# APPENDIX S Geochemical Trend Analysis

**S-1. Introduction**. An overview of the "geochemical" approach is presented from a statistical perspective via illustrations, and existing geochemical guidance (primarily from the Navy) is supplemented. The geochemical approach is an effective strategy for distinguishing anthropogenic from naturally occurring metal concentrations, particularly when it is used with traditional quantitative statistical evaluations. The approach often identifies naturally occurring metal concentrations that are erroneously identified as site-related by traditional evaluations (i.e., comparisons of study area metal concentrations to background 95% UTLs). The geochemical approach can not only be used to determine whether a study area has been impacted by anthropogenic metal contamination but can also identify the individual sampling locations that are suspected to possess the elevated metal concentrations.

S-1.1. Although the geochemical approach is typically extremely useful, the limitations of the approach should be noted. Its primary disadvantage is that it is subjective because it is predominately qualitative. In particular, decision errors are not quantified and well-defined criteria for distinguishing native from anthropogenic metal concentrations are not specified. In addition, although the approach distinguishes anthropogenic metal contamination from naturally occurring concentrations, it does *not* distinguish site-related contamination from non-site-related anthropogenic metal contamination. In other words, elevated contamination relative to background identified by the geochemical approach may be consistent with anthropogenic background. Statistical comparisons using a background study area would typically be needed to distinguish site-related contamination from total background metal concentrations (from anthropogenic and non-anthropogenic sources). Lastly, an additional limitation of the approach is that it implicitly assumes that, at most, only a portion of the site has been impacted by anthropogenic metal releases. This assumption is typically reasonable but can be violated if the study area is too small (i.e., is predominately limited to a "hot spot").

S-1.2. Geochemical evaluations may be categorized as "association" and "enrichment" analyses. Both are qualitative strategies used to distinguish anthropogenic from naturally occurring metal concentrations and rely upon the assumption that metal releases from waste handling activities impact only a portion of the study area. Geochemical "association" analysis primarily uses scatter plots to distinguish anthropogenic from naturally occurring metal concentrations. The approach exploits and relies upon the ability to observe correlations between different naturally occurring metals, while geochemical "enrichment" analysis primarily uses probability plots to accomplish this objective. Typically (for both geochemical approaches), at least 20 samples are collected for some environmental medium of interest at the study area (i.e., surface soils or groundwater that has been potentially impacted by metal contamination) and the samples are analyzed for TAL (target analyte list) metals (i.e., the set of 23 metals listed in the Contract Laboratory Program Statement of Work). Because metals such as Al, Mg, Ca, and Fe

are major components of naturally occurring minerals in rocks and soils in the earth's crust, these metals are typically considered to be non-site related.

S-1.3. When geochemical association analyses are done, correlations between suspected site-related metals (e.g., Cd, Pb, and Cu) and non-site related metals (e.g., Al, Fe, or Ca) are investigated by generating scatter plots. Typically, the concentrations of some potential site-related metal are plotted on the *y*-axis and the corresponding concentrations of some non-site-related metal are plotted on the *x*-axis. A strong correlation suggests that detected metal concentrations that are not consistent with the correlations in the scatter plots appear as "anomalies" or "outliers" that are attributed to anthropogenic contamination. When geochemical enrichment analysis is performed, probability plots are generated. Native metal concentrations give rise to continuous monotonic curves (i.e., straight lines). An abrupt increase in the slope of a curve, appearing as an inflection point in the upper portion of the curve, indicates anthropogenic contamination.

S-1.4. The strategies used to select the particular native metals of interest are beyond the scope of this document, which focuses upon only the statistical evaluation of the data once the metals of interest have been selected. The metals and the correlations of interest will depend on the nature of the environmental population being sampled. Native metals concentrations in soils and sediment depend on factors such as the nature of the parent rocks and component minerals, and organic material content. Metal concentrations tend to be directly proportional to total organic carbon and inversely proportional to particle size. Dissolved metal concentrations in groundwater tend to be greater at low pH and reducing conditions. It should be noted that metals usually exist as anions (negatively charged species) and cations (positively charged species) in environmental media such as groundwater, soil, and sediments. For example, metals such as As, Sb, Se, V, and Mo tend to form anionic species (i.e., containing oxygen atoms); metals such as Ba, Cu, Pb, Ni, and Zn tend to form cations, while certain metals such Cr form either as cationic or anionic species. At neutral pH, clays, which typically contain Al, possess strong negative surface charges that attract cationic metals such as Cu, Zn, and Pb. Therefore, for soils rich in clay or groundwater containing suspended clay particles, Al will often be strongly correlated with cationic metals. Similarly, at neutral pH, environmental matrices containing iron oxides and iron oxyhydroxides possess positive surface charges that attract anionic metal species.

**S-2.** Geochemical Association Approach. To illustrate the geochemical association approach, assume that soils at some study area contain significant concentrations of native Fe and the area is suspected to have been impacted by site-related Pb contamination. The concentration of Pb in each sample is plotted against the corresponding concentration of Fe to generate a "Pb-Fe" scatter plot for the study area (i.e., as discussed in Paragraph J-9). When a scatter plot is generated for a geochemical evaluation, the *x*-axis is usually the concentration of the non-site-related metal (Fe), but this is merely a convention (e.g., a comparable scatter plot may be generated if the *y*-axis were the concentration of the non-site related metal). Also note that when

a scatter plot is produced, the values for the X variable and those for the Y variables are not ordered prior to plotting the data, rather a set of paired measurements,  $(x_i, y_i)$ , where i = 1, 2, ...,*n* (*n* denotes the number of environmental samples) is plotted. A strong positive correlation between naturally occurring concentrations of Fe and Pb (i.e., where the concentration of Pb tends to increase as the concentration of Fe increases) would suggest that Pb is not an anthropogenic contaminant. Figure S-1 is an example of a Fe-Pb scatter plot.



**Figure S-1. Scatter plot of Pb and Fe.** Copyright 2004 From "Identifying Metals Contamination In Soil: A Geochemical Approach," *Soil & Sediment Contamination*, Vol. 13, No. 1, pp. 1– 16, by Myers, J. and K. Thorbjornsen. Reproduced by permission of Talyor & Francis Group, LLC.

S-2.1. The relatively strong linear relationship between Pb and Fe for the points that appear as blue diamonds suggests that these samples contain only native concentrations of Pb and Fe. Samples containing Pb in excess of naturally occurring concentrations appear as "outlying" points (e.g., the three red circles) above the linear trend (the blue diamonds), suggesting that these samples contain anthropogenic Pb contamination.

S-2.2. Two major advantages of the geochemical approach relative to classic statistical approaches are immediately apparent. A *background* study area (and the expense associated with doing a separate background study) is *not* required to identify study area concentrations that are elevated relative to native metal concentrations. Furthermore, the approach readily identifies the samples (locations) suspected to contain the elevated metal concentrations. Classic statistical evaluations do not readily provide this information. (Because classic statistical evaluations rely upon the assumption that samples are independent of one another, the presence of a correlation or contamination "pattern" would violate this assumption and compromise the validity of the evaluation.) For example, a typical statistical approach would entail comparing the mean concentration of Pb at the site study area to the mean concentration of Pb at a background study area. Although the evaluation may indicate that the mean site Pb concentration is statistically

greater than the mean background Pb concentration, the evaluation itself would not (at least directly) identify the sampling locations associated the elevated lead concentrations (though a geostatistical approach could potentially evaluate contamination that is spatially correlated).

S-2.3. It should also be noted that, although background data are not required to perform geochemical evaluations, background data can be plotted with site data to determine if site metals are elevated relative to native concentrations. This is illustrated in Figures S-2 and S-3.

S-2.4. In Figure S-2, the Cu surface soil samples (blue non-shaded triangles) generally plot above the background samples (green circles). Similarly, in Figure S-3, Pb surface soil samples (blue non-shaded triangles) plot above the background samples (green circles). This suggests that the site has been contaminated by both Pb and Cu. These plots were generated from soil samples collected from an artillery firing range, where Cu and Pb are frequently potential contaminants of concern. The scatter plots also indicate that Pb and Cu in the site surface soils are elevated relative to the subsurface soils, which, given the nature of the site, is consistent with the manner in which one would expect site-related contamination to be spatially distributed.

S-2.5. An additional advantage of the geochemical approach is that multiple scatter plots between different metals (i.e., using site or a combination of site and background data) can potentially be used to determine whether or not a site has been contaminated by metals. In this example, the anthropogenic Cu and Pb contamination identified in the Cu-Fe and Pb-Mn scatter plots, respectively, can be further evaluated by generating a scatter plot for Pb and Cu, as shown in Figure S-4. The moderate to strong correlation between Cu and Pb for the site surface soil samples but the poor correlation between Pb and Cu for the background samples suggests that the Cu and Pb are site-related contaminants from a common anthropogenic source.



**Figure S-2.** Log scale Cu-Fe scatter plots of site and **background soil samples.** Figure provided by J. Myers of Shaw Environmental, Inc., Knoxville, TN.



**Figure S-3.** Log scale Pb-Mn scatter plot for site and background soil samples. Figure provided by J. Myers of Shaw Environmental, Inc., Knoxville, TN.



Figure S-4. Log scale Cu-Pb scatter plot of background and site soil soils. Figure provided by J. Myers of Shaw Environmental, Inc., Knoxville, TN.

S-2.6. As stated previously, the primary disadvantage of the geochemical approach is that it is predominately qualitative and, therefore, subjective. The degree of correlation that is required to conclude the study area has not been affected by anthropogenic contamination and what constitutes an "outlier" when a correlation is observed is typically is not well defined (i.e., quantitatively criteria are not specified). To illustrate, consider the As-Fe scatter plot presented below in Figure S-5.

S-2.7. There appears to be a large of amount of dispersion in the scatter plot shown in Figure S-5. A qualitative visual evaluation of this plot does not clearly indicate whether or not As and Fe are strongly correlated with one another. However, as illustrated in Figure S-6, the same scatter plot could potentially be interpreted in a different way: Arsenic concentrations less than about 4 mg/kg could be viewed as strongly correlated with Fe (as shown by the red line in Figure S-6), and the As concentrations larger than 4 mg/kg (i.e., the set of circled points) could be interpreted as anthropogenic contamination. Unlike classical statistical strategies that are used to distinguish anthropogenic contamination from background values, decision errors for geochemical evaluations are not quantifiable. As geochemical evaluations are subjective, they can produce erroneous conclusions and are more vulnerable to challenge (e.g., by regulators) than quantitative statistical approaches.



**Figure S-5.** As-Fe scatter plot with a large amount of scatter. Copyright 2004 From "Identifying Metals Contamination In Soil: A Geochemical Approach," *Soil & Sediment Contamination*, Vol. 13, No. 1, pp. 1–16, by Myers, J. and K. Thorbjornsen. Reproduced by permission of Talyor & Francis Group, LLC.



Figure S-6. Misidentified trends for the scatter plot in Figure S-5. Copyright 2004 From "Identifying Metals Contamination In Soil: A Geochemical Approach," *Soil & Sediment Contamination*, Vol. 13, No. 1, pp. 1–16, by Myers, J. and K. Thorbjornsen. Reproduced by permission of Talyor & Francis Group, LLC.

S-2.8. However, the As results in Figure S-5 are probably naturally occurring. As shown in Figure S-7, a scatter plot of As versus the ratio Ln(As/Fe) exhibits a fairly strong linear relationship, suggesting that the As is natural.



**Figure S-7. Scatter plot of As and logarithm of As/Fe using the data set plotted in Figure S-5.** Copyright 2004 From "Identifying Metals Contamination In Soil: A Geochemical Approach," *Soil & Sediment Contamination*, Vol. 13, No. 1, pp. 1–16, by Myers, J. and K. Thorbjornsen. Reproduced by permission of Talyor & Francis Group, LLC.

S-2.9. The scatter plots presented above were generated using soils data, but similar geochemical association analyses may also be conducted for groundwater. Some scatter plots using log rather than linear scales for the *x*- and *y*-axes are presented below for groundwater data.

S-2.10. There is a relative good correlation between Al and Fe in Figure S-8, which suggests that both metals are non-site-related. The correlation between As and Fe in Figure S-9 suggests that As is not a site-related contaminant.

S-2.11. The scatter plots may also be used to examine the relationship between filtered and unfiltered samples, as well as between metal concentrations and parameters such as turbidity and oxidation-reduction potential (e.g., in single monitoring well over time or for a set of monitoring wells). Figure S-10 illustrates the relationship between filtered and unfiltered samples analyzed for Cr. There is an apparent linear relationship between the concentration of Cr in unfiltered groundwater and the ratio of filtered to unfiltered Cr, which could indicate naturally occurring Cr in suspended particles from the surrounding soils.



**Figure S-8.** Al-Fe log-scale scatter plot for a set of groundwater monitoring wells. Figure provided by J. Myers of Shaw Environmental, Inc., Knoxville, TN.



Figure S-9. Log-scale As-Fe scatter plot using Fe groundwater data for Figure S-8. Figure provided by J. Myers of Shaw Environmental, Inc., Knoxville, TN.



Figure S-10. Log-scale scatter plot of filtered and unfiltered groundwater analyzed for Cr. Figure provided by J. Myers of Shaw Environmental, Inc., Knoxville, TN.

S-3. Geochemical Enrichment Analysis. Geochemical enrichment analysis entails constructing quantile plots or normal probably plots (e.g., as discussed in Appendix J). To construct a quantile plot, the values of some variable are ordered from smallest to largest and the percentage or faction of the values less than or equal to each data point is then calculated. The measured values are then plotted on one axis (*y*-axis) and the corresponding percentages or proportions are plotted on the remaining axis *x*-axis). The approach is so named because the measured variable being plotted is called an "enrichment factor." An enrichment factor is calculated from an equation of the form:

 $Y' = (C_M / C_X)_{Site} / \mu_{Parent Rock}$ .

S-3.1. The quantity  $(C_M/C_X)_{Site}$  is the concentration of some site related metal (e.g., Cr)  $C_M$  divided or "normalized" by the corresponding concentration of some non-site-related metal (e.g., Al)  $C_X$ . The term  $\mu_{Parent Rock}$  is the true mean concentration of  $(C_M/C_X)$  concentration in the "parent rock" (i.e., the rock from which the site soil was geologically derived) and is typically obtained from the literature. However, as this term is simply a constant, it does not alter the shape of the quantile plots and is unnecessary for their evaluation. Quantile plots may be generated using the ratios

$$Y = (C_M / C_X)_{Site}$$

or the logarithms of these ratios

$$\operatorname{Ln}(Y) = \operatorname{Ln}\left\{ \left( C_M / C_X \right)_{Site} \right\}$$

S-3.2. The quantile plot is evaluated for trends indicative of naturally occurring metal concentrations and "deviations" that indicate anthropogenic contamination. Because environmental data are frequently normal or lognormal, it is usually convenient to construct normal probably plots for Y or Ln(Y) (i.e., the values of  $(C_m / C_x)_{Site}$  are plotted against the corresponding quantiles of a standard normal distribution or their associated probabilities). For normally distributed data, "deviations" appear as "breaks" in a straight line. This is illustrated in Figure S-11.



Figure S-11. Probability plot of  $Y = (C_M/C_X)_{Site}$  when a portion of the study area has been heavily impacted by anthropogenic contamination.

S-3.3. The plot is predominately linear from about 700 to 1300, where there appears to be either a "break" or inflection point in the graph. After this region, the graph is essentially linear from about 1800 to 2200. The linear portion of the plot from 700 to 1300 would be attributed to native background concentrations and the values greater than about 1300 would be attributed to anthropogenic contamination. It should also be noted that the probably plots may contain more than one inflection point. Multiple populations (i.e., differences in concentration between background soils, surface soils, and subsurface soils) will potentially give rise to multiple inflection points. Ideally, the total number of inflection points plus one will be equal the number of different populations.

S-3.4. There are two apparent inflection points for the probability plot in Figure S-12 (one near 120 and one near 180), which suggests that there are three distinct populations. For example, there may be a background data set and two different concentration regions for site-related waste handling activities, or there may be two distinct background data sets and one data set for sampling locations impacted by anthropogenic contamination. However, the identification of the background "trend" and the "deviations" are subjective components of the evaluation. The value at which the "break" or inflection point occurs cannot be precisely determined, and accuracy decreases as the variability increases and the average native concentrations approaches the average concentrations of anthropogenic contamination.



Figure S-12. Probability plot of  $Y = (C_M/C_X)_{Site}$  for three different populations.

S-3.5. Two different known data sets were actually combined to produce the plot in Figure S-13. The "background data set" consisted of 100 points from a normally distributed population with a mean of 1000 and standard deviation of 100. The second set, which represents the anthropogenic contamination, consisted of 10 points from a normally distributed population with a mean of 2000 and a standard deviation of 100. As the difference between the means is large, an inflection point can be easily obtained from the probability plot in Figure S-13. However, a very

different probability plot would result if the means of the two data sets were more similar. Consider the probability plot that would have been produced by combining the following data sets: i) a "background" data set, consisting of 100 points from a normally distributed "background" population with a mean of 1000 and standard deviation of 200, and ii) a "site" data set, consisting of 10 points (representing the anthropogenic contamination) from a normally distributed population with mean of 1300 and standard deviation of 200.

S-3.5. An inflection point is not apparent in the probably plot though the plot contains 10 data points from a population with a mean that is significantly greater than the background mean. Descriptive statistics for the two data sets are presented below:

Variable	Mean	Std. Dev.	Minimum	Maximum
Y <sub>Background</sub>	1004.3	212.2	548.9	1592.3
$Y_{Site}$	1306.6	211.6	837.9	1512.9

S-3.6. Assuming that the background areas are known, a two-sample Student's *t*-test could show that there is a significant difference between the means for the "background" and "site" data sets at well over the 95% level of confidence. Unlike the geochemical approach, this test would conclude that the "site" is elevated relative to "background." As in the geochemical association approach, the qualitative nature of enrichment factor approach can produce decision errors. Geochemical evaluations should typically be done with quantitative statistical evaluations to determine whether or not a study area has been impacted by metal contamination.



Figure S-13. Probability plot of  $Y = (C_M/C_X)_{Site}$  when a portion of the study area has been slightly impacted by anthropogenic contamination.

S-4. Recommendation for performing Geochemical Evaluations. Relatively detailed guidance for evaluating background concentrations using classic statistical as well as

geochemical evaluations is available from the Navy for soil, sediment, and groundwater at the following web link:

# http://web.ead.anl.gov/ecorisk/related/

However, some modifications to the Navy's approach are recommended as listed below.

S-4.1. In the Navy guidance, Ordinary Least Squares (OLS) (linear regression) is used to evaluate geochemical relationships (e.g., correlation), outliers that present contamination, and is used to estimate background concentrations. It is recommended that OLS calculations <u>not</u> be performed. The underlying assumptions required to perform linear regression of typically violated (as discussed in Paragraph P-4).

S-4.1.1. As discussed in Appendix P, when a regression line of the form  $Y = b_1 X + b_0$  is calculated, it is being assumed that X is an "independent" variable that possesses negligible uncertainty relative to the "dependent" variable Y. A change in X produces "explained" variation in Y; the "unexplained" variation is attributable to random error associated with the measurement of Y alone. However, this assumption is routinely violated for geochemical evaluations. In the Navy's guidance, non-site-related metals such as Al and Fe are plotted on the x-axis and potential site-related metals are plotted on the y-axis, but this is merely a convention. The variables X and Y are both measured quantities possessing comparable levels of uncertainty. In this context, there is no a prior justification for treating the two variables differently. Furthermore, other underlying assumptions required for regression fits are often (but not necessarily) violated (e.g., the residuals must be normally distributed and the variance cannot be a function of X or Y).

S-4.1.2. The violation of the underlying assumptions required to calculate the regression lines can produce erroneous conclusions. For example, when regression lines are calculated, the Navy guidance quantifies their certainty to calculate predication intervals, which are used to identify outliers indicative of anthropogenic contamination. (Points that lie outside the prediction intervals are suspected to be elevated relative to native concentrations.) However, when the assumptions required for the regression lines are violated, the prediction intervals will not necessary be valid, which may result in incorrect decisions.

S-4.2. Geochemical evaluations should focus (at least initially) on *correlation* rather than OLS regression. A correlation coefficient is a measure of the degree of association between two variables. Unlike regression, it does not require a "dependent" and "independent" variable. Three common measures of correlation are Pearson's r, Kendal's tau, and Spearman's rho (refer to Appendix O). However, Pearson's r is recommended only to screen the results for correlations (e.g., to generate the correlation matrix in Table 3-1 of the Navy's soil guidance).

S-4.2.1. Pearson's r measures only linear associations; is not appropriate when the data are not normal (a bivariate normal distribution is actually required), and is not invariant under logarithm transformations (e.g., Pearson's r calculated for an X-Y scatter plot will differ from that calculated for a Ln(X)-Ln(Y) scatter plot). Furthermore, it is not appropriate when a significant number of non-detects are reported (i.e., not robust to data censoring). In contrast, Kendal's tau and Spearman's rho are non-parametric correlation coefficients (i.e., normality is not required) that measure the degree of association for monotonic (linear and non-linear) relationships. They are invariant with respect to monotonic transformation, such as logarithm transformation, and are relatively robust to data censoring.

S-4.2.2. A statistical hypothesis test should be performed for a correlation coefficient calculated for two sets of measured variables (metals), *X* and *Y*, to determine if it is statistically different from zero at the 95 or 99% level of confidence. If the correlation coefficient is not statistically different from zero, there is insufficient evidence to conclude that two variables (metals) are correlated with one another. If the coefficient is statistically different from zero, then we may conclude that some degree of associate exists. Unfortunately, there is no quantitative criterion for the degree of association. Two metals may exhibit a statistically significant correlation, but the degree of correlation may be so weak that it is not of practical importance. However, some "rule-of-thumb" guidance for the degree of correlation is presented in Paragraph O-2. It is recommended that at least a weak to moderate relationship be required for geochemical associations.

S-4.2.3. When non-detects are reported (especially when the non-detects are reported at different detection limits), it is recommended that correlation be evaluated using Kendal's  $\tau$ -*b*: Kendal's  $\tau$ -*b* would typically be calculated using statistical software and is essentially Kendal's tau adjusted for tied values (see Appendix O).

S-4.3. A Kendal-Theil or "line of organic correlation" (LOC) should be plotted with scatter plots to help identify linear relationships (refer to Appendix P). A Kendal-Theil line passes through the medians of both variables X and Y that are linearly related. The slope of the Kendal-Theil line is not significantly different from zero if Kendal's tau is not significantly different from zero. Unlike the least-squares regression line, the Kendal-Theil line is non-parametric and is relatively robust to outliers and censored data. The calculation of a LOC constitutes an alternative parametric approach to examine a linear relationship that would be more appropriate than OLS. A LOC is appropriate to evaluate linear relationships for the geochemical approach because the uncertainty associated with both sets of metal measurements is taken into account. The LOC is calculated in a similar manner as OLS lines, but the X and Y variables are treated in the same manner (i.e., the approach does not require "dependent" and "independent" variables). The same LOC will be obtained whether Y is plotted against X or X is plotted against Y.

S-4.4. The Navy guidance recommends that only Ln(X)-Ln(Y) scatter plots be generated. However, X-Y (or Ln(X)-Y, and X-Ln(Y)) scatter plots can also be generated and may be useful for identifying associations between variables, as shown by the X-Y scatter plot in Figure S-1. Associations can also be identified by generating scatter plots of the form: "X versus X/Y" (e.g., where X denotes the concentration of a potential site-related metal and X/Y is the ratio of the metal to a non-site-related metal concentrations). A linear relationship between X and X/Y implies that a linear relationship will be obtained when Y is plotted against Ln(X). (If Y is proportional to Ln(X), then the first derivative dY/dX is proportional to 1/X and dX/dY is proportional to X.)

S-4.5. The Navy's groundwater guidance document does not promote the geochemical evaluations presented for soils and sediments in the Navy's soil and sediment background guidance documents. The geochemical evaluations for soils and sediments can substantively be applied to groundwater, as shown by groundwater scatter plots presented above.

S-4.6. For the geochemical enrichment approach, it is recommended that both the ratios  $(C_m/C_x)_{Site}$  and the logarithms of the ratios be plotted to identify trends characteristic of anthropogenic contamination. The normalization factor  $(C_m/C_x)_{Parent Rock}$  is not required and may be omitted if convenient to do so.



Figure S-14. Scatter plot for censored data.

S-4.7. Censored data (non-detects) should be included in scatter plots for the geochemical association analyses when only one of the variables is censored. The uncensored variable (which would typically be a non-site-related metal such as Fe or Al) should be plotted along the *x*-axis and the censored variable (the suspected site-related metal) should be plotted on the *y*-axis. To illustrate, a Pb and Al scatter plot is presented in Figure S-14 for a small data set. The black circles represent detected results and the red squares are the reporting limits for non-detects. The dashed lines indicate that the actual Pb concentration lies somewhere between the reporting limit

and the zero. One the basis of the detected results alone, there appears to be a strong correlation between Pb and Al. However, the correlations appears to be rather weak when the non-detects are also plotted