washington Department of Ecology (Ecology) about potential air pollution coming from a large integrated metallurgical smelter in Trail, British Columbia (B.C.), approximately 10 miles upstream of the U.S.-Canadian border. The Trail smelter is currently operated by Teck Metals Limited.

In response to community concerns, Ecology's Air Quality Program (AQP) and Toxics Cleanup Program (TCP) reviewed existing data to assess whether additional monitoring may be warranted.

AQP began monitoring aerosol [¹] element concentrations at several sites in the Northport area beginning in December 1992 [²] and continuing through December 1998 [³]. Teck (previously Teck Cominco) also began monitoring aerosol elements at one of the same Northport area sites in August 1993. They continued to monitor there until February 2009. Teck has also operated similar air quality monitoring stations in the Trail area, from 1971 through the present time.

Monitoring near Northport in the 1990s indicated particulate matter less than 10-µm in size (PM10) concentrations of arsenic (As), cadmium (Cd), and lead (Pb) significantly exceeded health impact screening concentrations.

Overview of Air Quality Monitoring Stations and Monitoring Parameters

Figure 1 presents air Pb monitor data from the decommissioned Teck monitoring station near Northport that operated from 1993 to 2009 (Northport-Cominco Station). Teck's reported annualized inventory of Pb air emissions in the same period is also plotted for comparison. The data from the station demonstrate decreased Pb emitted and transported downwind following the 1996/1997 Kivcet smelter furnace conversion. This suggests the last known large-scale process modification at the smelter facility resulted in substantially lower Pb emissions than before. Still aerosol Pb (and other elements) have continued to be emitted from the smelter facilities. A portion of this analysis attempts to estimate the likely range of concentrations of selected aerosol elements that presently occur in the upper Columbia River valley in the vicinity of Northport, Washington, using existing monitoring data obtained from U.S. and Canadian sources.

¹ Aerosol: Fine solid particles and liquid droplets suspended in air.

² Air Monitoring Data and Evaluation of Health Concerns in Areas of Northeast Tri-County. Washington State Department of Health. April 1994.

³ Northport, Washington Air Quality Study: Phase IV Final Report. Washington State Department of Ecology Air Quality Program. Publication No. 99-209. August 1999.



Figure 1. Northport-Cominco Station aerosol Pb concentrations from 1993 to 2009 relative to Teck facility modifications and reported Pb emissions.

Source of smelter complex modification information: *Trail Area Health & Environment Committee* (September 9, 2014 report).

An air quality monitoring hiatus has existed in the Northport/upper Columbia River area in Washington State since monitoring activities were suspended in 2009. Nonetheless, at that time, some of the aerosol elements data indicated potential risk worthy of further analysis.

To assess whether new monitoring is warranted, this analysis weighs uncertainties and potential concerns about contemporary concentrations of air pollution downriver from the smelter, specifically along the river valley between the international boundary and Northport.

To explore the most current air pollution in the Northport area potentially coming from the smelter facility, Ecology requested and obtained access to data from a series of Teck-managed monitoring stations via the British Columbia Ministry of Environment (BCMoE) Environmental

Monitoring System (EMS) Reporting System database [⁴]. Data obtained from the EMS, by permission of BCMoE, include analytical results from both public and private laboratories. The data in this analysis were collected by BCMoE and Teck staff (or their consultants) in accordance with BCMoE protocols and operating air permit requirements established for the Trail smelter.

As of September 2016, the data available via BCMoE EMS were current through the end of 2014. Some of the data are aerosol elements measured at locations downriver from Teck (Figure 2). AQP analyzed data that were efficiently comparable between monitoring stations in the Columbia River valley between Northport, Washington, and the Teck smelter complex in Trail, B.C.



Figure 2. Distribution of PM10 monitoring stations used in this analysis between Trail, B.C., and Northport, WA.

⁴ EMS is the Ministry's electronic repository of data on chemical, physical, and biological analysis performed on air, water, biological, solid waste discharge, and ambient monitoring locations throughout the province.

Data Selection and Analysis

Our selection of data for analysis was based on the monitoring location, sample timing, parameters measured, and analytical methods used. Specific details are provided in this section. Analysis of these data allowed us to preliminarily assess potential health risks to Washington State residents living in the area and make informed recommendations about the next steps.

Types of Air Monitoring Samplers Used

High-volume (Hi-Vol) samplers use a continuous duty blower and filter to collect particles up to 100-µm in aerodynamic diameter size. When fitted with a particle size classifier, a Hi-Vol sampler separates particles greater than 10-µm size from the air stream. The air stream is then passed through a filter paper to collect particles less than 10-µm in size (PM10). Gravimetric measurement gives the mass of suspended particulate matter (SPM) as the sum of the two fractions. SPM is often called total particulate matter (TPM). Material retained on the filters can be quantitated by laboratory methods such as inductively coupled plasma (ICP) used in conjunction with mass spectrometry (MS). Similar filter methods can be used to collect and analyze the 2.5-µm particle size fraction (PM2.5).

Rationale for Selective Use of PM10 Data

All of Teck's Northport-Cominco and Columbia Gardens data retrieved from EMS are "Hi-Vol Selective Size Inlet" with "N/P Dig(Filt+Wash);ICP". However, Teck and Ecology used two or more sampling methods and two or more analytical methods over time at some sites. For instance, the Butler Park monitor site near Trail, B.C., has had as many as four monitor types collocated simultaneously (Hi-Vol, Hi-Vol Selective size inlet, PM2.5 and PM10). The Hi-Vol Selective Size Inlet Sampler is for PM10, and the Hi-Vol Sampler is for Total Suspended Particulate (TSP) [⁵].

Since Northport-Cominco data consist of PM10 concentrations, and since data from other sites from 1994 up to 2015 were mainly also PM10 (rather than TSP or PM2.5), AQP concentrated on PM10 data and did not further examine TSP or PM2.5 data.

Other Data Exclusion Criteria

AQP also excluded concentration data obtained with non-ICP laboratory methods, or that did not have temporal overlap with data from other monitor locations in the study area.

Teck and AQP have monitored zinc (Zn) in PM10 in the Northport area. The amounts of Zn people there are exposed to by inhalation are too low to be harmful. Zn exposures at concentrations relevant to those in the area have not been implicated as causes of health

⁵ Particles of solid or liquid matter — such as soot, dust, aerosols, fumes, and mist — up to approximately 30 microns in size.

problems. In fact, Zn is an essential nutrient, and there are no regulatory risk-based concentration limits for it. Conversely, As, Cd, and Pb are well-known toxicants, and each has regulatory risk-based concentration limits. For these reasons, AQP assessed As, Cd, and Pb, but not Zn, data in this air quality assessment. Available daily average PM10 As, Cd, and Pb concentrations data are shown in Figures 3 through 6.



Figure 3. Sheep Creek, AQP

Figure 4. Teck-Cominco, Northport



Note that some of the lowest concentrations shown in Figures 3 through 6 are less than the concentrations that could be measured by ICPMS, but they are rendered as the corresponding quantitative concentration detection limits.

Sampling Time Periods

The PM10 elements monitored at stations shown in Figure 2 spanned partially overlapping time periods and so are comparable. Only data from times when station periods/parameters overlapped could be used to estimate concentrations in Northport in the post-monitoring period. To display timelines of the available PM10 As, Cd, and Pb data, AQP plotted the date of each sample event by monitor (Figure 7).



Figure 7. Timelines of reported PM10 samples analyzed by ICPMS from different air monitoring stations.

Overlapping monitoring intervals among the data from AQP's Sheep Creek PM10 monitor and the Northport-Cominco, Columbia Gardens, and Butler Park- Hi-Vol SSI ICP monitors are shown in Table 1.

Table 1. Monitoring Intervals common to stations downriver from Teck to Northport with PM10 ICMPS elements data.

17 August 1993 to 31 December 1998	7 November 2005 to 6 February 2009	7 February 2009 to 31 December 2014
AQP Sheep Creek		
Teck-Cominco Northport (early)	Teck-Cominco Northport (late)	
	Columbia Gardens (early)	Columbia Gardens (late)
	Butler Park (early)	Butler Park (late)

Below Quantitation Limit Data

All the As and Cd datasets and four of the seven Pb datasets from monitors in the Trail-to-Northport area contained some concentrations reported as less than the amount ICPMS was capable of measuring. One example is the Teck-Cominco Northport As dataset (Figure 8). Data are sorted by concentration to give an empirical cumulative distribution function (CDF) plot. The vertical axis provides the location function of each data point on a cumulative distribution. The horizontal axis gives each point's concentration. Inspection of the figure shows that the maximum As concentration in any sample was $0.39-\mu g/m^3$; the quantitation limit was $0.01-\mu g/m^3$; and 0.4 (40%) of the samples had concentrations less than that limit.



Figure 8. Cumulative distributions of Northport-Cominco Northport As concentration data (17 August 1993 – 31 December 1998).

All we really know about the samples with concentrations below quantitation limits is that the actual concentrations are somewhere between the limit and zero. However, when evaluating such data, some analysts ignore the below-quantitation-limit data or replace them with a fixed value such as zero or half the detection limit. Both these techniques may lead to biased results [⁶]. The potential for bias increases as the proportion of below-quantitation-limit data increases. It is especially important to reduce such bias in cases where the quantitation limit is close to the toxic level, as is the case for the Northport data. An effective alternative for working with such data is to use maximum likelihood estimation (MLE) or similar statistical methods [⁷]. Therefore, AQP

⁶ Helsel, D.R. 1990. "Less than obvious - statistical treatment of data below the detection limit." *Environ. Sci. Technol.* 24(12): 1766-74.

⁷ Gardner, M. 2012. "Improving the interpretation of 'less than' values in environmental monitoring." *Water and Environ. J.* 26: 285-90.

applied MLE procedures using statistical software R [⁸] with fitdistplus [⁹] to fit each dataset to different distributions including Lognormal, Log-logistic, Burr, Pareto, Weibull, and Gamma. Comparisons of the resulting goodness-of-fit statistics (Akaike and Schwarz's Bayesian information criteria) of the distributions guided the choice of which distribution best fit each dataset. Then, AQP used mixdist [¹⁰] and actuar [¹¹] procedures to obtain the mean concentration based on the best fitting distribution of each censored dataset. These means and the arithmetic means of the uncensored datasets are in Table 2.

Monitor, dates of operation (interval designation)	PM10	Estimate of the mean (μg/m³)	Fraction of dataset less than the reporting limit
	As	0.038	0.01
Butler Park, 7 November 2005 to 6 February 2009 (early)	Cd	0.007	0.06
	Pb	0.144	0
	As	0.018	0.07
Butler Park, 7 February 2009 to 31 December 2014 (late)	Cd	0.007	0.02
	Pb	0.153	0
	As	0.012	0.03
Columbia Gardens, 7 November 2005 to 6 February 2009	Cd	0.004	0.10
(earry)	Pb	0.082	0
	As	0.006	0.03
Columbia Gardens, 7 February 2009 to 31 December 2014	Cd	0.004	0.08
(late)	Pb	0.081	0
	As	0.006	0.14
Teck-Cominco Northport, 7 November 2005 to 6 February	Cd	0.001	0.48
2003 (late)	Pb	0.028	0.03
	As	0.026	0.40
Teck-Cominco Northport, 17 August 1993 to 31 December	Cd	0.011	0.68
1880 (early)	Pb	0.177	0.15
	As	0.026	0.50
AQP Sheep Creek, 17 August 1993 to 31 December 1998	Cd	0.011	0.65
	Pb	0.191	0.10

Table 2.	Descriptive statistics of eleme	nt concentration	datasets with	overlapping time-interview	erval
PM10 el	ements monitors.				

Contemporary Arsenic, Cadmium, and Lead Concentrations in the Northport Area

After addressing issues arising from insensitive element quantitation limits, AQP analyzed the existing monitor data to estimate recent mean PM10 As, Cd, and Pb concentrations near

⁸ R version 3.3.1 (2016-06-21) -- Copyright© 2016 The R Foundation for Statistical Computing <u>http://riskassessment.r-forge.r-project.org</u>.

⁹ Delignette-Muller M, Dutang C, Pouillot R, Denis J-B. (R package 'fitdistrplus') Help to Fit of a Parametric Distribution to Non-Censored or Censored Data, Version 1.0-7 (2016-7-2).

¹⁰ Macdonald P, Du J. (R Package 'mixdist') Finite Mixture Distribution Models, Version 0.5-4 (2011-10-18).

¹¹ Goulet V, Auclair S, Dutang Č, Milhaud X, Ouellet T, Pouliot L-P, Pigeon M. (R Package 'actuar') Actuarial Functions and Heavy Tailed Distributions, Version 2.0-0 (2016-11-12).

Northport. For this analysis, the average PM10 concentrations at the Northport-Cominco stations were assumed to be proportional to concentrations at Butler Park and Columbia Gardens. AQP calculated linear regressions of Northport As, Cd, and Pb concentrations as dependent on the concentrations at Butler Park and Columbia Gardens in the same monitoring intervals. We estimated contemporary (2/7/2009 to 12/31/2014) average concentrations of the elements near Northport using the resulting coefficients (Table 3).

	Ratios of means		Product of the ratio and corresponding recent mean (μg/m ³)	Predicted mean recent concentration near Northport (μg/m ³)
	Northport-Cominco/Butler Park	0.170		
٨٥	Northport-Cominco/Columbia Gardens	0.548		
AS	Butler Pk. – recent x Northport-Coming	co/Butler Park ratio	0.003	
	Columbia G recent x Northport-Cominco	/Columbia G. ratio	0.004	
				0.003
Cd	Northport-Cominco/Butler Park Northport-Cominco/Columbia Gardens Butler Pk. – recent x Northport-Cominco Columbia G. – recent x Northport-Cominco	0.202 0.381 co/Butler Park ratio o/Columbia G. ratio	0.001 0.001	0.001
Pb	Northport-Cominco/Butler Park Northport-Cominco/Columbia Gardens Butler Pk. – recent x Northport-Cominco Columbia G. – recent x Northport-Cominco	0.195 0.340 co/Butler Park ratio b/Columbia G. ratio	0.030 0.027	
				0.029

Table 3. Summary of regression analysis concentration ratios to derive Northport-area concentration estimates.

Estimated Concentrations from Northport to the International Border

To estimate average As, Cd, and Pb concentrations in areas upriver from Northport to the border where no PM10 speciation monitors have been deployed, AQP used SigmaPlot 10.0 [¹²] to apply a smoothing algorithm to the mean concertation estimates as functions of time and downriver distance. The previously noted data that were used in this procedure are consolidated into Table 4.

¹² SigmaPlot for Windows Version 10.0 Build 10.0.0.54. Copyright© 2006 Systat Software, Inc.

	Time Interval	Butler Park (1.34-Km)	Columbia Gardens (11.78-Km)	Northport Cominco/ Sheep Cr. (32.5-Km)		
٨c	First	0.038	0.012	0.007		
AS	Second	0.018	0.006	0.003		
Cd	First	0.007	0.004	0.002		
Cu	Second	0.007	0.004	0.001		
Dh	First	0.144	0.082	0.027		
FD	Second	0.153	0.081	0.029		
Notes:	First interval – 7 November 2005 to 6 February 2009					
	Second interval – 7 February 2009 to 31 December 2014					
	(Downriver distance from the Teck smelter complex)					
	Units = µg/m ³					

Table 4. Mean PM10 element concentration data used in Loess smoothing algorithm.

The best fitting data smoothing function for each dataset was a Loess second degree polynomial using the nearest neighbors bandwidth method [¹³]. The independent variable inputs to the Loess algorithm included two time intervals (first and second monitoring/modeling intervals) and six distance intervals (evenly spaced between 1.34-Km to 32.5-Km downriver from Teck). Figures 9 through 11 show the resulting mean concentration estimates as contour lines from Teck downriver to Northport and smoothed between early and late monitoring periods.



Figure 9. Observed and estimated mean As concentrations contour plot. (Note: 49N indicates where the Columbia River crosses the international boundary.)

¹³ The Loess algorithm is a tricube function used to weight data when quantifying a gradient.



Figure 10. Observed and estimated mean Cd concentrations contour plot. (Note: 49N indicates where the Columbia River crosses the international boundary.)



Figure 11. Observed and estimated mean Pb concentrations contour plot. (Note: 49N indicates where the Columbia River crosses the international boundary.)

The way to interpret Figures 9 through 11 can be exemplified by inspection of Figure 9. Notice that the As concentration contours that intersect the left vertical axis are the November 2005 through January 2009 average concentrations. Thus the estimated average concentration in that time interval at 17.95-Km (49°N, Columbia River at the U.S.-Canadian border 17.95-Km downriver from Teck) is about $0.010-\mu g/m^3$. Likewise, the contour that intersects the right vertical axis (February 2009 through December 2014 average concentrations) at 49°N is about $0.006-\mu g/m^3$.

The concentration estimates in Table 5 are taken from Figures 9 through 11. Ecology is not aware of any operational changes at the Trail smelter [¹⁴] that happened between 2005 and 2014 that might explain the apparent As concentration decrease.

Table 5.	Estimated recent average concentrations of PM10 As,	Cd, and Pb close to Northport and
the U.S	-Canadian border at the Columbia River.	-

	As		C	d	Pb	
	Nov. 2005 through Jan. 2009	Feb. 2009 through Dec. 2014	Nov. 2005 through Jan. 2009	Feb. 2009 through Dec. 2014	Nov. 2005 through Jan. 2009	Feb. 2009 through Dec. 2014
Columbia River Valley at U.SCanadian border (49°N)	0.010	0.006	0.003	0.003	0.066	0.066
Teck-Cominco Northport	0.007	0.004	0.002	0.002	0.027	0.028

Units = $\mu g/m^3$

Inhalation Characterization

AQP compared estimates of the mean PM10 As, Cd, and Pb concentrations at the U.S.-Canadian border (Table 5) and at the former Northport-Cominco and AQP Sheep Creek monitoring stations for the 2009 to 2014 interval to cancer unit risk factors and non-cancer health risk concentration thresholds (Table 6). The resulting risk estimates are presented in Tables 7 and 8.

¹⁴ Documented in a report titled *Trail Area Health & Environment Committee*. September 9, 2014.

	California Office of Environmental Health Hazard Assessment Cancer Risk Factor (/µg/m ³)	EPA Integrated Risk Information System Assessment Cancer Risk Unit Factor (/µg/m ³)	California Office of Environmental Health Hazard Assessment Chronic Reference Exposure Level (µg/m ³)	California Office of Environmental Health Hazard Assessment Acute Reference Exposure Level (µg/m ³)	Federal National Ambient Air Quality Standard (µg/m³)
	0.0033	0.0043	0.015	0.2 (4-hour average)	
As	Cancer: Gastrointestinal and urinary tracts, skin and lung		Toxicity to reproductive, cardiovascular and nervous systems, and to development, lungs and skin	Decreased fetal weight	
	0.0042	0.0018	0.02		
Cd	Cancer: Lung, trachea, bronchus		Toxicity to kidney, respiratory system, development, cardiovascular and nervous systems, skin		
	0.000012				1.5 (3-month average)
Pb	Cancer				Reproductive and neurobehavioral developmental toxicity

Table 6. Federal and California As, Cd, and Pb risk-based concentrations.

The relevant Chapter 173-460 Washington Administrative Code (WAC) Acceptable Source Impact Levels (ASIL) concentrations are based on cancer unit risk factors selected from either the U.S. Environmental Protection Agency (EPA) or the California Office of Environmental Health Hazard Assessment (OEHHA) [¹⁵]. However, as noted in Table 6, the factors are not equal. Variations between the methods EPA and OEHHA used to estimate unit risk factors for As and Cd produce different values. Instead of using one or the other of these unit risk factors, AQP used both to calculate higher and lower cancer risk estimates for As and Cd, as well as a single cancer risk estimate for Pb. The results for the Northport area are in Table 7, and the results for the Columbia River valley at the international boundary (49°N) are in Table 8. These tables also include sums of the three elements' cancer risks, and their non-cancer health hazard quotients.

¹⁵ 173-460 WAC ASIL concentrations are risk screening levels based on unit risk factors from the EPA or the OEHHA. The As, Cd, and Pb ASILs are:

^{• 0.000303-}µg/m³ (1-year Time-Weighted Average [TWA]) As and inorganic As compounds.

[•] $0.000238 - \mu g/m^3$ (1-yr TWA) Cd and compounds.

[•] $0.0833 - \mu g/m^3$ (1-yr TWA) Pb and compounds not otherwise specified.

 Table 7. Estimated potential additional lifetime cancer risk and chronic non-cancer health effect hazard posed by inhalation exposure to As, Cd, and Pb in ambient air in the Northport area.

	As	Cd	Pb		
Lower	1.08E-05	2.42E-06			
Higher	1.41E-05	5.65E-06	3.44E-07		
	Cancer risk sum				
Higher	2.01E-05				
Lower	1.36E-05				
Chronic hazard quotient	0.22	0.07			
	Developmental, cardiovascular and nervous systems, and skin hazard index				
	0.29				

Table 8. Estimated potential additional lifetime cancer risk and chronic non-cancer health effect hazard posed by inhalation exposure to As, Cd, and Pb in ambient air where the Columbia River flows into Washington, 49°N.

	As	Cd	Pb		
Lower	1.72E-05	5.22E-06			
Higher	2.24E-05	1.22E-06	7.92E-07		
		Cancer risk sum			
Higher	3.53E-05				
Lower	2.32E-05				
Chronic hazard quotient	0.35	0.15			
	Developmental, cardiovascular and nervous systems, and skin hazard index				
	0.49				

The proper interpretation of these estimated values is that a life-long Northport resident may have up to a 14-to-20-in-one-million chance (1.36E-05 to 2.01E-05) of developing cancer due to breathing As, Cd, and Pb in outdoor air at the most likely contemporary concentrations if these levels were to persist there for 70 years. This risk is in addition to cancer risks posed by other factors.

Likewise, a life-long resident dwelling within the lower elevations of the Columbia River valley at the international boundary may have a cancer risk of up to 23 to 35 in one million (2.32E-05 to 3.53E-05) due to inhalation exposure to As, Cd, and Pb. This again assumes exposure to contemporary levels of airborne As, Cd, and Pb over a 70-year timespan.

Non-cancer toxic health hazards from acute (short-term) and chronic (life-long) inhalation of As and Cd in outdoor air are unlikely at probable contemporary levels near Northport and in the

lower elevations of the Columbia River valley at the international boundary. Chronic As and Cd hazard ratios are 0.29 and 0.49 near Northport and near the Columbia River at 49°N, respectively, indicating there is little to no hazard of developmental, cardiovascular, nervous system, or skin toxicity (if the ratios were equal to or greater than 1, the hazards would be considered significant). Because Pb has no apparent effects threshold concentration, there are no published Federal or California inhalation risk-based concentration levels for it, and its potential to increase the risk of these problems is not accounted for in this analysis. Even small exposures to Pb appear to be slightly toxic in terms of impaired neurodevelopment and increased hypertension. Nonetheless, it is unlikely that any 3-month mean concentration of Pb during the 7 February 2009 to 31 December 2014 interval, at either location, exceeded the National Ambient Air Quality Standards.

Note that acute arsenic health hazards were significant before 1997. For example, daily (24-hr) average As concentrations exceeded the California OEHHA acute risk exposure level $(0.2-\mu g/m^3, 4-hr \text{ average})$ on a few occasions as late as 1997. Acute As hazards within the Columbia River valley at the international boundary cannot be determined without specific information on extremes in daily average concentrations there.

Quality Assurance/Uncertainty Analysis

To assess the speciation monitors data quality, AQP used datasets from the Butler Park station. Like with other Trail-Northport area data in the BCMoE's EMS database, Butler Park monitor data quality improved beginning in 2000, after which the database included no further TSP and PM10 element concentrations recorded as zero (0). Before then, however, some zero-value concentrations were placed in EMS. Zero concentrations are impossible to measure because of the limited sensitivity of the analytical methods used.

AQP also compared Butler Park element concentrations in different PM size fractions. With respect to the assumed quantified relationships between TSP, PM10, and PM2.5 in any given air sample, the mass of an element in TSP must be greater than its mass in PM10, which in turn must be greater than its mass in PM2.5. As such, simultaneously collected samples of different sizes at Butler Park should have greater masses of each element in larger size fractions relative to masses in smaller size fractions. Therefore, in instances when samples on the same day were available, AQP checked if element concentrations were relatively enriched/diminished in TSP versus PM10 size fractions. During the 8/3/1997 to 10/28/2001 interval, 17% of As, 11% of Cd, and 10% of Pb concentration ratios were less than one. Again, this is physically impossible, though in some instances, time-rounding may have been the cause, because TSP and PM10 samplers did not always finish at exactly the same time of day, and it was necessary to round sample end-times to the nearest whole day to match data together by date.

AQP compared our Sheep Creek monitor data to Northport-Cominco Hi-Vol SSI ICP data. The dates in the AQP data did not specify what time of day each sample started or ended, but the EMS data did. Both samplers operated (usually) every sixth day. Because there are no records of collection times in the AQP data, we could not determine if samples taken on the same reported date actually occurred in the same interval. Comparing ones that might not have been collected

in precisely overlapping intervals would produce uncertain results. In other words, pairwise comparison of individual samples from the AQP monitor to ones from the Teck's Northport-Cominco monitor cannot be interpreted with full confidence. As an alternative, AQP compared long-term averages and variances of both datasets. Side-by-side comparison of rounded Northport-Cominco data with AQP data (Table 9) indicate equal average concentrations across the As and Cd, and similar Pb concentrations.

Approximate monitoring interval 23 Aug. 1993 to 13 Dec. 1998 at:	PM10	Estimate of the mean (µg/m ³)
	As	0.026
Teck-Cominco Northport	Cd	0.011
	Pb	0.177
	As	0.026
AQP Sheep Creek	Cd	0.011
	Pb	0.191

Table 9.	Descriptive	statistics f	or PM10 As	, Cd,	and Pb	data from	co-located	I Teck-Cor	minco
Northpo	rt and AQP S	Sheep Cree	k monitorin	g sta	tions.				

Emissions inventory reporting from Trail Operations could not be verified and several observations suggest the value and representativeness of this data may be low. Data compiled from BCMoE and the EPA [¹⁶] reveal some anomalies evident, which call into question the emissions and other data. Year-to-year variations in PM emissions do not correspond to variations in As, Cd, Pb, and Zn emissions. TPM, PM10, and PM2.5 emissions are reported as unchanging ratios of what should be actual measurements, not estimates. The amounts do not appear to have been independently monitored and reported. As, Cd, Pb, and Zn are solid particle components yet their year-to-year emissions trends do not proportionately track emissions of PM. For example, the annual PM10, PM2.5, Pb, and Zn emissions data shown in Figure 12 reveal large variations in PM emissions but relatively small variations in metals emissions. It is unexpected that mass of Zn (the predominant element monitored in PM near Trail and Northport) exceeds the mass of PM2.5 emitted in 2003 and 2009, but emitted Zn mass is about half the PM2.5 mass in 2007 and 2012.

¹⁶ Data in Figure 12 were compiled from

http://ec.gc.ca/inrp-npri/donnees-data/index.cfm?do=facility_history&lang=En&opt_npri_id=0000003802&opt_rep_ort_year=2014

and http://www.epa.gov/ttn/chief/ap42/c00s00.pdf, both accessed August 22, 2016.



Figure 12. Teck emissions inventories.

Because most quality assurance/quality control (QA/QC) documentation is absent, any preliminary conclusions drawn from these data must be tempered accordingly. AQP performed this assessment without the benefit of instrumental method standard operating procedures, sample handling records, field or internal duplicates, blanks and spikes, etc. These supplemental QA/QC data would be needed to better evaluate the overall representativeness of these historical monitor data.

In summary, a comprehensive analysis of confidence in the accuracy and representativeness of all the available monitoring and emissions data compiled and reviewed as part of this evaluation is limited. The possibility of some PM samples actually having none of one or more elements is extremely low. Routinely finding none of some elements when analyzing PM samples is unrealistic. Yet some PM element concentrations prior to 2000 at Columbia Gardens and Butler Park were reported as $0-\mu g/m^3$.

Lastly, on certain days when both TSP and PM10 samples were collected, reported masses of one or more elements were greater in the PM10 fraction than in the TSP sample; analytically, this is not possible. Unqualified reporting of sample results where the PM10 sample mass exceeds the corresponding TSP sample mass diminishes AQP's overall confidence in these historical data.

Conclusions and Recommendations

Evaluation of Canadian monitors and extrapolation methods to assess potential air quality conditions near Northport between 2009 and 2014 indicates recent average PM10 As and Cd concentrations exceed State of Washington ASILs. However, the data have several recognized limitations. An expanded data quality assessment would be necessary to attempt a verification of the representativeness of these BCM0E EMS datasets to support air quality decision-making.

The following recommendations are provided as an outcome from this AQP evaluation of historical Northport-area air quality monitoring data:

- Updated upper Columbia River valley air quality monitoring in Washington State is recommended using current technologies, expanded methods, and consistent equipment at appropriate locations. Development of more contemporary air quality data will provide a better basis to assess current air quality conditions in the upper Columbia River valley of northeast Washington. This study should be scoped to assess current air quality conditions, including possible human health-related impacts attributable to nearby Trail, B.C., smelter emissions and potential re-dispersion of previously deposited particulates.
- 2. The suite of analytes should be expanded beyond just As, Cd, Pb, and Zn to allow for the quantification of certain metals/metalloids such as indium and thallium that also are known to be emitted from the smelter complex and may further contribute to potential human health impacts.