

**ALASKA DEPARTMENT OF ENVIRONMENTAL CONSERVATION
DIVISION OF SPILL PREVENTION AND RESPONSE
CONTAMINATED SITES PROGRAM**

Technical Memorandum

Date: August 2018

Guidance for Evaluating Metals at Contaminated Sites

I. PURPOSE

The purpose of this technical memorandum is to provide guidance on evaluating metals that are commonly found in the natural environment but may also be present from anthropogenic sources at a contaminated site. The guidance includes: how to determine when metal sampling and analysis is required; considerations in obtaining background samples; establishing and comparing background concentrations to the site; determining cleanup levels for the site; and how to evaluate cumulative risk. Although, the primary focus of this technical memorandum addresses arsenic and chromium, the same approach may be employed for other naturally occurring inorganic metals.

II. INTRODUCTION

Arsenic, chromium and many other metals are naturally occurring throughout Alaska. The naturally existing concentrations of these metals are typically referred to as “background.” However, these metals may also be present from anthropogenic activities. Anthropogenic is defined as “of human origin or resulting from human activity.” For example, anthropogenic arsenic sources include naturally occurring arsenic sources altered or disturbed by human activity, *e.g.* mine tailings, mobilization from soil to groundwater via another introduced contaminant such as gasoline, as well as manufactured products which contain arsenic released into the environment.

Arsenic is found naturally in two forms. Inorganic arsenic refers to arsenic atoms that occur in a pure, metallic form, or in compounds where they are bonded to other non-carbon elements (typically combined with oxygen, chlorine, and sulphur). Organic (*i.e.* carbon based) arsenic compounds contain covalently bonded arsenic atoms combined with carbon, oxygen, and hydrogen. The toxicity of arsenic depends very heavily on its form. Inorganic arsenic (arsenite, arsenate) is considered to be most toxic, whereas organic (methylated) forms of arsenic are common metabolites of the human body and are much less toxic. The soil cleanup levels listed in 18 AAC 75.341 Table B1 are associated with inorganic arsenic. These levels can also be applied to organic forms of arsenic, although this may be an overly conservative approach. Arsenic detected in environmental media should be assumed to be in its inorganic form unless proven otherwise by a laboratory and method approved by the Alaska Department of Environmental Conservation (ADEC). Arsenic poses significant non-cancer health risks to humans in addition to being a known human carcinogen.

Naturally occurring arsenic is released into the environment by volcanoes and through weathering of arsenic-containing minerals and ores. Anthropogenic arsenic sources include various commercial and industrial processes and materials. In industry, arsenic is a by-product of the smelting process for many metal ores, including lead, gold, zinc, cobalt, and nickel. It is also used in multiple commercial products such as fungicides, herbicides, wood preservatives, batteries, optical glass, semiconductors, ammunition, and pharmaceutical products.

Chromium is most often present in two forms: trivalent (chromium III), and hexavalent (chromium VI). Naturally occurring chromium is usually present as chromium III, whereas chromium VI is often derived from human activities (WHO 1990). Chromium VI is more toxic, soluble, mobile and

bioavailable in the environment compared with Chromium III. Typical baseline laboratory analysis for chromium reports total concentrations without speciation. In the past, the ADEC cleanup level calculations for total chromium used the most toxic oxidation state, chromium VI, which poses significant non-cancer health risks. However, concentrations of total chromium in soils throughout the State routinely exceed a calculated total chromium cleanup level that is based off of chromium VI toxicity. In addition, chromium VI has rarely been detected at contaminated sites in Alaska, as this metal is primarily associated with industrial and manufacturing processes (e.g., chrome electroplating, textile dyes, wood preservatives, anti-corrosion products used in paints/primers) that have not typically been utilized in Alaska. If an anthropogenic source of chromium is suspected to have been released, then ADEC will require chromium VI be analyzed.

Alaska cleanup levels are now established for chromium III and chromium VI and arsenic as follows:

Soil Cleanup Levels(mg/kg)	Arctic Zone	Under 40 Inch Zone	Over 40 Inch Zone	Migration to Groundwater
Chromium(III), Insoluble Salts	1.0 x 10 ⁵			
Chromium(VI)	4.9	3.9	3.2	0.089
Arsenic	12	8.8	7.2	0.2

	Groundwater Cleanup Level (micrograms/liter)
Chromium(III), Insoluble Salts	22000
Chromium(VI)	0.35
Arsenic	0.52

Site analytical data reporting total chromium results will be presumed to represent chromium III unless site-specific evidence suggests a potential chromium VI source. This allows chromium VI to be evaluated on a site-specific basis where an anthropogenic source is confirmed or suspected based on current or past activities at a site.

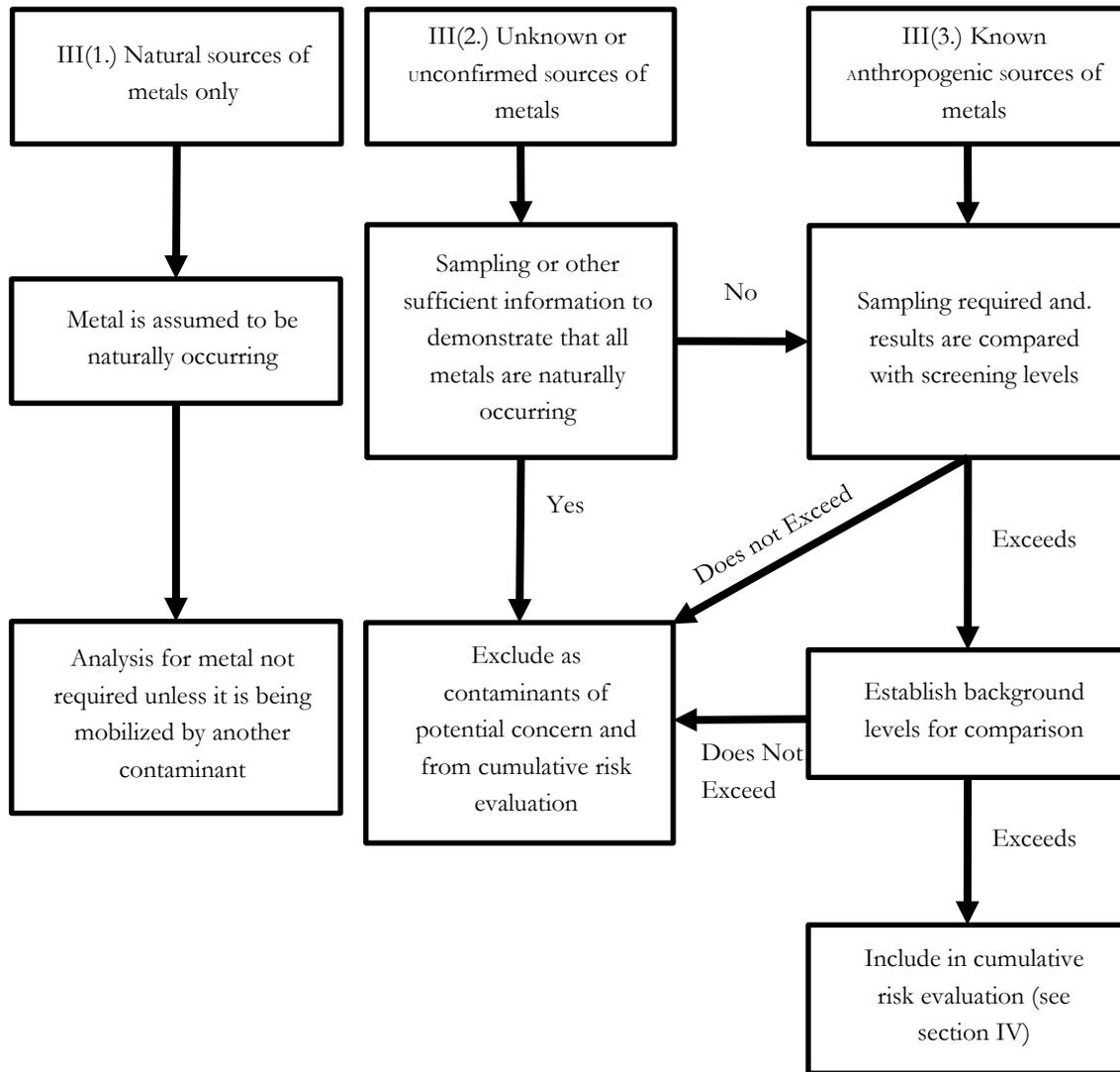
Please note that the requirement to evaluate background metals, the timing of background metal characterization in the cleanup process, and the level of effort needed to generate a background data set should be determined on a site-specific basis.

III. METALS IN THE ENVIRONMENT

The sources for metals in the environment at contaminated sites typically fall into one of three subcategories: natural sources, unknown or unconfirmed sources, and known anthropogenic sources.

Available knowledge about the potential source(s) of metals at a site and the initial evaluation will determine the need for conducting background sampling and cumulative risk calculations as presented in the flow chart (Figure 1).

Figure 1. Path for Evaluating Metals at Contaminated Sites.



1. Natural Sources of Metals

As a general rule, sampling and analysis for metals will not be required at sites presumed to only contain naturally occurring concentrations of metals. For example, if a site’s history is well known and there is no evidence of an anthropogenic source of metals being stored or released at the site, then there is usually no reason to sample for metals.

One exception is that in some site settings, certain contaminants can influence the surrounding geochemistry and promote mobilization of naturally occurring metals to more sensitive pathways like consumption of groundwater. In these instances where the natural occurring metal concentration in the

soil is high enough and conditions favor mobility to ground or surface water, monitoring may be required. An example of this type of mobilization is the natural breakdown of petroleum plumes in groundwater, which can temporarily result in anoxic conditions that mobilize arsenic into the water column. Studies suggest the mobilized arsenic may adsorb to aquifer sediment downgradient from the plume as the petroleum plume degrades (Cozzarelli et al., 2015). Cleanup will not generally be required for arsenic in these situations; however, monitoring of dissolved arsenic may be required as an indicator of biodegradation, or to ensure the groundwater is safe for consumption. Furthermore, arsenic must be included in cumulative risk calculations and institutional controls may be required until the groundwater geochemistry has reverted to its original conditions.

2. Unknown or Unconfirmed Sources of Metals

At many contaminated sites, contaminants and releases may fall under the unknown or unconfirmed category. For these sites, a lines-of-evidence approach should be considered when deciding whether elevated concentrations of a metal are related to a release or past activity or are naturally occurring. In general, no single line-of-evidence will provide sufficient justification to determine that a particular metal is not related to the release in question; multiple lines of evidence provide the necessary stronger case. Without sufficient justification to rule out a metals related release, one should proceed with the screening process as with any other anthropogenic contaminant release to determine if a reference background study and comparisons are required. All analytical results from an ADEC approved analytical method should be reported. For example, if EPA Method 6010C is run for 31 metals, then the results for all metals should be reported and not just the results for metals subject to the requirements of the Resource Conservation and Recovery Act (RCRA). The following lines-of-evidence are examples to consider when evaluating site assessment data to determine whether metals are naturally occurring:

- There is no record of a potential metal related release and/or historical usage or site activity related to metals.
- Site characterization data do not show any well-defined pattern of concentrations indicative of a release of the metal. Typically, a contaminant concentration gradient will lead back to the location of a release.
- The metal is associated solely with shallow soil near site features such as fences, sidewalks or buildings and is known to be a constituent of pesticides/herbicides that were likely used for their intended purpose and properly applied.
- The detection and analysis of a specific metal species or metal organic complex could be used to determine if a specific anthropogenic chemical source was released.

3. Known or Suspected Anthropogenic Sources of Metals

When a metal release is known or suspected to have occurred based on sources, site history, or site activities, one should proceed with metals analysis and screening as with any other anthropogenic contaminant release to determine if it is a contaminant of potential concern (COPC). Potential anthropogenic sources of metals include: landfills or waste dumps, batteries, glass, drilling muds, paints, metal plating, additive in cooling tower water, mining, pesticides, coal, electrical equipment, photography and film development, and wastewater treatment plants. Characterization at sites where used oil or waste oil has been released should include sampling and analysis for metals, including arsenic and chromium (see Contaminated Sites Program Field Sampling Guidance – Appendix F and UST Procedures Manual). The laboratory and method chosen to analyze metals in environmental media should be approved by the Contaminated Sites Program prior to the sampling effort. Disturbed

or altered naturally occurring arsenic sources (e.g., mine tailings or waste rock) are considered anthropogenic and should be compared with appropriate screening values or cleanup levels, and should be included in cumulative risk evaluations when exceedances occur. As with other COPCs, if the metal concentrations do not exceed screening values, the metal can be dropped from further assessment. Any other metals results quantified by a given analytical method specified in Appendix F of the field sampling guidance should be reported, but if a metal is not related to the release, it can be assumed to be naturally occurring and excluded from the screening process.

4. Obtaining Background Samples

The basic principle in identifying background sample locations is to find areas that represent the native soil characteristics of the site, have similar distribution of metal concentrations as the site, but have not been impacted by a discharge, release, or other site disturbance, such as the movement of soil or rock. Groundwater wells used to establish background conditions should be up-gradient of the impacted well(s). When possible, background samples should be collected within site boundaries, but outside of known or suspected anthropogenic sources and in accordance with a department approved work plan. If it is not defensible to establish a single background value; a range should be evaluated to account for the heterogeneity of environmental media. The selection of background sample locations is a matter of professional judgment, however the following points should be considered:

- The background sampling area must be clearly unaffected by releases from the subject site, or any other site. When characterizing natural background conditions, samples are best taken from areas with minimal anthropogenic impact (e.g., undisturbed natural areas). The following areas are inappropriate for background sampling:
 1. Fill areas;
 2. Areas where known or suspected hazardous substances, petroleum, solid or hazardous wastes or wastewaters are managed, treated, handled, stored or disposed;
 3. Areas affected by road runoff;
 4. Parking lots and areas affected by runoff from parking lots or other paved areas;
 5. Railroad tracks or railway areas or other areas affected by their runoff;
 6. Areas of concentrated air pollutant depositions or areas affected by their runoff;
 7. Storm drains or ditches presently or historically receiving industrial or urban runoff; or
 8. Groundwater wells down gradient or surface water and sediment downstream of the impacted area.

- Natural concentrations of inorganics vary with soil type and location. When determining natural background, the soil type and/or aquifer for the contaminated area and background locations should be similar in the physical, chemical and biological aspect of the media whenever possible. The following parameters should be similar when comparisons are made:
 1. pH/Eh
 2. salinity
 3. cation exchange capacity
 4. percent organic carbon
 5. particle size and distribution
 6. thickness of soil horizon
 7. soil type, structure

8. well screening interval

- Concentrations from background studies performed on one site may not be used on a different site, without prior approval, due to the potential for variability in the naturally occurring concentrations.
- When measuring chemical concentrations in background samples, the same analytical methods used for site samples should be employed, if possible.
- The background data set should be examined carefully for the presence of outliers, i.e., data that may not in fact represent background conditions. Formal outlier tests as well as professional judgment can be used in evaluating the background data set.
- Background samples should be collected randomly and be representative of the area and media of interest.
- For rivers, surface water and sediment background samples should be collected upstream of the impacted area.
- For surface water bodies, background samples can be collected near the inflow to the water body if it is not influenced by the contaminated site. Alternatively, for large surface water bodies, the background samples can be collected from the water body itself but as far away as possible from an anthropogenic source.
- The effect of tides should be considered for background sampling and if possible, background surface water, groundwater or sediment samples should be collected outside a zone of tidal influence.

Published background studies may be of value in determining whether a site-specific background data set lies within the normal range of observations. The size of the geologic area and the number of samples to be collected should be carefully considered prior to conducting a background study to ensure that any substantial difference in mean metal concentrations between background and the site can be reasonably determined with statistical significance. EPA's *Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites* (EPA, 2002) can assist an investigator in choosing the appropriate number of samples for a background study. As a general rule, a data set should have a minimum of 10 discrete observations or measurements. In some cases, 20 or more samples may be appropriate when an area exhibits significant heterogeneity. In addition, the laboratory analytical method used in the background study should be reviewed by ADEC to confirm it is suitable for its intended use and the quality of analytical data validated to ensure it meets regulatory standards and guidance. A background data set with significant metal concentration variability, may not be suitable to compare to a data set of site metal concentrations if statistical hypothesis testing is unable to detect a difference in mean metal concentrations between the site and background data sets. To reduce the variability in a data set, more samples could be collected or the size of the background area to be studied could be reduced. In general, a metal data set with a coefficient of variation greater than 3 is indicative of high variability or dispersion.

5. Establishing Statistical Background Concentrations and Comparing with Site Data

Comparisons between site and background data should occur by either conducting:

- A point by point comparison of site data to an upper tolerance limit (UTL) background concentration using a 95% confidence limit with 95% coverage; or
- A distributional comparison using hypothesis tests to determine whether the differences in the central tendency (i.e., mean or median) or upper tails are statistically significant.

ADEC recommends a point by point comparison of site data to a statistically derived UTL for evaluating background concentrations in groundwater or surface water. For comparison of soil or sediment data to background data, ADEC recommends a hypothesis testing in accordance with EPA guidance (USEPA 2002; USEPA 2007). Incremental Sampling Methodology (ISM) or a combination of ISM and discrete sampling may be utilized for hypothesis testing if approved by ADEC on a site-specific basis.

If an investigator proposes to use a parametric method for statistical testing or calculating a UTL, data distribution testing should be performed before running the test statistic since the appropriateness of a parametric method used to compute the test statistic is contingent on the distribution of the data. For example, the student's-T method for calculating a 95% upper confidence level (UCL) of the mean is not appropriate for data which has a distribution that is significantly skewed.

Additionally, prior to computing the background or site calculations, outlier testing should also be conducted and outliers should be removed if there is no justification to retain these values. EPA has available the free statistical software package ProUCL which allows the user to detect outliers and determine the distribution of a dataset, and calculate potential UCL and UTL values (ProUCL 2016). The UTL is recommended as a bright-line background threshold value using 95% confidence limit on the 95th percentile.

Censored data sets (i.e. data sets with nondetect values) should also be evaluated prior to computing background or site calculations. When nondetects are present in a data set, ADEC recommends utilizing the Chebyshev inequality or bootstrap methods in ProUCL for computing the upper limits to run a test statistic.

IV. DETERMINING CLEANUP LEVELS, CUMULATIVE RISK, AND INSTITUTIONAL CONTROLS

1. Sites where no Known or Suspected Source of a Metal has been Identified

The presence of a metal will be considered naturally occurring at sites that have no known or suspected anthropogenic sources. Sampling and analysis for metals is not necessary at such sites.

Where metal sampling and analysis have occurred in the past, and where no known or suspected anthropogenic source has been identified, the metal results will be considered as background unless the data strongly indicate a localized source. Furthermore, speciation of metals is not required unless specifically requested by ADEC.

Cleanup and/or institutional controls will be not be required for metals in these situations, nor will it be necessary to collect background samples for comparison. Cumulative risk calculations should be conducted in accordance with the ADEC's *Procedures for Calculating Cumulative Risk* and exclude the risk

contribution from the naturally occurring metals. However, depending on site specific circumstances, the risk posed by naturally occurring metals may need to be discussed qualitatively in an uncertainty risk analysis and managed appropriately.

2. Sites Where a Known or Suspected Anthropogenic Metal Source has been Identified

For sites where a known or suspected anthropogenic source of metals is identified, characterization of these metals is required and cleanup may be necessary.

A determination of naturally occurring background metal levels as described above will be necessary to separate the contribution of naturally occurring metal concentrations from any anthropogenic metal concentrations for purposes of setting a cleanup level and conducting any necessary cleanup. A statistical hypothesis test should be conducted to determine if site metal concentrations in soil or sediment represent background or an anthropogenic source. When conducting hypothesis testing, a null hypothesis should be proposed such that the mean site metal concentration exceeds the background mean metal concentration. The hypothesis test selected is then used to determine if a comparison of background data to site data support the rejection of the null hypothesis (i.e. statistically confirming an alternative hypothesis that site mean metal concentration is equal to or below the background mean metal concentration) with an acceptable amount of potential decision errors. Acceptable limits for Type I (false positive that the null hypothesis is rejected) decision error and Type II decision error (false negative that null hypothesis is not rejected) are 0.10, respectively. If the site and background populations have unequal variances, then standard parametric tests may not be appropriate. If an anthropogenic source is determined, and metal concentrations exceed one tenth an ADEC cleanup level, then a metal's maximum detected value or 95% UCL of the mean should be used as an exposure point concentration (EPC), and the EPC should be included in cumulative risk calculations.

For groundwater or surface water data, a 95% UTL can be developed to determine if site conditions exceed background levels. If a UTL is developed and approved by ADEC, water samples should be collected and analyzed for metals from on-site wells or from on-site surface water bodies. If metal concentrations in two consecutive water samples do not exceed the 95% UTL, then metals at the site can be determined to be naturally occurring. If a detected metal in groundwater or surface water is not determined to be naturally occurring based on its comparison to a 95% UTL, then the maximum detected value or 95% UCL of the mean should be compared to cleanup levels and potentially used as the EPC for cumulative risk calculations.

Additionally, if a metal, such as arsenic, is determined to be naturally occurring, then the metal may need to be discussed qualitatively in an uncertainty risk analysis. If a remedy includes an engineering control such as capping, or a cleanup does not completely achieve the site cleanup levels, institutional controls may be necessary to ensure that residual contamination is managed appropriately.

At a site where chromium VI has been confirmed through sampling as a contaminant of concern, confirmation sampling for chromium VI will be required in addition to total chromium. It is important to note that chromium speciation requires a short (typically 24 hours) turnaround time for laboratory analysis. A discussion with the DEC project manager is recommended to address this sampling and analysis consideration.

REFERENCES

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