

5 Geochemical Evaluations

Geochemical evaluation is a technique based on selected elemental ratios that is used to identify processes controlling element concentrations in soil and confirm or rule out the presence of contamination in individual samples. These ratios reflect trace elements' affinities to adsorb on the surfaces of specific minerals in soil. An anomalous ratio can indicate the presence of excess trace element from a contaminant source. While commonly used during site investigations to delineate contaminated areas and refine lists of COPC (([Myers and Thorbjornsen 2004](#)), ([Thorbjornsen and Myers 2007](#))), geochemical evaluation is also important during background studies, where the goal is to characterize representative background concentrations and conditions (([Thorbjornsen 2008](#)), ([Geiselbrecht et al. 2019](#))).

A notable feature of geochemical evaluation is that it employs the field observations and existing analytical data, such as environmentally available metals concentrations in discrete soil samples, that are acquired during standard environmental investigations. This minimizes overall project cost, because specialized analytical data are not required ([Thorbjornsen and Myers 2007](#)). Elemental ratios have long been used as a geochemical prospecting technique (([Hawkes and Webb 1962](#)), ([Boyle 1974](#)), ([Levinson 1974](#)), ([Whitney 1975](#))) and are well suited for the background applications discussed below.

The geochemical evaluation described in this guidance does not include stable isotope analyses, sequential extraction procedures, or other specialized analytical techniques. Not only are such techniques outside the scope of this guidance, but they are also not necessary for background determination at most sites. Geochemical evaluation is also not a statistical technique ([Section 5.1](#)), but rather it complements statistics by evaluating analytical results from a different perspective, thereby reducing decision errors that are inherent to any single methodology. Geochemical evaluations should be performed by experienced geochemists, because many potential geochemical processes need to be considered when evaluating soil datasets.

5.1 Geochemistry Is Not Statistics

There are many statistical procedures that are applied to environmental data, but they are not used during geochemical evaluation, which has as its aim the identification of geochemical mechanisms controlling element concentrations in soil. It is not a hypothesis test with associated probabilities; it does not assume linear relationships between elements, nor do linear models apply, for the reasons explained in [Thorbjornsen and Myers \(2007\)](#) and [ASTM E3242-20 \(ASTM 2020\)](#). A properly performed geochemical evaluation identifies geochemical mechanisms controlling element concentrations in individual soil samples, which procedures such as multivariate statistics cannot do. Geochemical considerations are an important complement to statistical evaluations and serve as an independent line of evidence when characterizing background concentrations in soil and during comparisons of site versus background data.

5.2 Uses of Geochemical Evaluations

Geochemical evaluations are used for the following purposes:

- to identify the processes controlling element concentrations
- to identify contaminated samples
- to determine whether statistical outliers should be retained in the background datasets
- to confirm or rule out the grouping of candidate background datasets

These purposes are described in the following sections.

5.2.1 Identify the processes controlling element concentrations

Many geochemical mechanisms can control element concentrations in soil, and they are highly localized phenomena due to effects such as pH and oxidation-reduction (redox) in soil pore fluid. It is important to understand these processes so that elevated concentrations, which may be perceived as unrepresentative of background, can be explained. [Section 5.5](#) provides further discussion of some of these geochemical mechanisms.

5.2.2 Identify contaminated samples

Geochemical evaluation identifies samples with element concentrations that are anomalous relative to uncontaminated samples. These anomalous concentrations are not always obviously elevated in terms of their absolute concentrations. Moderately contaminated and even slightly contaminated samples can be identified using geochemical evaluation. This includes concentrations that would pass statistical outlier tests and/or lie below regulatory screening levels. Exclusion of all

such contaminated samples results in a dataset that more appropriately represents background geochemical conditions. This becomes especially important later in the project life cycle, when site-to-background comparisons are performed that incorporate geochemical evaluation. Retaining a contaminated sample with anomalously high elemental ratio(s) in the background dataset means that contaminated site samples are more likely to be erroneously declared as uncontaminated.

5.2.3 Evaluate statistical outliers

Background data screening processes may include statistical outlier tests ([Section 11.5](#)) to identify unusually high or low concentrations that do not fit a mathematical model, typically the normal distribution. Such “unexpected” concentrations may look suspicious but should not be excluded without further inspection to verify that they are not representative of background. Removal of naturally elevated concentrations would bias descriptive and inferential statistics toward lower, unrepresentative values, and it would censor important geochemical information about site soils. As noted by USEPA (2006): “These [outlier] tests should only be used to identify data points that require further investigation. The tests alone cannot determine whether a statistical outlier should be discarded or corrected within a dataset. This decision should be based on judgmental or scientific grounds.”

Geochemical evaluation is a critical tool for determining whether statistical outliers represent contamination, in which case they should be removed from a background dataset; or have a natural source or are due to inherent variability, in which case they should be retained ([Thorbjornsen 2008](#)). [Section 14.3](#), [Section 14.4](#), and [Section 14.5](#) provide case studies of geochemical evaluations performed following statistical outlier tests.

5.2.4 Confirm or rule out the grouping of candidate background datasets

A common assumption is that background soil samples must be separated on the basis of soil type (such as the U.S. Department of Agriculture’s soil survey map units), location, or depth. Assumptions such as these should be tested using geochemical evaluation of selected elemental ratios ([Thorbjornsen 2008](#)). Similar elemental ratios provide a line of evidence for pooling soil background datasets that might otherwise be segregated based on *a priori* assumptions, at least during the geochemical evaluation phase of site-to-background comparisons if not also during the background study itself. Trace element concentrations in soil at a given site are controlled primarily by adsorption on fine-grained minerals such as clays and iron oxides, so grain-size effects ([Section 5.5](#)) have the largest influence on their concentrations. This means the various *a priori* classification schemes are often irrelevant for background purposes and separating samples confers no advantage. An example of using geochemical evaluation to test the validity of grouping samples follows. At a Georgia facility the candidate background dataset included surface soil samples collected from 0 to 2 feet below ground surface; and subsurface soil samples collected at 1-foot and 2-foot intervals with starting depths ranging from 2 feet below ground surface (the shallowest subsurface sample) to 42 feet below ground surface (the deepest subsurface sample). Of interest was whether the surface and subsurface samples could be combined (pooled), because during subsequent site investigations the project risk assessors would be evaluating hypothetical receptors’ exposure to “total” (surface and subsurface) soil. Geochemical evaluation was performed that included comparisons of elemental ratios. The two sets of background samples exhibited consistent elemental ratios for the evaluated elements, including cobalt ([Figure 5-1](#) and [Figure 5-2](#)). Natural cobalt concentrations in soil at this facility are controlled primarily by adsorption on manganese oxide minerals, which is reflected as consistent Co/Mn ratios regardless of absolute cobalt concentration. The surface soil Co/Mn ratios span the same range as the subsurface soil ratios ([Figure 5-2](#)), even though the depth intervals vary greatly. It was concluded in this situation that a combined (“total”) background soil dataset was appropriate for the facility, in addition to separate background surface soil and background subsurface soil datasets. Descriptive statistics and inferential statistics were subsequently provided for the three background datasets.

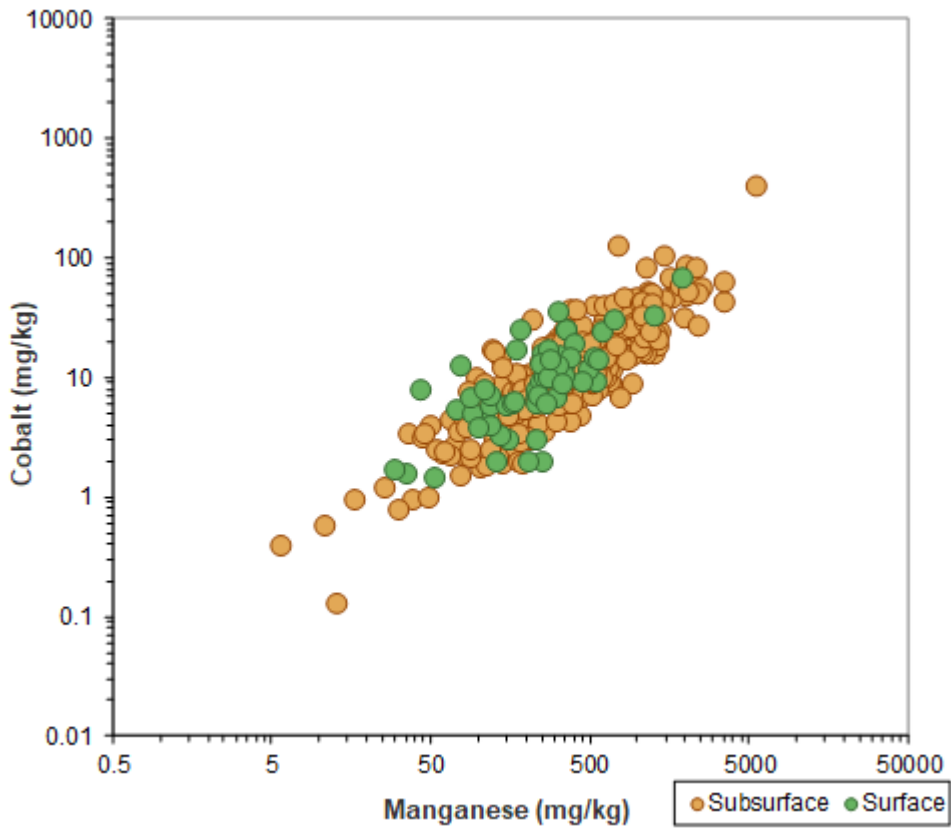


Figure 5-1. Cobalt vs. manganese in background surface and subsurface soil samples.
 Source: Karen Thorbjornsen, APTIM.

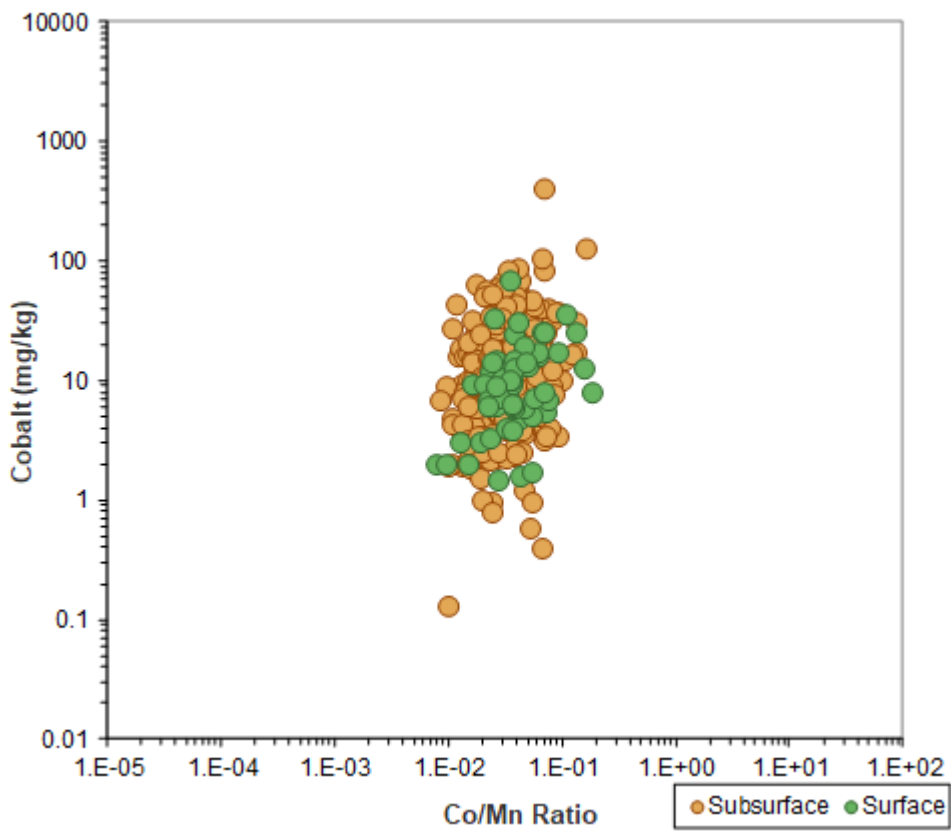


Figure 5-2. Cobalt vs. Co/Mn ratios in background surface and subsurface soil samples.
 Source: Karen Thorbjornsen, APTIM.

Geochemical evaluation can complement statistical tests that compare the absolute concentrations of groups of data (for example, Wilcoxon rank sum test [also referred to as the “Wilcoxon-Mann-Whitney test” or “Mann-Whitney U test”] or

Kruskal-Wallis test). When the statistical tests indicate no statistically significant difference among the data groups *and* geochemical evaluation indicates similar elemental ratios among the data groups, then that provides multiple lines of evidence that the data groups can be combined into one background dataset. This is preferable to relying only on a statistical approach.

An advantage of combining datasets (where demonstrated to be appropriate) is that the summary background statistics will be based on a larger number of samples, thus providing greater confidence in the estimates of the population properties.

5.3 General Methodology

Geochemical evaluation is based on natural associations between elements and minerals in soil and employs all available field observations, analytical data, and information about the facility or area. Major element analyses (including aluminum, calcium, iron, magnesium, and manganese) are required to properly evaluate the trace elements of interest (such as arsenic, chromium, and lead). In soil, “major” elements are defined as having concentrations greater than 100 mg/kg and “trace” elements have concentrations less than 100 mg/kg ([Sposito 2016](#)). Where project budgets allow, the USEPA Target Analyte List of 23 elements should be analyzed because it includes most of these elements, thereby permitting a more thorough evaluation. If the analyte list is too restrictive (for example, only the trace element of interest and one major element, such as arsenic and iron), then important information may be lost that would otherwise explain the concentrations of the element of interest.

In addition to the examination of trace versus major element ratios (described below), information that should be examined includes field geologists’ soil descriptions (found on drilling logs, sample collection forms, or field logs), site photographs, soil pH measurements, site history and physical setting, and interviews with personnel familiar with the site or facility operations. All lines of evidence should be brought to bear when drawing conclusions about the presence or absence of inorganic contamination in soil samples.

In support of the geochemical evaluation, scatter plots and ratio plots are constructed to explore the elemental associations and identify potentially contaminated samples (([Myers and Thorbjornsen 2004](#)), ([Thorbjornsen and Myers 2007](#))). A useful starting point is to examine the relationship between aluminum and iron concentrations in the soil samples. Covariance of these major elements does not reflect a geochemical association (such as adsorption effects) but rather a grain-size effect. In oxic soils, samples with high aluminum and iron concentrations have a high proportion of clay minerals and iron oxide minerals, which are very fine-grained. As noted in [Section 5.5](#), these minerals have affinities to adsorb specific trace elements, so samples with more of these minerals will contain higher background concentrations of the associated trace elements, including higher natural background concentrations. Coarser-grained soils will generally contain lower background concentrations of trace elements.

To evaluate trace elements, scatter plots are constructed to depict the detected concentrations of the trace element of interest against the detected concentrations of the major element that represents the mineral to which the trace element may be adsorbed. In the absence of contamination, the samples will tend to exhibit a common trend and similar elemental ratios. Uncontaminated samples with higher trace element concentrations will have proportionally higher major element concentrations and lie on the background trend. Contaminated samples will have anomalously high elemental ratios; on the scatter plot they will lie above the trend formed by the other samples. Such samples contain more trace element than can be explained by the soil mineral content, and they may contain a component of contamination. Ratio plots depicting trace element concentrations versus the corresponding trace versus major element ratios are prepared to accompany the scatter plots. The major elements against which trace elements are evaluated reflect the affinities that the trace elements have for specific minerals, which is a function of the specific trace element and geochemical environment. This is discussed in more detail in [Section 5.5](#), which also includes example scatter and ratio plots.

5.4 Nondetects

The intent of geochemical evaluation is to determine whether detected element concentrations have a natural source or are impacted by anthropogenic or site releases and/or activities, by considering the geochemical mechanisms controlling the concentrations in soil. Nondetects, while typically indicating very low (below the detection limit) concentrations, are a function of a laboratory process; they have no meaning in the geochemical context and provide no geochemical information for the site. Nondetects are therefore excluded from the evaluation ([Myers and Thorbjornsen 2004](#)). Estimated concentrations, such as “J” flagged (or “qualified”) concentrations, are included in geochemical evaluation datasets. Although they have more analytical uncertainty than unqualified concentrations, estimated concentrations still contain useful information. The higher analytical uncertainty associated with their values may result in additional variability in the data presented in scatter plots and greater spread in ratio plots, particularly at the low end of the trace element

concentration range, where most J-qualified concentrations tend to reside.

5.5 Key Geochemical Processes

Trace element concentrations in soil are controlled by multiple processes, including solubility (which is a function of pH, redox, temperature, etc.) and adsorption/desorption (“sorption”) reactions. Typically, the most important control is sorption reactions on specific mineral surfaces, which are driven by solute and surface charges. A detailed discussion of geochemical mechanisms is outside the scope of this guidance, but they are more fully explained in other sources, including Stumm and Morgan (1996), Cornell and Schwertmann (2003), and Sposito (2016).

Trace elements have affinities to adsorb on specific soil-forming minerals (such as clays), represented by major elements (such as aluminum). These adsorption affinities are manifested as consistent trace versus major element ratios in a set of uncontaminated soil samples. Samples with excess trace element from a contaminant source are identified by their anomalously high elemental ratios. Section 5.5.1 through Section 5.5.3 provide a few common element associations that are explored through the use of scatter and ratio plots. Other associations should be explored beyond those listed below, to ensure a thorough evaluation of concentration data for soil at a given site.

5.5.1 Clay minerals

Clay minerals contain aluminum as a primary component. They tend to maintain net negative surface charges under circumneutral pH conditions and attract cationic species such as barium (Ba^{2+}), cadmium (Cd^{2+}), and zinc (Zn^{2+}), among others (Kabata-Pendias 2010). Concentrations of barium versus aluminum, cadmium versus aluminum, and zinc versus aluminum are typically examined. In the example scatter plot of Figure 5-3, barium concentrations are plotted along the y-axis and the corresponding aluminum concentrations are plotted along the x-axis.

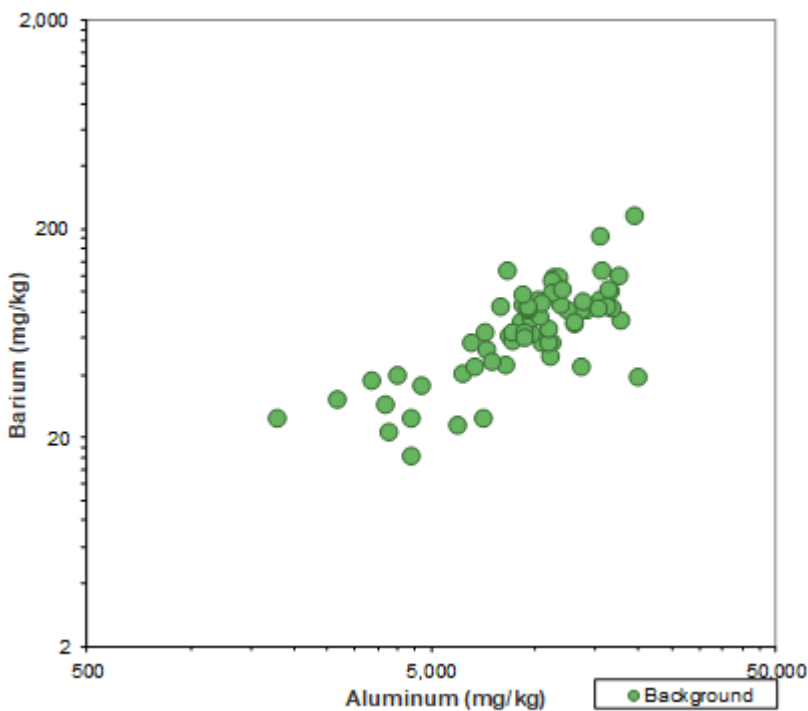


Figure 5-3. Barium vs. aluminum in background soil samples.

Source: Karen Thorbjornsen, APTIM.

The covariance of barium and aluminum concentrations exhibited by these samples (barium concentrations tend to increase as aluminum concentrations increase) suggests that the barium concentrations are controlled by adsorption on clay minerals. Another way of looking at the same data is provided by a ratio plot (Figure 5-4), in which the barium concentrations are plotted along the y-axis and the corresponding Ba/Al ratio for each sample is plotted along the x-axis.

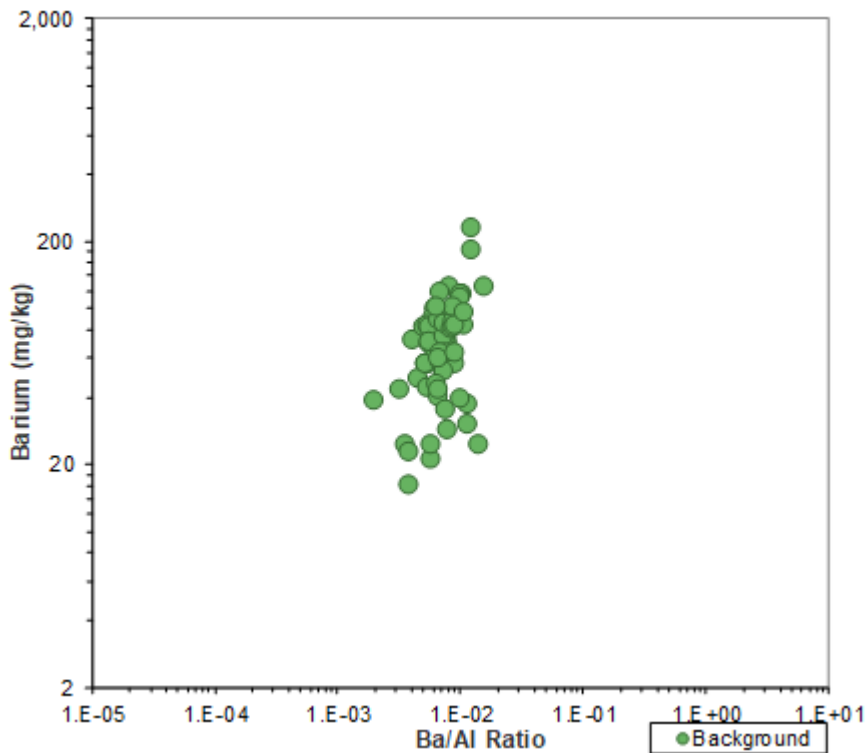


Figure 5-4. Barium vs. Ba/Al ratios in background soil samples.

Source: Karen Thorbjornsen, APTIM.

The background samples exhibit a relatively narrow range of Ba/Al ratios (Figure 5-4), which is expected in the absence of barium contamination. Anomalously high ratios (which are not present in this example dataset) are sometimes more readily seen on ratio plots than on scatter plots; samples with anomalously high ratios lie to the right of uncontaminated samples in a ratio plot. Because the ratios are calculated, they are reproducible, objective, and can be individually inspected in spreadsheets. Some scatter is expected at the low end of the trace element concentration range, due in part to the analytical uncertainty surrounding estimated concentrations.

5.5.2 Iron oxides

Iron oxides are a large group of minerals that contain iron as a primary component (Cornell and Schwertmann 2003). They tend to maintain net positive surface charges under circumneutral pH and oxidizing redox conditions and attract oxyanion species such as arsenic (HAsO_4^{2-} , H_2AsO_4^-) and vanadium (H_2VO_4^- , HVO_4^{2-}), among others. Concentrations of arsenic versus iron and vanadium versus iron would be examined, for example.

A scatter plot of vanadium concentrations versus iron concentrations (Figure 5-5) in a set of site-specific background soil samples reveals a common trend with a positive slope. The samples' V/Fe ratios span a narrow range (0.0013 to 0.0043; Figure 5-6), which is consistent with a natural source for the vanadium concentrations. A sample with excess vanadium from a contaminant source would lie above the trend in Figure 5-5 and would be shifted to the right of the other samples in Figure 5-6, but that is not observed for this dataset.

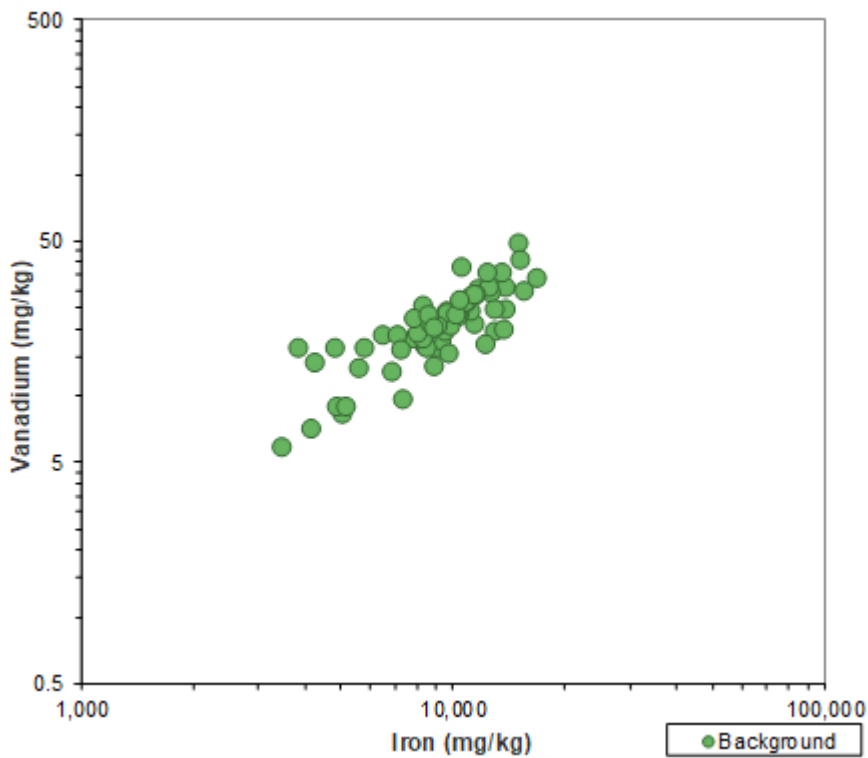


Figure 5-5. Vanadium vs. iron in background soil samples.

Source: Karen Thorbjornsen, APTIM.

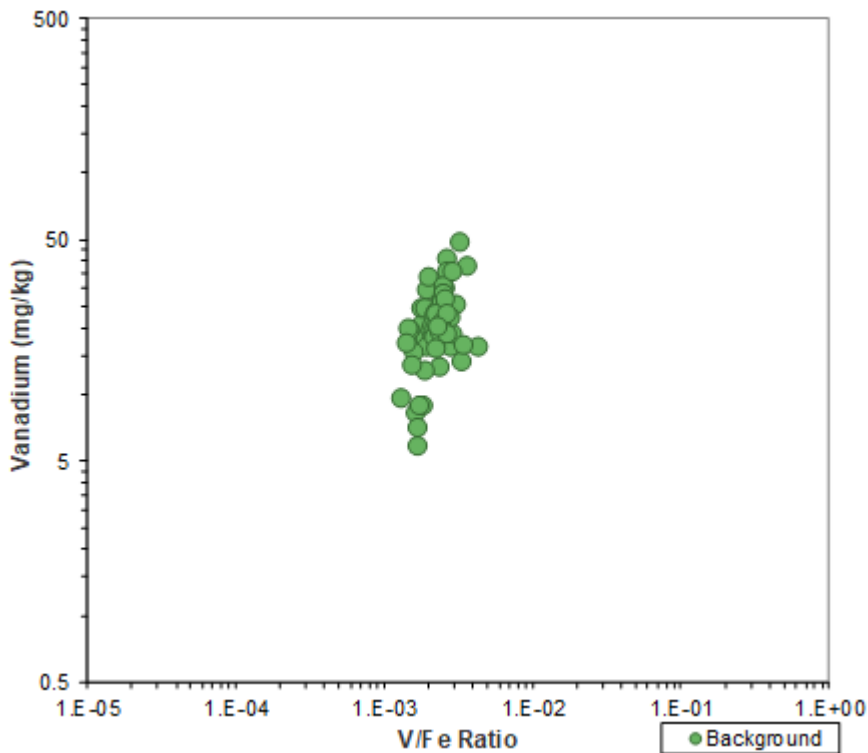


Figure 5-6. Vanadium vs. V/Fe ratios in background soil samples.

Source: Karen Thorbjornsen, APTIM.

5.5.3 Manganese oxides

Manganese oxides are a large group of minerals that contain manganese as a primary component; where present in oxic soils, they tend to maintain strong negative surface charges and attract positively charged species such as cobalt (Co^{2+}) and lead (Pb^{2+}), among others (Kabata-Pendias 2010). Concentrations of cobalt versus manganese and lead versus manganese

would be examined, for example.

In the example below, a site-specific background soil dataset contains two samples with relatively high cobalt concentrations (Figure 5-7); however, the two samples also contain proportionally higher manganese. The two samples were determined to be preferentially enriched in manganese oxide minerals and therefore contain naturally higher concentrations of associated trace elements, such as cobalt.

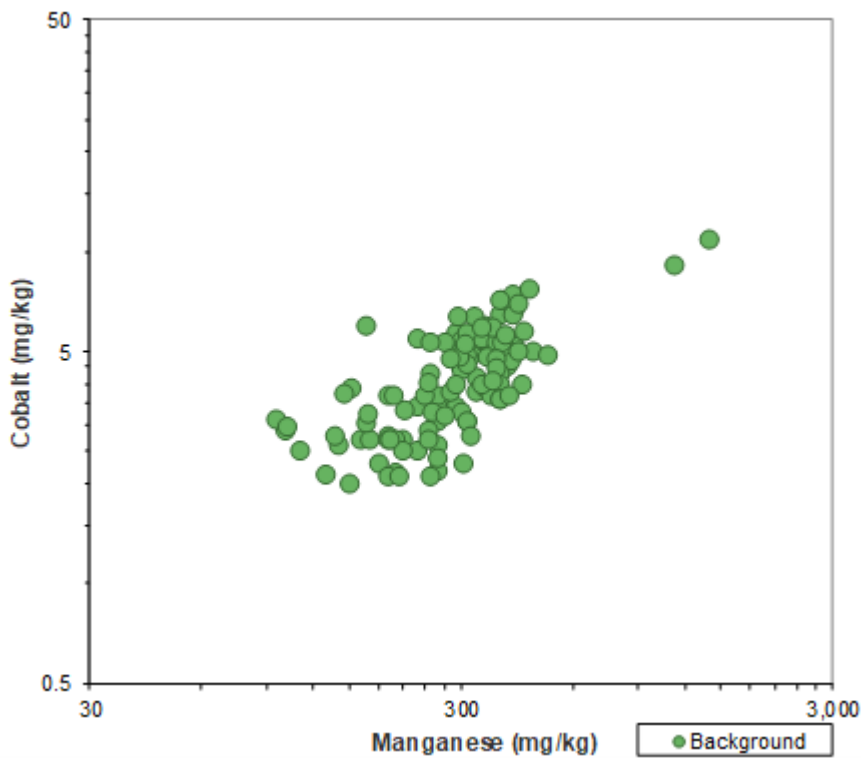


Figure 5-7. Cobalt vs. manganese in background soil samples.

Source: Karen Thorbjornsen, APTIM.

The Co/Mn ratios of the two samples are consistent with those of the other background samples (Figure 5-8), which is indicative of a natural source for the cobalt detections. If the samples contained excess cobalt from a contaminant source, then their Co/Mn ratios would be elevated relative to those of the other background samples, but that is not observed. The two samples reflect the natural variability of the site soils.

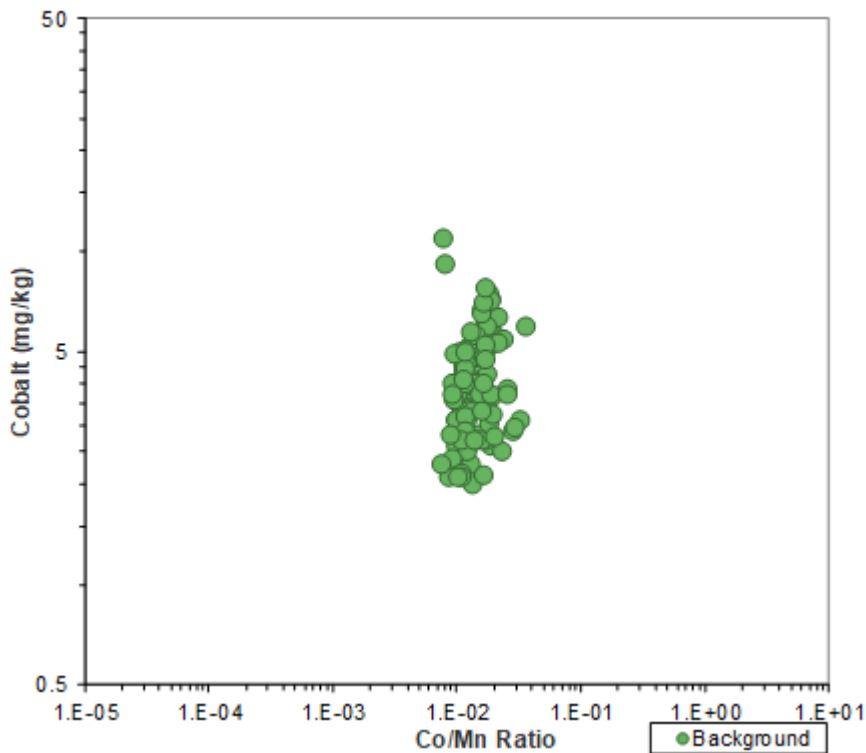


Figure 5-8. Cobalt vs. Co/Mn ratios in background soil samples.

Source: Karen Thorbjornsen, APTIM.

5.5.4 Additional geochemical processes

Additional geochemical processes need to be considered, along with relevant non-geochemical processes. They include:

- other trace-versus-major element associations not described above, such as adsorption of cadmium and zinc on iron oxides ([Kabata-Pendias 2010](#))
- adsorption of specific trace elements such as mercury and copper on organic particles, which would be evaluated via comparison of trace element concentrations versus total organic carbon concentrations (for example, see Xue et al. ([2019](#)))
- the presence of evaporite minerals in arid soils
- the effects of weathering of certain rock types, such as mafic and ultramafic units (for example, see Morrison et al. ([2009](#)))
- the presence of mineralized zones that may have localized areas with high concentrations of specific elements
- strong soil profile development that may cause vertical redistribution of elements
- the effects of bioconcentration, such as microbial or “biofilm” coatings on soil particles (for example, see Pal and Paul ([2008](#)))
- physical weathering of rock (for soils that are dominated by mechanical fragments rather than chemical weathering products)
- the effects of low redox in hydric soils

Geochemical evaluation is not simply a graphical approach. All available data and information must be examined when evaluating the concentration data, as noted in [Section 5.3](#), and the evaluation should be documented in writing. It is recommended that an experienced geochemist perform the geochemical evaluation because of the complexity that may be encountered at any given site. Conclusions must be explained and supported by applicable citations from the scientific literature, and they must often be defended during regulatory review.

5.6 Extracting Background Data from Existing Data

Geochemical evaluation should be used to examine candidate background samples, in addition to the use of statistical procedures. Extracting background data from existing datasets can minimize the number of new background samples that may need to be collected, thereby saving money. Multiple procedures are typically performed when background data are extracted, with the goal of identifying uncontaminated samples that represent background conditions. Statistical procedures

are most commonly performed, but those procedures can only identify elevated concentrations or attempt to distinguish “subpopulations” among a set of concentrations without consideration of their geochemical and scientific context. Some statistical procedures erroneously assume that data must fit a statistical distribution (such as the normal or gamma distribution); violations of the distribution or failures of statistical tests are often assumed to indicate the presence of contamination or other undesirable attributes. This is an unreasonable assumption for naturally heterogeneous geogenic materials such as soil. Statistics, being based in mathematics, cannot explain the reasons for detected concentrations of elements in soil. That is the province of geochemistry and related sciences. Geochemical evaluation can be used to screen out contaminated samples, if present, in the candidate background dataset (([Thorbjornsen 2008](#)), ([ASTM 2020](#))). Note that soil samples will need to be analyzed for major elements (for example, aluminum, calcium, iron, magnesium, manganese) in addition to trace elements of interest to support geochemical evaluation of metals.