Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation

Addendum B:

Protocol for the Estimation of Site-Specific Adsorption Co-efficients, K_d

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**Report to the British Columbia
Ministry of Water, Land and Air Protection,
Ministry of Transportation and Highways,
British Columbia Buildings Corporation, and the
Canadian Association of Petroleum Producers**

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Introduction

Many environmental fate models used to predict the movement of contaminants in subsurface soils via groundwater-mediated transport require an estimation of how a substance partitions between soil particles and the surrounding soil interstitial water. This in turn influences the degree to which a substance is retarded in its transport in the saturated zone, relative to the expected groundwater velocity. Often, the tendency of substances to interact with the external surface of soil particles within the saturated zone, and to partition between the immobile soil phase and the mobile groundwater phase, is summarized as an "adsorption co-efficient" or K_d.

The K_d is formally defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium.

It was previously determined (Bright and Addison, 2002a) that modeling calculations for chloride, using the BC WLAP model and default assumptions, were very sensitive to the assumed magnitude of the adsorption coefficient, K_d. It is generally considered that chloride ions are conservative tracers of groundwater movement, and in most soil types it is generally accepted that chloride ions exhibit very little if any potential to interact ionically or otherwise with the surfaces of soil particles in the saturated zone. The K_d for chloride, therefore, is often assumed to be zero ml/g. We noted earlier (Bright and Addison, 2002b) that some United States regulatory agencies recommended use of a chloride ion K_d of 0.1 ml/g, toward the modeling of subsurface fate of radionuclides, using the RESRAD model.

The interaction of chloride with soil particles, leading to limited retardation relative to groundwater flow velocities is theoretically possible, as would be a site-specific K_d value that departs from zero. It has long been recognized that the K_d values for any potentially ionic substance will vary as a function of soil and groundwater pH, as well as soil properties (proportion of soil particles with negatively or positively charged chemical ligands on and extending from the exterior surface, including clays, organic matter such as humic substances, or some carbonate- and phosphate-containing minerals). Whereas the degree of soil adsorption tends to decrease at lower pHs (under more acidic conditions) for many cations such as cupric ion (Cu^{2+}), anions such as Cl^- or HSO_4^- tend to exhibit less soil adsorption at higher pHs (more alkaline soils). On the other hand, recently recognized processes such as anion exclusion, can further enhance anion mobility. Overall, the tendency of a substance to partition onto soil particle external surfaces from groundwater will be influenced by a combination of ionic interactions, van der Waals forces, covalent bonding, and – in the case of non-ionic, relatively non-polar substances – hydrophobic interactions.

In the absence of a reasonable scientific knowledge base, it is assumed that coarse, low organics soils (sands and coarse glaciofluvial materials, for example) would exhibit very limited ability to retain chloride ions. Soils that include less than 10% by weight of soil

fractions with a least some potential to transiently retain chloride ions (clays, organic matter, some complex oxides) are likely to exhibit chloride K_d values of zero. On the other hand, it is conceivable in the absence of better scientific information that medium-grained (10 to 30% clay/organic matter/oxide content) to fine (> 30% clay/organic matter/oxide content) to fine-grained soils would exhibit K_ds that could approach 0.1 ml/g or higher. Given the uncertainty in these estimates, experimental analysis of chloride ion K_ds would be invaluable in allowing more accurate model predictions.

Adsorption co-efficients are not part of the intrinsic properties of a specific substance. Rather, they are site-specific values that may vary across soil types and – to a lesser extent – other site conditions. As such, they are often estimated through empirical studies. An up-to-date and very thorough review of methods used for the estimation of adsorption co-efficients was recently completed by the US Environmental Protection Agency and US Department of Energy (Krupka *et al.*, 1999).

This addendum report summarizes the pros and cons of various methods that have been used for the site- and soil-specific estimation of K_d, based on information provide in Krupka et al., (1999) and provides a proposed method for the determination of site-specific K_d values at British Columbia, Canada, sites as part of site investigation and remediation planning.

Brief Overview of Methods for the Estimation of K_d Values

K_d values are variously referred to as "adsorption co-efficients", "partition co-efficients", "distribution co-efficients" or other terms. Regardless, they are often used in practical settings to quantify a contaminant retardation factor, R_f.

Methods used to derive K_d values can be roughly divided into five major categories:

1. Laboratory batch (static to semi-static) methods
2. *In-situ* batch methods
3. Laboratory flow-through (soil column) methods
4. Field modeling methods.
5. K_{OC} (for non-ionic, non-polar contaminants only).

For a more detailed discussion of these, their theoretical basis, and their application for estimation of retardation factors, please refer to Krupka *et al.* (1999).

For many ions, the estimated K_d values can vary by over six orders of magnitude, with serious consequences for our ability to predict contaminant fate, based on the complexity of aqueous and solid-phase chemistry. In parallel with the aforementioned major methods for determining K_d, there has been considerable effort devoted to the development of mechanistic models that better explain the underlying chemical reactions. Mechanistic models used within the research community are intended to more explicitly accommodate the dependency of K_d values on contaminant concentration, competing ion concentration, variable surface charge on the absorbent, solution species distribution, redox reactions and the dependence of other interactions on both redox conditions and pH. Ultimately, it is desirable to incorporate a better mechanistic understanding into working groundwater models, so that they become more accurate, more generalizable, and more robust. The technical challenges associated with this, given our current level of understanding, are not trivial.

Prior to summarizing K_d estimation methods, a very brief discussion is provided on soil sorption processes. When a substances is sorbed by the solid-phase in a soil environment, rarely is it possible to distinguish between the processes involved. Sorption can involve adsorption onto the outside of soil particles, absorption into the interior of particles, and/or precipitation as a 3-dimensional molecular complex onto the surface of soils.

Of these –

- **Dissolution/precipitation** is more likely to be the major controlling process where chemical non-equilibrium exists. This has important implications for fate predictions at a point source, for an area where high contaminant concentrations exist, or where steep pH or redox gradients exist.

- **Adsorption/desorption** will likely be the key process controlling contaminant migration in areas where chemical equilibrium exists, such as in areas far from the point source, or at lower contaminant concentrations.

Absorption processes have been discussed recently in the scientific literature with regard to the possible tendency of some organic contaminants to exhibit a decreased bioavailability and mobility in progressively older soil/contaminant systems.

One advantage of K_d estimates is that there is no requirement to differentiate between the major sorption mechanisms. On the other hand, experimentally-derived estimates of K_d are highly susceptible to the experimental conditions, since these influence the degree to which the different sorption mechanisms operate. A precautionary note is warranted, therefore: Experimentally derived K_d values are likely to be influenced by the concentration of contaminant present in a field or laboratory setting, the influence of equilibrium versus non-equilibrium conditions, and both the absolute value of and gradients in pH and redox.

The constant partition co-efficient, K_d, as a measure of total sorption is defined as the ratio of quantity of the adsorbate (e.g., contaminant mass) adsorbed per unit mass of solid-phase (soil) to the amount of adsorbate remaining in solution at equilibrium:

$$K_d \text{ (mL/g)} = \quad A_i / C_i \tag{1}$$

Where –

A_i = adsorbate on the solid at equilibrium (μg/g).
C_i = total dissolved adsorbate remaining in solution at equilibrium (μg/ml).

According to Krupka et al. (1999) –

> "Essentially all of the assumptions associated with the thermodynamically defined K_d value are violated in the common protocols used to measure K_d values for use in contaminant transport codes. Typically, the K_d for a given absorbent is determined in the laboratory using soil from the study area and actual or simulated groundwater to which an adsorbate is added at some trace concentration. The values of C_i and A_i are operationally defined as the adsorbate concentrations measured in the fractions that passed through or were retained by, respectively, filtration by some known filter pore size, such as 0.45-μm diameter. An important practical limitation of the measurement of K_d values is that the total concentration or radioactivity of the adsorbate is measured, thereby treating the adsorbate as a single species. This assumption is not an inherent requirement, but it is generally applied for convenience."

A practical limitation of K_d values is that they apply only to the conditions used to derive them. One way around this problem is to establish "parametric" or regression based models. In this case, it is assumed that K_d values vary as a function of other predictor variables such as clay content, cation exchange capacity, or pH. A generalized form of a multiple-linear regression is –

$$K_d = \quad a + b_1(\text{variable1}) + b_2(\text{variable2}) + \ldots + b_n(\text{variable } n) \tag{2}$$

Exercises to derive K_d values using a multiple regression or factorial design are likely to be more robust in that they can be generalized across a broader range of environmental conditions. The use of a regression-based approach also provides for quantitative estimates of the range of uncertainty around K_d estimates for any given set of environmental conditions.

Given the possibility of incorporating a more mechanistic understanding of co-variates of K_d values, it is sometimes desired to produce a series of isotherm plots that capture the soil and groundwater conditions under which different K_d values would be expected. Isotherm models can be constructed by observing experimentally derived K_d values while holding one variable constant and systematically varying others. This is often useful where the response between K_d and other values is strongly non-linear; for example, if the underlying mechanisms for sorption follow Langmuir, Freundlich, or Dubinin-Radushkevich models.

K_d values are likely to vary with the degree of soil saturation in addition to other soil and solute properties. According to Krupka *et al.* (1999) –

> "There are theoretical reasons for believing that K_d values vary as a function of volumetric water content. First, as the soil becomes increasingly unsaturated there will be a smaller percentage of the total exchange sites in contact with the aqueous phase. For example, if only half of the exchange sites of a soil come into contact with the aqueous phase, then the effective exchange capacity of the soil is only half of that, had all the available exchange sites come into contact with the aqueous phase. Therefore, as less mineral surface is exposed to the aqueous phase, the lower the effective exchange capacity becomes because less of the surface is exposed to the solute of interest. On the other hand, the clay fraction of the soil constitutes the largest exchange capacity and smallest pore sizes. Because the smaller pores are involved in unsaturated flow, there may be little measurable effect on the exchange capacity of the soil in unsaturated conditions. Another reason for believing that K_d values would vary with degree of saturation is because in the unsaturated systems the aqueous phase is in closer contact with the soil surfaces. Solutes in the middle of large pores have less interaction with soil surfaces than solutes nearer to the soil surfaces. In unsaturated conditions, the middle of large pores tend to be empty, resulting in a greater percentage of pore water being in close contact with the soil surface. Finally, the ionic strength of the aqueous phase tends to increase closer to the clay surfaces. Thus, as a soil dehydrates, the system tends to have a higher ionic strength. The K_d value for many cations tends to decrease with increases in ionic strength."

For the purpose of this exercise, it is assumed that the primary purpose of K_d determinations is to predict the fate of contaminants in the saturated zone. Such values may not be applicable to the unsaturated zone, however, and different experimental approaches may be required for estimating K_d in unsaturated soil conditions.

Finally, there may be other conditions under which experimentally-derived K_d values may over-estimate sorption relative to natural systems. Dissolved chloride, bromide, and nitrate are usually reported to travel through natural systems or soil columns at the same rate as, or faster than, water owing to "anion exclusion". (Krupka *et al.* 1999). Anion exclusion occurs when anions are repulsed by an extension of a particle's negative surface charge into the surrounding solution. By excluding anions from the negatively charged diffuse double layer around soil particle surfaces, where water is relatively immobile, the system restricts anions to the faster moving pore water, resulting in an average rate of anion transport that is greater than the average pore water velocity defined by Darcy's Law. Anion exclusion is more pronounced with higher cation exchange capacity (*i.e.*, negative charge) of the soil or rock. The implication of anion exclusion for anionic contaminants (*e.g.*, nitrates, chloride) is that they might actually travel through the subsurface environment at a rate greater than water.

Having noted important, generically-applicable provisos regarding the interpretation of empirically derived K_d values, we now turn to a brief summary of possible methods, including their advantages and disadvantages. Table 1 provides a brief summary.

Table 1: Summary of K_d Estimation Methods (After Krupka et al., 1999)

Method	Data Requirements	Advantages	Disadvantages	Assumptions
Batch - Laboratory	M_{soil} (mass of soil) C_i (conc. in solution at equilibrium) C_0 (initial conc. in solution) V_W (solution volume)	Inexpensive Quick	Assumes equilibrium Solids more homogenous than *in situ* Uses larger ratio of groundwater to solids than found at site. Measures adsorption, not desorption (the kinetics of the latter being slower) Speciation not considered	Equilibrium Adsorption rate = desorption rate Only one type of surface adsorption A>>>>Ai Mass of Ai = 1 (conserved) No influence of suspended colloids No. precip. of adsorbate due to $[C_0]$ exceeding solubility limit
Batch - Field	C_i (conc. in solution at equilibrium) A_i (conc.on solid at equil.)	*In-situ* Equilibrium conditions Aqueous and solid phases are precisely those of the field site	Expensive to collect samples Commonly have high detection limits for solid-phase measurements Very site-specific; not generalizable	Same as for lab. batch Measurement of adsorbed contaminant (Ai) can differentiate between adsorbed, precipitated and structural constituents
Flow-through (column)	C_0 (initial conc. in solution) C_0 tracer n, θ, or n_e Particle density Time >10 data pts for $C_{elutriate}$	Measures sorption at field flow rates (non-steady state) Captures hydrodynamic effects Can measure result of chemical speciation and other related phenomena	Not at equilibrium and non-equil. conditions may not be the same as in field setting. Must make assumptions about rel'n between Kd and Rf. Kd values tend to vary with infiltration velocity and column dimensions Requires more expensive equipment Time consuming Data tend to be non-linear.	Assumed relationship between Rf and Kd Water flow and dispersion co-efficeint is constant

Field modeling	$C_{release}$ C_{well} Time Distance n, θ, or n_e Diffusion or disperion co-efficients	Derived Kd has the precise geochemical and flow conditions of the study site.	Kd is truly site-specific and not generalizable. Kd is transport model-specific. Requires other (simplifying) assumptions about groundwater flow. Measures Rf and then Kd; assumptions required about relationship between the two. Not a thermo-dynamic Kd: may or may not reflect equilibrium. Kd value greatly improves with more field data collected. Calculations are quite involved.	Assumed relationship between Rf and Kd Knowledge of n_e or n Must know flow path and ground-water velocity Sorption is uniform through the subsoil mass (no channelized flow)
K_{OC}	f_{OC} K_{OC}	Well demonstrated and accurate indirect method Foc is easy measurement Good look-up tables available for Koc (or Kow, which correlates well)	For hydrophobic organic contaminants only. Lower Kow compounds lead to less accurate Kd predictions.	Organic constituents adsorb only to organic matter in soil; no sorption to inorgnaics Adsorption rate = desorption rate

Recommended Method for Estimating K_d Values at British Columbia Sites Under the Framework of the Contaminated Sites Regulation

The following method is adapted from standard methods used by researchers at the Pacific Northwest National Laboratory in Richland, Washington, US, for the measurement of K_d values, as reproduced in Appendix C of Krupka *et al*.(1999). It is adapted from the procedure described in Relyea *et al*. (1980). Note that the procedure was originally derived in consideration of radionuclide behaviour in geological materials, and has been adapted herein for non-radioactive, ionic substances.

1.0 Applicability

This procedure includes descriptions for the estimation of K_d in unconsolidated, loosely consolidated, consolidated porous, and intact, impermeable geological materials. Its use is adapted here for use in British Columbia for the investigation of and remediation planning for contaminated sites.

The procedure is best suited to estimating K_d in saturated environments, and may lead to erroneous predictions of K_d values for unsaturated matrices. While batch procedures as described herein are both relatively inexpensive and quick relative to other techniques such as column flow-through studies, they may create departures in the estimated versus true solids substrate-groundwater partitioning. Groundwater flow conditions, especially near a contaminant source or otherwise across steep gradients are not always at equilibrium, while batch K_d estimation techniques assume equilibrium. Furthermore, batch techniques usually generate less spatial heterogeneity in the solids matrix than occurs at many sites, and may involve unrealistically high groundwater: solids volume ratios relative to site conditions. The batch methodology determines adsorption from contaminants added to a model groundwater sample, and then interacted with solids, rather than measuring desorption. Adsorption of various ions typically occurs much faster than desorption. While this may not influence equilibrium distribution co-efficients, it will influence the extent to which a zone within a field site is in equilibrium. Finally, chemical speciation is not considered.

Parties interested in non-equilibrium partitioning, K_d values in the unsaturated zone, or non-homogenous matrices may be required to investigate alterate techniques.

2.0 Definitions

Background equilibration:
    Contact of solids (soil, sub-soil, or sediment) sample with non-contaminated groundwater for purposes of establishing chemical equilibrium with aqueous constituents other than the substance of interest.

Adsorbant: Substance of interest added to groundwater solution to measure extent of sorption to a solids sample.
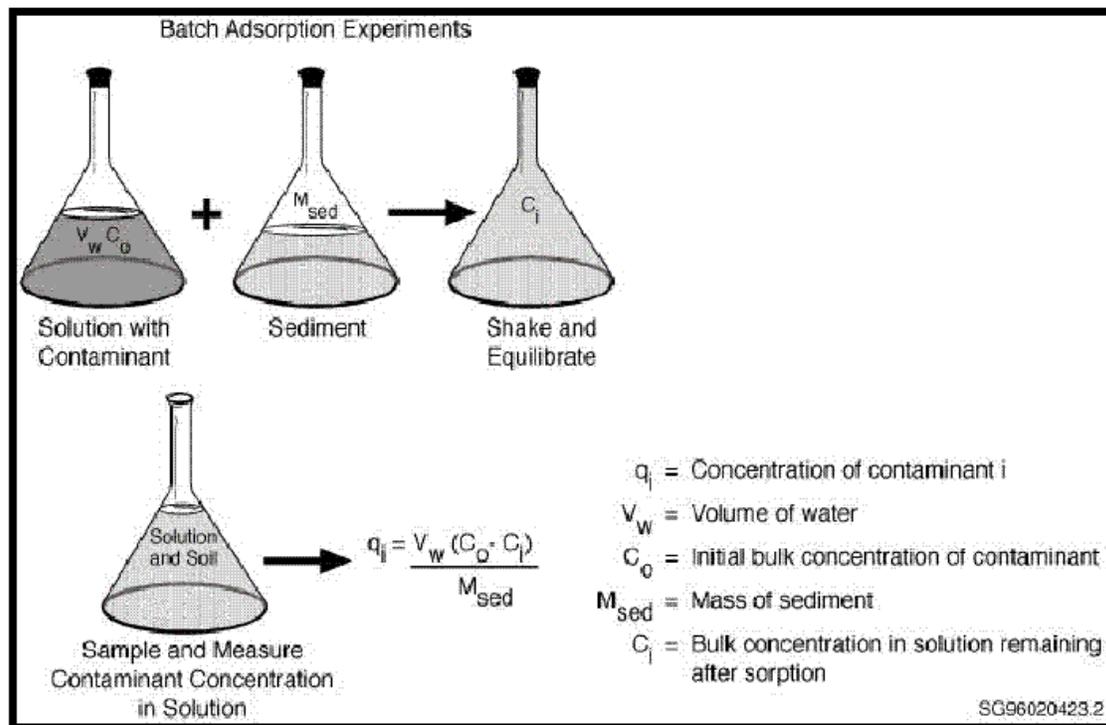*Spiked groundwater:* Groundwater with adsorbant of interest.
Blank tube: Centrifuge tube containing spiked groundwater but no solids (included to assess degree of partitioning onto experimental apparatus.

3.0 Procedure

Briefly, the procedure involves the preparation of (i) an appropriate solids sample, chosen to be representative of soil, sub-soil, or sediment types in the zone of interest with regard to subsurface contaminant fate, (ii) a representative groundwater sample without the adsorbant of interest, (iii) a representative groundwater sample with the adsorbant of interest, and (iv) static test combinations of spiked groundwater samples and solids samples.

For each adsorbant – soil combination, it is desirable to estimate the K_d value under equilibrium batch conditions using at least three to five different spiked groundwater concentrations, bracketed around an environmentally relevant concentration.

Batch Adsorption Experiments

$$q_i = \frac{V_w (C_o - C_i)}{M_{sed}}$$

q_i = Concentration of contaminant i
V_w = Volume of water
C_o = Initial bulk concentration of contaminant
M_{sed} = Mass of sediment
C_i = Bulk concentration in solution remaining after sorption

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from Krupka *et al.,* 1999.

In order to maximize reproducibility of the test, the solids samples are first pre-conditioned using unspiked groundwater until the solids-groundwater conditions are at equilibrium, as measured by a constant pH with progressive additions of groundwater aliquots to the solids material (Background equilibration).

After the solids material is equilibrated, spiked groundwater is added and the container is agitated until equilibrium is reached ($\sim$ 7 days). The loss of concentration from groundwater (C_0-C_i) is attributed to adsorption onto the solids present.

In addition, a parallel control is run which includes the spiked groundwater and container, but no solids sample, in order to assess concentration loss through adsorption onto the test apparatus.

3.1 Materials

pH meter
pH combination electrode 0-14 pH
pH buffers
Pre-cleaned sample vials
Magnetic stirrer
Stir bars
Groundwater
Mortar and pestle
No. 18 stainless steel sieve (1 mm)
No. 50 sieve (0.3 mm)
Analytical balance (accuracy within $\pm$ 0.01 g
Teflon tape
50 ml polycarbonate centrifuge tubes with screw caps
Orbit shaker
Centrifuge
Vacuum pipets
0.45-micrometer polycarbonate membrane filters
Plastic bags

Additional as required to measure adsorbant concentration in water and soil samples

3.2 Sample Characterization

Before the K_d study, perform the following analyses to characterize solid and groundwater samples. Ensure that field collected samples are collected, stored, and analyzed according to accepted procedures that prevent sample deterioration or other sampling and analytical artifacts.

Include the following:

3.2.1 For groundwater

- pH
- electrical conductivity
- bulk chemistry (Ca, Mg, Na, K, Cl, NO_3, SO_4, CO_3, HCO_3)

3.2.2 <u>For solids</u>
- Mineralogy
- Surface area
- Cation exchange capacity
- Moisture content
- Particle size analysis
- Organic C content
- Concentration of freely dissociable adsorbant of interest, prior to running trials for determination of K_d.

Record all results.

3.3 Sample Preparation

3.3.1 <u>Groundwater (synthetic or uncontaminated)</u>

3.3.1.1   Filter groundwater through a 0.45-µm non-contaminating polycarbonate membrane before it is used in a batch K_d measurement.

3.3.1.2   If retardation parameters (such as pH, ionic strength, and complexing ligand concentration) are to be studied, chemically analyze the synthetic or altered groundwater after preparation and filtration and record results.

3.3.2   <u>Solid (Representative Soil or Sub-soilSample for Site and Zone of Interest)</u>

3.3.2.1   **Unconsolidated Material**. To remove particles greater than one millimeter (>1.0 mm), the sample shall be wet-sieved with uncontaminated artificial or filed-collected groundwater by passing the sample through a No. 18 stainless steel sieve. If tests with the material are to be conducted in an inert atmosphere or in a controlled atmosphere, soil/sub-soil samples are to be prepared under those same atmospheric conditions. This requires minimum contact of the material with air from the time it is removed from the earth until the time the experiment is concluded. This condition holds for Sections 3.3.2.2 as well. The particle size shall be determined and reported with results from Section 3.2.

3.3.2.2   **Loosely Consolidated Material**. The sample shall be disaggregated by an ultrasonic method or by hand with a mortar and pestle. Disaggregation shall proceed no farther than that required to reduce the sample to its natural grain size. Fresh surfaces will be exposed to weathering, but this procedure should reduce fracturing of particles to a minimum. Remove particles >1.0 mm as in Section 3.3.2.1. The particle size distribution after disaggregation shall be reported with results in Section 3.2.

3.3.2.3   After samples have been sized (Sections 3.5.2.1-2), they must be homogenized to ensure that the same particle size distribution is obtained for each subsample to be studied.

3.3.3 <u>Background Equilibration</u>

3.3.3.1   Prepare 50 ml polycarbonate centrifuge tubes with screw caps by first assigning identifications which are unique to each sample tube obtaining and then recording tare weights to the nearest 0.0001 of a gram.

3.3.3.2   After homogenizing, 5.0 g (5.0 g ± 0.05 g) samples are to be weighed (and weights recorded) into centrifuge tubes. Record the weight after addition to the nearest 0.0001 g. Wrap centrifuge tube threads with Teflon tape to prevent leaks, if necessary. If this is done, re-weigh, recording the added weight of the Teflon tape, again to the nearest 0.0001 g.

3.3.3.3   Thirty milliliters (30 mL) of filtered, nonspiked (no adsorbant) groundwater is added to each tube, including blanks with no soil, for background equilibration. The tube caps are to be replaced before the tubes are placed on a shaker for a gentle overnight agitation (about one oscillation per second). Background equilibration and the remainder of the batch testing should be conducted at either room temperature (20 – 22 deg. C) or at the expected field temperature for which the fate of the adsorbant is being predicted.

3.3.3.4   Next centrifuge the tubes to separate solids and liquids. Following centrifugation, gently remove the overlying solution (supernatant) with a vacuum or other type of pipette to prevent removal of the solids sample (some liquid will remain in the tube).

3.3.3.5   Repeat the wash procedure twice more for a total of three unspiked groundwater washes. Before the centrifuge step on the third wash, measure and record the pH of the solid-solution. If the pH has changed from its natural equilibrium value as measured in the field, the solids sample and groundwater have not yet re-established equilibrium. Alternatively, continue to wash the solids sample with unspiked groundwater until three consecutive pH readings show no variation.

Continue to wash until the pH is stable. A change in pH is most likely to occur with samples of rock crushed during the disaggregation of semi-consolidated materials (Section 3.3.2.2) because fresh surfaces (either rock or cementing agents) have been exposed.

3.3.3.6   After removal of the third wash solution, each tube must be reweighed and the weight must be recorded to determine the volume of excess solution left in each sample. Secure the cap of each tube to prevent evaporation, which would result in an increased salt concentration in the remaining solution. The excess solution volume is found by dividing the excess solution weight by the solution density.

3.4 Addition of Spiked Groundwater

3.4.1   The adding of the adsorbant in groundwater to a solution represents a critical step in the execution of contaminant migration studies. Two items must be carefully considered: (1) the total amount of spike added must be soluble in the volume of solution used and (2) the chemical composition of the

groundwater or synthetic groundwater must remain unchanged, except for the addition of the adsorbants(s) to be studied.

3.4.2   Using the previously filtered, uncontaminated groundwater (field collected or synthetic: must be similar to that encountered at a site) make up a series of spiked solutions with the adsorbant(s) of interest. The substances of interest should be of analytical grade and high purity. A concentration series should be established along a geometric scale (e.g. 1 x environmentally relevant conc.; 0.1, 0.63, 6.3 and 10x conc.). Unless there is a specific reason to do otherwise, establish the environmentally relevant concentration as the BC CSR Aquatic Life Standard (Schedule 6 of the BC CSR).

3.4.3   Allow the spiked groundwater solutions to sit for 48 h under conditions to be used in the experiment (in equilibrium with air if the aquifer is in equilibrium with air, or under controlled atmosphere conditions if the aquifer is not in equilibrium with air). Make any necessary adjustments to pH during the equilibration time. Solution is to be filtered (0.45 µm) after equilibration prior to contact with the geologic material.

3.4.4   Set aside sufficient aliquots of the spiked groundwater for chemical analysis to confirm the actual spiked concentrations. Record the nominal concentration in groundwater of spiked adsorbant (mg/l) present in the groundwater just prior to contact with the geologic material. Additionally, report any companion ions or carrier added with the spiked adsorbant and any natural occurrence of the element in groundwater.

3.5 Soil or Sub-soil and Groundwater Contact

3.5.1   Thirty milliliters (30 ml) of filtered groundwater containing the adsorbant spike is added to each sample tube containing five grams (5.0 g) of solid. In addition, 30 ml of spiked groundwater is placed in each of three empty (blank) centrifuge tubes (prewashed as in Section 3.3.3). The blank tubes are needed to detect sorption of the substance by centrifuge tube walls.

3.5.2   After replacing the tube caps, the tubes are placed on a shaker (for linear reciprocating shaker, place tubes horizontally) so that the solid-solution mixture makes maximum contact. Set the shaking speed to 0.8 to 1.2 oscillations per second to ensure mixing of solid and liquid but to reduce grinding of particles.

3.5.3   If time is not a parameter being studied, then contact between solid and liquid is to be seven days (7 days). Record the actual contact time allowed. The samples are then removed from the shaker and the tubes are visually checked for leaks (decontaminate if necessary and discard leaky tubes).

3.5.4   It is possible to deviate from the seven day equilibration period. If the period is shortened, however, at least one time series should be run measuring the concentration of the adsorbant in the spiked groundwater. The equilibration time is sufficiently long if the time-series of adsorbant concentration shows a decrease in concentration relative to the original spiked water and the exposure period occurs within the asymptotic portion of the curve.

3.5.5   The blank and sample tubes are centrifuged for twenty minutes (20 min) at 10,000 g (g = 980 cm/sec2) or more, and fifteen milliliters (15 ml) of effluent is withdrawn through a pre-washed, non-contaminating 0.45 μm polycarbonate-membrane-type filter. This can be practically carried out by withdrawing the sample using a new, non-contaminating syringe to which a 0.45 μm luehr filter has been added. (Pre-wash with groundwater from Section 3.3.1 to remove foreign particles and soluble impurities).

3.5.6   Analyze filtered effluent samples for adsorbant concentration using an appropriate, approved analytical method.

3.5.7   Analyze an aliquot of effluent for pH. Record any deviations between observed pH and that obtained in section 3.3.3.

3.5.8   Next, an aliquot of the effluent is decanted from the blanks and analyzed as per 3.5.6. This allows an assessment of the degree of sorption to the sample container. If sorption to the blank tube walls is determined to account for greater than 10 percent of the total blank concentration (using a one-tailed "t" test and combined counting error and statistical variation between blanks), do not use the nominal blank influent concentration for K_d calculation.

3.5.9   If sorption of the substance of interest occurs, as determined in 3.5.7, then it will be necessary to not only determine adsorption by loss of from the initial to final spiked concentration, but also to measure the increase in adsorbed concentration in the solid phase (refer to Section 4.2)

4.0 Batch K_d Calculations

4.1   When the substance of interest (adsorbant) is not sorbed by blank tube wall

4.1.1   Data needed for K_d calculation are:

(1) excess solution volume, V_{excess}, (ml) left from the third cold wash (weight of excess solution divided by solution density);
(2) mass of solid aquifer material, M_{sed}, (g);
(3) volume of groundwater with adsorbant added, V_{spike} (ml);
(4) activity or concentration of tracer in the effluent solution, $C_{effluent}$ (dpm/ml); and
(5) the tracer activity or concentration in the influent blank, C_{blank}, (dpm/ml).

4.1.2   The concentration on the solid phase (A_i) estimated by loss from the spiked ground water is -

$$A_i \ = \ q_i \ = [(C_{blank} \ x \ V_{spike}) - C_{effluent} \ (V_{spike} + V_{excess})]/M_{sed} \qquad \textbf{(1)}$$

The Kd is then given by –

$$K_d = \ \frac{(C_{blank} \ x \ V_{spike}) - C_{effluent} \ (V_{spike} + V_{excess})}{C_{effluent} \ x \ M_{sed}} \qquad \textbf{(2)}$$

4.2   When the substance of interest (adsorbant) is sorbed by blank tube wall

When adsorption to the test apparatus is significant, then the degree of sorption to the tube wall as opposed to geological material can either be measured directly using the geological material, or the actual spiked and final equilibrated groundwater concentration can be corrected using the measured adsorption of the triplicate blank tubes. The first of these is the preferred method:

4.2.1   If the substance of interest (adsorbant) is adsorbed by the walls of blank tubes $[(C_{initial} - C_{final})/C_{initial} >$ than 10%], determine the mass of adsorbant adsorbed by the solid by direct measurement.

4.2.2   For this procedure, after the sediment and spiked groundwater have been equilibrated over a 7 day period (or suitable alternative, where a time series is included to establish time to equilibrium), the samples are centrifuged to separate solids from liquids, then the liquid effluent is decanted from the sample tube using a vacuum or other pipette. The sample is then weighed to determine the excess effluent solution volume (V_{excess}). The solid sample is then dried (it should be "air dried" in the same manner as when originally weighed (either in air or in a controlled atmosphere), and transferred to a clean sample container. The weight of the dry sample M_{sed} (g) is then determined.

4.2.3   The concentration of the freely dissociable (adsorbed) substance is determined using a suitable sensitive and approved analytical method. In some cases, the substance of interest will also occur naturally in the geological material, often in a mineral form that contributes to the analyte concentration. It may be necessary to estimate the mass of substance adsorbed by difference in concentration between the equilibrated, non-contaminated soil (Section 3.3.3) and the soil or sub-soil from the equilibrated, spiked groundwater trial. This may in turn require the addition of additional experimental units under Section 3.3.3.

4.2.4   The K_d can then be calculated from:

$$K_d = \frac{C_{solid} - (C_{effluent\ x}\ V_{excess})}{C_{effluent}\ X\ M_{sed}} \qquad \textbf{(3)}$$

5.0 Reporting Results

The following indicates the information to be obtained:

5.1   Attribution of Test Data
- *Name and Address* of person who performed experiments
- *Date* that experiment was started
- *Detailed Comments* regarding deviations from procedures, anomalies, other pertinent information.

5.2   *Experimental Details*
- *Method* refers to standard batch method, alternatives such as column, major co-variates of sorption tested to establish parametric or isotherm-type model, *etc.*
- *State of Geological Media* for each sample tests as of time of receipt in the laboratory
- *Ratio* of solids to solution for batch Kd determinations or analogous information for other methods.
- *Spiked Concentrations* at which determinations were carried out.
- *Replication:* replicate number of blank tubes and spiked, soil-containing tubes for each spiked concentration used.
- *Time of Contact* including shaking time for batch determinations (hours or days)
- *Temperature* (deg. C) including variations at which analysis was conducted.
- *Equilibrating Atmosphere* [ambient, inert (N_2, argon, helium, other), CO_2, *etc.*]
- *Separation Techniques* – Information on filter type and effective pore size, centrifugation, other.
- *Associated analytical techniques* used to measure adsorbant concentration in aqueous and solids samples, including method or sample-specific detection limit, relative standard deviation (RSD) of method, and expected bias relative to known standards.

5.3   *Geological Media (Soil, Sub-soil, Sediment)*
- *Site Name:*
- *Location (x,y,z coordinates)* within site
- *Name* (soil classification scheme)
- *Chemical composition as oxides* (SiO_2, $Al_2O_3TiO_2$, FeO, Fe_2O_3, MnO, CaO, MgO, K_2O, Na_2O, P_2O_5 – in %)
- *Carbonate* content of geological material
- *Organic matter* content of geological material
- *OX* = hydrous Fe, Mn, Al oxides content of geological material
- *CEC* = cation exchange capacity (meq/100 g).Specify pH of system.
- *AEC* = anion exchange capacity (meq/100 g). Specify pH of system.
- *Surface area*

5.4   *Aqueous Phase*
- *Macro constituents (*pH, Eh, salt ions, sulphate, SiO_4)
- *Trace constituents* (nitrate, organic C, trace metals)
- *Post-equilibration composition* as macro and trace constituents.

5.5   *Adsorption Function*
- *Kd values* – each individually determined value (show calculations where appropriate)
- *Statistical method* used to determine final effective Kd value (Section 6)

6.0   Final Reported K_d.

The analytical procedure as described above should yield one or more K_d determinations. A K_d value should be calculated for each spiked concentration and replicate in the analysis. Where other co-variates are investigated, such as pH or groundwater concentration of the substance of interest, additional values will be generated. The reported K_d can include either –

6.1   *the statistically defined relationship* between calculated K_d and the predictor variables, including the goodness of fit as estimated by the r^2 value, and the regression parameters, using either a least-squares linear regression or appropriately applied non-linear regression procedure.

6.2   *the geometric mean K_d value* for all similarly estimated and applicable K_d estimates.

References

Bright. D.A. and J.A. Addison, 2002b Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation Addendum Report - Technical Options Analysis for a Soil Chloride Standard for Drinking Water Protection (Aesthetic) (Jan. 23, 2002). 15 pp.

Bright. D.A. and J.A. Addison, 2002b Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation (Final Draft, February, 2002). 132 pp plus appendices.

Krupka, Kenneth, M., Daniel I. Kaplan, Gene Whelan, R. Jeffrey Serne, and Shas V.Mattigod, 1999. Understanding Variation in partition Coefficient, Kd, Values. Vol. 1. The Kd Model, Methods of Measurement, and Application of Chemical Reaction Codes. USEPA, 212 pp. (http://www.epa.gov/radiation/docs/kdreport/vol1/kdvol1.pdf)

Relyea, J. F., R. J. Serne, and D. Rai. 1980. *Methods for Determining Radionuclide Retardation Factors: Status Report*. Pacific Northwest Laboratory, Richland, Washington