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British Columbia Ministry of Environment

K_D (Chloride) Analytical Method Validation Interlab Study (CSR # 12355)

2006 June 28

FINAL

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INTRODUCTION

Background Regarding KD (Chloride) Issue

As a consequence of Environment Canada's declaration of salt as a CEPA toxic substance in 2001, the BC provincial government is now working to adopt standards for the regulation of salts under the BC Contaminated Sites Regulation (CSR). Draft standards intended to regulate sodium and chloride were developed for the BC Ministry of Environment (formerly BC Ministry of Water, Land, and Air Protection) by Dr. Doug Bright and Dr. Jan Addison, and were released for public comment in June 2002.

The proposed chloride standard is expected to pose significant challenges for BC sites related to road salt storage and handling, and to sites affected by produced water from the oil and gas industry. In order to allow options for release from the lowest standards, matrix numerical soil standards as a function of the site-specific partitioning co-efficient (KD) for chloride (KD-Cl) have been proposed (see APPENDIX A).

Under the salt standards derivation project, Dr. Bright also proposed a generic analytical procedure to measure KD entitled "Protocol for the Estimation of Site-Specific Adsorption Co-efficients, KD". Members of the Technical Sub-committee of the BC Environmental Laboratory Quality Assurance Advisory Committee (BCELQAAC) evaluated this procedure for chloride, and found it inadequate to meet the requirements of the proposed standard.

It is important to note that the draft standards require accurate determination of KD values to place them within the following ranges:

<0.05

0.05 - <0.1

0.1 - < 0.15

0.15 - <0.2

≥0.2

Difficulties with the Determination of KD for Chloride

There are three primary reasons why the determination of partitioning co-efficient for chloride is difficult:

1. According to Dr. Bright, most soils would be expected to exhibit KD values of between zero and 0.1[1]. Soils that contain less than 10% fractions of clays, organic matter, or complex

[1] From "Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation", June 2002, Doug Bright and Jan Addison. Note that a K_D value of 0.1 means that in an equilibrated mixture of equal weights of water and soil, 10% of the chloride present will be adsorbed to the soil and 90% will be dissolved in the water. A K_D value of zero means that 100% of the chloride will be dissolved in the water.

oxides are expected to exhibit KD values of zero. Thus very little, if any, adsorption of chloride is expected with most soil types.

2. At low KD values, it is difficult to measure the degree of adsorption that may occur onto a soil. This is because adsorption must be measured indirectly as the difference between pre- and post-exposure aqueous chloride spike concentrations, which are expected to be almost identical in most cases. The problem is actually a function of measurement uncertainty (MU). Using the originally proposed method, a cumulative measurement uncertainty of less than 1% in the chloride analysis would be required to characterize a sample as having a KD of 0.05 (which is the lowest category for KD-Cl within the standard).

3. Virtually all soils contain appreciable levels of background chloride, which must either be removed prior to the KD determination process or (if background values are sufficiently low) included in KD calculations.

Due to the expected uncertainty of the proposed method at KD values that are relevant to the draft salt standards and that are likely to occur in natural soils, the BCELQAAC could not endorse the proposed method. Further work was required to improve and validate the method for KD-Cl in order to ensure that it could be applied successfully to support the salt standards.

BCELQAAC Recommendations

The BCELQAAC Technical Sub-committee recommended that if the Ministry wished to pursue approval of the Matrix Numerical Soil Standards for Chloride Ion (MNSS-Cl) as a function of site-specific KD that a study should be funded to evaluate whether a suitable cost-effective method could or could not be developed for the accurate determination of KD (chloride) down to values as low as 0.05.

The primary objectives of this study would be to:

1. Further revise the proposed KD methods to develop a procedure that was optimized to minimize analytical measurement uncertainty;

2. Evaluate the revised KD method through a round-robin study involving a representative group of major BC laboratories;

3. Locate and test a suitable "negative control sample" that laboratories could use in future applications as a Quality Control reference sample. A negative control sample for KD would be a commonly available soil type (e.g. a clean sand matrix) that would be verified as having a KD value of zero or near-zero.

The recommended study was launched on 2005 Sep 23. This report outlines the outcomes from this study.

STUDY METHODOLOGY

Participants

Five major laboratories were invited to participate in an interlab study that would analyze three native uncontaminated soils and one negative control sample using a revised KD Chloride (KD-Cl) method. These laboratories included:

- ALS Environmental - Vancouver - Contact: Mark Hugdahl (Mark.Hugdahl@alsenviro.com)
- Cantest Ltd. - Burnaby - Contact: Charles LeBlanc (CLeblanc@cantest.com)
- Levelton Analytical Services - Contact: Brent Mussato (BMussato@levelton.com)
- Maxxam Analytics - Burnaby - Contact: Rob Gilbert (Rob.Gilbert@maxxamanalytics.com)
- Norwest Laboratories - Surrey - Contact: Bill Warning (Bill.Warning@norwestlabs.com)

All invited laboratories agreed to participate. Each of the participant Laboratories was randomly assigned a numeric identifier (i.e. 001 through 005). These numeric identifiers are used through-out this report to protect the anonymity of the participant laboratories.

Norwest Laboratories was contracted to sample and process three native uncontaminated soil samples. The three areas chosen were felt to be near sites applicable to and indicative of soil types appropriate to applications of the MNSS-Cl. These samples are generally described (i.e. rigorous characterization was not carried out) as follows:

- A sandy loam from near Edmonton, AB
- A clay sample from near Fort St John, BC
- A sand from the Fraser Valley, BC

ALS Environmental was contracted to further revise the proposed KD-Cl method to minimize analytical measurement uncertainty.

JRD Consulting was contracted to plan and manage the study elements and to draft the final report upon completion of the study.

Revised Proposed KD Chloride Method

Both the original and the revised KD-Cl method attempt to measure the adsorption co-efficient by equilibrating an aqueous solution of chloride at known concentration with a known amount of soil, and then detect a change in the aqueous chloride concentration due to adsorption to the soil.

In order to minimize analytical uncertainty for the KD determination, the originally proposed method was modified as follows:

1) The soil : spike solution ratio in the adsorption test samples was minimized (default ratio was set to 1:1, versus the originally proposed 6:1 ratio). KD is a concentration ratio (i.e. the ratio of soil-adsorbed chloride : aqueous chloride). Therefore, if we maximize the amount of soil in the adsorption study, we maximize the mass of chloride that can

potentially be adsorbed from an aqueous solution, which increases the likelihood of detecting a difference in the aqueous concentration. This was the most important modification.

2) Soil blanks were incorporated into the method to determine how much native chloride is present in each soil sample. Background native chloride concentrations are incorporated into adsorption calculations. This was also a crucial step to the method.

3) Control solutions were incorporated into the method. Control solutions are blank samples that use the same chloride spike solutions that are added to the subject soil samples. Control solutions are analyzed alongside the test sample solutions under identical analytical conditions. Ratios of the measured concentrations (i.e. pre versus post exposure to the test sample) are used to measure adsorption amounts. This approach minimizes uncertainty associated with the instrumental analysis, and with preparation of the spike solutions.

4) A leaching step was incorporated in an attempt to remove most native chloride from the test samples prior to initiating the adsorption test. This aspect of the method was later re-assessed.

A copy of the Revised Proposed KD-Cl Method used during this study is included in this report (see APPENDIX B).

Native Sample Processing

Grab samples of approximately 10 Kg were taken for each of the three native materials by Norwest Labs. These three native materials were dried at 65 C to constant weight then lightly disaggregated and sieved through 10 mesh. The less than 10 mesh portion of each of the samples was homogenized and riffle split into 5 discrete 500 g portions. These discrete sample were dispensed into wide mouth LPE bottles and labeled:

Sample A – Edmonton (Loam),

Sample B – Fort Saint John (Clay),

Sample C – Abbotsford (Sand).

Negative Control Sample

Three (3) kilograms (kg) of a commercially available sand was purchased from Fisher Scientific (product code: S23-3 product description: SAND OTTAWA 20-30 MESH 3 KG). This material was split into ~500 g sub-samples and labeled:

Sample D – Ottawa (Control Sand);

Production of Sampling Kits

Five sampling kits were generated consisting of one ~500 g portion of each of the native materials, one ~500 g portion of the negative control sand, a set of processing instructions (see APPENDIX C) and a copy of the Revised Proposed KD-Cl Method (see APPENDIX B).

One sampling kit was delivered to each of the participant labs on or before 2005 Oct 19.

An electronic reporter in the form of a pre-formatted MS Excel spread sheet was emailed to all participant labs on 2005 Oct 28.

Interlab Study to evaluate suitability of proposed method

The inter-laboratory round robin was initiated on 2005 Oct 20. Each of the participant labs was instructed to process the five materials according to the Revised Proposed KD-CI Method and to report data on or before 2005 Nov 21 using the electronic reporter provided.

All data was received on or before 2005 Nov 28. A complete set of the KD-CI data is included in APPENDIX D.

STUDY RESULTS AND OBSERVATIONS

Key Elements of the Revised Proposed KD-Cl Method

The Revised Proposed KD-Cl Method (The Revised Method) attempted to minimize the introduction of Measurement Uncertainty. The key elements of The Revised Method are:

- Ratio of test sample mass to volume of chloride spike solution was maximized, to maximize the concentration change in solution for a given concentration adsorbed to the soil;
- Use of a Soil Blank to account for the effect of native chloride in the material being tested;
- Use of Control Samples to minimize the effect of variability in Spike Solution preparation and chloride analysis;
- Test sample pre-leaching step introduced to remove native chloride levels.

Issues Related to the Revised Method Observed During the Interlab Study

Issue 1 – Pre-extraction of Naturally Occurring Chloride from Test Soil

The Revised Proposed Method required a pre-extraction procedure described as follows:

> *"Weigh approximately 150g dry weight of the soil sample into a pre-cleaned container (e.g. 1L Erlenmeyer flask)…. Add 750 mL of deionized water to the wet soil sample to create approximately a 5:1 water:soil slurry. Agitate the slurry for 2 hours by shaking or stirring. Allow to settle. Separate soil from water by filtration through a large Buchner funnel fitted with Whatman No. 5 or equivalent filter paper. Collect the leachate for chloride analysis. When filtration is complete, rinse the soil and the filter apparatus with an additional 3 x 100 mL portions of deionized water (discard the rinsings). Test the leachate for chloride. If the chloride concentration in the leachate exceeds 50 mg/L, perform additional 5:1 deionized water leaches until a leachate concentration of below 50 mg/L is achieved."*

This pre-extraction procedure was designed to remove native chloride from the soil to minimize its effects on the variability of the overall method.

All labs reported that the pre-extraction procedure posed significant technical challenges when processing the native materials labeled Sample A - Edmonton (Loam). A new in situ pre-extraction procedure was developed in the early stages of this study in an attempt to reduce the technical challenges associated with this procedure. The new procedure is described as follows:

> "*Weigh 10g dry weight of the soil sample into a pre-cleaned centrifuge tube of appropriate volume (e.g. 100mL). Add 50 mL of deionized water to the wet soil sample to create approximately a 5:1 water:soil slurry. Agitate the slurry for 2 hours by shaking or stirring. Allow to settle. Separate soil from water by centrifuge. Decant the supernatant leachate. Collect the leachate for chloride analysis.. Test the leachate for chloride. If the chloride concentration in the leachate exceeds 50 mg/L, perform additional 5:1 deionized water leaches until a leachate concentration of below 50 mg/L is achieved. Dry the remaining washed soil at 60 C. Lightly disaggregate the soil after drying."*

All labs reported that while the new procedure greatly reduced the technical challenges associated with the pre-extraction it did not eliminate them.

Two of the five labs indicated they observed obvious physical changes to Sample A post pre-extraction. One of the five labs measured changes in the pH of Sample A post pre-extraction. Both these observations indicated that the pre-extraction procedure was physically and chemically altering the material to be analysed, and that the washing procedure may therefore alter the anion exchange or adsorption capacity of a test sample. BCELQAAC members therefore decided that the pre-extraction procedure should be omitted from the KD-Cl procedure.

RECOMMENDATION 1: Eliminate the procedure for pre-extraction of naturally occurring chloride from the KD-Cl method. Introduction of a Soil Blank in The Revised Method has effectively eliminated the need for the pre-extraction step. However, to assist in selection of appropriate chloride Spike Sample levels (see ISSUE 2) each test sample should be tested for native chloride prior to starting the test procedure. The Method should include an outline of this test for native chloride.

Issue 2 – Preparation of Spike Samples and Effects of Native Chloride

As stated previously under ISSUE 1, high levels of native chloride have an adverse effect on the performance of this method. Where native chloride from the test sample approaches the concentration of a given Spike Sample, variability in the test increases due to uncertainty in the exact amount of chloride that may leach from the test sample. It is therefore recommended that the Spiked Sample concentrations not be prescriptive. Rather, these concentrations should be set to at least two times the concentration of leachable native chloride in a given test sample.

RECOMMENDATION 2: Include a pre-screen for native chloride followed by an adjustment of the Spike Sample chloride concentrations (where necessary) such that the lowest chloride spike concentration is at least two times the concentration of the measured native chloride in a 1:1 soil : water leachate.

Issue 3 – Impact of Measurement Uncertainty on Method Detection Limit (MDL) for KD-Cl

The BCELQAAC established that MU was one of the key issues associated with the proposed method.

Uncertainty of measurement (i.e. Measurement Uncertainty or MU) is a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand (Eurachem, 2000, sec 2.1.1). There are a number of approaches which can be employed to derive MU.

Because the proposed KD-Cl method requires a minimum of 4 replicate KD-Cl measurements per sample, it affords a simple approach to the estimation of the minimum measurement uncertainty within each test, as follows:

$$U(c) = (t_{n-1} * s_n)/ \sqrt{n}$$

Where: U(c) = Expanded Measurement Uncertainty (minimum)

t_{n-1} = two tailed students t value for 95% CI at n-1 degrees of freedom

s_n = the standard deviation of n KD results

Measurement Uncertainty values determined in this fashion for all samples analyzed in this study (see TABLE 1).

TABLE 1 – Measurement Uncertainty Estimates for Each Sample by the Revised KD-Cl Method

LAB ID	Sample A		Sample B		Sample C		Sample D	
	n	KD ± MU	n	KD ± MU	n	KD ± MU	n	KD ± MU
001	4	0.06 ± 0.14	4	0.004 ± 0.021	4	-0.033 ± 0.040	4	0.005 ± 0.056
002	4	-0.147 ± 0.057	12	0.001 ± 0.009	4	-0.037 ± 0.023	4	0.005 ± 0.008
003	8	-0.057 ± 0.023	12	0.002 ± 0.012	8	-0.032 ± 0.013	8	0.008 ± 0.008
004	4	-0.057 ± 0.38	11	-0.016 ± 0.010	4	-0.061 ± 0.033	4	-0.004 ± 0.020
005	6	0.13 ± 0.20	12	0.026 ± 0.033	4	-0.029 ± 0.055	4	-0.036 ± 0.039

MU values are expressed in units of mL/g.
n is the number of data points used to calculate KD (and MU).

The Measurement Uncertainty values determined in TABLE 1 are excellent measures of the Method Detection Limits (MDL) for KD-Cl for each of these samples. It is obvious from TABLE 1 that MU values and consequently the achievable KD-Cl MDL varied considerably from sample to sample and laboratory to laboratory.

Data for Samples B (Fort Saint John – Clay) and D (Ottawa – Control Sand) indicated that both were non detectable for KD-Cl (i.e. KD-Cl values were below their average MU values). It should be noted that Sample D was designed to become a negative control for KD-Cl and appears to be fit for this purpose. Data produced from the analysis of Sample B and D was used to assess the sensitivity of The Revised Method under a best case scenario. MU data for Samples A and B indicate that even with optimal test samples, it would be very difficult to achieve a KD-Cl detection limit of 0.05.

Data generated on Sample A (Edmonton – Loam) exhibited an extremely high degree of variability. In addition the native concentration of chloride in this sample obscured data generated on the lowest concentration Spike Sample, further compounding the issue of variability on this sample. This is evident in the calculated MU value for this sample, which was far too high to allow an assessment of KD-Cl against the proposed salt standard KD-Cl ranges.

Data generated on Sample C (Abbotsford – Sand) exhibited a slight but significant negative bias for KD-Cl, which could not be explained. As a consequence no clear assessment of KD-Cl could be made on this sample.

Considering that the lowest two MNSS-Cl ranges for KD-Cl are <0.05 and 0.05 - <0.1, it is clear that sensitivity (i.e. MDL) and the ability to effectively quantify near the MDL (i.e. the Quantitation Limit or QL) will impact assessments of KD-Cl as it relates to the MNSS-Cl.

RECOMMENDATION 3: Raise the lowest KD-Cl range within the MNSS-Cl to a level that exceeds the MDL and Quantitation Limit of the KD-Cl method (under ideal circumstances). It is recommended that the lowest KD-Cl range be set to <0.1 mL/g.

RECOMMENDATION 4: Broaden the KD-Cl ranges within the MNSS-Cl to improve compatibility with the uncertainty of the KD-Cl method (i.e. set the MNSS-Cl at: <0.1, 0.1 – <0.2, ≥0.2).

RECOMMENDATION 5: Add a recommendation to use Ottawa Sand (Fisher Scientific product code: S23-3 product description: SAND OTTAWA 20-30 MESH 3 KG, or a comparable product) as a negative control sample to the methodology.

RECOMMENDATION 6: Increase the number of replicates required for each analysis to 8. Increased replication will maximize precision in the test, and will improve confidence in final results.

RECOMMENDATION 7: Require the reporting of MU with all KD-Cl results. Include the required protocol for calculation of MU within the method.

Issue 4 – Specific Issues Related to Test Soil

None of the samples analyzed exhibited a KD-Cl value significantly different than zero. In other words, the study did not reveal a sample which was positive for KD-Cl. No concrete conclusion can there-fore be presented regarding the effectiveness of this method to measure a statistically significant positive KD-Cl value.

As noted under Issue 3, KD-Cl data for Samples A and C were inconclusive, even under the highly controlled conditions of this study. Sample C (Abbotsford – Sand) produced a slightly negative but statistically significant KD-Cl value (negative KD values are undefined). KD-Cl values for Sample A were highly variable.

Based on the above it is clear that further evaluation of the method is required with a broader cross-section of test samples, to determine whether the method can produce consistently valid results for KD-Cl in the hands of experienced chemists. For this reason it is recommended that a draft method be issued such that additional data can be gathered to further assess the methods effectiveness.

Additional evaluation will also illustrate whether samples with detectable positive KD-Cl values are commonly encountered. Furthermore, if positive results for KD-Cl are encountered with some frequency, it would be valuable to review additional information regarding relevant physical and bulk properties of these samples. This may allow a simpler approach to estimation of KD-Cl in future. It is there-fore recommended that samples amenable to this method be characterized for soil texture (detailed particle sizing) and Total Organic Carbon (TOC) content.

The draft method should stand until such time as sufficient data had been collected to further refine both the soil types amenable to the MNSS-Cl Standard and the method itself. A six month time frame is estimated to be a minimum for this period.

RECOMMENDATION 8: Issue a revised KD-Cl method as a draft (see APPENDIX E) with a planned review after a minimum of six months (i.e. the BCELQAAC would commit to reviewing the performance of the draft method on or after 2006 September 01, pending sufficient available data).

RECOMMENDATION 9: Require that samples analyzed by the KD-Cl method (for comparison with the draft BC Salt Standards) also be analyzed for Texture and Total Organic Carbon.

REFERENCES

Bright, 2002 — Doug Bright and Jan Addison, “Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation”, June 2002.

Eurachem, 2000 — Joint EURACHEM/CITAC Working Group, “Quantifying Uncertainty in Analytical Measurement”, 2000.

APPENDIX A
Matrix Numerical Soil Standards for Chloride Ion

Table 8.2:

SCHEDULE 5

MATRIX NUMERICAL SOIL STANDARDS[1]

CHLORIDE Ion (Cl^-)

COLUMN I	COLUMN II	COLUMN III	COLUMN IV	COLUMN V	COLUMN VI	Note
	SOIL STANDARD FOR PROTECTION OF SITE-SPECIFIC FACTOR					
Site-specific Factor	Agricultural (AL)	Urban Park (PL)	Residential (RL)	Commercial (CL)	Industrial (IL)	2
HUMAN HEALTH PROTECTION						
Intake of contaminated soil	>1 000 mg/g	>1 000 mg/g	>1 000 mg/g	>1 000 mg/g		3,4
Groundwater used for drinking water						
Kd < 0.05	50	50	50	50	50	5
Kd 0.05 - < 0.1	90	90	90	90	90	5
Kd 0.1 - <0.15	130	130	130	130	130	5
Kd 0.15 - <0.2	170	170	170	170	170	5
Kd ≥ 0.2	210	210	210	210	210	5
ENVIRONMENTAL PROTECTION						
Toxicity to soil invertebrates and plants	370	370	370	2 500	2 500	
Livestock ingesting soil and fodder	NS					6
Major microbial functional impairment	NS					7
Groundwater flow to surface water used by aquatic life						
Kd < 0.05	440	440	440	440	440	5,8
Kd 0.05 - < 0.1	820	820	820	820	820	5,8
Kd 0.1 - <0.15	1200	1200	1200	1200	1200	5,8
Kd 0.15 - <0.2	1600	1600	1600	1600	1600	5,8
Kd ≥ 0.2	2000	2000	2000	2000	2000	5,8
Groundwater used for livestock watering	NS					6
Groundwater used for irrigation watering						
Kd < 0.05	20	20	20			5
Kd 0.05 - < 0.1	35	35	35			5
Kd 0.1 - <0.15	50	50	50			5
Kd 0.15 - <0.2	70	70	70			5
Kd ≥ 0.2	85	85	85			5

Notes

1. All values in ug/g unless otherwise stated. Substances must be analyzed using methods specified in protocols approved under section 53 or alternate methods acceptable to the director.
2. The site-specific factors of human intake of contaminated soil and toxicity to soil invertebrates and plants specified in this matrix apply at all sites.
3. Intake pathway of exposure modeled is inadvertent ingestion of soil.
4. Standard established based on toxic reference dose (Tolerable Daily Intake) derived for NaCl. Toxicity attributed primarily to cation (Na^+), not anion (Cl^-).
5. The Kd is the Kd of the soil at a site.
6. NS - no standard. No appropriate standard, guideline or criterion exists to use to develop a soil quality standard.
7. NS - no standard. Insufficient acceptable scientific data exists, so no standard is calculated.
8. Standard to protect freshwater aquatic life, based on USEPA (1988) chloride water quality guideline of 230 mg/L.

APPENDIX B
Revised Proposed KD Chloride Method
(The method used during this study.)

Round Robin DRAFT – Determination of Site-Specific Soil-Water Partitioning Co-efficients (Kd) for Chloride (Prescriptive Method)

Parameter

Soil Adsorption Co-efficient (Kd) for Chloride.

Analytical Method

Calculation of Kd value for chloride requires the indirect measurement of chloride ion concentration that is retained on soil particles of a particular soil sample, as well as a direct measurement of the concentration of chloride ions in the interstitial water of the soil at equilibrium.

Chloride analysis is by any approved analytical method with sufficient precision and sensitivity to meet the Performance Requirements of the method.

Introduction

The BC MOE groundwater fate model, used to predict the movement of contaminants in subsurface soils via groundwater-mediated transport, requires an estimation of how a substance partitions between soil particles and the surrounding soil interstitial water (Soil Adsorption Coefficient: Kd). 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.

BC CSR Soil Matrix Standards (Schedule 5) for either drinking water or aquatic life protection are back-calculated soil concentrations estimated in part using a range of plausible Kd values. This method is intended to provide an estimate of actual site-specific Kd - Chloride values, which in some cases may provide some release from the Standards.

Kd is defined as the ratio of the contaminant concentration associated with the solid (µg substance/ g dry soil) to the contaminant concentration in the surrounding aqueous solution (µg substance / mL solution) when the system is at equilibrium. The units for Kd therefore are mL/g or similar.

$$Kd\ (mL/g) = A_i / C_i$$

Where:
A_i = adsorbate concentration on the solid at equilibrium (µg/g).
C_i = concentration of dissolved adsorbate remaining in solution at equilibrium (µg/mL).

The (draft) BC Matrix Numerical Soil Standards for Chloride utilize the following five categories for Kd Chloride: 0-0.05 mL/g, 0.05-0.10 mL/g, 0.10-0.15 mL/g, 0.15-0.20 mL/g, and ≥0.20 mL/g.

Chloride is often considered to be a conservative tracer of groundwater movement by hydrogeologists, and is often assumed to have a Kd value of 0.0 mL/g. There is some evidence, however, that viable mechanisms for the limited adsorption of chloride to soil particles exist. On a site-specific basis, therefore, Kd values in to range of 0.05 to 0.20 may be possible.

In the absence of a reasonable scientific knowledge base, it is assumed that coarse, low organics soils (e.g. sands and coarse glaciofluvial materials) 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, complex oxides) are likely to exhibit chloride Kd 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 Kd values that could approach 0.10 mL/g or higher.

It has long been recognized that the Kd 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 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).

Most soil particles are negatively charged, but some anions are also bound by, for example, metal oxides or hydroxides (MO or MOH). In particular, at relatively low pH, metal oxides can react as follows:

$MOH + H^+ \leftrightarrow MOH_2^+$
$MO + H^+ \leftrightarrow MOH^+$

Soil organic matter, including humic and fulvic substances, may also have functional groups, which form positive sites: e.g. $R\text{-}H_3^+$. These positive functional groups collectively contribute to an anion exchange capacity of soils, which can be experimentally measured. Overall, the anion exchange capacity of soils is likely to be much lower than the cation exchange capacity (i.e. – typically 5% or less of the CEC), but may nonetheless be closely related to chloride ion soil sorption tendency.

Because chloride ions have a very limited potential to adsorb to soil particles, the measurement of Kd for chloride presents challenges that are different from the vast majority of other inorganic or polar organic substances (primarily due to measurement uncertainty). This method was specifically developed within British Columbia for undertaking chloride Kd determinations.

For further information on this topic, please refer to "*Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulations*", June 2002, Doug A. Bright and Jan Addison (Report to BC WLAP, MOTH, BCBC, and CAPP), and to "*Determination of Site-Specific Soil-Water Partitioning Co-efficients (Kd) for Inorganic Ions and Polar Substances other than Chloride*" (BC Environmental Lab Manual).

Method Summary

A soil sample is pre-extracted by a 5:1 aqueous leach to remove the majority of naturally occurring chloride ions which may be present. The sample is oven dried at low temperature, and 4 x 20g portions of the sample are equilibrated for 7 days with 20 mL volumes of deionized water or site groundwater containing sodium chloride at 320 mg/L, 1000 mg/L, 3200 mg/L, and 10000 mg/L. Four Control Samples are prepared with the same spiking solutions, but without soil, to act as relative indicators of adsorption. Two Soil Blank Samples are prepared by mixing the soil with deionized water, to determine chloride background levels. Samples are centrifuged and filtered prior to analysis of the equilibrated aqueous fraction by an appropriately sensitive and precise analytical method for chloride (e.g. Ion Chromatography). Adsorption co-efficient values are calculated for each of the 4 Spike Samples, and a final Kd value is determined.

In order to meet the requirements of the BC salt standards, this method must be able to accurately determine Kd values as low as 0.05 mL/g, which is extremely challenging. In order to achieve this objective, the following key elements have been incorporated into this method:

- The ratio of dry soil weight to aqueous spike solution volume for test sample equilibrations has been maximized (defaulting to 1:1), as this ratio has a direct factor on the sensitivity of the Kd determination.
- Final Kd estimates are determined by averaging up to 4 independent Kd test measurements, performed at 4 different chloride concentrations.
- Control Spike solutions are used, such that relative adsorption values can be measured (as opposed to absolute comparisons with nominal target values).
- Test samples are pre-extracted to remove most naturally occurring chloride ions, which would otherwise limit the sensitivity of the method.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Kd (Chloride)	0.05 mL/g	

Matrix

Soil samples, collected as being representative of subsurface soils along groundwater flow paths. Soil Samples must not be heavily contaminated with chloride, hydrocarbons, or other contaminants.

Interferences and Precautions

Obtaining representative and valid results is dependent on performing the following procedure exactly as written. Deviations from this method will likely result in erroneous data.

The primary difficulty with this method is related to analytical precision and measurement uncertainty. Under the stated conditions of this method, a 5% error in the measured ratio of 2 analytical results (Spike Sample Results versus Control Sample Results) translates to an error in Kd value equal to at least 0.05 mL/g.

Sample Handling and Preservation

No preservation is required.

Stability

Holding and Storage Time and Particulars: Soils may be stored refrigerated at 4°C, or (preferably) frozen at approximately –20°C, for up to 28 days.

Soil anion exchange capacity is highly pH dependent. Handling and storage conditions should not alter soil pH or anion exchange capacity.

Positively charged amino acids may also occur on soil organic matter. The prescribed storage conditions should limit microbial activity. Much of chloride ion exchange sites are expected to reside on longer chain, complex, and relatively non-labile organic matter (humics, fulvics), so effects of shorter term heterotrophic microbial activity during storage should be minimal.

Procedure

1. Selection of Soils for Analysis

It is the responsibility of the submitter to provide samples that adequately capture the range of site conditions of interest, including spatial and vertical variations in soil texture or other properties which may influence groundwater flow and groundwater quality. Typically, the soil samples will have originated in connection with the assessment and/or environmental risk assessment of salt contaminated sites (e.g. from produced water releases or road salt storage/release).

Chloride Kd determinations must be conducted on soil samples representative of the site (and strata within it) but which are not contaminated with salt ions or other contaminants.

2. Pre-extraction of Naturally Occurring chloride from Test Soil

At least 100g dry weight of each sample is required to perform this test, assuming analysis will be conducted using one Spike Sample at each of the four solute test concentrations plus the Soil Blank. If the test sample as submitted is over-saturated, decant and discard overlying water before proceeding. Determine the moisture content on a sub-sample. Weigh approximately 150g dry weight of the soil sample into a pre-cleaned container (e.g. 1L Erlenmeyer flask). The wet weight amount to be measured is:

$$\text{Wet wt. amount} = 150\text{g} / [(100-M)/100] \qquad \text{where } M = \text{Moisture in \%}$$

Add 750 mL of deionized water to the wet soil sample to create approximately a 5:1 water : soil slurry. Agitate the slurry for 2 hours by shaking or stirring. Allow to settle.

Separate soil from water by filtration through a large Buchner funnel fitted with Whatman No. 5 or equivalent filter paper. Collect the leachate for chloride analysis. When filtration is complete, rinse the soil and the filter apparatus with an additional 3 x 100 mL portions of deionized water (discard the rinsings).

Test the leachate for chloride. If the chloride concentration in the leachate exceeds 50 mg/L, perform additional 5:1 deionized water leaches until a leachate concentration of below 50 mg/L is achieved.

3. Drying and Preparing the Test Soil

Dry the test soil completely by spreading it thinly in a large beaker, and placing it in a 60°C drying oven for at least 16 hours (or to constant weight).

Disaggregate the soil and sieve through a 10 mesh sieve. Do not mechanically grind the soil. Discard the > 10 mesh fraction.

4. Optional: Testing of Site Groundwater for Chloride

The most representative Kd test results should be obtained when groundwater obtained from the site of the test sample is used as the spiking solution medium. If site groundwater is available and appropriate for use with this test, it is recommended that it be used. Otherwise, deionized water may be used. Note: Kd results using deionized water for the spiking solution are expected to be equal to or less than the Kd values that would be obtained using site groundwater.

If groundwater is to be used, approximately 4 x 50mL will be required per sample. The groundwater must be tested for chloride prior to use (ensure the required quantity is well mixed in a single container prior to testing).

Site groundwater can only be used to prepare spike solutions that require nominal concentrations that exceed the groundwater chloride concentration.

If the groundwater chloride concentration is greater than the nominal concentration required for a particular spike solution, then deionized water must be used to prepare that spike solution.

5. Preparation of Spike Solutions

For each sample to be tested, prepare at least 50 mL of a chloride spike solution into deionized water, at the following nominal sodium chloride concentrations: 320 mg/L, 1000 mg/L, 3,200 mg/L, and 10,000 mg/L. These NaCl concentrations translate to chloride concentrations of 194 mg/L, 606 mg/L, 1,940 mg/L, and 6,060 mg/L. It is imperative that all spike solutions be thoroughly mixed prior to each use.

If site groundwater is used to prepare any of the solutions, the groundwater chloride concentration must be taken into account when preparing each spike solution.

Samples with high water holding capacity may require more than 50 mL of each spike solution.

6. Preparation of Spike Samples, Control Samples, and Soil Blanks.

Each Kd test requires 4 Spike Samples (at different spike concentrations), 4 Control Samples, and 2 Soil Blanks.

Spike Samples: For each Spike Sample, weigh (20.0 ± 0.2) grams of air-dried soil sample into a 50 mL glass or Teflon round-bottom centrifuge tube. Then add (20.0 ± 0.2) mL of the relevant spike solution to the centrifuge tube.

Check to ensure that 20 mL of spike solution is sufficient to cover and saturate the soil after it has been completely wetted. If necessary, add more spike solution as required to permit the removal of approximately 1 - 2 mL of the aqueous solution for analysis of chloride ion concentration (after centrifuging) at the completion of the test. Record the exact soil weight used, and the exact amount of spike solution added to each sample (to 3 significant figures). Cap tightly. If the actual values used are within the stated ranges (e.g. 20.0 ± 0.2 grams or mL), then the nominal values (20 g and 20 mL) may be used for Kd

calculations.

> **Note:** As greater volumes of spike solution is added, the detection limit of the Kd test increases proportionately. Addition of more than 25-30mL of spike solution should be avoided if possible.

Control Samples: Add (20.0 ± 0.2) mL of each spike solution to a 50 mL centrifuge tube. Control Samples are used as a relative reference point against which adsorption of chloride by test samples is measured. Cap tightly.

> **Note:** If multiple Kd tests are being performed, the same 4 Control Samples can be used for each sample. However, each test sample and its corresponding control spike **must** be prepared from the same batch of spike solution.

Soil Blanks: For each soil sample being tested, prepare 2 Soil Blanks. Soil Blanks are used to determine the amount of chloride contributed to the test solutions from the leaching of the soil. Cap tightly.

For each blank, weigh (20.0 ± 0.2) grams of air-dried soil sample into a 50 mL centrifuge tube. Then add (20.0 ± 0.2) mL of deionized water to the centrifuge tube.

7. Equilibration of Test Samples

All test samples (Spike Samples, Control Samples, and Soil Blanks) must be mixed either with a spatula or a mechanical shaker to ensure that the soil and spike solutions are well-mixed so that contact is maximized.

Allow all test samples to equilibrate at ambient temperature for 7 days. Store samples right-side up to prevent leaking.

8. Filtration of Test Samples

When equilibration is complete, mix all samples thoroughly (e.g. using a spatula or mechanical shaker) to ensure that a representative sub-sample is taken for analysis. Centrifuge all Spike Samples and Soil Blanks to permit removal of a portion of the aqueous layer for analysis.

Remove at least 1 - 2 mL (more if accessible) of each Spike Sample, Control Sample, and Soil Blank. Filter all samples (including Control Samples) through dry, non-contaminating 0.45 µm polycarbonate-membrane type syringe filters (pre-test filters for chloride contamination potential; if necessary, pre-clean and dry filters before use).

9. Analysis of Test Samples for Chloride

Analyze all test samples for chloride using an approved, highly precise analytical procedure. If the analytical procedure employed requires more than the 1-2 mL sample volume available, or if the concentrations of the test samples exceed the range of the technique, then dilutions can be performed before analysis. Any dilutions conducted must be highly accurate (e.g. < 1% error). If a Spike Sample is diluted, its corresponding Control Sample must be diluted identically.

Any chloride test method used for this procedure must have a detection limit (after accounting for dilutions) of no more than 1 mg/L in at least the lowest concentration test samples.

During instrumental analysis, each Spike Sample (for a given spike level) must be analyzed immediately before or after its associated Control Sample. If a set of Control Samples is being applied to more than one test sample, the Control Samples must be analyzed once for each test sample.

The following example analysis sequence meets these requirements:

A. Calibration Standards
B. Control Standard / LCS
1. Chloride Method Blank
2. Soil Blank (Sample X)
3. Spike Sample X (320 mg/L)
4. 320 mg/L Control Sample
5. Spike Sample X (1000 mg/L)
6. 1000 mg/L Control Sample
7. Spike Sample X (3200 mg/L)
8. Spike Sample X - Duplicate (3200 mg/L)
9. 3200 mg/L Control Sample
10. Spike Sample X (10000 mg/L)
11. 10000 mg/L Control Sample
12. Calibration Verification Standard
13. Soil Blank (Sample Y)
14. Spike Sample Y (320 mg/L)
15. ...

10. Calculation of Kd results

For each test sample, the following measured concentrations must first be determined:

SB = $[Chloride]_{(aq)}$ (measured) of Soil Blank sample (mg/L)
Spk_n = $[Chloride]_{(aq)}$ (measured) of Spike Sample level n (mg/L)
CS_n = $[Chloride]_{(aq)}$ (measured) of Control Sample level n (mg/L)

Other data required to calculate Kd includes the following:

SBVol = Volume of Deionized water added to Sample Blank (mL, normally 20)
SBWt = Weight of soil used for Soil Blank sample (g, normally 20)
$SpkVol_n$ = Volume of Level n Spike Solution added to Spike level n (mL, normally 20)
$SoilWt_{SPk,n}$ = Dry Weight of Soil used for Spike level n (g, normally 20)
$CS_{nom,n}$ = nominal chloride concentration of spike solution level n (mg/L)

For each test sample, first calculate the Adsorption Fraction (AF) value for each spike level, as follows. Adsorption Fraction is the fraction of the total chloride amount (mass) from the spike solution that was adsorbed to the soil after equilibration, expressed as a decimal fraction. AF is unitless:

$$\mathbf{AF_n = 1 - [(Spk_n - SB_{equiv}) / CS_n]}$$

where:

$$\mathbf{SB_{equiv} = SB * (SBVol / SpkVol_n) * (SoilWt_{spk,n} / SBWt)}$$

SB_{equiv} is the equivalent Soil Blank concentration that would be expected in the Spike sample due to chloride ions leaching from the sample itself. If the volumes and weights of the Soil Blank and the Spike sample are the same, then SB_{equiv} = SB. These equations assume that the amount of residual chloride adsorbed to the sample prior to spiking is small in comparison to the spike level. The adsorption fraction AF_n relates only to adsorption of chloride from the spiking solution. It is assumed that any chloride that would have leached from the unspiked soil sample (i.e. SB_{equiv}) would not re-adsorb.

Note that the nominal concentrations of the spike solutions do not enter into this calculation (therefore, error in nominal concentrations does not translate to error in the measured Kd values).

Next, the Adsorption Fraction values must be converted to Adsorption Co-efficients (Kd values) as follows. This converts the amount fraction into a concentration ratio. Derivation

of the formula to be used begins with the definition of Kd:

Kd (mL/g) = A_i / C_i

Where:
A_i = adsorbate concentration on the solid at equilibrium (mg/g)
C_i = concentration of dissolved adsorbate remaining in solution at equilibrium (mg/mL)

A_i and C_i may be calculated directly from the adsorption fraction AF_n and the nominal chloride concentration of the Control Sample and Spike Sample for each level. The A_i term represents what is sorbed to the soil mass (mg/g), calculated on the basis of mass loss from solution, divided by the soil mass in the container:

$A_{i,n}$ = [AF_n (unitless)] * $CS_{nom,n}$ (mg/L) * $SpkVol_n$ (mL) * 0.001 L/mL] / $SoilWt_{Spk,n}$ (g)

$C_{i,n}$ = [1 – AF_n (unitless)] * $CS_{nom,n}$ (mg/L) * 0.001 L/mL

Substituting the above equations for $A_{i,n}$ and $C_{i,n}$ into the Kd equation above leads to the following final equation for calculation of Kd_n. Use this equation to calculate Kd for each spike level:

Kd_n = [AF_n / (1 – AF_n)] * $SpkVol_n$ (mL) / $SoilWt_{Spk,n}$ (g)

The units for Kd are mL/g. For each sample, Kd values are determined for each of the 4 spiking levels. Kd values for most samples should be near zero (typical results are expected to be in the 0.00 - 0.20 range). Although not meaningful, small negative Kd values may occur due to analytical variability.

Compute the average and standard deviation of the 4 Kd values (including any negative values obtained). If the standard deviation (not the RSD) of the Kd values is less than 0.05, report the mean Kd result as the Kd for the sample.

If the standard deviation (SD) of the 4 mean Kd results is >0.05, exclude the result furthest from the mean, and re-compute the mean and SD from the remaining 3 results. If the SD of the closest 3 results is ≤0.05, report their mean as the final Kd value. If the standard deviation is still >0.05, exclude the next furthest result from the mean, and re-compute the mean and SD from the remaining 2 results. If the SD of the closest 2 results is ≤0.05, report their mean as the final Kd value, otherwise repeat the entire test for the sample.

Note: If the test as written does not provide sufficient precise Kd values for a given sample or application, then it is recommended that it be conducted using between two to five replicates of each Spike Sample, Control Sample, and Soil Blank, with averages used in all calculations. The recommended degree of replication depends on the importance of the test result. The required amounts of soil and spiking solutions for the test increase proportionately to the number of replicates used.

11. Reporting Requirements

All of the following results must be reported within the lab report for any test for Kd - Chloride that relates to compliance of the BC MOE Salt Standards:

- Report Kd results for all four spiking levels, reported to 3 decimal points (including any negative values obtained).
- Report the final Kd result, based on the above-described protocols, to 3 decimal points. If the final Kd estimation is a negative value between -0.05 and zero, report a final Kd value of zero. Otherwise, report the value obtained, or repeat the test (Note: negative Kd values are not theoretically possible; large negative values indicate an unacceptably large degree of error within the test).
- If any significant deviations were required from this method, these deviations must be reported.

Performance Requirements

Precision Requirement (of Chloride Method): The analytical method selected for chloride should be sufficiently precise such that the RSD of within-batch sequential chloride measurements of standards or reference materials is well below 5%.

Accuracy Requirement (of Chloride Method): The analytical measurement for chloride should demonstrate recoveries in the range of 90% to 110% on aqueous standards or aqueous reference materials.

Sensitivity Requirement (of Chloride Method): The analytical method selected for chloride measurements must have a detection limit (after accounting for any necessary sample dilutions) of no more than 1 mg/L in the lowest concentration level test samples.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Chloride Method Blank	One per batch	< 2 mg/L
Kd Method Blank	One per batch (1 level)	Kd between -0.10 and 0.10
Chloride Control Std (LCS-Chloride)	One per batch	Within 10% of Target
Chloride Lab Duplicates	One instrumental duplicate per test sample.	5% RPD (based on measured Chloride in solution)
Kd Lab Duplicate	Optional	Not Specified
Laboratories should report qualified data when any of these DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.		

Chloride Method Blank: Required. Minimum one per Kd test batch. The Chloride Method Blank is prepared by adding 20 mL of deionized water directly to an empty centrifuge tube and carried through the entire process (including filtration steps and any dilution steps).

Chloride Lab Duplicates: Required (Instrumental duplicate only). Minimum one per Kd sample test.

Chloride Control Standard or LCS-Chloride: Required. One per batch. Acts as a second source check on calibration standard accuracy.

Kd Method Blank: Required. Minimum one per Kd test batch. A Kd Method Blank is a complete Kd test, conducted on an inert solid matrix (e.g. clean, solvent rinsed, oven baked sand, or a suitable reference material), that would be expected to exhibit a Kd value of zero. To minimize the level of effort, a Kd Method Blank may be conducted using a single chloride concentration level. Using a single concentration level, the Kd Method Blank value should fall within the range of -0.10 to 0.10.

Kd Lab Duplicate: Recommended for crucial test samples. However, the test protocols already include 4 independent Kd measurements for each test sample. The difference between Kd Lab Duplicate results should ideally be less than 0.05 mL/g.

Note: "Soil Blanks" are not related to Kd Method Blanks or Chloride Method Blanks. Soil Blanks are used to determine the amount of chloride contributed to the equilibrated sample solutions by any given soil sample.

Prescribed Elements

This is not a performance based method. All steps must be performed as written.

As a minimum component of laboratory method validation, laboratories must conduct a full Kd Method Blank test (using all 4 concentration levels) on at least one inert solid matrix or suitable reference material, and must achieve a final Kd result of between -0.05 and 0.05. This demonstration of capability must be completed before using the method for environmental samples.

References

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/vol1/402-r-99-004a.pdf).

Revision History

October 18, 2005	First draft as BC PBM & version used for validation Round Robin.

APPENDIX C
Instructions to Participant Laboratories

JRD CONSULTING COMPANY

603 First Street
New Westminster, BC V3L 2H3
Canada
604.889.3732

21 October 2005

Dear Participant Lab,

Thank you for agreeing to participate in the British Columbia Ministry of Environment (BCMOE) *Kd (Chloride) Analytical Method Validation Interlab Study (CSR # 12355)*. As discussed at the last meeting of the Technical Subcommittee of the BC Environmental Laboratory Quality Assurance Advisory Committee (held on 23 September 2005), this Interlab Study is designed to evaluate a reliable reference method for the analysis of Kd for Chloride in support of the pending draft BC CSR salt standards.

Please find included with this letter the following:

1. A set of four (4) bottles containing three (3) native materials and one (1) control material labeled as follows:
    a. *Sample A – Edmonton (Loam),*
    b. *Sample B – Fort Saint John (Clay),*
    c. *Sample C – Abbotsford (Sand),*
    d. *Sample D – Ottawa (Control Sand);*
2. A detailed set of instructions describing the preparation and reporting requirements for the study,
3. A copy of *DRAFT – Determination of Site-Specific Soil-Water Partitioning Coefficients (Kd) for Chloride (Prescriptive Method) [18 October 2005].*

An MS Excel spreadsheet for reporting of results in electronic format will be sent out via email on or before Friday 21 October 2005.

Your laboratory has been assigned the following Identification number: ### . Please refer to this number in all correspondence relating to this study.

Final results are due at the JRD Consulting Company on or before **16 November 2005.**

Just a reminder that work associated with this study should be:

1. invoiced **on or after** 01 December 2005;
2. the invoice must be made out to *Maxxam Analytics Inc.*;
3. please ensure you reference *BCMOE Kd (Chloride) Analytical Method Validation Interlab Study (CSR # 12355)*;
4. include a summary of completed work with your invoice; and
5. **send all invoices to James Downie (JRD Consulting Company)** who will forward them onto Maxxam.

Sincerely;

Signature Valid

Digitally signed by James R. Downie
DN: cn=James R. Downie, o=JRD Consulting Company, c=CA
Date: 2005.10.21 13:12:17 -07'00'
Reason: Document is certified
Location: New Westminster, BC, CANADA

James R. Downie
JRD Consulting Company
jamie.downie@Telus.net

Attachments (2)
Enclosures (1)

Cc Steve Horvath (BCMOE)
Glyn Fox (BCMOE)

jrd/JRD

ATTACHMENT 1

INSTRUCTIONS

Introduction

As a consequence of Environment Canada's declaration of salt as a CEPA toxic substance in 2001, the BC provincial government is now working to adopt standards for the regulation of salts under the BC Contaminated Sites Regulation (CSR). Draft standards intended to regulate sodium and chloride were developed for the Ministry of Environment by Dr. Doug Bright and Dr. Jan Addison, and were released for public comment in June, 2002.

The proposed chloride standard is expected to pose significant challenges for BC sites related to road salt storage and handling, and to sites affected by produced water from the oil and gas industry. In order to allow some options for release, matrix numerical soil standards as a function of the site-specific partitioning co-efficient (Kd) for chloride have been proposed.

Under the salt standards derivation project, Dr. Bright also proposed a generic analytical procedure to measure Kd entitled "Protocol for the Estimation of Site-Specific Adsorption Co-efficients, KD". Members of the Technical Subcommittee to the BC Environmental Laboratory Quality Assurance Advisory Committee (BCELQAAC) evaluated this procedure for chloride, and found it to be inadequate. As a result of this feedback from the BCELQAAC, Dr. Bright worked with the BCELQAAC members to develop a modified version of the Kd method, which is intended to be more applicable to the determination of Kd for chloride.

The primary objectives of this study are to:

1. Evaluate this modified version of the Kd method through an interlab study involving the major BC commercial laboratories and a number (three) of native uncontaminated materials;
2. Locate and test a suitable "negative control sample" that laboratories could use in future applications as a Quality Control reference sample. A negative control sample for Kd would be a commonly available soil type (e.g. a clean sand matrix) that would be verified as having a Kd value of zero or near-zero.

You have been sent four (4) 500g containers of dried, disaggregated and sieved homogenized material. This material is a composite of three (3) “real world” native non-contaminated soils (Samples A, B & C) and one (1) commercially available sand (Sample D). Sample D is intended to become our negative Quality Control reference material. You will be instructed (see General Instructions for details) to analyze sub-samples from all of these containers. One of the four containers will be analyzed in triplicate.

Please follow the BCMOE *DRAFT – Determination of Site-Specific Soil-Water Partitioning Coefficients (Kd) for Chloride (Prescriptive Method) [18 October 2005]* exactly as written.

A total of 6 data sets will be generated by each participating lab.

General Instructions:

All samples have been labelled as follows:

Sample A – Edmonton (Loam);
Sample B – Fort Saint John (Clay);
Sample C – Abbotsford (Sand);
Sample D – Ottawa (Control Sand).

Sample Handling and Storage

The samples have been processed and stabilized such that degradation should be minimal at room temperature (i.e. 20 C). However, to further guarantee minimal degradation it is recommended that the samples be stored at or below 4 C during this study.

All normal safety precautions applicable to the handling of potentially hazardous material should be observed.

Preparation and Analytical Methodology

Please analyze:

- a single sub-sample from the containers labeled Sample A, C & D;
- triplicate sub-samples from the container Labeled Sample B;
- all required Quality Control as outlined in the DRAFT Method

Process all sub-samples as follows:

1. As per DRAFT – Determination of Site-Specific Soil-Water Partitioning Coefficients (Kd) for Chloride (Prescriptive Method) [18 October 2005] exactly as written,

WARNING:
The reference method must be followed as written.

2. analyze Chloride by the most precise method available (e.g. Ion Chromatography),
3. report the resulting 6 data sets as per Reporting Requirements listed below.

Reporting Requirements

Please use the electronic file provided with this paperwork to report the data. This file is an MS Excel spreadsheet with protection applied to specific cell ranges. There should be no need to unprotect these ranges. However if the participant does require protection to be turned off please contact Mr. James R. Downie at (604) 889-3732 or via email at jamie.downie@Telus.net for the password. Participant definable cells have been highlighted in YELLOW all other cells are protected. YELLOW cells have also been preformatted to simplify the data entry process.

Please report the results data (sheet labelled SAMPLES) and quality control (sheet labelled QA_QC) in the appropriate worksheet. Explanatory Comments have been added to various cells. To activate these Comments place your pointer over a specific cell and the Comment will appear in the resulting bubble.

If there are any questions related to reporting of data please direct them to:

James (Jamie) R. Downie
(604) 889-3732 C or
jamie.downie@Telus.net

Once the data file has been completed please email or courier the file on disk to:

James (Jamie) R. Downie
603 First Street
New Westminster, BC V3L 2H3
Canada
(604) 889-3732 C or
jamie.downie@Telus.net

DATA IS DUE AT THE ABOVE COORDINATES ON OR BEFORE

Wednesday 16 November 2005

Material sent to you and left over from this study is provided to you free of charge in appreciation for the time and effort you have provided to this project.

All data reported during this project will be kept in strict confidence. The association between Laboratory IDs and reported results will only be known to James R. Downie (of the JRD Consulting Company) for the purposes of data analysis. Participating labs will be listed in the final published report. Data sets will be reported anonymously in the final published report.

Once again, thank-you for agreeing to participate in this study.

ATTACHMENT 2

Refer to APPENDIX B for a copy of the method included in these instructions

APPENDIX D
KD Chloride Data

RAW DATA
2005 KD Choride Interlab Study

Lab_ID	Sample_Label	Rep_No	Start_Date	Stop_Date	Analysis_Date	No_Prewash	Prewash_Tech	Anal_Tech	MDL_Anal	Kd_Value_Source	Kd_Value
001	A	3.1	2005-11-15	2005-11-21	2005-11-21	2	NEW	IC	2 mg/L	320	-0.012
001	A	3.1	2005-11-15	2005-11-21	2005-11-21	2	NEW	IC	4 mg/L	1000	0.012
001	A	3.1	2005-11-15	2005-11-21	2005-11-21	2	NEW	IC	20 mg/L	3200	0.061
001	A	3.1	2005-11-15	2005-11-21	2005-11-21	2	NEW	IC	40 mg/L	10000	0.186
001	A	3.1	2005-11-15	2005-11-21	2005-11-21	2	NEW	IC		FINAL	0.020
002	A	3.1	2005-11-03	2005-11-10	2005-11-18	2	NEW	IC	0.5 mg/L	320	-0.196
002	A	3.1	2005-11-03	2005-11-10	2005-11-18	2	NEW	IC	0.5 mg/L	1000	-0.138
002	A	3.1	2005-11-03	2005-11-10	2005-11-18	2	NEW	IC	5 mg/L	3200	-0.143
002	A	3.1	2005-11-03	2005-11-10	2005-11-18	2	NEW	IC	5 mg/L	10000	-0.110
002	A	3.1	2005-11-03	2005-11-10	2005-11-18	2	NEW	IC		FINAL	-0.147
003	A	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	0.767
003	A	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	-0.068
003	A	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	-0.061
003	A	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	-0.025
003	A	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	-0.051
003	A	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	-0.089
003	A	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	-0.021
003	A	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	-0.086
003	A	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	-0.074
003	A	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	-0.068
003	A	2.1	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	5 mg/L	320	0.474
003	A	2.1	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	5 mg/L	1000	0.330
003	A	2.1	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	50 mg/L	3200	0.231
003	A	2.1	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	50 mg/L	10000	0.438
003	A	2.1	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR		FINAL	0.456
003	A	2.2	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	5 mg/L	320	0.236
003	A	2.2	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	5 mg/L	1000	0.383
003	A	2.2	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	50 mg/L	3200	0.369
003	A	2.2	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR	50 mg/L	10000	0.333
003	A	2.2	2005-11-11	2005-11-17	2005-11-17	1	NEW	COLOUR		FINAL	0.361
003	A	3.1	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	5 mg/L	320	-0.002
003	A	3.1	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	5 mg/L	1000	-0.059
003	A	3.1	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	50 mg/L	3200	-0.055
003	A	3.1	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	50 mg/L	10000	-0.042
003	A	3.1	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR		FINAL	-0.039
003	A	3.2	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	5 mg/L	320	-0.058
003	A	3.2	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	5 mg/L	1000	-0.078
003	A	3.2	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	50 mg/L	3200	-0.100
003	A	3.2	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR	50 mg/L	10000	-0.063
003	A	3.2	2005-11-11	2005-11-17	2005-11-17	2	NEW	COLOUR		FINAL	-0.075
004	A	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	320	0.305
004	A	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	1000	-0.188
004	A	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	3200	-0.171
004	A	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	10000	-0.172
004	A	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR		FINAL	-0.177

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Lab_ID	Sample_Label	Rep_No	Start_Date	Stop_Date	Analysis_Date	No_Prewash	Prewash_Tech	Anal_Tech	MDL_Anal	Kd_Value_Source	Kd_Value
005	A	3.1	2005-11-03	2005-11-09	2005-11-09	2	NEW	IC	1 mg/L	320	-0.156
005	A	3.1	2005-11-03	2005-11-09	2005-11-09	2	NEW	IC	1 mg/L	1000	-0.120
005	A	3.1	2005-11-03	2005-11-09	2005-11-09	2	NEW	IC	10 mg/L	3200	-0.113
005	A	3.1	2005-11-03	2005-11-09	2005-11-09	2	NEW	IC	10 mg/L	10000	-0.030
005	A	3.1	2005-11-03	2005-11-09	2005-11-09	2	NEW	IC		FINAL	-0.087
005	A	1.1	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	1 mg/L	320	-1.854
005	A	1.1	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	1 mg/L	1000	4.386
005	A	1.1	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	10 mg/L	3200	0.147
005	A	1.1	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	10 mg/L	10000	0.144
005	A	1.1	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE		FINAL	0.146
005	A	1.2	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	1 mg/L	320	-1.878
005	A	1.2	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	1 mg/L	1000	2.677
005	A	1.2	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	10 mg/L	3200	
005	A	1.2	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE	10 mg/L	10000	
005	A	1.2	2005-11-30	2005-12-06	2005-12-07	0	NONE	ISE		FINAL	0.399
005	A	2.1	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	1 mg/L	320	0.338
005	A	2.1	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	1 mg/L	1000	0.077
005	A	2.1	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	10 mg/L	3200	-0.049
005	A	2.1	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	10 mg/L	10000	-0.009
005	A	2.1	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE		FINAL	-0.029
005	A	2.2	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	1 mg/L	320	0.398
005	A	2.2	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	1 mg/L	1000	0.041
005	A	2.2	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	10 mg/L	3200	
005	A	2.2	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE	10 mg/L	10000	
005	A	2.2	2005-11-30	2005-12-06	2005-12-07	1	NEW	ISE		FINAL	0.219
005	A	3.1	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	1 mg/L	320	-0.126
005	A	3.1	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	1 mg/L	1000	-0.075
005	A	3.1	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	10 mg/L	3200	-0.115
005	A	3.1	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	10 mg/L	10000	-0.102
005	A	3.1	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE		FINAL	-0.104
005	A	3.2	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	1 mg/L	320	-0.085
005	A	3.2	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	1 mg/L	1000	-0.115
005	A	3.2	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	10 mg/L	3200	
005	A	3.2	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE	10 mg/L	10000	
005	A	3.2	2005-11-30	2005-12-06	2005-12-07	2	NEW	ISE		FINAL	-0.100

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Lab_ID	Sample_Label	Rep_No	Start_Date	Stop_Date	Analysis_Date	No_Prewash	Prewash_Tech	Anal_Tech	MDL_Anal	Kd_Value_Source	Kd_Value
001	B	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	2 mg/L	320	-0.003
001	B	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	4 mg/L	1000	-0.002
001	B	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	20 mg/L	3200	0.023
001	B	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	40 mg/L	10000	-0.004
001	B	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC		FINAL	0.004
002	B	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	320	0.006
002	B	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	1000	0.000
002	B	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	3200	-0.006
002	B	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	10000	0.018
002	B	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC		FINAL	0.004
002	B	1.2	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	320	-0.017
002	B	1.2	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	1000	-0.001
002	B	1.2	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	3200	0.012
002	B	1.2	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	10000	0.025
002	B	1.2	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC		FINAL	0.005
002	B	1.3	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	320	-0.019
002	B	1.3	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	1000	-0.004
002	B	1.3	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	3200	-0.010
002	B	1.3	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	10000	0.012
002	B	1.3	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC		FINAL	-0.005
003	B	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	0.024
003	B	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	-0.014
003	B	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	0.023
003	B	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	-0.011
003	B	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	0.006
003	B	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	0.001
003	B	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	-0.020
003	B	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	0.022
003	B	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	-0.008
003	B	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	-0.001
003	B	1.3	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	-0.004
003	B	1.3	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	-0.025
003	B	1.3	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	0.025
003	B	1.3	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	0.010
003	B	1.3	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	0.001
004	B	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	320	
004	B	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	1000	-0.018
004	B	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	3200	-0.003
004	B	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	10000	-0.031
004	B	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR		FINAL	-0.017
004	B	1.2	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	320	-0.024
004	B	1.2	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	1000	-0.031
004	B	1.2	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	3200	-0.005
004	B	1.2	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	10000	-0.006
004	B	1.2	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR		FINAL	-0.016

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Lab_ID	Sample_Label	Rep_No	Start_Date	Stop_Date	Analysis_Date	No_Prewash	Prewash_Tech	Anal_Tech	MDL_Anal	Kd_Value_Source	Kd_Value
004	B	1.3	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	320	-0.038
004	B	1.3	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	1000	-0.028
004	B	1.3	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	3200	-0.002
004	B	1.3	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	10000	0.0042
004	B	1.3	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR		FINAL	-0.016
005	B	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	1 mg/L	320	0.173
005	B	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	1 mg/L	1000	0.062
005	B	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	10 mg/L	3200	0.105
005	B	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	10 mg/L	10000	0.031
005	B	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC		FINAL	0.066
005	B	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	320	0.038
005	B	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	1000	0.042
005	B	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	3200	0.104
005	B	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	10000	-0.003
005	B	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC		FINAL	0.045
005	B	1.2	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	320	0.019
005	B	1.2	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	1000	-0.058
005	B	1.2	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	3200	0.008
005	B	1.2	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	10000	-0.004
005	B	1.2	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC		FINAL	-0.009
005	B	1.3	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	320	0.026
005	B	1.3	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	1000	-0.027
005	B	1.3	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	3200	0.044
005	B	1.3	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	10000	0.129
005	B	1.3	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC		FINAL	0.014

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Lab_ID	Sample_Label	Rep_No	Start_Date	Stop_Date	Analysis_Date	No_Prewash	Prewash_Tech	Anal_Tech	MDL_Anal	Kd_Value_Source	Kd_Value
001	C	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	2 mg/L	320	-0.023
001	C	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	4 mg/L	1000	-0.07
001	C	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	20 mg/L	3200	-0.026
001	C	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	40 mg/L	10000	-0.014
001	C	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC		FINAL	-0.033
002	C	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	320	-0.053
002	C	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	1000	-0.040
002	C	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	3200	-0.035
002	C	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	10000	-0.019
002	C	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC		FINAL	-0.037
003	C	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	-0.019
003	C	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	-0.025
003	C	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	-0.022
003	C	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	-0.029
003	C	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	-0.024
003	C	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	-0.052
003	C	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	-0.056
003	C	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	-0.016
003	C	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	-0.039
003	C	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	-0.041
004	C	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	320	-0.089
004	C	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	1000	-0.064
004	C	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	3200	-0.048
004	C	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	10000	-0.043
004	C	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR		FINAL	-0.061
005	C	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	320	-0.075
005	C	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	1000	-0.022
005	C	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	3200	-0.029
005	C	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	10000	0.009
005	C	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC		FINAL	-0.029

RAW DATA
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Lab_ID	Sample_Label	Rep_No	Start_Date	Stop_Date	Analysis_Date	No_Prewash	Prewash_Tech	Anal_Tech	MDL_Anal	Kd_Value_Source	Kd_Value
001	D	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	2 mg/L	320	-0.009
001	D	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	4 mg/L	1000	-0.019
001	D	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	20 mg/L	3200	0.058
001	D	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC	40 mg/L	10000	-0.009
001	D	1.1	2005-11-15	2005-11-21	2005-11-21	0	NONE	IC		FINAL	0.005
002	D	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	320	0.003
002	D	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	0.5 mg/L	1000	0.000
002	D	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	3200	0.006
002	D	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC	5 mg/L	10000	0.011
002	D	1.1	2005-11-01	2005-11-08	2005-11-10	0	NONE	IC		FINAL	0.005
003	D	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	0.011
003	D	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	0.007
003	D	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	0.010
003	D	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	-0.004
003	D	1.1	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	0.006
003	D	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	320	-0.005
003	D	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	5 mg/L	1000	0.018
003	D	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	3200	0.006
003	D	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR	50 mg/L	10000	0.020
003	D	1.2	2005-11-04	2005-11-10	2005-11-11	0	NONE	COLOUR		FINAL	0.010
004	D	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	320	-0.01
004	D	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	1000	-0.019
004	D	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	3200	0.0035
004	D	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR	0.5 mg/L	10000	0.0083
004	D	1.1	2005-11-16	2005-11-23	2005-11-23	0	NONE	TITRATOR		FINAL	-0.004
005	D	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	1 mg/L	320	-0.011
005	D	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	1 mg/L	1000	0.018
005	D	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	10 mg/L	3200	0.020
005	D	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC	10 mg/L	10000	-0.013
005	D	0.1	2005-11-03	2005-11-09	2005-11-09	1	OLD	IC		FINAL	0.004
005	D	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	320	-0.013
005	D	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	1 mg/L	1000	-0.030
005	D	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	3200	-0.071
005	D	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC	10 mg/L	10000	-0.030
005	D	1.1	2005-11-03	2005-11-09	2005-11-09	0	NONE	IC		FINAL	-0.036

RAW DATA
2005 KD Chloride Interlab Study

Table Key

Lab_ID = Participant laboratory's numeric identifier
Sample_Label = Sample identifier
Rep_No = Replicate number, where:

0.x =	the x replicate of a sample which was pre-extracted using original technique (i.e. KD-Cl Method version 2005-10-18).
1.x =	the x replicate of a sample which was not pre-extracted.
2.x =	the x replicate of a sample which was pre-extracted once using the modified technique outlined under ISSUE 1 of study report.
3.x =	the x replicate of a sample which was pre-extracted twice using the modified technique outlined under ISSUE 1 of study report.

Start_Date = Date Equilibration of Test Samples was commenced.
Stop_Date = Date Equilibration of Test Samples was ceased.
Analysis_Date = Date chloride analysis was carried out on extracts.
No_Prewash = Number of pre-extractions carried out on sample (see Rep_No)
Prewash_Tech = The type of pre-wash carried out (see Rep_No), where:

OLD =	Original technique (i.e. KD-Cl Method version 2005-10-18) used.
NONE =	Sample was not pre-extracted.
NEW =	Modified technique outlined under ISSUE 1 of study report was used.

Anal_Tech = Analytical technique used to analyze chloride, where

IC =	Ion Chromotograophy.
COLOR =	Colorimetric.
TITRATOR =	Titrimetric.
ISE =	Ion Selective Electrode.

MDL_Anal = Estimated Method detection limit of analytical technique employed correcting for dilution.
Kd_Value_Source = The concentration of the Spike Solution from which this KD value was derived, where:

FINAL =	Final data derived from all or a number of the Spike Solution resluts.

Kd_Value = Calculated KD Chloride value.

APPENDIX E
Draft KD Chloride Method

Determination of Site-Specific Soil-Water Partitioning Co-efficient (Kd) for Chloride (Prescriptive Method)

Parameter

Soil Adsorption Co-efficient (Kd) for Chloride.

Analytical Method

Calculation of Kd value for chloride requires the indirect measurement of chloride ion concentration that is retained on soil particles of a particular soil sample, as well as a direct measurement of the concentration of chloride ions in the interstitial water of the soil at equilibrium.

Chloride analysis is by any approved analytical method with sufficient precision and sensitivity to meet the Performance Requirements of the method.

Introduction

The BC MOE groundwater fate model, used to predict the movement of contaminants in subsurface soils via groundwater-mediated transport, requires an estimation of how a substance partitions between soil particles and the surrounding soil interstitial water (Soil Adsorption Coefficient: Kd). 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.

BC CSR Soil Matrix Standards (Schedule 5) for either drinking water or aquatic life protection are back-calculated soil concentrations estimated in part using a range of plausible Kd values. This method is intended to provide an estimate of actual site-specific Kd - Chloride values, which in some cases may provide some release from the Standards.

Kd is defined as the ratio of the contaminant concentration associated with the solid (µg substance/ g dry soil) to the contaminant concentration in the surrounding aqueous solution (µg substance / mL solution) when the system is at equilibrium. The units for Kd therefore are mL/g or similar.

$$Kd\ (mL/g) = A_i / C_i$$

Where:
A_i = adsorbate concentration on the solid at equilibrium (µg/g).
C_i = concentration of dissolved adsorbate remaining in solution at equilibrium (µg/mL).

The (draft) BC Matrix Numerical Soil Standards for Chloride utilize the following five categories for Kd Chloride: 0-0.05 mL/g, 0.05-0.10 mL/g, 0.10-0.15 mL/g, 0.15-0.20 mL/g, and ≥0.20 mL/g.

Chloride is often considered to be a conservative tracer of groundwater movement by hydrogeologists, and is often assumed to have a Kd value of 0.0 mL/g. There is some evidence, however, that viable mechanisms for the limited adsorption of chloride to soil particles exist. On a site-specific basis, therefore, Kd values in to range of 0.05 to 0.20 may be possible.

In the absence of a reasonable scientific knowledge base, it is assumed that coarse, low organics soils (e.g. sands and coarse glaciofluvial materials) 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, complex oxides) are likely to exhibit chloride Kd 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 Kd values that could approach 0.10 mL/g or higher.

It has long been recognized that the Kd 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 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).

Most soil particles are negatively charged, but some anions are also bound by, for example, metal oxides or hydroxides (MO or MOH). In particular, at relatively low pH, metal oxides can react as follows:

$MOH + H^+ \leftrightarrow MOH_2^+$
$MO + H^+ \leftrightarrow MOH^+$

Soil organic matter, including humic and fulvic substances, may also have functional groups, which form positive sites: e.g. $R\text{-}H_3^+$. These positive functional groups collectively contribute to an anion exchange capacity of soils, which can be experimentally measured. Overall, the anion exchange capacity of soils is likely to be much lower than the cation exchange capacity (i.e. – typically 5% or less of the CEC), but may nonetheless be closely related to chloride ion soil sorption tendency.

Because chloride ions have a very limited potential to adsorb to soil particles, the measurement of Kd for chloride presents challenges that are different from the vast majority of other inorganic or polar organic substances (primarily due to measurement uncertainty). This method was specifically developed within British Columbia for undertaking chloride Kd determinations.

For further information on this topic, please refer to "*Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulations*", June 2002, Doug A. Bright and Jan Addison (Report to BC WLAP, MOTH, BCBC, and CAPP), and to "*Determination of Site-Specific Soil-Water Partitioning Co-efficients (Kd) for Inorganic Ions and Polar Substances other than Chloride*" (BC Environmental Lab Manual).

Method Summary

Test samples are oven dried at low temperature, and 8 x 20g portions of the sample are equilibrated for 7 days with 20 mL volumes of deionized water or site groundwater containing sodium chloride at 320 mg/L, 1,000 mg/L, 3,200 mg/L, and 10,000 mg/L (alternative spike levels may be used where leachable native chloride for a sample exceeds 100 mg/L). Four Control Samples are prepared with the same spiking solutions, but without the test soil, to act as relative indicators of adsorption. Two Soil Blank Samples are prepared by mixing the soil with deionized water, to determine chloride background levels. Samples are centrifuged and filtered prior to analysis of the equilibrated aqueous fraction by an appropriately sensitive and precise analytical method for chloride (e.g. Ion Chromatography or Colourimetry). Adsorption co-efficient values are calculated for each of the 8 Spike Samples. Grubbs outliers are removed if necessary, and a final average Kd value is determined. A measurement uncertainty value is calculated for the Kd value to determine whether the Kd value is significantly different from zero.

In order to meet the requirements of the BC salt standards, this method must be able to accurately determine Kd values as low as 0.05 mL/g, which is extremely challenging. In order to help achieve this objective, the following key elements have been incorporated into this method:

- The ratio of dry soil weight to aqueous spike solution volume for test sample equilibrations has been maximized (defaulting to 1:1), as this ratio has a direct factor on the sensitivity of the Kd determination.

- Final Kd estimates are determined by averaging up to 8 (or more) independent Kd test measurements, performed at 3 - 4 different chloride concentrations.

- Control Spike solutions are used, such that relative adsorption values can be measured (as opposed to absolute comparisons with nominal target values).

A Measurement Uncertainty value is calculated for every Kd result determined by this method, which acts as a check on the relevance of the final result.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Kd (Chloride)	0.05 – 0.10 mL/g *	

Achievable MDLs for this method are sample dependent, and are related to measurement uncertainty calculations that must be conducted for each Kd test result.

Matrix

Soil samples, collected as being representative of subsurface soils along groundwater flow paths. Soil Samples must not be heavily contaminated with chloride, hydrocarbons, or other contaminants.

Interferences and Precautions

Obtaining representative and valid results is dependent on performing the following procedure exactly as written. Deviations from this method will likely result in erroneous data.

The primary difficulty with this method is related to analytical precision and measurement uncertainty. Under the stated conditions of this method, a 5% error in the measured ratio of 2 analytical results (Spike Sample Results versus Control Sample Results) translates to an error in Kd value equal to at least 0.05 mL/g.

Sample Handling and Preservation

No preservation is required.

Stability

Holding and Storage Time and Particulars: Soils may be stored refrigerated at 4°C, or (preferably) frozen at approximately –20°C, for up to 28 days.

Soil anion exchange capacity is highly pH dependent. Handling and storage conditions should not alter soil pH or anion exchange capacity.

Positively charged amino acids may also occur on soil organic matter. The prescribed storage conditions should limit microbial activity. Much of chloride ion exchange sites are expected to reside on longer chain, complex, and relatively non-labile organic matter (humics, fulvics), so effects of shorter term heterotrophic microbial activity during storage should be minimal.

Procedure

1. Selection of Soils for Analysis

It is the responsibility of the submitter to provide samples that adequately capture the range of site conditions of interest, including spatial and vertical variations in soil texture or other properties which may influence groundwater flow and groundwater quality. Typically, the soil samples will have originated in connection with the assessment and/or environmental risk assessment of salt contaminated sites (e.g. from produced water releases or road salt storage/release).

Chloride Kd determinations must be conducted on soil samples representative of the site (and strata within it) but which are not contaminated with salt ions or other contaminants.

2. Drying and Preparing the Test Soil

Dry the test soil completely by spreading it thinly in a large beaker, and placing it in a 60°C drying oven for at least 16 hours (or to constant weight). A minimum of 220 dry grams will be required for each test sample.

Disaggregate the soil and sieve through a 10 mesh sieve. Do not mechanically grind the

soil. Discard the > 10 mesh fraction.

3. Determination of Leachable Native Chloride in Test Soil

Weigh (20.0 ± 0.2) grams of the air-dried soil sample into a 50 mL glass or Teflon round-bottom centrifuge tube. Then add (20.0 ± 0.2) mL of deionized water to the centrifuge tube.

Check to ensure that 20 mL of water is sufficient to cover and saturate the soil. If necessary, add more water as required to permit the removal of approximately 1 - 2 mL of the aqueous solution for analysis of chloride ion concentration (after centrifuging) at the completion of the test. Record the soil weight used, and the amount of water added to the sample (to 3 significant figures). Cap tightly.

Agitate the slurry for 2 hours by mechanical shaking. Centrifuge and remove a small portion of the leachate for chloride analysis. Filter the leachate through a dry, non-contaminating 0.45 µm polycarbonate-membrane syringe filter that is known to be free of detectable chloride.

Test the leachate for chloride.

Note that this test is not applicable to samples that are contaminated with chloride (i.e. from anthropogenic chloride sources). If chloride levels in the test soil appear abnormally high, it is recommended that submitter of the test sample be contacted before proceeding. Non-contaminated samples that otherwise represent the site conditions should be obtained.

4. Optional: Testing of Site Groundwater for Chloride

The most representative Kd test results should be obtained when groundwater obtained from the site of the test sample is used as the spiking solution medium. If site groundwater is available and appropriate for use with this test, it is recommended that it be used. Otherwise, deionized water may be used. Note: Kd results using deionized water for the spiking solution are expected to be equal to or less than the Kd values that would be obtained using site groundwater.

If groundwater is to be used, approximately 300 – 500 mL will be required per test sample (more for samples with high a water holding capacity). The groundwater must be tested for chloride prior to use (ensure the required quantity is well mixed in a single container prior to testing).

Site groundwater can only be used to prepare spike solutions that require nominal concentrations that exceed the groundwater chloride concentration. If the groundwater chloride concentration is greater than the nominal concentration required for a particular spike solution, then deionized water must be used to prepare that spike solution.

5. Preparation of Spike Solutions

If the leachable native chloride concentration from Step 3 is less than or equal to 100 mg/L, then the default spike levels specified below should be used (2 soil spikes and 1 control will be conducted at each level). If the leachable native chloride concentration from Step 3 exceeds 100 mg/L, then the spike levels should be altered such that the lowest spike level is at least 2x the leachable native chloride concentration.

Examples of Suitable Spike Concentrations as a Function of Native [Chloride]

Native [Cl]	[NaCl] Spike 1	[NaCl] Spike 2	[NaCl] Spike 3	[NaCl] Spike 4
< 100 mg/L	2 x 320 mg/L	2 x 1,000 mg/L	2 x 3,200 mg/L	2 x 10,000 mg/L
100 – 300 mg/L	2 x 1,000 mg/L	3 x 3,200 mg/L	3 x 10,000 mg/L	-
500 mg/L	2 x 1,600 mg/L	2 x 3,200 mg/L	2 x 6,400 mg/L	2 x 12,800 mg/L

Note: For NaCl solutions, NaCl concentrations are 1.65 times Chloride concentrations as mg/L.

At least eight spikes are required, using at least 3 different spike concentrations, with no more than 3 spikes at the same level. Successive spike concentrations should increase by a constant factor of 2-4x. Examples are provided in the table above.

Prepare a sufficient volume of each spike solution for the test. For each test sample where the leachable native chloride concentration is <100 mg/L, prepare at least 100 mL each of four chloride spike solutions in deionized water at the following nominal sodium chloride concentrations: 320 mg/L, 1,000 mg/L, 3,200 mg/L, and 10,000 mg/L. These NaCl concentrations translate to chloride concentrations of 194 mg/L, 606 mg/L, 1,940 mg/L, and 6,060 mg/L. It is imperative that all spike solutions be thoroughly mixed prior to each use.

If site groundwater is used to prepare any of the solutions, the groundwater chloride concentration must be taken into account when preparing each spike solution.

Samples with high water holding capacity may require more than 100 mL of each spike solution.

6. Preparation of Spike Samples, Control Samples, and Soil Blanks.

Each Kd test requires 8 Spike Samples (using at least 3 different spike concentrations), 4 Control Samples, and 2 Soil Blanks.

Spike Samples: For each Spike Sample, weigh (20.0 ± 0.2) grams of air-dried soil sample into a 50 mL glass or Teflon round-bottom centrifuge tube.

Determine the spike solution:soil ratio that will be used for each test sample spike. Refer to the water:soil ratio that was used in Step 3 for the native chloride leachate step. A 1:1 ratio should be used if at all possible. If a 1:1 ratio is not sufficient, determine the minimum ratio that will permit the removal of approximately 1 - 2 mL of the aqueous solution for analysis of chloride ion concentration (after centrifuging) at the completion of the test.

Add the appropriate volume of the applicable spike solution to the dry test soil in the centrifuge tube. If possible, use the default amount of (20.0 ± 0.2) mL.

Check to ensure that the spike solution fully saturates the soil after it has been completely wetted. Record the exact soil weight used, and the exact amount of spike solution added to each sample (to 3 significant figures). Cap tightly. If the actual values used are within the stated default ranges (e.g. 20.0 ± 0.2 grams or mL), then the nominal values (20 g and 20 mL) may be used for Kd calculations.

> **Note:** As the spike volume : soil ratio increases beyond 1:1, the detection limit of the Kd test will increase proportionately!

Control Samples: Add (20.0 ± 0.2) mL of each spike solution to a 50 mL centrifuge tube. Control Samples are used as a relative reference point against which adsorption of chloride by test samples is measured. Cap tightly.

> **Note:** If multiple Kd tests are being performed, the same 4 Control Samples can be used for each sample. However, each test sample and its corresponding control spike **must** be prepared from the same batch of spike solution.

Soil Blanks: For each soil sample being tested, prepare 2 Soil Blanks. Soil Blanks are used to determine the amount of chloride contributed to the test solutions from the leaching of the soil. Cap tightly.

For each blank, weigh (20.0 ± 0.2) grams of air-dried soil sample into a 50 mL centrifuge tube. Then add (20.0 ± 0.2) mL of deionized water to the centrifuge tube.

7. Equilibration of Test Samples

All test samples (Spike Samples, Control Samples, and Soil Blanks) must be mixed either with a spatula or a mechanical shaker to ensure that the soil and spike solutions are well-mixed so that contact is maximized.

Allow all test samples to equilibrate at ambient temperature for 7 days. Store samples right-side up to prevent leaking.

8. Filtration of Test Samples

When equilibration is complete, mix all samples thoroughly (e.g. using a spatula or mechanical shaker) to ensure that a representative sub-sample is taken for analysis. Centrifuge all Spike Samples and Soil Blanks to permit removal of a portion of the aqueous layer for analysis.

Remove at least 1 - 2 mL (more if accessible) of each Spike Sample, Control Sample, and Soil Blank. Filter all samples (including Control Samples) through dry, non-contaminating 0.45 µm polycarbonate-membrane type syringe filters (pre-test filters for chloride contamination potential; if necessary, pre-clean and dry filters before use).

9. Analysis of Test Samples for Chloride

Analyze all test samples for chloride using an approved, highly precise analytical procedure. If the analytical procedure employed requires more than the 1-2 mL sample volume available, or if the concentrations of the test samples exceed the range of the technique, then dilutions can be performed before analysis. Any dilutions conducted must be highly accurate (e.g. < 1% error). If a Spike Sample is diluted, its corresponding Control Sample must be diluted identically.

Any chloride test method used for this procedure must have a detection limit (after accounting for dilutions) of no more than 1 mg/L in at least the lowest concentration test samples.

During instrumental analysis, each Spike Sample (for a given spike level) must be analyzed immediately before or after its associated Control Sample. If a set of Control Samples is being applied to more than one test sample, the Control Samples must be analyzed once alongside each test sample.

The following example analysis sequence meets these requirements:

A. Calibration Standards
B. Control Standard / LCS
1. Chloride Method Blank
2. Soil Blank (Sample X)
3. Spike Sample X (320 mg/L)
4. 320 mg/L Control Sample
5. Spike Sample X (1000 mg/L)
6. 1000 mg/L Control Sample
7. Spike Sample X (3200 mg/L)
8. Spike Sample X - Duplicate (3200 mg/L)
9. 3200 mg/L Control Sample
10. Spike Sample X (10000 mg/L)
11. 10000 mg/L Control Sample
12. Calibration Verification Standard
13. Soil Blank (Sample Y)
14. Spike Sample Y (320 mg/L)
15. ...

10. Calculation of Kd results

For each test sample, the following measured concentrations must first be determined:

SB = Average $[Chloride]_{(aq)}$ (measured) of Soil Blank samples (mg/L)
Spk_n = $[Chloride]_{(aq)}$ (measured) of Spike Sample level n (mg/L)
CS_n = $[Chloride]_{(aq)}$ (measured) of Control Sample level n (mg/L)

Other data required to calculate Kd includes the following:

SBVol = Volume of Deionized water added to Sample Blank (mL, normally 20)
SBWt = Weight of soil used for Soil Blank sample (g, normally 20)
$SpkVol_n$ = Volume of Level n Spike Solution added to Spike level n (mL, normally 20)
$SoilWt_{SPk,n}$ = Dry Weight of Soil used for Spike level n (g, normally 20)
$CS_{nom,n}$ = nominal chloride concentration of spike solution level n (mg/L)

For each test sample, first calculate the Adsorption Fraction (AF) value for each spike level, as follows. Adsorption Fraction is the fraction of the total chloride amount (mass) from the spike solution that was adsorbed to the soil after equilibration, expressed as a decimal fraction. AF is unitless:

$$\mathbf{AF_n = 1 - [(Spk_n - SB_{equiv}) / CS_n]}$$

where:

$$\mathbf{SB_{equiv} = SB * (SBVol / SpkVol_n) * (SoilWt_{spk,n} / SBWt)}$$

$\mathbf{SB_{equiv}}$ is the equivalent Soil Blank concentration that would be expected in the Spike sample due to chloride ions leaching from the sample itself. If the volumes and weights of the Soil Blank and the Spike sample are the same, then $\mathbf{SB_{equiv}}$ = SB. These equations assume that the amount of residual chloride adsorbed to the sample prior to spiking is small in comparison to the spike level. The adsorption fraction AF_n relates only to adsorption of chloride from the spiking solution. It is assumed that any chloride that would have leached from the unspiked soil sample (i.e. $\mathbf{SB_{equiv}}$) would not re-adsorb.

Note that the nominal concentrations of the spike solutions do not enter into this calculation (therefore, error in nominal concentrations does not translate to error in the measured Kd values).

Next, the Adsorption Fraction values must be converted to Adsorption Co-efficients (Kd values) as follows. This converts the amount fraction into a concentration ratio. Derivation of the formula to be used begins with the definition of Kd:

$$Kd\ (mL/g) = A_i / C_i$$

Where:
A_i = adsorbate concentration on the solid at equilibrium (mg/g)
C_i = concentration of dissolved adsorbate remaining in solution at equilibrium (mg/mL)

A_i and C_i may be calculated directly from the adsorption fraction AF_n and the nominal chloride concentration of the Control Sample and Spike Sample for each level. The A_i term represents what is sorbed to the soil mass (mg/g), calculated on the basis of mass loss from solution, divided by the soil mass in the container:

$$A_{i,n} = [AF_n\ (unitless)] * CS_{nom,n}\ (mg/L) * SpkVol_n\ (mL) * 0.001\ L/mL] \ / \ SoilWt_{Spk,n}\ (g)$$

$$C_{i,n} = [1 - AF_n\ (unitless)] * CS_{nom,n}\ (mg/L) * 0.001\ L/mL$$

Substituting the above equations for $A_{i,n}$ and $C_{i,n}$ into the Kd equation above leads to the following final equation for calculation of Kd_n. Use this equation to calculate Kd for each spike level:

$$\mathbf{Kd_n = [\, AF_n / (1 - AF_n) \,] * SpkVol_n\ (mL) / SoilWt_{Spk,n}\ (g)}$$

The units for Kd are mL/g. For each sample, Kd values are determined for each of the 3-4 spiking levels. Kd values for most samples should be near zero (typical results are expected to be in the 0.00 - 0.20 range). Although not meaningful, small negative Kd values may occur due to analytical variability.

Compute the average and standard deviation of the 8 Kd values (including any negative values obtained).

11. Outlier Checking and Calculation of Final Kd Value

If necessary, run the 8 or more Kd values for each test sample through a Grubbs outlier test using no greater than a 5% risk of false rejection. If justified, up to 2 statistical outliers may be removed by this process.

Determine the mean Kd value after removal of any outliers. Report the mean Kd result as the Kd value for the sample.

12. Determination of Measurement Uncertainty for Kd

Determine an estimated measurement uncertainty value for the mean Kd value as follows:

$$U(c) = (t_{n-1} \times s_n) / \sqrt{n}$$

Where:
U(c) = Expanded Measurement Uncertainty (minimum)
t_{n-1} = Two tailed students t value for 95% CI at n-1 degrees of freedom
s_n = The standard deviation of n final Kd results
n = The number of Kd replicates for a sample, after outlier removal

Compare the mean Kd value with the computed measurement uncertainty value. If the Kd value is less than or equal to the MU value, it should be reported as below detection limit, with the DL set equal to or greater than the calculated MU value.

13. BC MOE Reporting Requirements

All of the following results must be reported within the lab report for any test for Kd - Chloride that relates to compliance of the BC MOE Salt Standards:

- Report Kd results for all eight (or more) spikes, each reported to 3 decimal points (including any negative values obtained).
- Report the final mean Kd result, based on the above-described protocols, to 3 decimal points. Report the actual value obtained, even if negative (Note: negative Kd values are undefined, but can occur; large negative values indicate an unacceptably large degree of error within the test).
- Report the estimated Measurement Uncertainty value for the Kd result, as described in section 12.
- If any significant deviations were required from this method, these deviations must be reported.

It is strongly recommended that any sample tested for Kd chloride also be tested for Total Organic Carbon and Soil Texture, as these parameters may show correlations with Kd chloride values.

Performance Requirements

Precision Requirement (of Chloride Method): The analytical method selected for chloride should be sufficiently precise such that the RSD of within-batch sequential chloride measurements of standards or reference materials is less than 5%.

Accuracy Requirement (of Chloride Method): The analytical measurement for chloride should demonstrate recoveries in the range of 90% to 110% on aqueous standards or aqueous reference materials.

Sensitivity Requirement (of Chloride Method): The analytical method selected for chloride measurements must have a detection limit (after accounting for any necessary sample dilutions) of no more than 1 mg/L in the lowest concentration level test samples.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Chloride Method Blank	One per batch	< 2 mg/L
Kd Method Blank	One per batch (1 level)	Kd between -0.10 and 0.10
Chloride Control Std (LCS-Chloride)	One per batch	Within 10% of Target
Chloride Lab Duplicates	One instrumental duplicate per test sample.	5% RPD (based on measured Chloride in solution)
Kd Lab Duplicate	Optional	Not Specified
Laboratories should report qualified data when any of these DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.		

Chloride Method Blank: Required. Minimum one per Kd test batch. The Chloride Method Blank is prepared by adding 20 mL of deionized water directly to an empty centrifuge tube and carried through the entire process (including filtration steps and any dilution steps).

Chloride Lab Duplicates: Required (Instrumental duplicate only). Minimum one per Kd sample test.

Chloride Control Standard or LCS-Chloride: Required. One per batch. Acts as a second source check on calibration standard accuracy.

Kd Method Blank: Required. Minimum one per Kd test batch. A Kd Method Blank is a complete Kd test, conducted on a suitable negative control sample (Ottawa Sand, 20-30 mesh, e.g. Fisher Scientific S23-3). This inert material is should exhibit a Kd value of zero. To minimize the level of effort, a Kd Method Blank may be conducted using a single chloride concentration level. Using a single concentration level, the Kd Method Blank value should fall within the range of -0.10 to 0.10.

Kd Lab Duplicate: Recommended for crucial test samples. However, the test protocols already include 8 independent Kd measurements for each test sample. The difference between Kd Lab Duplicate results should ideally be less than 0.05 mL/g.

Note: "Soil Blanks" are not related to Kd Method Blanks or Chloride Method Blanks. Soil Blanks are used to determine the amount of chloride contributed to the equilibrated sample solutions by any given soil sample.

Prescribed Elements

This is not a performance based method. All steps must be performed as written.

As a minimum component of laboratory method validation, laboratories must conduct a full Kd Method Blank test (using all 4 concentration levels) on at least one inert solid matrix (e.g. Ottawa Sand), and must achieve a final Kd result of between -0.10 and 0.10. This demonstration of capability must be completed before using the method for environmental samples.

References

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/vol1/402-r-99-004a.pdf).

Revision History

February 14, 2006	Revised based on Round Robin study recommendations.
October 18, 2005	First draft as BC PBM & version used for validation Round Robin.