Estimation of a Generic Adsorption Coefficient Kd for Barium

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1. INTRODUCTION

The British Columbia Ministry of Environment is currently developing matrix numerical soil standards for barium. The Barite-Barium Issues Committee and the BCLQAAC Barite Task Group recommended that a study be conducted to determine an appropriate value of the adsorption coefficient Kd for barium in subsoil to use in developing soil quality guidelines protective of groundwater use. The determination of Kd of barium was conducted by Darlene Lintott of Bodycote Testing Group, in consultation with Miles Tindal of Axiom Environmental. This report documents the results of that study.

The primary purpose of Kd determination is to predict the fate of contaminants in a (*sub-*) soil zone, by describing the relative proportion of a chemical that is sorbed to the solid phase and in solution. This is an empirical, site-specific value, and may vary with soil type, water chemistry and other site-specific conditions. The objective of this study was to determine a single value for Kd that could be conservatively applied under a range of soil types and site conditions. To that end, this study included Kd determinations for barium in four subsoils considered representative of northern BC, using a wide range of barium exposure concentrations. If a simple, linear relationship of barium partitioning between soil and water could be established across soil types and concentration ranges, then a single representative Kd could be estimated and applied to development of generic numerical soil standards.

2. EXPERIMENTAL METHODOLOGY

2.1. PREPARATION OF TEST SOILS

Four field soils were used for the Kd study. Two soils, including a clay soil and a sandy soil, were collected from northeastern BC sites as background samples and have likely not been exposed to industrial contaminants. The clay soil and sandy soil were collected and supplied by Husky Energy and were received at Bodycote Testing Group (BTG, formerly Norwest Labs), Edmonton AB on September 1 2006 (referred to as "Husky Sand and Clay", or "Clay"). The sand was later omitted from the Kd evaluation but analytical characterization is included here for comparison. Three additional soils were collected by Northern Envirosearch Inc. from a northeastern BC site known to have been historically associated with drilling waste disposal. These soils, referred to as "CNRL #1, #2 and #3" were collected at 1.0 to 1.5 m in depth, from a background area, an encapsulation pit and in vicinity of a former drilling sump. The CNRL soils were received at BTG Edmonton on October 30, 2006.

The native soils were prepared by drying at 30°C, then disaggregated to <2 mm (but were not pulverized). The soils were characterized extensively for physical and chemical parameters (presented in Appendix 1). Key characteristics of the soils that are most pertinent to behavior of barium in soil are provided in Table 1. The CNRL soils were colluvial in nature. The gravel fraction was removed prior to completing any analytical characterization, in order not to bias the particle size and texture analysis.

Table 1. Primary Characteristics of Soils for Kd Determination

Parameter Name	Units	Clay	CNRL#1	CNRL#2	CNRL#3
Texture	%	Clay	Sandy Loam	Sandy Loam	Sandy Loam
Sand	%	14	75	72	68
Silt	%	26	17	17	20
Clay	%	59	8	11	13
CEC	meq/100g	25	7.8	10.3	10.3
Barium by Fusion	mg/kg	1000	200	1800	7700
Barium (EPA 3050B)	mg/kg	333	75	1590	5760
Barium (BC SALM)	mg/kg	176	102	506	647
BC Soluble Barium	mg/kg	16	nd	28	52
Sulfate-S	mg/kg	1120	4	137	199

2.2. Kd TEST METHOD SELECTION

Kd is defined as the ratio of the substance concentration associated with the solid (μ g substance/ g soil) to the substance concentration in the surrounding aqueous solution (μ g substance / mL solution) when the system is at equilibrium.

Reference was made to a list of method descriptions, including a draft BC protocol, and ASTM and USEPA protocols (see references provided at the end of this document). Essentially, the method involves exposure of a solution of analyte at varying concentrations to the soil of interest. The loss of the analyte from solution is used to infer the concentration of analyte sorbed to the solid phase in the calculation of Kd. Variations in these reference methods included ratio of test solution to soil, test soil pretreatment, test solution pretreatment, mixing methods and length of the exposure period to reach equilibrium.

The methodology adopted for measuring Kd which was most applicable for this study's objectives is the ASTM "Standard Test Method for 24 hour Batch-Type measurement of Contaminant Sorption by Soils and Sediments" (D4646-03). Certain elements from the other reference methods were included in the test design. In essence the method involves taking solutions of soluble barium over a range of concentrations, adding a soil sample, and measuring the loss of barium from the solution following 24 hours equilibration.

2.3. Kd RANGE FINDING TESTS WITH CLAY

A successful determination of Kd is dependant on test methodology, including exposure concentrations, volume of solute and solution, exposure length and method of solids removal from solution. In order to investigate these potentially confounding variables, preliminary testing was conducted using the background clay in order to refine the final test method.

The preliminary clay Kd test was completed using broadly ranging exposure concentrations from near detection limit (0.1 mg/L) to near the maximum solubility of barium chloride (100,000 mg/L Ba). Test soil was exposed to soluble barium solutions at a rate of 20:1 solution to soil. For each clay treatment, a blank at the same concentration was included for comparison (test solution, no clay) to examine if loss of barium was occurring by other mechanisms than soil sorption such as binding to test vessels or precipitation of barium compounds. Additional replicates for each treatment were included to allow analysis at Day 1 (24 h), Day 3 and Day 25, in order to establish time to equilibrium. Treatments were

agitated by end to end shaking for the first 24 h, then again for 6 hours on Day 2. On day 24, treatments were agitated for about 18 h, and then allowed to settle on Day 25. At each exposure point, the solutions were decanted, filtered through a 0.45 um membrane filter, the filtrate was preserved with nitric acid and barium was analyzed by ICP-MS.

The results of the preliminary study are presented for Day 1, Day 3 and Day 25 in Table 2. The "Blank" treatment is barium analyzed in test solution without exposure to clay. Kd was calculated as per the ASTM method as:

Kd (mL/g) =
$$\frac{(C_{blank} - C_{soil}) \times V}{M \times C_{soil}}$$

Where:

 C_{blank} = Concentration of barium in the blank solution (mg/L)

C_{soil} = Concentration of barium in solution after contact with test soil

V = Volume of test solution (mL)

M = Mass of soil (g))

Table 2. Kd and Barium Concentrations in Solution and Solution Exposed to Clay – Range Finding Study

	Trt		Trt		Trt	_	Trt	-	Trt	_	Tri		Tri	
	0 mg	g/L	0.1 m	ng/L	10 m	10 mg/L		ng/L	1000 mg/L		50000 mg/L		10000	0 mg/L
	Blank	Clay	Blank	Clay	Blank	lank Clay B		Clay	Blank	Clay	Blank	Clay	Blank	Clay
Time					Meas	ured E	Barium Concentrations (mg/			/L)				
Day 1	0.01	0.03	0.16	0.03	9	9 0.08		0.07	726	0.07	29000	30500	50000	51000
Day 3	0.002	0.03	0.08	0.04	11	0.06	270	0.05	839	0.06	46800	35500	50300	54400
Day 25	0.001	0.03	0.10	0.05	9	0.05	460 0.04 9		900 0.04		56000	52200	97000	75000
Kd						С	alculate	ed Kd	(ml/g)					
Day 1	-1:	2	81	1	220)2	1104	128	2199	980	-0.	98	-0.	39
Day 3	-19	9	24	1	340	3409		480	262	168	6.3	37	-1.	51
Day 25	-19	9	17	7	356	3	2486	529	428551		1.46		5.8	37

At very low barium test concentrations (control, 0.1 mg/L), the results are confounded by proximity to the detection limit and cannot be interpreted as meaningful Kd values. At intermediate barium test concentrations (approximately 10 to 1000 mg/L), essentially all the dissolved barium was removed from solution, presumably by precipitation of barium sulphate and/or cation exchange with clay. The resulting Kd is high, indicating a strong affinity for clay. The Kd increases to 1000 mg/L as the Kd value is dependant on the exposure concentration. At high barium exposure concentrations (50,000 and 10,000 mg/L), the cation exchange capacity of the soil was saturated by barium, and excess barium remains in solution, resulting in a low "effective Kd". Between these two extremes, there will be a concentration range where the sulphate in the soil is exhausted, but there is still cation exchange capacity available. This is the target range of concentrations for definitive Kd determination.

The concentration of barium in test solutions not exposed to clay (blank) indicated reduced recovery of barium compared to nominal concentrations, for treatments 500, 50,000 and 100,000 mg/L on Days 1

and 3. This loss of soluble barium in higher test concentrations was evaluated with additional studies which examined the effect of filtration, potential sorption to test vessels and effects of nitric acid preservation on the Kd supernatant. It was determined that the likely cause for reduced recovery in the blank test solutions was the addition of nitric acid preservative to highly concentrated solutions, resulting in formation of relatively insoluble barium nitrate precipitate. This practice was discontinued for subsequent tests. There was no measurable indication of loss of barium by either filtration or from sorption to test vessels,

2.4. DEFINITIVE Kd TESTS

Based on the results of the preliminary tests with clay, Kd determinations for the four field soils proceeded with the following experimental design:

- Test Series: a range of soluble barium solutions which comprise of two treatments per concentration, including
 - o "blank" treatment, which is the test solution without exposure to subsoil
 - o "clay" treatment, which is the test solution exposed to subsoil.
- Exposure solutions prepared with barium chloride (BaCl₂.2H₂0).
- Each treatment was duplicated.
- 10 g soil exposed to 200 mL test solution in 500 mL plastic bottles
- Agitated horizontally on shakers for 24 hours.
- 1 hour settling period
- Decant supernatant, filter (0.45µ membrane filter)
- Analyze for barium by ICP-MS or ICP-OES within 24 hours.

The clay range finding experiments suggested that at low initial barium concentrations, the equilibrated barium concentrations are low and likely controlled by BaSO₄ precipitation and/or sorption to clay. At sufficiently high concentrations, there seems to be little loss of barium on equilibration, and this is postulated to be because the mass of barium available significantly exceeds both the availability of sulphate to form precipitates, and the cation exchange capacity of the soil, and thus the additional loss of barium from solution is limited.

In order to target a range of concentrations below the sorption saturation point of barium for Kd determinations, calculations were made to estimate the critical initial barium concentrations required to: i) precipitate all of the available sulphate in the soil sample; and, ii) saturate the available cation exchange capacity (CEC) of the soil.

2.4.1. Critical Barium Concentration – Barite Precipitation

Barite (barium sulphate) is highly insoluble, and hence barite precipitation is expected to control the concentration of barium in solution until the concentration is high enough to precipitate effectively all of the available sulphate. The critical barium concentration where there is just enough barium present to precipitate all the available sulphate was calculated using the following equation:

$$C_{{\scriptscriptstyle Ba.PPT}} = C_{{\scriptscriptstyle s.SO4}} \times \frac{137.33}{32.07 \times 20}$$

Where:

$C_{Ba.PPT}$	=	critical initial concentration of barium in solution required to precipitate all
		available sulphate (mg/L);
$C_{\text{s.SO4}}$	=	measured initial concentration of sulphate as sulphur in soil sample (mg/kg);
137.33	=	relative atomic mass of barium (mol/g);
32.07	=	relative atomic mass of sulphur (sulphate measurements are presented on an "as
		sulphur" basis; mol/g); and,
20	=	dilution ratio of solution volume to soil mass in Kd equilibration experiments
		(L/kg).

The critical barium concentration for precipitation, calculated using the above equation for each of the 3 test soils, is summarized in Table 3. Based on the data in Table 3, a treatment of greater than 50 mg/L for the CNRL soils and greater than 250 mg/L for clay would ensure there is sufficient barium available to exhaust the available sulphate.

2.4.2. Critical Barium Concentration – CEC Saturation

As noted previously, at sufficiently high initial barium concentrations, the cation exchange capacity (CEC) of the soil may become saturated, thus precluding the potential for further barium to be sorbed to the soil. The critical initial barium concentration where sufficient barium is present to saturate the available CEC of the soil was calculated as follows:

$$C_{Ba,CEC} = C_{Ba,PPT} + \frac{CEC \times 10 \times 137.33}{2 \times 20} - \frac{C_{Ba,Ex}}{20}$$

Where:

$C_{Ba.CEC}$	=	critical initial concentration of barium in solution required to saturate CEC
		capacity of soil (assumes all exchange sites occupied with barium (mg/L);
$C_{\text{Ba.PPT}}$	=	critical initial concentration of barium in solution required to precipitate all
		available sulphate (calculated in previous section) (mg/L);
CEC	=	measured cation exchange capacity of soil (meq/100 g);
10	=	conversion factor from 100g to kg (100 g/kg);
137.33	=	relative atomic mass of barium (mol/g);
2	=	charge on the barium ion (meq/mmol);
20	=	dilution ratio of solution volume to soil mass in Kd equilibration experiments
		(L/kg); and,
$C_{Ba.Ex}$	=	measured extractable barium concentration in soil (mg/kg).

The critical barium concentration for saturating the CEC, calculated using the above equation for each of the 4 test soils, is summarized in Table 3.

TABLE 3. CRITICAL BARIUM CONCENTRATIONS

Parameter	Unit	CNRL #1	CNRL #2	CNRL #3	Clay	Sand
Measured Soil Clay Content	%	8.0	11.0	12.6	59.4	1.6
Measured Sulphate-S concentration in Soil	mg/kg	4.0	137	199	1120	3.4
CEC of Soil	meq/100 g	7.76	10.3	10.3	24.6	1.3
Measured extractable barium concentration in soil	mg/kg	0.05	8.4	8.3	1.1	9.4
Total Barium (EPA 3050)	mg/kg	75	1590	5760	333	64
Critical Barium concentration for barite precipitation	mg/L	0.9	29	43	240	0.7
critical barium concentration to saturate CEC	mg/L	267	383	396	1084	45

The definitive tests for the Kd determinations in the four field soils were designed based on the critical concentrations presented in Table 3. Barium concentrations of most interest for determining a practical Kd value for barium would be those that were high enough to precipitate all the available sulphate, but not so high as to saturate the available cation exchange capacity.

3. RESULTS

A complete set of the definitive test data for the four field soils are included in Appendix 2 through 5, and are summarized in Table 4. Barium concentrations in the blank solutions for all four soils were near nominal concentration, indicating that barium was not lost by other mechanisms than soil partitioning such as sorption to test vessels or membrane filters.

The behavior of barium exposed to the four soils demonstrates the dependency of Kd on soil type. A log plot of the concentration of barium in blank solutions compared to solutions exposed to test soils is presented in Figure 1. For clay, loss of barium is near complete for concentrations where the cation exchange capacity remains undersaturated, resulting in very high Kd concentrations, reaching a maximum of 164000 mL/g. The CEC saturation point, apparently reached near the 3000 mg/L barium treatment resulted in a Kd of only 17 mL/g. This all or nothing effect was not observed for the three CNRL soils. The measured concentration of barium in solutions exposed to clay increased proportionally with increasing exposure concentration. Kd was generally highest in the lowest exposure concentration of 20 mg/L, gradually decreasing from 387 mL/g for CNRI#3, the highest Kd measured for the 3 soils, to less than 10 mL/g in exposure solutions of 1000 mg/L barium and higher.

Sulfur concentrations were also measured in blank and clay-exposed test solutions for the clay series and are presented in Appendix 2. It had been assumed that the formation of insoluble barium sulfate from available sulfate from the soil would be the primary cause of loss of soluble barium from solution, until available sulfate had been consumed. However, the results of the clay series suggest that sorption of barium to soil cation exchange sites is a more significant mechanism of partitioning. Sulfur is detected in treatments 1 through 5 (0 to 500 mg/L Ba) at > 200 mg/L. However, essentially no barium is available in these solutions. At Treatment 6 (1000 mg/L barium), however, sulfur in solution is reduced to 82 mg/L, and is undetectable in Treatment 7 (3000 mg/L barium). Concurrently, barium was 53% of the exposure concentration in the Treatment 7. The results indicate that barium is quickly sorbed to cation exchange sites first, and when the saturation point is reached, barium sulfate then becomes available to precipitate from solution with soil available sulfate. Once available sulfate is removed from solution by barium sulfate formation, excess barium then remains in solution. The

significance of soil sorption relative to formation of barium sulfate in the environmental fate of barium was underestimated in a USEPA Barium factsheet (2006) which stated that "barium does not bind to most soils and may migrate to ground water".

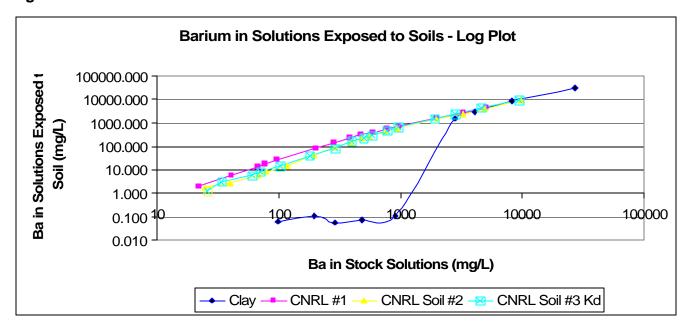


Figure 1. Barium in Solution in Blank and Soil Treatments

The results for clay also suggest that the degree of mobility of barium in a specific soil type could be simply predicted by equating barium concentration to the soil CEC and available sulfate concentration. However, the behavior of barium in the CNRL soils suggests that this simplistic approach may not be applicable for all soil types. Other soil cations may preferentially impact the availability of cation exchange sites for sorption, and barium may form other precipitates such as carbonate and nitrate salts.

The results of the Kd tests for the four soils, CNRL samples #1 to #3, and the Husky Clay, are summarized in Table 4. The left hand column represents the nominal concentration of barium (mg/L) in the test solution prior to equilibration. For each of the four soil samples, two columns of results are provided. Cw is the measured concentration of barium (mg/L) in the supernatant solution following equilibration with the soil, and is less than the nominal concentration since some of the barium has been sorbed to the soil. Cs is the calculated concentration of barium added to the soil through the equilibration process. Cs was calculated using the following formula:

$$Cs = 20 * (Nominal - Cw)$$

Where:

20 = soil to solute dilution ratio in Kd test (kg/L);

Nominal nominal concentration of barium added to test solution (mg/L); and,

measured concentration of barium in supernatant at the end of Cw

equilibration.

Table 4. Results of Kd Tests for Four Soils

Soil:	CNF	RL #1	CNF	RL #2	CNI	RL #3	Husky	y Clay
Nominal	Cw	Cs	Cw	Cs	Cw	Cs	Cw	Cs
mg/L	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg
20	1.9	362	1.7	366	1.3	375	nm	nm
40	5.9	683	2.7	746	3.2	735	nm	nm
60	13	942	5.9	1,083	6.0	1,080	nm	nm
80	17	1,255	8.3	1,434	8.5	1,431	nm	nm
100	26	1,472	15	1,701	15	1,706	0.062	1,999
200	79	2,412	44	3,119	41 3,178		0.112	3,998
300	145	3,100	88	4,231	4,231 81 4,378		0.055	5,999
400	233	3,350	161	4,780	169	4,630	nm	nm
500	310	3,800	225	5,510	223	5,550	0.072	9,999
600	395	4,100	280	6,400	285	285 6,300		nm
800	565	4,710	440	7,200	455	6,900	nm	nm
1,000	755	4,900	605	7,900	650	7,000	0.111	19,998
2,000	1,700	6,000	1,550	9,000	1,550	9,000	nm	nm
3,000	2,730	5,400	2,435	11,300	2,440	11,200	1,500	30,000
5,000	4,650	7,000	4,300	14,000	4,450	11,000	2,850	43,000
10,000	nm	nm	9,465	10,700	9,435	11,300	8,600	28,000
30,000	nm	nm	nm	nm	nm	nm	30,350	nc

Notes:

nc = not calculated

4. DISCUSSION

The objective of this project was to determine an appropriate value of the Kd for barium to use in developing soil quality guidelines protective of groundwater uses. Kd describes the relative proportion of a chemical (barium in this case) that is i) sorbed to the solid phase and ii) in solution. When there is a simple linear relationship between the sorbed and dissolved phases, a single value of Kd can be determined. Figure 2 illustrates the relationship between barium in the sorbed and dissolved phases for the three CNRL soils (only the lower concentration part of the dataset is presented, to allow relevant details to be resolved clearly).

[&]quot;Nominal" is the concentration of barium added to the initial test solution (mg/L).

[&]quot;Cw" is the measured concentration of barium in solution following equilibration with the soil (mg/L)

[&]quot;Cs" is the calculated concentration of barium added to the soil following equilibration (mg/kg) nm = not measured:

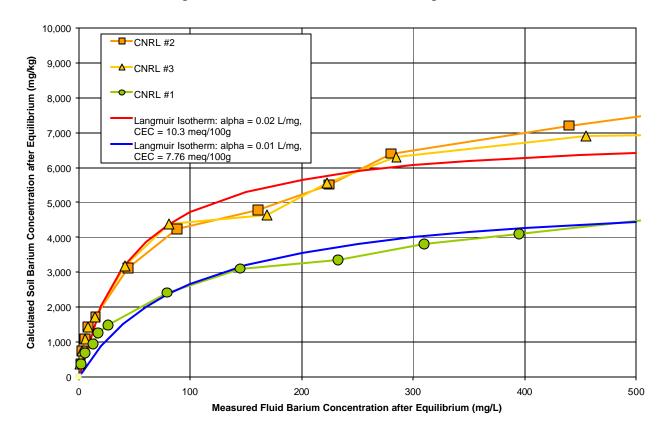


Figure 2. Kd Data for CNRL Soils Fitted to Langmuir Isotherms

As can be seen in Figure 2, the relationship between barium in the sorbed and dissolved phases is not linear over the range presented.

The Langmuir sorption isotherm was developed with the concept that a solid surface possesses a finite number of sorption sites. When all the sorption sites are filled, the surface will no longer sorb solute from solution. The form of the Langmuir sorption isotherm is (Fetter, 1993):

$$Cs = \frac{abCw}{1 + aCw} \tag{1}$$

Where:

Cs = concentration of barium sorbed to soil (mg/kg)

 α = absorption constant related to the binding energy (L/mg);

 β = the maximum amount of solute that can be absorbed by the solid (mg/kg);

Cw = the concentration of barium in solution after equilibrium (mg/L).

Now β is related to the cation exchange capacity as follows:

$$\mathbf{b} = \frac{CEC \cdot 10 \cdot 137.33}{2} \tag{2}$$

Where:

 β = the maximum amount of solute that can be absorbed by the solid (mg/kg);

CEC = cation exchange capacity of soil (meq/100g);

10 = conversion factor from 100g to kg; 137.33 = relative atomic mass of barium; and,

2 = charge on a barium ion.

Thus the value of β for the 3 CNRL soils can be calculated as follows

Soil	CEC (meq/100g)	β (mg/kg)
CNRL #1	7.76	5,330
CNRL #2	10.3	7,070
CNRL #3	10.3	7,070

Using the values of β calculated above, and varying alpha in equation 1 allows Langmuir isotherms to be fitted to the CNRL Kd data, as indicated in Figure 2.



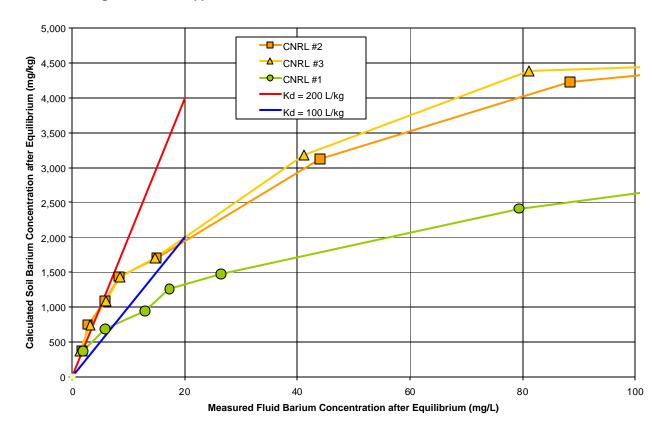


Figure 3 indicates that the barium Kd data collected for the CNRL soils are consistent with the Langmuir assumptions. Thus a complete description of how Cs and Cw are related may be obtained by using equation 1 together with the following values:

Soil	α (L/mg)	β (mg/kg)
CNRL #1	0.01	5,330
CNRL #2	0.02	7,070
CNRL #3	0.02	7,070

However, the existing CSST model for groundwater guidelines uses a single value for Kd, and thus it is necessary to determine the most applicable range of concentration values to calculate an appropriate value for Kd. Data collected for this and other related projects indicate that for field samples with total barite-barium up to 7,700 mg/kg, and for barite spiked samples with total barium up to 50,000 mg/kg, the CaCl₂ exchangeable barite is below 400 mg/kg (and often much lower than this). Since Kd describes the sorption of barium to the soil, the relevant concentration is the soluble/exchangeable barium concentration as measured by the CaCl₂ extraction. Comparing the exchangeable barium value of 400 mg/kg with Figure 3, it is clear that the relevant part is the extreme low concentration range of this graph. The corresponding Kd value is the slope of this graph.

20000 Calculated Soil Barium Concentration after Equilibrium (mg/kg) 18000 Kd = 150,000 L/kg Husky Clay 16000 14000 12000 10000 8000 6000 4000 2000 0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20 Measured Fluid Barium Concentration after Equilibrium (mg/L)

Figure 4. Kd Data for the Husky Clay at Low Soluble Barium Concentration

Figure 3 illustrates the low concentration part of the relationship shown in Figure 2, and shows that at soluble barium concentrations in the range 0 to 500 mg/kg, a linear approximation for the value of Kd would lie in the range 100 to 200 L/kg.

Data for the Husky clay are less easy to interpret (Figure 4), and data are not available for soil barium concentrations as low as 500 mg/kg. However, considering only the lower concentration part of the dataset, it is clear that the data are consistent with a much higher value of Kd, as would be expected for a clay. Figure 4 shows that the low concentration Husky Clay data appear to be consistent with a Kd value of the order of 150,000 L/kg, and thus the Kd range (100 to 200 L/kg) determined for the CNRL soils in Figure 3 will be conservative for the Husky clay soils too.

5. RECOMMENDATION

In the CSST soil standard calculations, lower values of Kd are conservative (i.e., they produce lower standard values). The range of Kd values estimated from the four soils tested was 100 to 150,000 L/kg. Overall, therefore, it is recommended that the lower end of this range, 100 L/kg be used as a conservative estimate of Kd in the CSST calculations. The soil standard thus calculated would be applicable to measurements of soluble, rather than total barium.

6. REFERENCES

ASTM 2006. D4646-03 Standard Test Method for 24-h Batch Type Measurement of Contaminant Sorption by Soils and Sediments. Standards Volume 11.04

Bright, Doug. 2002. Protocol for the Estimation of Site-Specific Adsorption Co-efficients, Kd. Prepared for BC WALP. Addendum B to the Derivation of Matrix Soil Standards for Salt Under the British Columbia Contaminated Sites Regulations. Royal Roads University, Draft Feb 19, 2002.

EPA 1991. Site Characterization for Subsurface Remediation. Seminar Publication. EPA/625/4-91/026.

EPA 2006. Consumer Factsheet on: Barium. National Primary Drinking Water Regulations.

Appendix 1. Detailed Characterization of Background Soils

					Phase and	782) e 1, 2	CNRL Soils (503905) Phase 3 and Kd Studies				
Method		Parameter Name	Unit	Detection Limit	Sand	Clay	#1	#2	#3		
Physical and	Moisture	Moisture	%	0.1	1.6	23					
Aggregate Properties	Particle Size Analysis -	Texture			Sand	Clay	Sandy Loam	Sandy Loam	Sandy Loam		
GS		Sand	%		96.4	14.4	74.6	71.6	67.6		
		Silt	%		1.2	26.2	17.4	17.4	19.8		
		Clay	%		2.4	59	8	11	12.6		
Salinity Saturated		рН	рН		8.4	7.7	7.9	8.3	7.4		
Paste ir		EC	dS/m	0.01	0.21	4.05	0.38	2.55	2.22		
General Soil		SAR			0.2	1	0.1	1.8	0.2		
		% Saturation	%		35	108	31	46	42		
		Calcium	meq/L	0.01	1.89	26.9	3.32	21.8	25.2		
		Calcium	mg/kg		13.1	583	20.3	198	213		
		Magnesium	meq/L	0.02	0.38	36.9	0.68	1.36	4.13		
		Magnesium	mg/kg		1.6	484	2.5	7.5	21.1		
		Sodium	meq/L	0.04	0.19	5.89	0.17	6.14	0.79		
		Sodium	mg/kg		2	147	1	64	8		
		Potassium	meq/L	0.03	0.06	0.69	0.13	0.93	0.58		
		Potassium	mg/kg		<1	29	2	16	10		
		Chloride	meq/L	0.03	0.07	1.31	0.19	9.84	5.1		
		Chloride	mg/kg		1	50	2	159	76		
		Sulfate-S	meq/L	0.06	0.61	64.9	0.81	18.8	29.5		
		Sulfate-S	mg/kg		3.4	1120	4	137	199		
		TGR	T/ac		<0.1	<0.1	<0.1	<0.1	<0.1		
	Total Barium	Fusion-XRF or ICP	mg/kg	0.1	450	1000	200	1800	7700		
	Methods	EPA3050	mg/kg	0.1	64	333	75	1590	5760		
		BCSALM* AENV	mg/kg	0.1	82	176	102	506	647		
Barium	Barium 0.1 M CaCl ₂ Extractable Barium		mg/kg	0.05	9.4	1.1	8.4	8.3	18.4		
1.0 M CaCl ₂ Soluble Barium		BC	mg/kg	0.05	40	16	nd	28	52		
Cation Exchange		Calcium	mg/kg	4	1970	7720	2930	5250	4280		
(CEC) for Genera	I Soil	Magnesium	mg/kg	2	34	1910	100	160	150		
		Potassium	mg/kg	20	<20	260	50	200	100		
		Sodium	mg/kg	12	<10	213	10	130	20		

				Phas and Stu	782) e 1, 2 l Kd dies	Pha	Soils (50 se 3 and Studies	Kd
Method	Parameter	Unit	Detection	Sand	Clay	#1	#2	#3
	Name Base Saturation	%	Limit 1	780	227	202	278	224
	Calcium	meq/100g	0.0003	9.81	38.5	14.6	26.2	21.3
	Magnesium	meq/100g	0.0008	0.28	15.7	0.85	1.3	1.3
	Sodium	meq/100g	0.003	<0.5	0.925	0.05	0.55	0.088
	Potassium	meq/100g	0.003	<0.5	0.68	0.1	0.5	0.2
	ESP	%	0.2	<4	3.76	0.7	5.4	0.85
	TEC	meq/100g	2	10	56	16	29	23
	CEC	meq/100g		1.3	24.6	7.76	10.3	10.3
Carbon and Nitrogen in Soil	Organic matter	%	1	<1	2	<1	4	3
	Carbon	%	0.05	<0.05	1.13	0.45	2.04	1.74
Hot Water Soluble Boron	Boron	ug/g	0.1	<0.1	1	0.3	0.4	0.6
Metals Strong Acid Digest (EPA 3050)	Mercury	ug/g	0.01	0.01	0.08	0.02	0.02	0.02
(EFA 3030)	Antimony	ug/g	0.2	<0.1	<0.2	<0.2	<0.2	<0.2
	Arsenic	ug/g	0.2	2.4	10.5	8.6	8.5	8.9
	Barium	ug/g	1	64	333	75	1590	5760
	Beryllium	ug/g	0.1	0.1	1.2	0.4	0.5	0.5
	Cadmium	ug/g	0.01	0.06	0.42	0.09	0.14	0.13
	Chromium	ug/g	0.5	3.4	34.4	9	12.6	12
	Cobalt	ug/g	0.1	2.2	12.8	5.4	6.2	6.2
	Copper Lead	ug/g	1	3	32	3	9	7
	Molybdenum	ug/g ug/g	0.1	2.3	14.1	6.4	9.3	9.9
	Nickel		1	<1	<1	<1	1	<1
	Selenium	ug/g ug/g	0.5 0.3	6.1 <0.2	38.3	26.7	26.9	29.9
	Silver	ug/g ug/g	0.3	<0.2	1.4 0.2	<0.3 <0.1	0.6 <0.1	0.4 <0.1
	Thallium	ug/g ug/g	0.05	0.06	0.2	<0.05	0.1	0.08
	Tin	ug/g	1	1	<1	<1	<1	<1
	Vanadium	ug/g	0.1	6	65.4	19.4	25.9	24.5
	Zinc	ug/g	1	12	111	50	53	61

Appendix 2. Kd Test Results for Clay

		Test Solution # Test Solution as Ba (mg/L)	0	100	3 200	300	5 500	6 1000	7 3000	8 5000	9	10 30000
Barium	Test Solution Test Solution Mean % Recovery	Rep A Rep B	<0.001 <0.001 <0.001	100 98 99 99	190 204 197 99	287 294 291 97	480 480 480 96	940 880 910 91	2910 2700 2805 94	3900 4200 4050 81	8200 8300 8250 83	26600 27800 27200 91
	Clay Clay Mean % Recovery (Nominal) % Recovery (Measured)	Rep A Rep B	0.025 0.028 0.027	0.065 0.059 0.062 0.1 0.1	0.061 0.162 0.112 0.1 0.1	0.056 0.054 0.055 0.0	0.078 0.066 0.072 0.0 0.0	0.108 0.114 0.111 0.0 0.0	1400 1600 1500 50 53	2800 2900 2850 57 70	8800 8400 8600 86 104	29800 30900 30350 101 112
	Kd			31915	35316	105616	133313	163944	17	8	-1	-2
Sulfur	Test Solution Test Solution	Rep A Rep B	<0.3 <0.3	<0.3 <0.3	<0.3 <0.3	<0.3 <0.3	<0.3 <0.3	<0.3 <0.3	<0.3 <0.3	<0.3 <0.3	<3 <3	<3 <3
	Clay Clay Mean	Rep A Rep B	332 272 302	286 294 290	281 281 281	218 293 256	203 210 207	82.3 81.5 82	<0.3 <0.3 <0.3	<0.3 <0.3 <0.3	<3 <3 <3	<3 <3 <3

Appendix 3. Kd Test Results for CNRL#1

		Test Solution # Test Solution as Ba	1 0	2 20	3	4 60	5	6	7 200	8	9	10 500	11	12 800	13	14	15 3000	16 5000
		(mg/L)																
Barium	Test Solution	Rep A	0.016	22	41	66	79	98	190	279	380	480	616	760	950	2040	3500	5220
	Test Solution	Rep B	0.008	22	41	67	75	97	214	288	380	470	580	786	1000	2000	3070	5000
	Mean		0.012	22	41	67	77	97.5	202	284	380	475	598	773	975	2020	3285	5110
	% Recovery			110	102	111	96	98	101	95	95	95	100	97	98	101	110	102
	Clave	Dan A	0.000	2.0	5 4	40	4.0	20	70	450	004	240	440	FC4	740	4000	2020	4000
	Clay	Rep A	0.036	2.0	5.4	13	16	28	79	150	234	310	410	561	740	1800	2630	4600
	Clay	Rep B	0.029	1.8	6.3	12	18	25	80	140	231	310	380	568	770	1600	2830	4700
	Mean		0.033	1.9	5.9	13	17	26	79	145	233	310	395	565	755 70	1700	2730	4650
	% Recovery (Nominal)			9.5	15	22	22	26	40	48	58	62	66	71	76	85	91	93
	% Recovery (Measured)			8.6	14	19	22	27	39	51	61	65	66	73	77	84	83	91
	Kd			212	120	83	69	54	31	19	13	11	10	7	6	4	4	2
Sulfur	Test Solution	Rep A	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<3	<3	<3	<3	<3	<3
Juliui	Test Solution	Rep B	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<3	<3	<3	<3	<3	<3
			10.0				-0.0											
	Clay	Rep A	0.5	0.4	0.3	0.4	0.3	0.4	<0.3	<0.3	<0.3	<0.3	<3	<3	<3	<3	<3	<3
	Clay	Rep B	0.5	0.4	0.4	0.3	0.4	0.4	< 0.3	< 0.3	< 0.3	< 0.3	<3	<3	<3	<3	<3	<3
	Mean		0.5	0.4	0.4	0.4	0.4	0.4	<0.3	<0.3	<0.3	<0.3	<3	<3	<3	<3	<3	<3
	Mean		0.5	0.4	0.4	0.4	0.4	0.4	<0.3	<0.3	<0.3	<0.3	<3	<3	<3	<3	<3	

Appendix 4. Kd Test Results for CNRL#2

		Test Solution #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
		Test Solution as Ba (mg/L)	0	20	40	60	80	100	200	300	400	500	600	800	1000	2000	3000	5000	10000
Barium	Test Solution	Rep A	0.011	23	39	72	77	116	190	290	390	470	543	730	930	1900	3460	5000	9930
	Test Solution	Rep B	0.001	27	39	64	81	121	200	288	410	500	574	776	950	2020	3110	4800	9780
	Mean		0.006	25	39	68	79	119	195	289	400	485	558.5	753	940	1960	3285	4900	9855
	% Recovery			124	98	113	99	119	98	96	100	97	93	94	94	98	110	98	99
	Clay	Rep A	0.026	1.5	2.6	5.6	8.4	16	45	90.8	157	224	280	430	600	1600	2440	4200	9700
	Clay	Rep B	0.033	2.0	2.8	6.1	8.2	14	43	86.1	165	225	280	450	610	1500	2430	4400	9230
	Mean	<u>-</u>	0.030	1.7	2.7	5.9	8.3	15	44	88	161	225	280	440	605	1550	2435	4300	9465
	% Recovery (Nominal)			8.6	6.8	9.8	10.4	15	22	29	40	45	47	55	61	78	81	86	95
	% Recovery (Measured)			6.9	6.9	8.6	11	13	23	31	40	46	50	58	64	79	74	88	96
	Kd			268	269	212	170	139	69	45	30	23	20	14	11	5	7	3	1

Appendix 5. Kd Test Results for CNRL#3

		Test Solution #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
		Test Solution as Ba (mg/L)	0	20	40	60	80	100	200	300	400	500	600	800	1000	2000	3000	5000	10000
Barium	Test Solution	Rep A	0.013	25	34	60	71	101	180	290	400	506	580	782	970	1900	2930	4600	9610
	Test Solution	Rep B	0.012	27	34	60	71	102	180	288	400	500	582	770	940	1900	2700	4600	9230
	Mean		0.013	26	34	60	71	102	180	289	400	503	581	776	955	1900	2815	4600	9420
	% Recovery			129	85	100	89	102	90	96	100	101	97	97	96	95	94	92	94
	Clay	Rep A	0.226	1.2	2.3	5.9	7.1	14	42	81	156	226	280	440	610	1600	2430	4500	9520
	Clay	Rep B	0.097	1.3	4.2	6.1	9.8	15	40	81	181	219	290	470	690	1500	2450	4400	9350
	Mean	•	0.162	1.3	3.2	6.0	8.5	15	41	81	169	223	285	455	650	1550	2440	4450	9435
	% Recovery (Nominal)			6.4	8.1	10.0	10.6	15	21	27	42	45	48	57	65	78	81	89	94
	% Recovery (Measured)			4.9	10	10	12	14	23	28	42	44	49	59	68	82	87	97	100
	Kd			387	189	180	148	118	68	51	27	25	21	14	9	5	3	1	0