ECF-Hanford-11-0165
Revision 1

Evaluation of Hexavalent Chromium Leach Test Data Conducted on Vadose Zone Sediment Samples from the 100 Area

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

CH2MHILL
Plateau Remediation Company
P.O. Box 1600
Richland, Washington 99352

Approved for Public Release;
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T. J. Budge
CH2M HILL Plateau Remediation Company

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CH2MHILL
Plateau Remediation Company
P.O. Box 1600
Richland, Washington 99352

APPROVED
By Shauna E. Adams at 2:56 pm, Mar 21, 2012

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Environmental Calculation Cover Page

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Preparer: TJ Budge	• **Basis of Qualification:** Education & Experience
Checker: N Hasan	• **Basis of Qualification:** Education & Experience
Senior Reviewer: S Mehta	• **Basis of Qualification:** Education & Experience

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Preparer:	TJ Budge / Senior Modeler (CHPRC) NAME/POSITION	
	SIGNATURE	2/13/2012 DATE
Checker:	N Hasan / Modeler (INTERA) NAME/POSITION	
	SIGNATURE	2/14/2012 DATE
Senior Reviewer:	S Mehta / Environmental Scientist (CHPRC) NAME/POSITION	
	SIGNATURE	2/13/12 DATE
Responsible Manager:	AH Aly / Risk and Modeling Integration Manager (CHPRC) NAME/POSITION	
	SIGNATURE	2/14/12 DATE

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Terms

CHPRC	CH2M-Hill Plateau Remediation Company
ECDF	empirical cumulative distribution function
ECF	environmental calculation file
HISI	Hanford Information System Inventory
HLAN	Hanford Local Area Network
K_d	linear distribution coefficient
m	meter(s)
mg/kg	milligrams per kilogram
mL/g	milliliters per gram
PNNL	Pacific Northwest National Laboratory
PRG	preliminary remediation goal
PQL	practical quantitation limit
OU	operable unit
SAP	sampling and analysis plan
SSL	soil screening level
STOMP	Subsurface Transport Over Multiple Phases (modeling software)
µg/L	micrograms per liter
µg/g	micrograms per gram
WAC	Washington Administrative Code

1. Purpose

The results of leach tests described in Calculation 0100K-CA-V0081, 0100K-CA-V0081, 0100X-CA-V0058, 0100X-CA-V0059, and 0100X-CA-V0060 have been analyzed to estimate the distribution coefficient (K_d) based on the assumption of linear sorption isotherm for residual Hexavalent Chromium (Cr(VI)) in the vadose zone. The soil samples were taken as part of River Corridor remedial investigation (RI) efforts, predominately from beneath previously remediated waste sites. This memorandum relies on collected field data and the corresponding lab analysis outlined in the sampling and analysis plan (SAP) DOE/RL-2009-41, Rev. 0, to recommend a K_d value for use in the 100-Area. All methods used to calculate a value for K_d were outlined in the various RI SAPs for the River Corridor. The objective of this environmental calculation (ECF) is to give a brief background associated with Cr(VI) leaching studies at the Hanford site and how these data relate to previous studies, summarize the data and analyses that are available to assess K_d in the River Corridor, analyze the results of the leach tests for trends, and recommend a K_d for use in the River Corridor based on the leach test results. These objectives are discussed in the following sections.

1.1 Introduction

Chromium (Cr) occurs naturally in Hanford soils in trivalent oxidation state [Cr(III)] but hexavalent Chromium [Cr(VI)] occurs as a common contaminant in the subsurface at reactor operations areas in the 100 Areas along the Columbia River. Historical records show that Cr [predominantly Cr(VI)] was released into the subsurface during the addition of sodium dichromate to cooling water for use in the reactors and by discharge of cooling water from the reactors. After a single pass through these reactors, the cooling waters were discharged to the surrounding environment by various routes. These disposal practices have resulted in contamination of the subsurface with Cr. Discharged Cr exists both in hexavalent state, Cr(VI), and a reduced trivalent state, Cr(III). Interim actions along the River Corridor have previously been completed that targeted the removal of Cr(VI) soil contamination above 2 – 8 mg/kg.

Fate and transport of different forms of Cr is an important factor in assessing the risk posed by the contamination. Various remedial strategies have already been implemented to reduce the amount of Cr(VI) in the 100-Area. Further, studies specific to attenuation of Cr(VI) at the Hanford site have been conducted to evaluate Cr(VI) migration and attenuation in the vadose zone and saturated groundwater aquifers. A detailed description of leaching experiments in soils retrieved below the 116-D-7 retention basin is provided in Serne and Parker (1999). Also, a detailed leaching and characterization study has been completed using near surface soils (less than 3 m [10 ft]) bgs collected near sodium dichromate storage tanks and railroad tracks in the 100BC Area (PNNL-17674). Other Cr leaching studies have also been performed for residual soils at other 100 Area waste sites, and a range of K_d values are available in literature. A summary of the 116-D-7 and the 100-BC study follow.

<u>116-D-7 Leach Study</u>

Serne and Parker (1999) studied soils in the 100-D Area to estimate a K_d value and/or leach rate of Cr(VI) in Hanford formation sediments. They conducted both batch adsorption experiments and flow through column leach tests to retrieve data for the estimation of these values. The batch adsorption tests were conducted on clean Hanford sediment samples. These samples were exposed to Hanford groundwater spiked with Cr(VI) until the dissolved concentration reached a steady level. The experiment indicated that the dissolved phase Cr(VI) is poorly adsorbing and recommended a K_d value for 0.0 mL/g for dissolved phase Cr(VI)

interacting with Hanford sediments. However, the report indicates and recommends "when attempting to measure the K_d of a very weakly adsorbing species some other technique than batch method is advised." As part of the study, Serne and Parker conducted a flow through column leach test to estimate the leach rate of Cr(VI) from soil. The contaminated soil had a Cr(VI) concentration of around 6 mg/kg. The results indicated that the Cr(VI) is not readily leachable from the Hanford sediments and that less than 1% of the Cr(VI) was removed from the sample over 43 days of leaching. In fact in order to leach an appreciable amount of Cr(VI) from the sediment a method similar to that described in the SAP (DOE/RL-2009-41, Rev. 0) was utilized. This indicates that residual Cr(VI) in Hanford sediments is not readily leachable. Subsequent batch tests conducted on contaminated samples using distilled and deionized water also indicate very limited desorption.

100-BC Leach Study

A detailed leaching and characterization study was completed using near surface soils (less than 4 m bgs) collected near sodium dichromate storage tanks, sodium dichromate carrying pipeline, and from the unplanned release site (surface spill) near railroad tracks in the 100-BC geographic area (PNNL-17674). The initial concentration of Cr(VI) in these samples range from 100 to 1000 mg/kg and therefore much larger than the soil concentration in the study described above. The results indicated that a large fraction of the Cr(VI) mass present in the sediments (about 65%) was removed in the first pore volume of effluent and traveled quickly through the column. However, only about 3.5% of Cr(VI) mass was removed in the next five pore volumes indicating a slower release. After 25 pore volumes of flushing the cumulative mass of Cr(VI) leached was about 70 to 87% in different soil columns indicating that a substantial amount of Cr(VI) remained on the sediments. Greater Cr(VI) mass remained associated with sediments that were contaminated with the old spill thereby indicating that aging of sediments could have had some effect on reducing the leachable fraction. The results indicate that after first few pore volumes have been flushed the desorption rate reduces significantly and the long-term slow release is controlled by sorption sites that have high surface site binding energies and therefore higher desorption K_d. A two-site sorption modeling was undertaken and was deemed to adequately describe the desorption profiles of both aged and freshly contaminated sediments.

These experimental results suggest that after Cr(VI) discharged to the soil column, two primary chemical stages of chromium reactivity occur, which influence its transport characteristics. First, a large fraction of initial Cr(VI) in a contaminated sediment remains mobile, transports readily, and contributes to groundwater concentrations commensurate with source term strength. Second, some Cr(VI) is sequestered by a variety of mechanisms that retard further migration rates and reduce groundwater concentrations. The effectiveness of these sequestration processes increases over time. In the soil column underneath the retention basins, it appears that the initial highly mobile component of discharged Cr(VI) has already been flushed from the sampled soil. This is expected, given the high leakage volume from the retention basins during operations. Conversely, the soil column underneath the reactor area that is contaminated with Cr(VI) has been contacted by much smaller volumes of water since the contaminating event. Extensive flushing of the soil has not been completed in the natural setting.

The leach tests designed as part of the RI/FS process and described in DOE/RL-2009-41, Rev. 0, were completed to assess attenuation of Cr(VI) and various other contaminants. The leach tests were conducted on soil samples from a large number of locations across the River Corridor including both high concentration/low volume waste sites, low concentration effluent waste sites, and boreholes not associated with a waste site. This ECF focuses on recommending a K_d for Cr(VI) based on these data and identifying the assumptions and

uncertainties associated with this recommendation. The following sections discuss how this was completed.

2. Methodology

A total of 509 soil samples were collected and quadruplicate analysis performed on the bulk sample for metals (arsenic, barium, calcium, chromium, hexavalent chromium, lead, silver, and selenium) under the RI. Soil samples were submitted for leaching using ASTM D3987-06, *Standard Test Method for Shake Extraction of Solid Waste with Water* at three ratios of soil to leachant (1:1, 1:2.5: and 1:5) by weight. Thus, for every 100 g of soil used in the leaching method 100 g, 250 g, and 500 g of water was added for leaching metals from the contaminated soil. One of the three ratios was randomly selected to be run as a duplicate analysis totaling four analyses for each of the 509 soil samples.

The K_d values were determined for each metal based on the bulk sample and leachate results. For the purpose of this ECF only Cr(VI) K_d determinations are evaluated further. Analyzed Cr(VI) concentration magnitudes of the soil samples collected for this study ranged from 4.31 mg/kg to undetectable levels. For samples that had detectable levels of hexavalent chromium in both the soil and leachate solution, a K_d was calculated as the ratio of contaminant sorbed concentration in soil to the contaminant concentration in solution by the following equation:

$$K_d = \frac{(C_S \times M_S) - (C_L \times V_L)}{M_S} \times \frac{1}{C_L} \times \frac{1000\ mL}{1\ L} \qquad \text{Equation 1}$$

Where:

K_d = Distribution coefficient (mL/g)
C_S = Contaminant concentration in bulk soil matrix prior to leaching (µg/g)
M_S = Dry mass of soil used for leaching (g)
C_L = Contaminant concentration in leachate (µg/L)
V_L = Liquid volume used for leaching (L)

If the sorbed mass on any of the four bulk soil samples were flagged as a non-detect (i.e., flagged “U” by the laboratory as a non-detect), the average was reported as N/A and the K_d calculation was not performed because the inherent variability in the concentration near the detection limit precludes a K_d determination that is reliable. Thus, the K_d results were reported as N/A.

If Cr(VI) was quantified in the four bulk soil sample analyses but an associated leachate result was non-detect (i.e., flagged “U” by the laboratory), the K_d was reported as a greater than value based on calculating the K_d using the practical quantitation limit (PQL) as the solute concentration (0100K-CA-V0081, 0100X-CA-V0058, 0100X-CA-V0059, 0100X-CA-V0060).In these cases the estimated lower limit on K_d was used in the analysis. However, the value used is a conservative estimate as the PQL is higher than the limit at which Cr(VI) can be detected.

A summary of the results from the K_d calculations is found in Table 1. A total of 509 samples from 58 locations resulting in a total of 2036 analyses were completed. Only 38 analyses from 4 locations had detections of Cr(VI) in both the soil and solute while 154 analyses exist where Cr(VI) was detected in the soil sample but not detected in the leachate following the leaching experiment. Comparing these two populations of data (Table 1) demonstrates that the range of

K_d values given by the group with calculated K_d (based on 38 analyses) and estimated K_d (based on 154 analyses) are similar. However, medians and averages are more different. Given that many of the locations for these tests were selected to increase the likelihood of detection, it should be noted that the majority of the sites were not contaminated with detectable levels of Cr(VI) and those with detectable levels, the majority showed no detectable leaching of Cr(VI) into the water during the leaching experiment, further illustrating the lack of leachability for residual Cr(VI) after the interim remediation actions are implemented.

The leaching results were also grouped based on the geologic formation where the sample was taken. Thirty-eight samples from the Hanford formation from 14 locations produced data where a K_d could be calculated. While 10 samples from 4 locations were collected from the Ringold formation. The K_d values calculated for the Hanford formation samples have a significantly higher minimum value (7 mL/g) over the minimum value for samples from the Ringold (0 mL/g). Median and average values for the Hanford formation are also larger in magnitude than the results in the Ringold.

Table 1 – Summary of leach tests and K_d results used in analyzing K_d for use in the river corridor

Sample Group	Locations	Samples	Analyses	Minimum	Average	Median	Maximum
All Samples	58	509	2036	--	--	--	--
By Detection							
Soil Detection Only	15	39	154	0	27	25	66
Soil and Solute Detection	4	10	38	0.03	14	3.5	55
By Geologic Formation							
Hanford	14	38	152	7	28	26	66
Ringold	4	10	40	0	12	2.0	54

* K_d calculated by assuming dissolved concentration is at the practical quantitation limit

3. Assumptions and Inputs

Several attributes exist that may influence the results of the leaching tests and the estimated K_d value associated with each leaching test. In this analysis depth below ground surface, dilution factor at which the leach experiment was conducted, type of waste site where the sample was collected, the operable unit where the sample was collected, geologic formation, and lithology were investigated to evaluate if there was an apparent influence of any of these attributes on the results. The analysis included plotting the cumulative distribution function for K_d results and illustrating the attributes listed above through the symbology of the points, creating scatter plots of depth vs. K_d, creating scatter plots of K_d with dilution factor 1:1 versus dilution factor of 1:2.5 and 1:5 for the same samples, and creating a scatter plot of Cr(VI) soil concentration versus estimated K_d. Because the evaluation includes only visual analysis of plots of these data, the analysis is qualitative.

Figure 1 shows the empirical cumulative distribution function (ECDF) created for K_d analysis values based on Weibull plotting position formula. It indicates that the probability at 10th, 50th, and 90th percentile is about 1.2 mL/g, 24 mL/g, and 48 mL/g, respectively. Converting this into a complimentary cumulative distribution function indicates a 90th, 50th, and 10th percentile exceedance of approximately 1.2 mL/g, 24 mL/g, and 48 mL/g, respectively. Note that the 90th

percentile exceedance means that there is 0.9 probability that the K_d value will be greater than or equal to 1.2 ml/g. Based on visual inspection of the ECDF a cluster of results near the minimum can be observed from 0th Percentile to 10th Percentile. These low values (indicating greater than 90th percentile exceedance) are attributable to two primary locations, C7695 and C7866. In each case the estimated K_d values come from samples taken below a depth of 50 ft bgs. According to the field log for this location, this places these sediments within the Ringold formation. This indicates that the K_d results may be affected by attributes associated with the collection and analysis of the samples.

To investigate what attributes of the sample locations and analysis might influence or bias the resulting K_d values the ECDF is presented where portions of the ECDF are isolated on the plot based on common attributes. Figures 2 through 5 illustrate the ECDF based on waste site type, reactor (geographic) area, geologic unit, and sediment lithology, respectively. The following paragraphs discuss trends in each of these figures.

Waste Site Type – Where possible, soil borings were designated based on the type of waste site (high concentration/ low volume sites, low concentration liquid effluent sites, or not assigned) were close to the boring. When plotting the ECDF based on waste site type (see Figure 2) one noticeable feature is that K_d values from sites of low concentration liquid effluent sites don't have any K_d values lower than 6 ml/g (Figure 2a). High concentration/low volume waste sites (Figure 2b) indicate that the majority of the lower K_d values result from samples taken at these sites. This supports the idea that low concentration liquid effluent sites tend to have higher minimum K_d values than high concentration/low volume sites.

Reactor Area – The values shown in Figure 3 indicate that operable unit does not significantly affect the value of K_d. Only the B/C Area does not have values that span the majority of the range of K_d Values. B/C Area K_d values (Figure 3c) range from 6 ml/g to 22 ml/g. However, this may be due to the limited number of detections from samples in the B/C Area.

Geologic Unit – Visual inspection of the ECDF separated based on geologic unit (see Figure 4) indicates that values from the units in the Ringold Formation tend to be lower than those values in the Hanford formation. Although, it is noted that some K_d values from samples taken from the Ringold formation are as high as the upper percentiles of the range of the Hanford formation.

Lithology - Figure 5 shows the portions of the ECDF for each lithology on a separate plot. The lithology descriptions typically show a large range of K_d values except for "gravel" designation shown in Figure 5b. The range of K_d values for the gravel appears to be limited to a lower range of the entire K_d data set.

Figure 6 illustrates the variability of K_d with depth in the form of a scatter plot with superimposed trendlines. The dataset was plotted where Cr(VI) was detected in both soil and solute and when detection occurred in soil only (assuming PQL for solute concentration). The soil and solute detection data seem to indicate a strong depth trend while the soil only data does not appear to trend heavily with depth. The sparse amount of data with depth in the soil and solute data is likely to be causing the strong depth trend. All of the data with depth comes from two sample locations. Any change in those two locations would greatly affect the trend. Also, the R-squared fits to each of the trends is low. Therefore, the trend is considered to be an artifact of sparse data availability rather than a reflection of an existing trend.

Scatter plots of K_d values based on dilution factors used in the leaching analyses are shown in Figure 7. These figures illustrate that dilution factor may be affecting the resulting K_d value. Only K_d values resulting from samples where the soil and solute detection occurred are shown in this figure. The upper boundary value (PQL), used to estimate K_d when only a soil concentration was measured, is constant. The constant value used is based on the analytical method of Cr(VI) detection. Therefore, it may not illustrate a dilution effect. Any resulting trend that was inferred using this data could result as an artifact of the PQL used to estimate K_d. Therefore, these data were not included in the figures. Trend line analysis of the remaining data of K_d resulting from the 1:1 dilution versus the 1:5 (Figure 7a) and 1:2.5 (Figure 7b) dilution show that there is a 2.9 multiplier and a 2.1 multiplier in the trend in each case. This indicates that a larger dilution factor may result in a larger estimate of K_d. This may be attributable to the amount of mass available for leaching from the soil column. If the mass available for leaching is similar in each case, the resulting solute concentration would be lower for larger dilution factors. Thus, a larger K_d value would be estimated. While the dilution factor seems to have an effect, this analysis does not provide a methodology for determining which dilution factor provides more appropriate K_d values. Therefore all of the dilution factors were treated with equal weight so no particular dilution factor was an average of the K_d values estimated from all the analyses.

Figure 8 shows a scatter plot of Cr(VI) soil concentrations versus the corresponding K_d value from the leaching experiment. In general, the K_d values for soils with a soil concentration below 1 mg/kg tend to have a relatively limited range of K_d values ranging from 0 to 4 mL/g. Approaching and after a soil concentration of 1 mg/kg the range of K_d values increases significantly to values from near 0 to 56 mL/g. Soil detection only K_d results were not plotted because due to the constant PQL used to calculate K_d, a linear trend is displayed that is an artifact of the PQL used for estimating a conservative value for K_d.

3.1 Method Uncertainties

Several uncertainties exist in the methodology used to determine K_d values. These include uncertainties in the ASTM D3987-06 leaching method, sample concentration range, the drilling of wells, and the equation (Equation 1) used to calculate the K_d value. These uncertainties and a discussion of the effect they have on the results are discussed below.

3.2 Leaching Method

One source of uncertainty in the results is identified in the ASTM D3987-06 documentation. The method specifies that the soil sample and water be placed in a batch reactor that is turned end over end for 18 hours. While appropriate for mixing these two substances together it is not necessarily representative of field conditions. The method specifies that it “is not intended to provide an extract that is representative of the actual leachate produced from a solid waste in the field.” (ASTM, 2006). This may or may not have an impact on the K_d results depending on how well the results would match field conditions. It is also recognized that the amount of water that is used in the batch leach experiments exceeds the pore volume of the soil samples under saturated field conditions. Unfortunately, there is no analysis that can be made with the current data to quantify the level of uncertainty this produces in the results.

As part of the leaching methodology the water added to the soil sample was prescribed to have a pH of 5 in order to simulate rain water infiltration at the Hanford Site. No data exist that can determine the final pH of the added water after mixing water with the soil. Figure 9 presents the Eh-pH diagram for chromium and indicates the oxidation states and chemical forms that exist

within specified Eh and pH ranges (Palmer and Wittbrodt, 1991; EPA, 2000). The figure shows that Cr(VI) remains stable when pH >4 and under oxygenated conditions that would be encountered in leaching experiments. The dominant species are $HCrO_4^-$ and CrO_4^{2-}. Any increase in pH alone would not lead to change in oxidation state of Cr(VI) and conversion to Cr(III). However, Cr(III) could undergo hydrolysis with increasing pH to form chromium hydroxy species [$CrOH^{+2}$, $Cr(OH)_2^+$]. Reduction of Cr(VI) to Cr(III) can only occur when reductants are introduced, such as, reduced manganese oxide (MnO), soil organic matter, soluble ferrous iron [Fe(II)], and reduced sulfur compounds.

It is possible that desorption characteristics from leaching at higher pH may be different due to speciation of chromium ions and surface complexation with the mineral surfaces where surface charge varies as a function of pH.

3.3 Sample Concentration Range

Analyzed Cr(VI) concentration magnitudes of the soil samples collected for this study ranged from 4.31 mg/kg to undetectable levels. Experimental results from flow through leaching experiments discussed previously show minimal leaching of Cr(VI) from soil concentrations as high as 6.0 mg/kg (Serne and Parker, 1999). Therefore, the recommended use of a K_d value in this report should only be applied to locations where Cr(VI) concentrations are below a concentration of 6 mg/kg. Application of the recommended K_d value outside of this range may introduce uncertainty that is not quantifiable based on the current dataset. In order to better quantify K_d outside of this concentration range may require soil samples with concentrations that cover a broader range. This is not to suggest that the soil samples were specifically targeted for a limited range of Cr(VI) concentrations. Rather, the locations were selected to maximize the likelihood that a broad concentration range was identified.

3.4 Sample Collection

A concern about the drilling and sample collection procedure may be a source of uncertainty in the K_d values. The wells and boreholes were drilled using the cable tool method. Periodically, water was added to the hole to allow removal of drill cuttings from the dry, unconsolidated sediments of the Hanford formation and Ringold Formation. The intent is to provide sufficient water for removing cuttings and advancing the borehole without disturbing the underlying material which is being tested for a variety of mobile and immobile contaminants. Typically, one gallon (0.13 cubic ft) of water was sufficient to provide some cohesion to the cuttings. However, occasionally 5-15 gallons (0.67 to 2.01 cubic feet) were used. Most of the additions were completed at least 2 feet above the planned split-spoon sample interval.

The hydraulic evidence indicates that the large majority of the samples are unlikely to be significantly disturbed. For scale, one gallon (0.13 cubic feet) of added water would fill a sphere of approximately 1 foot in diameter assuming a 20 percent porosity. Fifteen gallons (2.01 cubic feet) would fill a sphere of 2.7 feet in diameter. The high matric potential combined with the higher horizontal conductivity would tend to flatten the sphere out as water preferentially wets in the horizontal direction. This is generally confirmed by the results of neutron logging in the wells and boreholes that show close correlation between the depth of water addition and the presence of elevated water in the adjacent formation indicating water has moved laterally away from the borehole and away from the target split-spoon sample interval vertically below. While there could be a few samples impacted, there does not appear to be a significant bias introduced to these data that would cause significant impact to the dataset used in this memorandum for recommending a K_d value for Cr(VI).

3.5 Dilution Factor

The trend analysis discussed in a previous section indicated that the K_d value increased as the dilution factor used in the ASTM method increased. This can partly be explained by the amount of mass that is leached from the soil sample. Figure 10 compares the amount of mass leached from the soil samples using a 1:1 dilution factor to the mass leached for both a 1:2.5 and 1:5 dilution factor. A trend line for each of the datasets shows a slope of 1.2 and 1.04 for the 1:2.5 and 1:5 dilution factor, respectively. The nearness to a slope of 1 indicates that on average the same amount of mass leached for one dilution factor is the same amount of mass leached for another dilution factor. This would indicate that the rise in the K_d value for a given dilution factor is simply an artifact of the volume of water added to the system (i.e., the same mass added to a larger volume of water result in lower concentration causing an increased value of K_d based on equation 1).

A basic normalization factor that would account for the difference in volume of water used in the leaching method can be applied to Equation 1. Equation 2 shows an alternate version of Equation 1 with a correction factor included. The factor (D_f) is achieved by dividing the volume of water added to the leaching method by the amount of water used at the lowest dilution factor in the ASTM method (100 g). This results in values for D_f of 1, 2.5, and 5 for the dilution factors 1:1, 1:2.5, and 1:5, respectively.

$$K_d = \frac{(C_S \times M_S) - (C_L \times V_L)}{M_S} \times \frac{1}{C_L * D_f} \times \frac{1000\ mL}{1\ L} \qquad \text{Equation 2}$$

Where:

K_d = Distribution coefficient (mL/g)
C_S = Contaminant concentration in bulk soil matrix prior to leaching (µg/g)
M_S = Dry mass of soil used for leaching (g)
C_L = Contaminant concentration in leachate (µg/L)
V_L = Liquid volume used for leaching (L)
D_f = The batch-leach-ratio specific dilution factor (i.e., 1, 2.5, or 5)

Figure 11 shows the ECDF for the K_d values adjusted based on the dilution factor. The ECDF indicates a 90th, 50th, and 10th percentile exceedance of approximately 0.8 mL/g, 9 mL/g, and 29 mL/g, respectively. The results of correcting based on the dilution factor have the impact of shifting the values of key Percentile points on the ECDF to a lower value.

Another method for normalizing the K_d values from the batch leach experiments is based on the moisture content of the sample at saturated conditions. This would mimic the concentration of the pore water if the same mass leached in the leaching tests were to leach at field conditions. Assuming a bulk density of 1.90 g/ml and a porosity of 0.28 for the 100 Area (PNNL-14702) results in dilution factors of 6.8, 17 and 34 for K_d values derived from the 1:1, 1:2.5, and 1:5 dilution ratios, respectively. When these dilution factors are applied the range of resulting K_d values is from a high 7.9 mL/g to a low of 0 mL/g with a 90th, 50th, and 10th percentile exceedance of approximately 0.11 mL/g, 1.3 mL/g, and 4.3 mL/g, respectively. Figure 12 shows the ECDF of the K_d values normalized to an assumed saturation condition from average 100 Area bulk density and porosity. It must be stated that no measurements of Cr(VI) concentrations are available for this lower end of water content range. It is not known whether the same mass of Cr(VI) would have been detected at that water content. Therefore results in Figure 12 are not meant to be representative of K_d values, rather the results present a clear

lower bound on these K_d values. The recommended value of 0.8 mL/g (discussed below) is clearly within the range of these lower bounds on K_d.

4. Software Applications

Excel® spreadsheets were used to calculate ECDF distributions and evaluate linear trends in the K_d data presented as part of this ECF. These calculations were performed on a laptop computer with USDOE ID WF16209. The hardware is a Dell® Latitude® E6400 with a 2.26-GHz Intel Core™ 2 Duo CPU E8200 processor and 3 GB of RAM loaded with the HLAN Windows® XP Image Version 3.0.1.0 operating system.

This use of Excel® software is exempt from the requirements of PRC-PRO-IRM-309 because it constitutes a "flat-file" spreadsheet that is wholly incorporated into this ECF and the calculations, mathematical formulas, and input data can be exactly verified during the technical review of this ECF (PRC-PRO-IRM-309, Rev. 1, Section 1.3, Exemptions).

5. Calculation

Each percentile from the ECDF value can be estimated based on linear interpretation of the values closest to the given percentile. Hence, the 10th percentile can be estimated through linear interpolation of the two values closest to it. Figure 11 shows the ECDF for the K_d values adjusted based on the dilution factor. The ECDF indicates a 90th percentile exceedance of can be calculated based on the two values in Table 2. The resulting value for the 90th percentile exceedance is 0.8 mL/g.

6. Results/Conclusions

6.1 Summary

A large number of samples were collected (509) that generated results from leach tests (192) that are usable for evaluating the leaching potential of residual Cr(VI) in the River Corridor. Out of the attributes selected for evaluation, two (dilution factor and geologic formation) were noted as potentially having an effect on calculated K_d values. The trend with respect to geologic formation is likely attributable to the small sample size (the majority of these results came from two locations C7695 and C7866). The range of the K_d values from these samples was smaller than the results from shallower formations. Further, there appears to be a relationship between the dilution factor and the resultant K_d. When the dilution factor of soil to leachant was higher, a slightly larger K_d was typically estimated for the sample but the range of variability is well within the range of natural variability for the estimated values. \

Table 2 – ECDF locations used to calculate the 90th percentile exceedance for the dilution factor corrected ECDF.

Point ID	Weibull Plotting Position	K_d (mL/g)
1	0.098	0.74
2	0.103	0.99
Interpolation	0.1	0.8

6.2 Recommendations

The large number of K_d measurements and the lack of correlation of calculated K_d with possible explanatory parameters allows a conservative value to be used across the River Corridor for evaluation of future fate and transport of residual Cr(VI) after interim remedial actions have been implemented for source waste sites in the vadose zone. The ECDF of K_d for the soil samples indicates that more than 90% of the values are higher than 1.2 mL/g and greater than 95% of the values are higher than 0.65 mL/g. If the K_d values are adjusted for the amount of water used during the tests, the 90th percentile drops to about 0.8 mL/g. Based on the presented results in the previous section a K_d value of 0.8 mL/g is recommended as a conservative estimate for the lower limit on residual Cr(VI) K_d value for the River Corridor. This value is conservative relative to values available in literature (e.g., a K_d of 19 mL/g was selected for promulgation under WAC 173-340). The 0.8 mL/g value is based on K_d estimates from soils contaminated with a maximum concentration of 6 mg/kg. Therefore, using this value for soils contaminated at concentrations above this range should use a K_d value appropriate for concentrations above 6 mg/kg.

7. References

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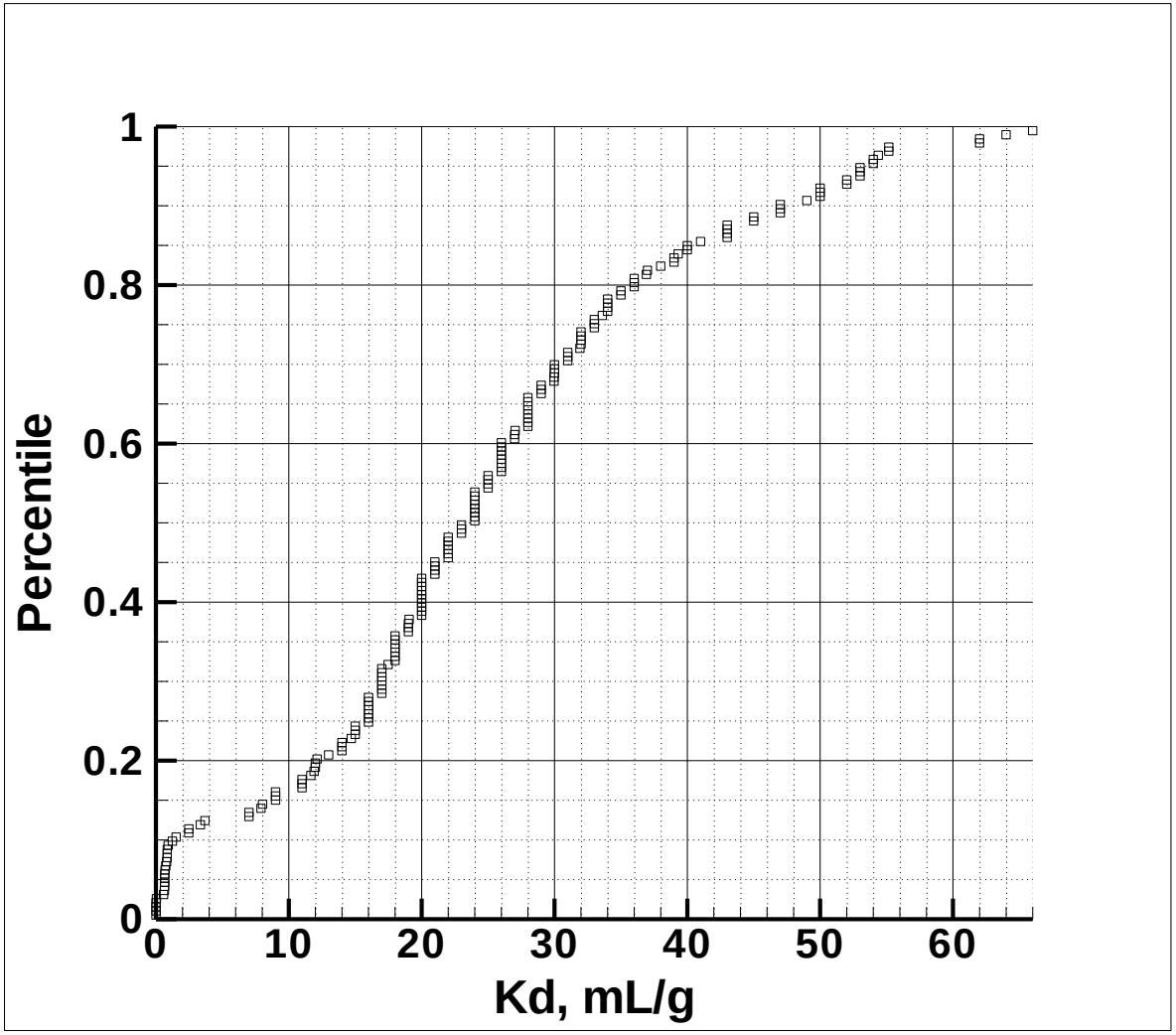


Figure 1 – Empirical cumulative distribution function for K_d estimates from leaching tests.

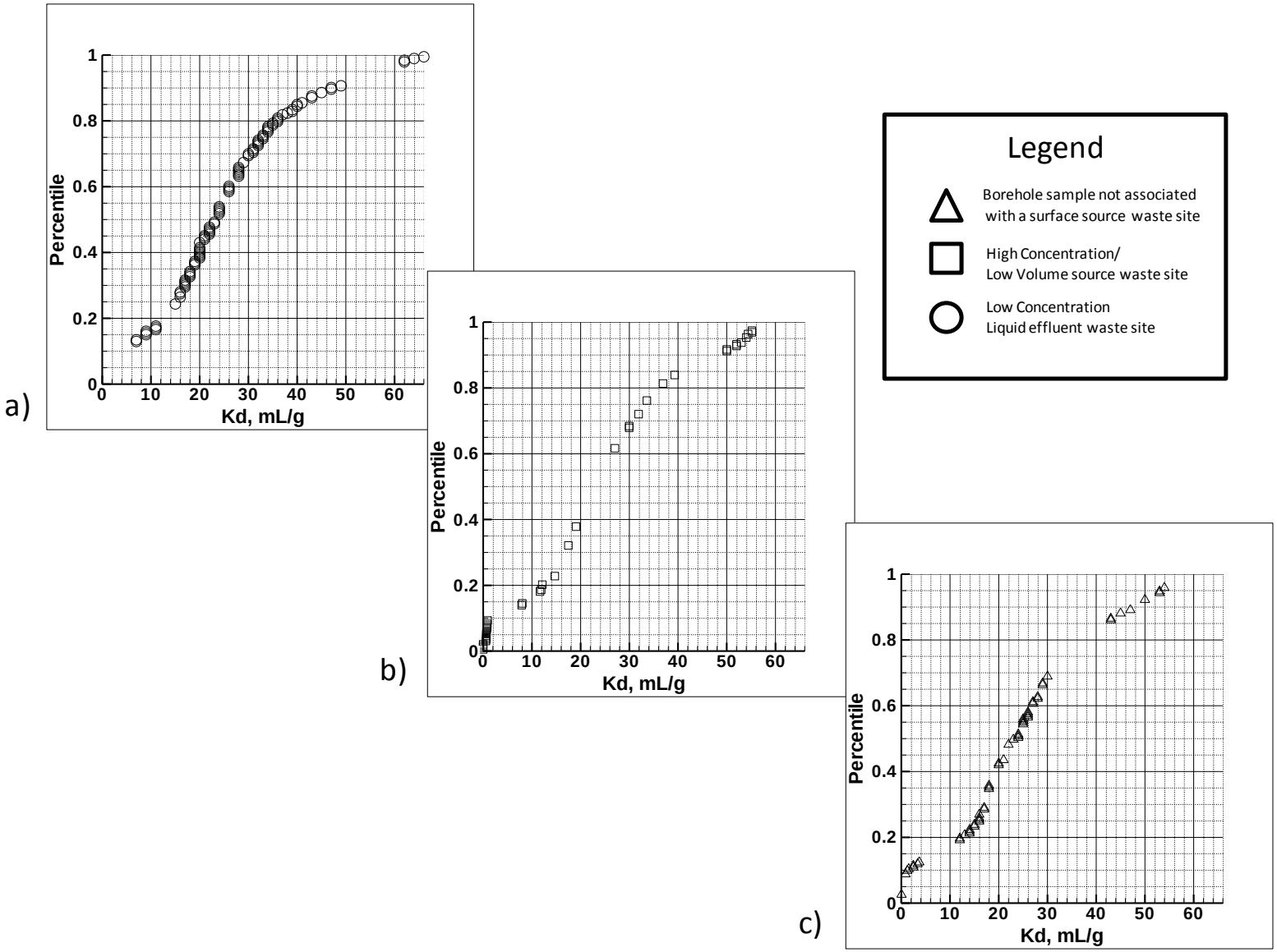


Figure 2 – Empirical cumulative distribution function for K_d estimates from leaching tests broken up by waste site type.

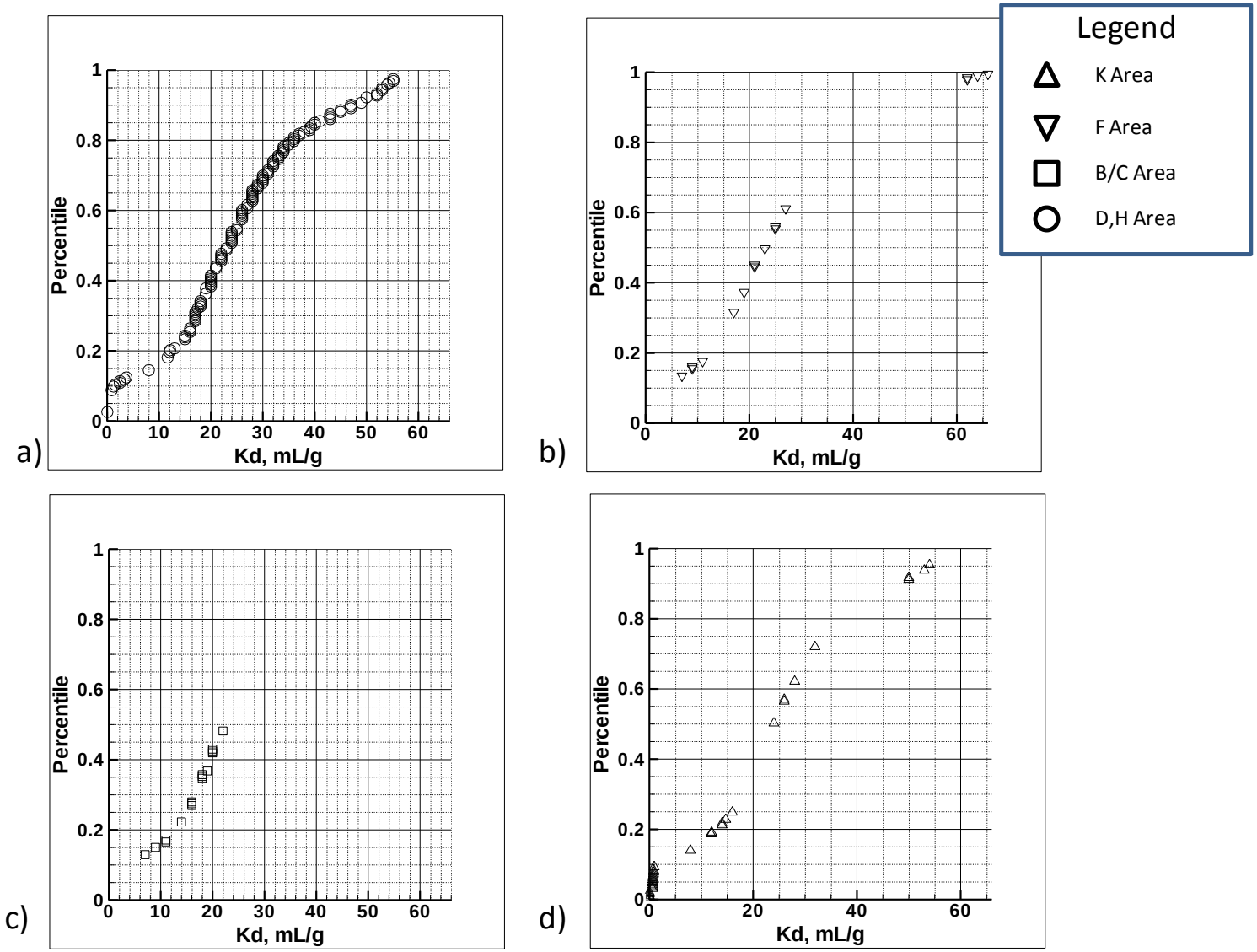


Figure 3 – Empirical cumulative distribution function for K_d estimates from leaching tests symbolized to indicate reactor area within the River Corridor.

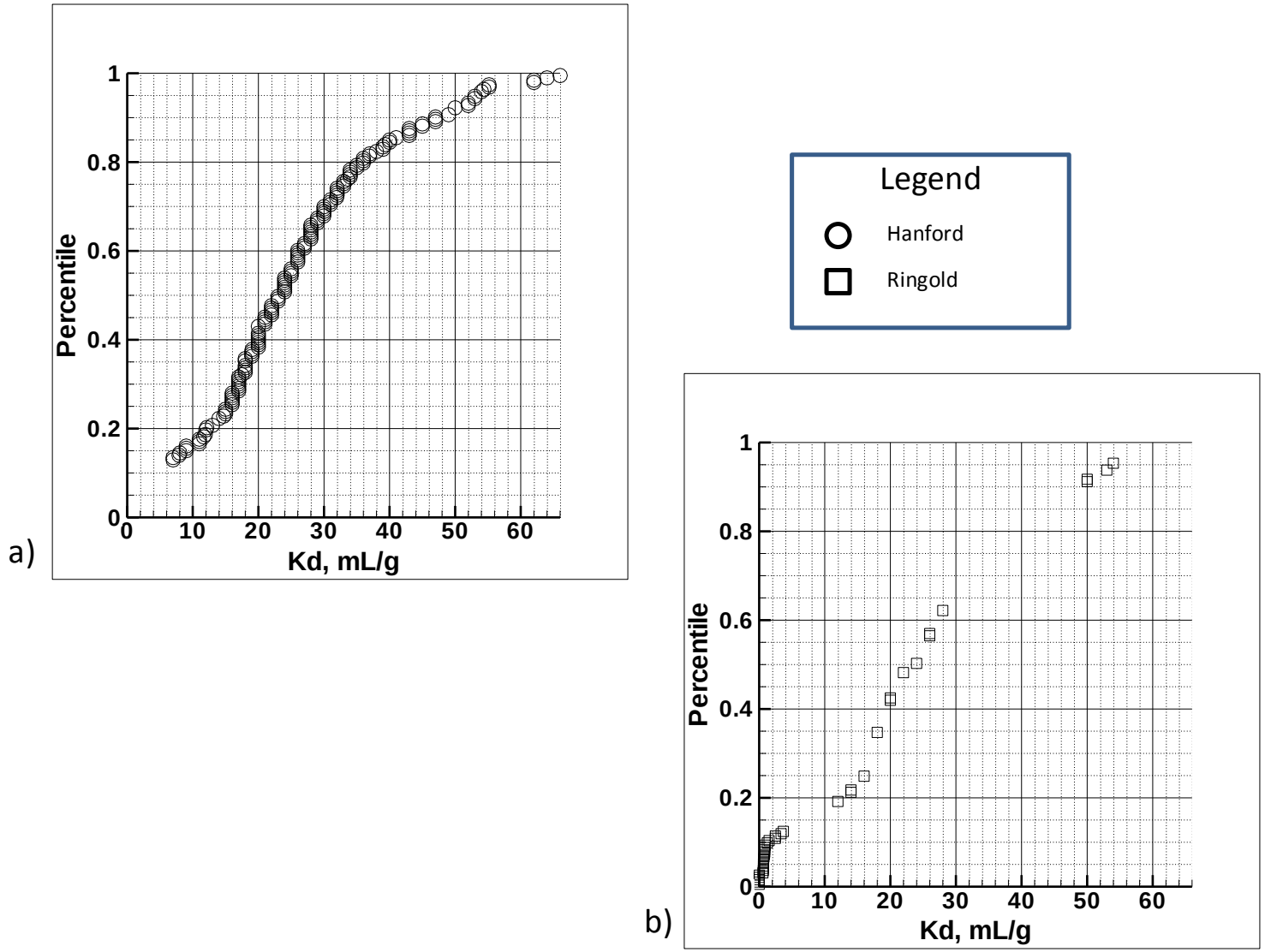


Figure 4 – Empirical cumulative distribution function for K_d estimates from leaching tests symbolized to indicate geologic formation of sediments.

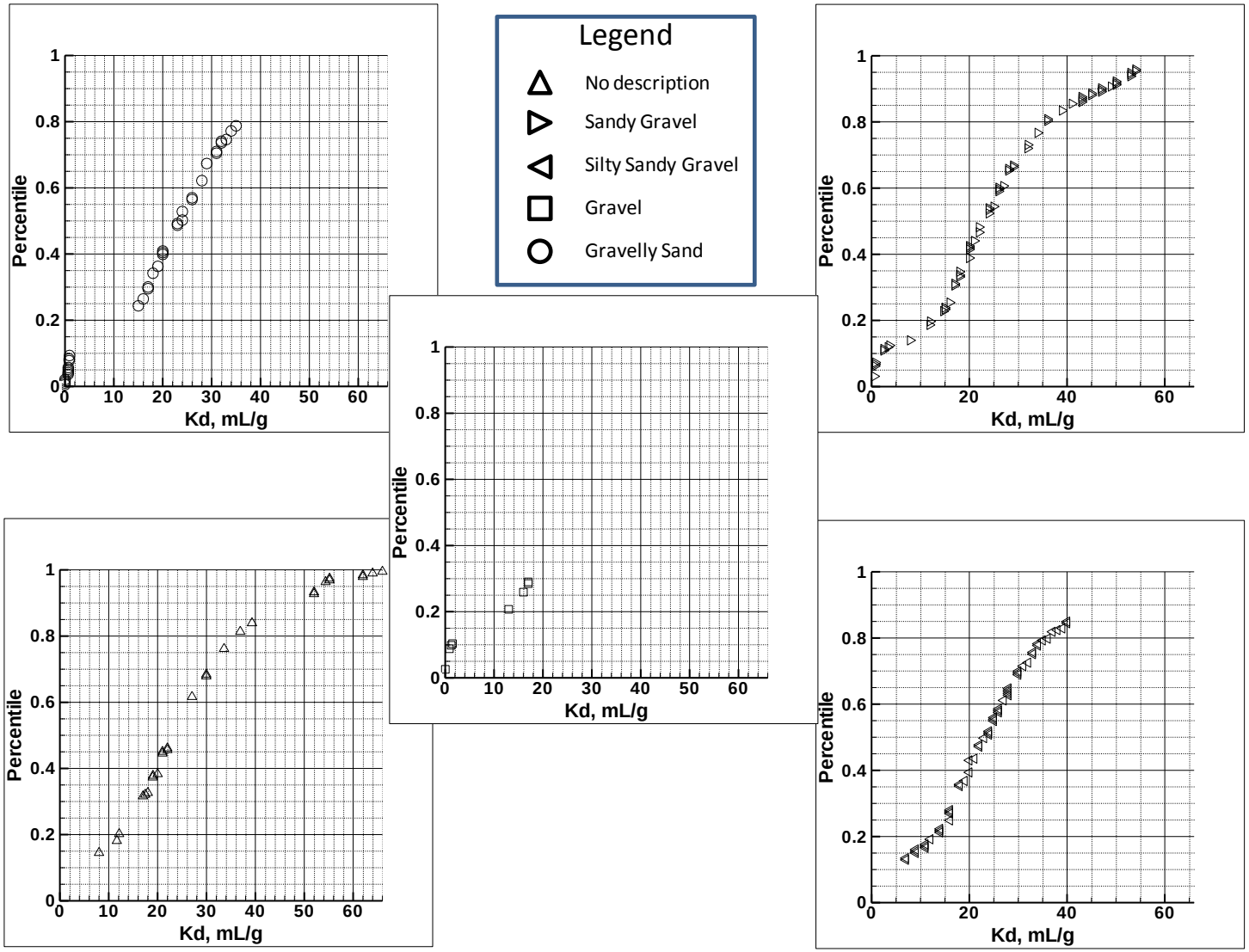


Figure 5 – Empirical cumulative distribution function for K_d estimates from leaching tests symbolized to indicate lithology of sediments.

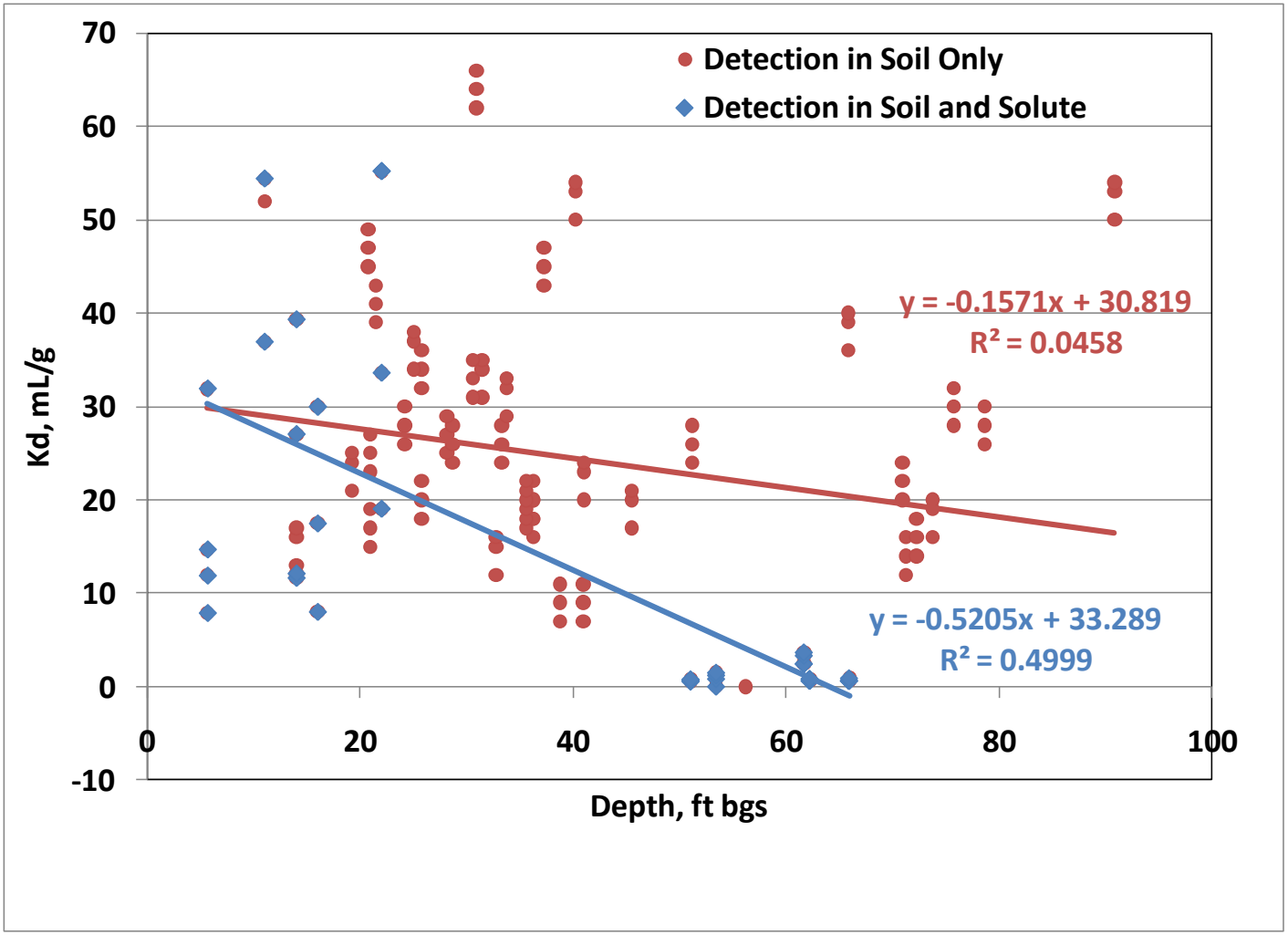
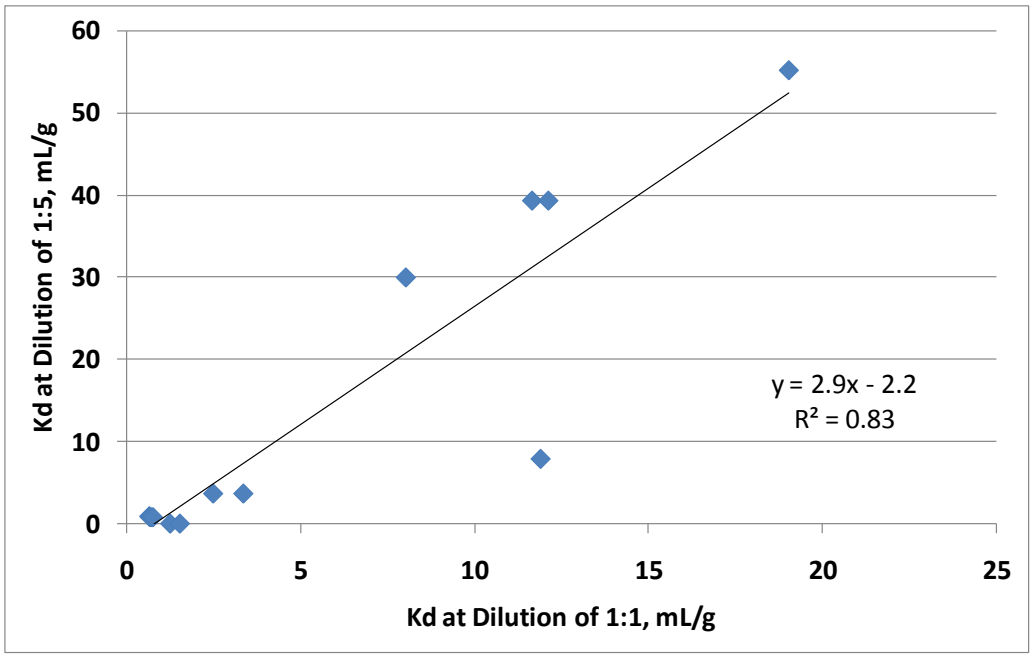
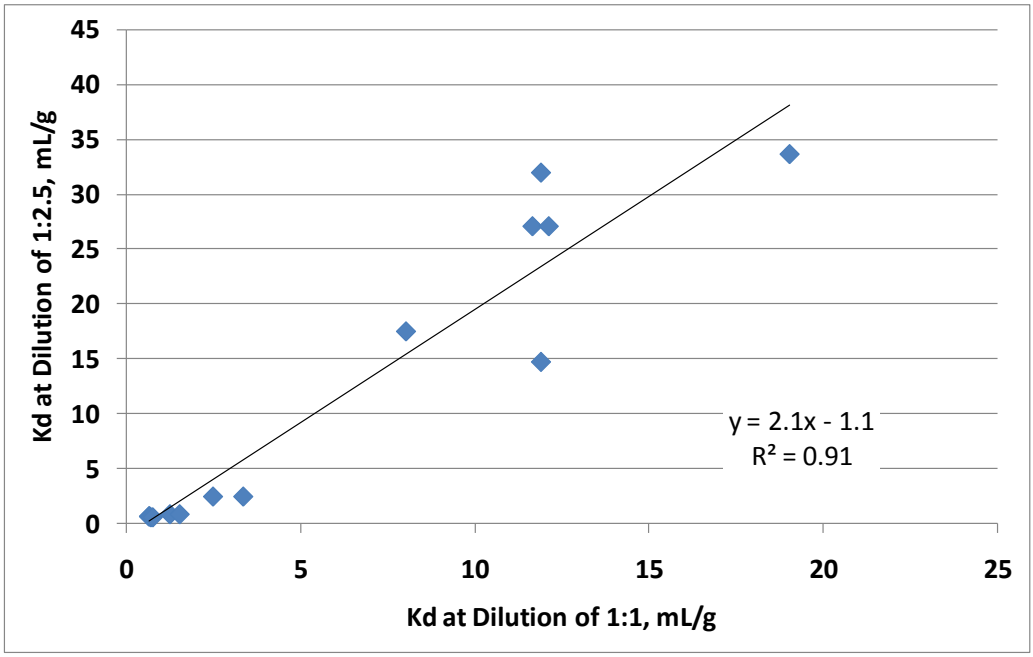


Figure 6 – Scatter plot of K_d versus depth with trend lines used to illustrate possible relationship between the two data.



a)



b)

Figure 7 – Scatter plot of K_d value based on dilution factor 1:1 versus dilution factor 1:5 (a) and 1:2.5 (b) with corresponding trendline

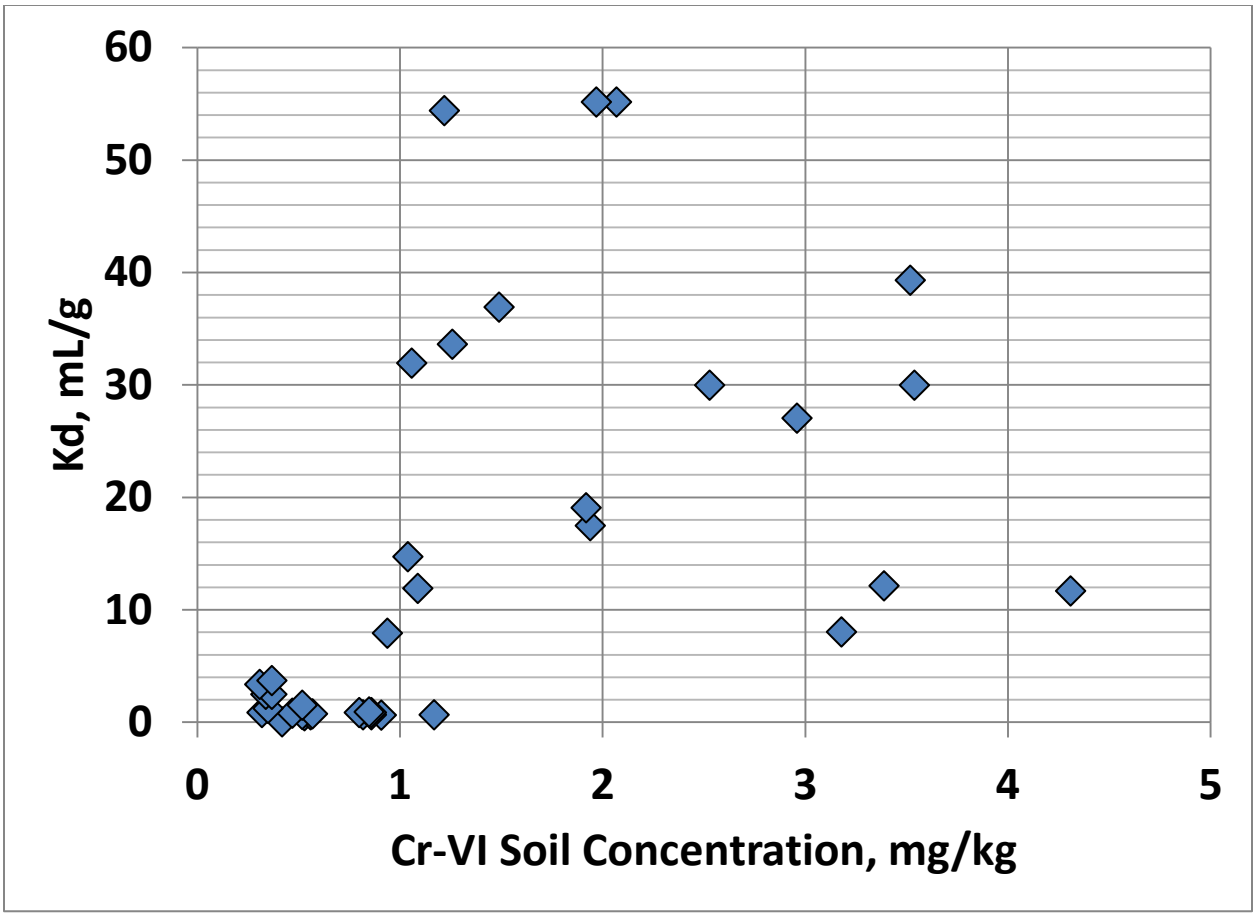


Figure 8 – Scatter plot of soil concentration versus estimated K_d for analyses where both soil and solute concentrations of Cr(VI) were detectable.

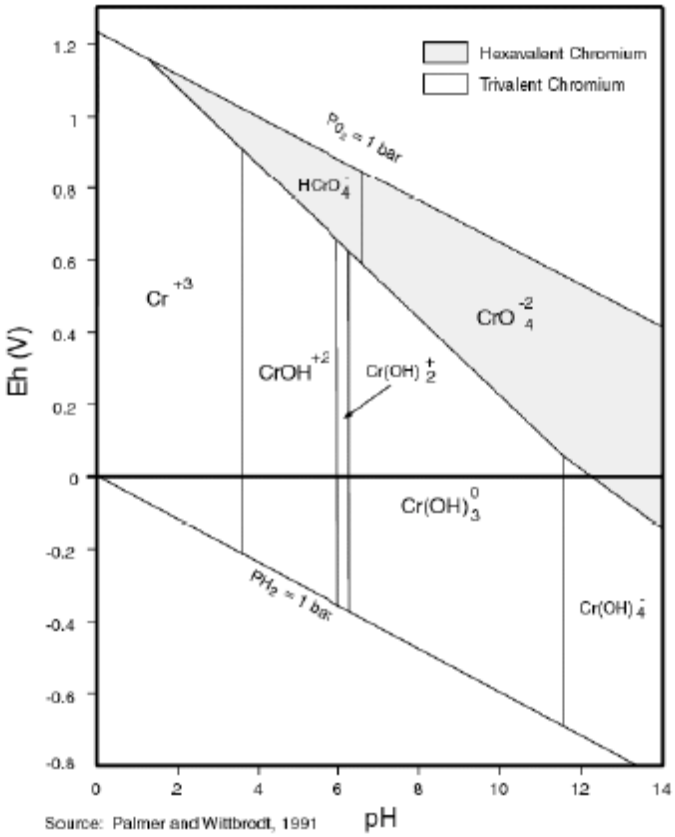


Figure 9 – Eh-pH diagram for Chromium

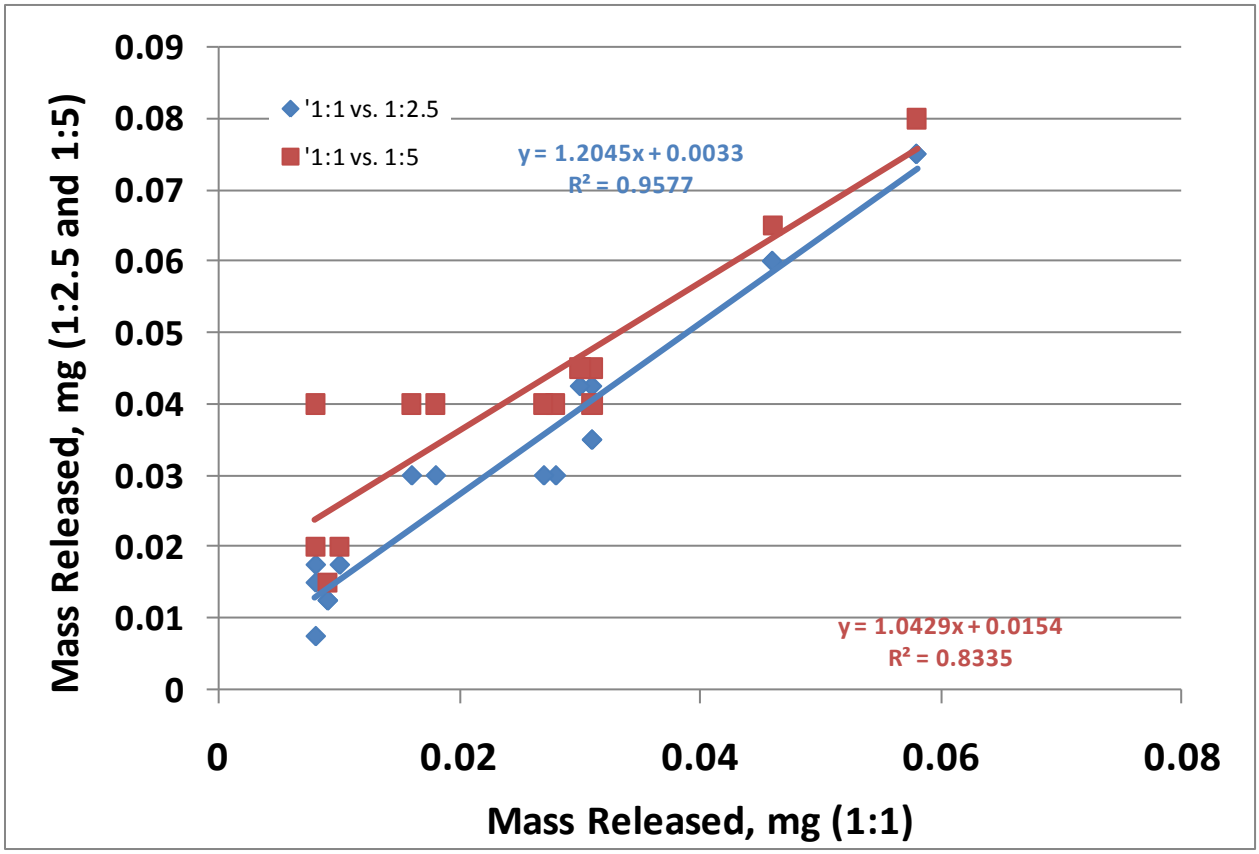


Figure 10 – Scatter plot of mass leached for dilution factor 1:1 versus mass leached for a dilution factor of 1:2.5 and 1:5.

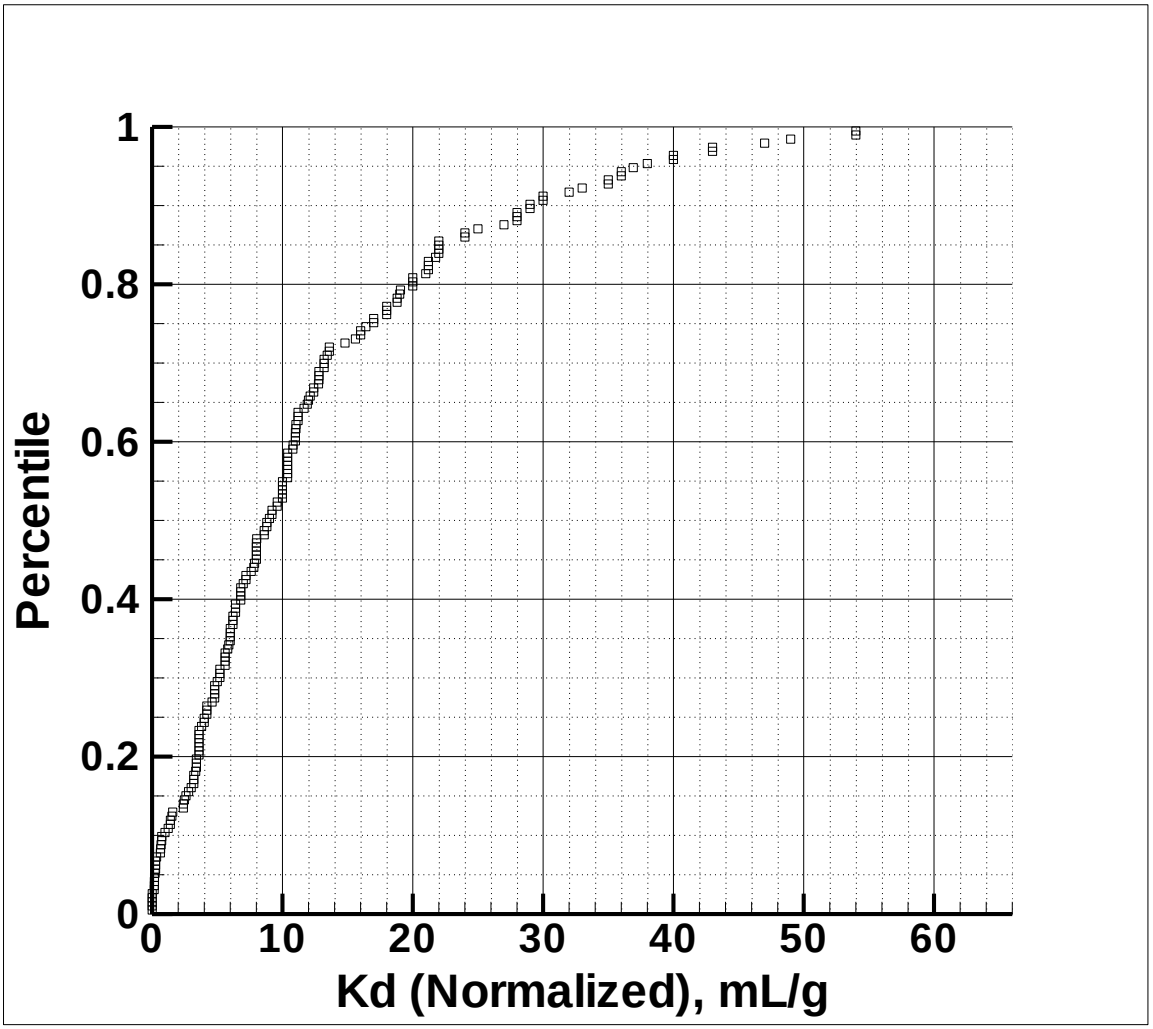


Figure 11 – Empirical cumulative distribution function for K_d estimates normalized based on the dilution factor used during leaching tests.

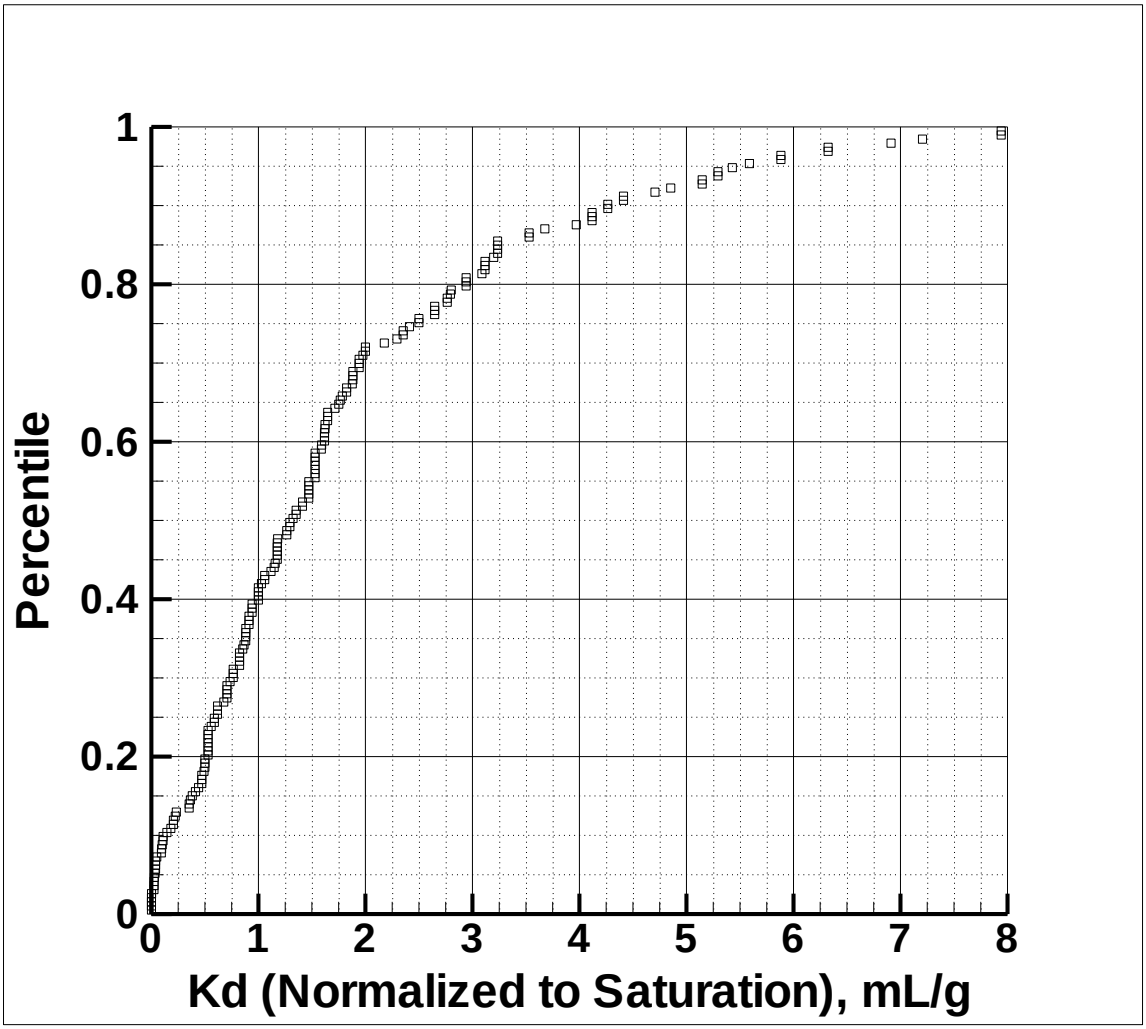


Figure 12 – Empirical cumulative distribution function for K_d values normalized to an assumed saturation condition from average 100 Area bulk density and porosity.