

DEVELOPMENT OF BC CSR ANALYTICAL METHOD FOR SOLUBLE BARIUM

PHASE 2: OPTIMIZATION AND RUGGEDNESS TESTING FOR SOLUBLE AND TOTAL BARIUM METHODS

June 5, 2007

Prepared for:

BC Upstream Petroleum Environmental Task Group,
Barite-Barium Issues Subgroup

By:

BCLQAAC BARITE TASK GROUP

Mark Hugdahl,
Chair, BCLQAAC Technical Subcommittee,
ALS Laboratory Group, Environmental Division,
Vancouver, BC

Darlene Lintott,
Bodycote / Norwest Labs,
Edmonton, Alberta

Dr. John Ashworth,
ALS Laboratory Group, Environmental Division,
Edmonton, Alberta

Miles Tindal,
Axiom Environmental,
Calgary, Alberta

Table Of Contents

1.0	INTRODUCTION.....	4
2.0	PHASE 2 OUTLINE AND OBJECTIVES.....	5
3.0	EXPERIMENTAL METHODOLOGY	7
3.1	PREPARATION OF TEST SOILS	7
3.2	PHASE 2A - CALCIUM CHLORIDE EXTRACTION METHOD	8
3.3	PHASE 2B - STRONG ACID AND TOTAL BARIUM TEST METHODS	9
3.3.1	US EPA 3050B	9
3.3.2	BC Strong Acid Leachable Metals (SALM).....	10
3.3.3	Fusion - X-Ray Fluorescence (Fusion-XRF)	11
3.4	PHASE 2B BARIUM METHOD SIDE STUDIES	11
2b-1.	Acid Volume to Soil Mass Ratios	12
2b-2.	Acid Strength	12
2b-3.	Digest Hold Time and Temperature	12
2b-4.	Effect of Final Dilution of Digest for ICP Analysis	12
2b-5.	Solubility of Barite in CaCl ₂ and Strong Acid.....	13
2b-5a.	Solubility of Barite in Calcium Chloride	13
2b-5b.	Maximum Recovery of Barium from Pure Barite in Strong Acid Digests	13
2b-6.	Sample Weight.....	14
2b-7.	Salt Concentrations in Soil.....	14
4.0	RESULTS AND DISCUSSION.....	15
4.1	PHASE 2A - OPTIMIZATION OF CALCIUM CHLORIDE EXTRACTION METHOD.....	15
4.3	BARIUM METHOD SIDE STUDIES.....	20
2b-1.	Acid Volume.....	20
2b-2.	Acid Strength	20
2b-3.	Digest Hold Time and Temperature	22
2b-4.	Effect of Final Dilution of Digest.....	23
2b-5.	Solubility of Barite in CaCl ₂ and Strong Acid.....	23
2b-5a.	Solubility of Barite in Calcium Chloride	23
2b-5b.	Maximum Recovery of Barium from Pure Barite in Strong Acid Digests	23
2b-6.	Sample Weight.....	23
2b-7.	Salt Concentrations in Soil.....	23
2b-7a.	BC Soluble Barium.....	23
2b-7b.	BC SALM Barium.....	23
2b-7c.	EPA 3050 Barium.....	23
5.0	RECOMMENDATIONS AND CONCLUSIONS	23
6.0	REFERENCES.....	23
	Appendix 1. Detailed Characterization of Background Soils.....	23
	Appendix 2. Phase 2a Results: Calcium Chloride/Total Barium Methods	23
	Appendix 3. Phase 2b Data Tables	23
	Appendix 4. Phase 2b Side Study Data Tables (mg/kg).....	23
	Appendix 5. Phase 2b-7SS Data Tables	49

List of Tables

Table 1. Primary Characteristics of Background Soils	8
Table 2. Measured Barium by BC Soluble Barium (1.0 M CaCl ₂) in Chloride and Sulfate Spiked Sand and Clay.....	23
Table 3. Measured Barium by BC SALM Total Barium in Chloride and Sulfate Spiked Sand and Clay.....	23
Table 4. Measured Barium by EPA 3050 Total Barium in Chloride and Sulfate Spiked Sand and Clay.....	23
Table 2a-1. Barium Chloride in Sand	23
Table 2a-2. Barium Chloride in Clay	23
Table 2a-3. Barium Sulfate in Sand	23
Table 2a-4. Barium Sulfate in Clay	23
Table 2b-1. Barium Sulfate in Sand	23
Table 2b-2. Barium Sulfate in Clay	23
Appendix 4. Phase 2b Side Study Data Tables	23
Table A5-1. Barite Solubility in CaCl ₂	23
Table A5-2. Chloride Spiked Sand.....	23
Table A5-3. Sulfate Spiked Sand	23
Table A5-4. Chloride Spiked Clay	23
Table A5-5. Sulfate Spiked Clay	23

List of Figures

Figure 1. Recovery of Spiked Barium Using Total Ba Methods	16
Figure 2. Calcium Chloride Extractable Barium	17
Figure 3. Calcium Chloride Extractable Barium	18
Figure 4. Phase 2b Recovery of Spiked Barium Using Total Barium Methods.....	19
Figure 5. Barium Recovery in Sulfate Spiked Soils with EPA 3050B.....	21
Figure 6. Barium Recovery in Sulfate Spiked Soils with BC SALM	22
Figure 7. Effect of Hold Time and Temperature of Digest on Barium Recovery	23
Figure 8. Barite Solubility in Calcium Chloride Extractions	23
Figure 9. BC Soluble Barium in Chloride and Barium Spiked Sand.....	23
Figure 10. BC Soluble Barium in Sulfate and Barium Spiked Sand.....	23
Figure 11. BC Soluble Barium in Chloride and Barium Spiked Clay	23
Figure 12. BC Soluble Barium in Sulfate and Barium Spiked Clay	23
Figure 13. BC SALM Barium in Chloride and Barium Spiked Sand.....	23
Figure 14. BC SALM Barium in Sulfate and Barium Spiked Sand	23
Figure 15. BC SALM Barium in Chloride and Barium Spiked Clay	23
Figure 16. BC SALM Barium in Sulfate and Barium Spiked Clay	23
Figure 17. EPA 3050B Barium in Chloride and Barium Spiked Sand	23
Figure 18. EPA 3050B Barium in Sulfate and Barium Spiked Sand	23
Figure 19. EPA 3050B Barium in Chloride and Barium Spiked Clay	23
Figure 20. EPA 3050B Barium in Sulfate and Barium Spiked Clay	23

1.0 INTRODUCTION

The British Columbia Ministry of Environment is currently developing matrix numerical soil standards for barium. Barium soil standards will impact the operations of the BC oil and gas sector, because barite (barium sulfate) is regularly used as a weighting agent for drilling muds. The BC Upstream Petroleum Environmental Task Group – Barite Barium Issues Committee was formed to provide an inter-governmental and industry expert advisory body for collaboration on scientific and technical aspects needed to support the development of barium standards. Government representation on the Barite Barium Issues Committee includes BC MOE, the BC Oil and Gas Commission, and the BC Ministry of Energy, Mines, and Petroleum. Axiom Environmental and the Technical Sub-Committee of the British Columbia Laboratory Quality Assurance Advisory Committee (BCLQAAC) are represented on the committee in a scientific advisory capacity.

Because of the extremely low aqueous solubility and low toxicity of barite, the Barite-Barium Issues Committee is recommending that BC develop and endorse an analytical method for *soluble* barium for use by the Oil and Gas sector of BC at sites where detailed documentary evidence of barite usage exists. An appropriate analytical method for soluble barium should generate relatively low results for barite-barium in soils, but quantitative or near-quantitative results for more toxic forms of barium with higher aqueous solubilities and mobilities than barite (e.g. barium chloride, barium acetate), unless they are strongly sequestered onto soil cation exchange sites.

Prior to endorsing the regulation of soluble barium, BC MOE requires that development and validation of an appropriate method be conducted to ensure that it will be environmentally relevant and sufficiently protective for soluble forms of barium where they may be present.

The BCLQAAC Technical Subcommittee was tasked with the development and validation of a suitable analytical method for the determination of soluble barium in soils and solids. A task group was formed for this purpose, consisting of Mark Hugdahl (Chair, BCLQAAC Technical Sub-committee, ALS Laboratory Group), Darlene Lintott (Bodycote/ Norwest Labs), and Dr. John Ashworth (ALS Laboratory Group). Miles Tindal (Axiom Environmental) also participated in an advisory capacity.

The BC CSR soluble barium method development project is being conducted in three stages:

- Phase 1: Evaluation of Viable Soluble Barium Analytical Methods
- Phase 2: Optimization and Ruggedness Testing of Analytical Method for Soluble Barium
- Phase 3: Interlaboratory Testing of Analytical Method for Soluble Barium

Phase 1 investigations assessed various candidate soluble barium methods for their efficacy and recovery when applied to barite impacted soils of various textures. These investigations established the primary candidate for a soluble barium method as a Calcium Chloride extraction method. This method is based on the calcium chloride extraction method that is prescribed by Alberta Environment for their regulation of soluble barium. Recommendations for further work identified by the Barite-Barium

Issues Committee and the BCLQAAC Barite Task Group included evaluating soluble barium recoveries with the selected method using coarse textured soils with higher concentrations of barite (as would actually be encountered at drilling waste sites), to determine whether there is an upper ceiling for soluble barium by these techniques, and what it may be. The Phase 1 report also recommended that any optimized method should also be more extensively evaluated with more soluble forms of barium than barite (e.g. barium chloride), which would likely be necessary to establish a CSR standard for soluble barium by the method.

Total barium methods were also evaluated in Phase 1 work. Results suggested that there is likely an upper limit of barite that can be measured using acid digestion methods such as the BCSALM or EPA 3050, and that this limit may have an impact on whether an acid digest method could be used to accurately characterize the true total barium concentration at a barite site. It was also established that small differences in method procedures can have a strong impact on barium recovery from soil. The use of a numeric regulatory standard for total barium in soil demands that laboratory results are capable of capturing consistent, replicable soil recoveries of barium that represent true soil concentrations, over a range of concentrations which may occur at typical drilling waste sites.

The recommended course of action for further investigations included examining the correlation of strong acid digestion barium recoveries versus true total barium concentrations, and evaluating the impact of procedural modifications to total barium techniques. Variables suggested for consideration included digestion temperatures, times, acid:solid ratios, and other potentially significant method variables.

This report documents Phase 2 of the project.

2.0 PHASE 2 OUTLINE AND OBJECTIVES

Phase 2 of the project was divided into 2 components:

- 2a. Optimization of Calcium Chloride Extraction Method for Soluble Barium
- 2b. Detailed Evaluation of Methods for Total Barium.

The primary objective of the first component of the study was to refine the Calcium Chloride extraction method to optimize its effectiveness at distinguishing between soluble and insoluble barium in two contrasting soil textures. It is important to note that the intent of a soluble barium method is to be able to discriminate between soluble and insoluble forms of barium. Thus an ideal method for soluble barium will achieve quantitative or near quantitative recovery of soluble and mobile forms of barium, with a much lower recovery of barite barium.

The candidate soluble barium method was established in Phase 1 and was based on the Alberta Environment Barite Guidelines calcium chloride extraction method. The intended principle behind the AENV soluble barium method is that an increased concentration of barium in the extraction solution occurs because barium cations that are sorbed to the soil can be solubilized when excess calcium ions exchange with barium (and other cations) on the cation exchange sites of clay particles. The cation exchange mechanism should have minimal effect on insoluble barite salts, which should not

interact with cation exchange sites because they are uncharged (unless they become solubilized).

It was recognized from Phase 1 work investigations that the concentration of calcium may increase the recoveries of soluble barium from soils with a higher cation exchange potential. This work was continued in this phase of the study by investigating the impact of increasing the calcium chloride concentration in the extraction solvent on several concentrations of barium spiked soils.

The Phase 2a study consisted of a laboratory evaluation of the proposed soluble barium calcium chloride extraction method using differing strengths of extraction solvent and two types of barium spiked field soils. Total barium methods were also included for reference. After completion of Phase 1 studies, the barite subcommittee decided to establish the solvent:soil ratio at 10:1, which is the ratio used in the Alberta Environment method for soluble barium.

The Phase 2a study design was as follows:

- 6 analytical methods:
 - Extraction using CaCl_2 at ionic strengths of 0.1, 0.5 and 1.0 M
 - Total barium methods EPA 3050, BC SALM and fusion-XRF
- 2 soil types: sandy soil and clay soil
- 2 spiked barium species: insoluble barium sulfate and soluble barium chloride
- 4 spiked barium concentrations; 0, 2000, 10000 and 50000 mg/kg as Ba
- 2 replicates per treatment

An additional study component in Phase 2a included evaluating the impact of extraction hold time and temperature on soluble barium recovery. This side study was included to determine if these variables would be significant as a source of interlab variability and/or cause for reduced recovery, and therefore would require prescribed procedures in the recommended method.

The second component of the Phase 2 study consisted of a laboratory evaluation of total barium methods, including the acid digest methods EPA 3050B and BC SALM. Fusion-XRF was also included for comparison. The objective of Phase 2b was to determine the upper practical concentration (if any) at which BC SALM and EPA 3050B can effectively measure total barium concentration in barite samples by comparing BC SALM, EPA 3050B and fusion-XRF analyses over a range of spiked barite concentrations.

The Phase 2b experimental design agreed to by the committee included:

- 3 analytical methods:
 - Total barium acid digest methods BC SALM and EPA 3050,
 - Fusion-XRF
- 2 soil types: sandy soil and clay soil
- 1 spiked barium species: barium sulfate
- 7 spiked barium concentrations; 0, 100, 300, 1000, 3000, 10000, and 100000 mg/kg as Ba
- 2 replicates per treatment

Acid digest methods were performed as prescribed by the reference method, using mandatory requirements, or minimum requirements where performance based procedures were prescribed.

Additional side studies were conducted in Phase 2b to investigate the significance of several key variables associated with the acid digest methods on the recovery of barium from spiked soils. It had been established in Phase 1 that small changes in procedures could have an impact on measured barium concentrations. The degree of impact on barium recovery from each of these variables needed to be resolved in order to establish potential for interlaboratory variability, and to determine whether additional mandatory elements were required in future analytical method protocols.

The Phase 2b key variables investigated for their effects on barium recovery from two spiked soils of differing textures using EPA 3050B and BC SALM included:

- 2b-1. Acid Volume Ratios
- 2b-2. Acid Strength
- 2b-3. Digest Hold Time and Temperature
- 2b-4. Effect of Final Dilution of Digest
- 2b-5. Solubility of Barite in CaCl_2 and Strong Acid
- 2b-6. Sample Weight
- 2b-7. Salt Concentrations in Soil

3.0 EXPERIMENTAL METHODOLOGY

3.1 PREPARATION OF TEST SOILS

Two barite-spiked background reference soils were prepared for analysis for Phase 2a and 2b investigations. The background reference soils included sandy soil ("sand") and clay soil ("clay"). These soils were provided by Husky and were collected from sites as background samples and have likely not been exposed to industrial contaminants. These same soils were also used for investigations completed in Phase 1. The soils were dried and ground, then spiked with drilling-mud grade barite or laboratory grade barium chloride dihydrate at the required concentrations (spiked barium concentrations were in addition to background barium concentrations).

These soils were characterized extensively for physical and chemical parameters (presented in Appendix 1). Key characteristics of the two soils that are most pertinent to barium methods are provided in Table 1.

Table 1. Primary Characteristics of Background Soils

Parameter Name	Units	Sand	Clay
Sand	%	96.4	14.4
Silt	%	1.2	26.2
Clay	%	2.4	59.4
CEC	meq/100g	1.3	24.6
Barium (EPA 3050B)	mg/kg	64	333
Extractable Barium	mg/kg	9.4	1.1
Sulfate-S	mg/kg	3.4	1,120

The soils were prepared by drying at 30°C, then disaggregating to <2 mm (but were not pulverized or sieved). Soils were spiked with a supply of barite (Canamara United Supply, provided by Newalta) that is commonly used in drilling muds. For Phase 2a, soils were also spiked with laboratory grade barium chloride dihydrate, added directly to the dry background soils to achieve the required target concentrations (mg/kg as barium) above background barium levels. The barium background levels in these soils are given in Table 1. The spiked dry soils were mixed using end-over-end rotation overnight. The soils were then hydrated with deionized water to achieve a saturated paste, in order to allow for soil chemical and physical interactions to occur. The hydrated soils were allowed to equilibrate for 24 hours, then were dried at 30°C. The dried soils were disaggregated to pass through a 2mm sieve, then separated into two replicate samples per treatment. Treated soils were stored at room temperature.

3.2 PHASE 2A - CALCIUM CHLORIDE EXTRACTION METHOD

The Alberta Environment extraction methodology for soluble barium in soils may be summarized as follows. The sample is prepared by air drying and sieving to <2 mm. 5 g of prepared sample is added to 50 mL of 0.1 M calcium chloride solution, and is agitated for 2 hr on a platform shaker or end-over-end rotator. The extract is filtered to yield a clear filtrate, ready for analysis. After appropriate dilution, samples are analyzed for barium by ICP.

Barium chloride and barium sulfate spiked sand and clay were extracted using the Alberta Environment soluble barium method, with modified calcium chloride concentrations of 0.1, 0.5 and 1.0 M. One of each replicate of each treatment described included in the Phase 2a study design was analyzed by this same extraction method by Bodycote/Norwest Labs and ALS-Edmonton.

As a side study, the impact of hold time and temperature on barium recovery by the calcium chloride extract was examined by extraction of selected samples of barium sulfate and barium chloride spiked sand and clay, using 0.1 M calcium chloride. Each extract was divided into 5 aliquots. One was analyzed the same day the extraction was performed. Two of the aliquots were stored at room temperature, then analyzed on day 3 and 7 after extraction. The remaining two aliquots were refrigerated (4°C) and analyzed for barium seven days after extraction.

Total barium methods BC SALM and EPA 3050B were analyzed on Phase 2a samples by NWL using mandatory elements of the respective procedures. Fusion-XRF analysis was performed on the same samples by ALS-Chemex. These methods are described in sections 3.3.

3.3 PHASE 2B - STRONG ACID AND TOTAL BARIUM TEST METHODS

Three methods for measuring total or strong acid extractable barium were included in this study. The US EPA 3050B Method is a strong acid digestion method, followed by ICP analysis. It is one of the most commonly-employed digestion methods in North America for the analysis of metals in environmental soil samples. The BC SALM method is another strong acid digestion technique, and is used specifically for analysis of “total” metals in soils under the BC Contaminated Sites Regulations as directed by the Ministry of the Environment. Fusion, or “whole rock analysis” is a dissolution technique commonly employed for geochemical analysis. It is not normally applied for environmental analysis, because constituents of rock matrices are not considered environmentally available. Fusion-X-Ray Fluorescence (Fusion-XRF) is an analytical method that combines the fusion dissolution technique with XRF quantitation, resulting in a total metals assay with an extremely high effective analytical concentration range for barium and other major compositional elements. Both Fusion-ICP and Fusion-XRF are considered likely to achieve true estimates of total barium in soils, including highly bound or complexed barium species. Fusion-ICP was not included in this study due to cost and time constraints, but is expected to achieve similar recovery to the fusion-XRF method.

These tests were included to give a true measure of the total barium in test samples, and to allow an examination of the limitations of each of the strong acid methods for measuring high concentrations of barite barium in soil.

3.3.1 US EPA 3050B

Modified versions of the US EPA 3050B method were used by Norwest/Bodycote Edmonton (NWL) and ALS Edmonton (ALS-EDM) for total barium analysis. Samples are normally dried, disaggregated (e.g. by flail grinder), and sieved prior to digestion, with the >2mm fraction discarded (spiked samples in this study were not sieved).

Soil sub-samples are digested with concentrated nitric acid, with the addition of hydrogen peroxide. Neither NWL nor ALS-EDM used hydrochloric acid in this digestion, which is an option within the 3050B method that might also be expected to influence recoveries. Exact weight and digestion volume requirements are not prescribed by the 3050B method. For barite analyses, these variables may result in significant differences among laboratories. Digestion times and temperatures varied slightly between the two labs.

NWL EPA 3050B method used for the Phase 2 studies is described as follows:

- A 0.5 g soil sample is wetted with 10 mL of deionized water
- 10 mL of concentrated nitric acid is added to soil samples
- The acid:soil mixtures are digested at a hot block temperature of 120°C for 3 hours

- 6 mL of 30% hydrogen peroxide is added to soils after cooling
- An additional 5 mL of nitric acid is added, and samples are digested for an additional 15 minutes
- Digests are centrifuged to clarify, then brought to a final volume of 50 mL for analysis
- Further dilutions with deionized water are completed prior to analysis by ICP-OES or ICP-MS

3.3.2 BC Strong Acid Leachable Metals (SALM)

The BC SALM method is a performance-based method. Reference conditions are specified, and known critical elements are prescribed, but labs may otherwise make changes to the method where equivalence is demonstrated. However, the effects of changes to digestion variables on recoveries of barite may be more pronounced than on typical soil samples.

The BC SALM reference method specifies digestion for 2 hours at 90+/-5°C using a 1:1 ratio of nitric and hydrochloric acids, with at least 5mL of concentrated 1:1 HCl:HNO₃ acid mixture per gram of sample. Digestion time and temperature are not prescribed elements of the method, and may be varied if equivalence is demonstrated. Digests are typically diluted to a final volume of 50 mL prior to analysis by ICP for barium and other metals.

For this study, NWL used a performance-based modification of the BC SALM method, which followed the prescribed mandatory elements of the BC SALM. The procedure used for this study is described as follows:

- 1.00 g of dry sample
- 2.5 mL of nitric acid and 2.5 mL of HCL. (BC MOE prescribed method mandates a minimum acid to sample ratio must be 5 mL per 1 g of dry sample).
- Swirl the sample to mix, allow to sit at room temperature for at least 1 hour before digesting.
- Bring sample to 50 mL with deionized water (performance based modification).
- Digest sample for 2 hours \pm 15 minutes at 90 \pm 5°C.
- Dilute the sample to final volume of 50 mL (not prescribed)
- Centrifuge or filter the digestate within 4 h of dilution
- Further dilutions with deionized water are completed prior to analysis by ICP-OES or ICP-MS

The reference conditions of the BC SALM method do not specify dilution of the acid prior to digestion, but some labs employ this technique to prevent evaporation to dryness (the BC MOE method states as a mandatory element that samples must not be allowed to dry out). This change essentially alters the acid strength of the digest solution from 100% to 10%, although the concentration will increase as excess water evaporates. Acid strength used during digestion is a performance based variable. The impact of this difference is addressed in study 2b-2.

3.3.3 Fusion - X-Ray Fluorescence (Fusion-XRF)

ALS Chemex (North Vancouver, BC) conducted analysis of the test soils for total barium by Fusion X-Ray Fluorescence (XRF). In this method, the solid sample is first digested using the metaborate fusion dissolution technique. Barium analysis is then conducted by XRF.

In XRF, a homogeneous sub-sample of either a pulverized and pelletized soil, or in this case, of a fusion digest, is irradiated with x-rays. When an atom absorbs these x-rays, low energy electrons may be dislodged from the innermost shells of the atom, creating vacancies which are then filled by electrons from higher energy outer electron shells. This transition radiates energy in the form of x-rays with wavelengths that are characteristic of the given atom. Measurement of the intensity of the x-ray fluorescence emitted at specific wavelengths can be used to quantify the concentration of the atom in the sub-sample.

EPA SW-846 Method 6200 is one official reference method for the XRF technique. Method 6200 describes a portable screening procedure for field quantitation of selected metals in soils, including barium. However, field application of XRF may be prone to inaccuracies and interferences, and has a limited upper concentration range.

Laboratory applications of the method in combination with the fusion dissolution technique do not suffer from inhomogeneity problems, and can have a range of up to at least 50% barium.

3.4 PHASE 2B BARIUM METHOD SIDE STUDIES.

Phase 2b Acid Digest Method Side Studies were conducted by NWL using the exact BC SALM and EPA 3050B methods described above and used for Phase 2a and 2b primary investigations. However, key variables were manipulated to examine significance on barium recovery from treated soils. Two calcium chloride extraction side studies were also included. The objectives and experimental methods for the barium method side studies are described below:

2b-1. Acid Volume to Soil Mass Ratios

The objective of this side study is to determine if the acid volume used during digestion has an impact on barium recovery from barium sulfate spiked soils.

- BC SALM acid volume doubled to 5 mL nitric acid and 5 mL HCl (keeping soil mass constant). Taking the pre-digestion dilution step into consideration, this essentially doubled the initial acid concentration from 10% to 20%.
- EPA 3050B acid volume doubled to 20 mL HNO₃ (keeping soil mass constant)

Thus, this side study investigated the effect of doubling the acid to soil ratio.

2b-2. Acid Strength

The objective of this side study was to determine if acid strength used during digestion has an impact on barium test result. Both acid digest methods used in

Phase 2a and 2b by NWL use concentrated acids, which are diluted with deionized water to prevent overheating and drying out of the sample. The BC SALM method used elsewhere in the Phase 2 studies added 50 mL deionized water prior to digestion, and the EPA 3050B method added 10 mL of deionized water prior to addition of acid. This side study examines the impact of addition of water during digestion, which reduces acid strength. This may reduce liberation of barium from cation exchange sites and insoluble salts due to reduced acid strength. However, barium solubility may be increased due to the greater volume of extracting solution present.

- For the Phase 2b-2 studies, both acid digest methods used only the required soil and acid volumes. No further addition of water was added to digestion tubes until after heating, where final sample volumes were brought to 50 mL.

2b-3. Digest Hold Time and Temperature

The objective of this side study was to determine if extracted barium concentrations would be reduced if the sample digest was held at either room temperature or was refrigerated for a period of time prior to analysis by ICP. For each digest generated in 2b-2, the final 50 mL volume was divided into 5 aliquots. One aliquot was analyzed within 24 hours (results of 2b-2). Two aliquots were stored at room temperature and analyzed at 3 and 7 days, respectively, diluted to within instrumental linear range, then analyzed by ICP. The other two aliquots were stored under refrigeration (approximately 4°C) for 3 and 7 days, prior to final dilution and analysis.

2b-4. Effect of Final Dilution of Digest for ICP Analysis

The objective of this side study was to determine if the final dilution rate of the acid digest for ICP analysis would have an impact on the final test result. The sample digest solution must undergo further dilution to bring the expected barium concentration to within the linear range of the analytical instrument. This dilution rate is sample specific as well as instrument specific, and therefore, may vary greatly within and between labs for a given barium concentration. Barium recovery in solution will depend in part on the solubility of the barium salts in question (e.g., barium sulfate, nitrate or carbonate). Increased dilution prior to analysis at a given concentration may result in greater barium recovery due to increased solubility of barium salts.

Soils spiked with barium sulfate at a concentration of 3000 mg/kg, were digested and diluted to 50 mL prior to analysis. At the time of analysis, aliquots of each digest were further diluted to 50 mL, 100 mL and 200 mL. These dilution rates maintained the barium concentration in solution to within the linear range of the instrument, but allowed for comparison of dilution rates.

2b-5. Solubility of Barite in CaCl₂ and Strong Acid

2b-5a. Solubility of Barite in Calcium Chloride

The solubility of barium sulfate (barite) is a primary controlling variable for barium detected by the soluble (i.e., calcium chloride extract) or acid digest methods. Results from Phase 1 and 2 work clearly demonstrate that increased soluble barium

can be detected in a range of soils using a higher strength calcium chloride extraction solution. However, it wasn't apparent if this finding was caused by a solubilization of barium sulfate, or was a result primarily from barium and calcium exchange at positively charged clay sites. Therefore, this "side study" investigated the effect of increasing calcium chloride (CaCl_2) molar concentration on barium sulfate solubility.

Laboratory grade barium sulfate as solid material was weighed into Erlenmeyer flasks, and extracted with 0.1 M CaCl_2 and 1.0 M CaCl_2 , using the AENV Extractable and BC Soluble Barium Methods (10:1 solvent to solid ratio, 2 hour extraction). The barium recovered (in units of mg/kg) was calculated based on the barium added to the flask (i.e., nominal concentration), and including the weight of soil that would be added for a soil test (as if there were 5 g of inert material present in addition to the pure barite solid).

2b-5b. Maximum Recovery of Barium from Pure Barite in Strong Acid Digests

The objective of this study was to determine if there is a maximum concentration of barium that could be recovered from pure barite, without the impact of soil physical and chemical influence. The key constraint variable would therefore be barium sulfate solubility in strong acid under specified conditions. Barite product was weighed directly into digestion tubes, without any additional material added. Calculations of recovery were based on the mg/kg barium concentration if the same amount of barium sulfate was present in a corresponding "inert" soil weight which would normally be digested.

2b-6. Sample Weight

The objective of this study was to determine if the sample amount that undergoes digestion by EPA 3050B and BC SALM has an impact on the final barium concentration determined. Potentially, the smaller sample volume may reduce sulfate concentrations present in the digest mix, and therefore, reduce concentrations of insoluble barium sulfate. It may also be impacted by barium nitrate solubility. Therefore, expected outcome is increased recovery of barium with lower amounts of soil that are digested. This variable should be similar in outcome to the results of 2b-2 for Acid Volume.

Barium sulfate spiked soils were digested using the same techniques for EPA 3050B and BC SALM, however, only a 0.1 g soil weight was digested. Thus, this side study investigated the effect of increasing the acid to soil ratio by a factor of 5.

2b-7. Salt Concentrations in Soil

Drilling waste disposal sites and areas impacted by produced water spills may be associated with high levels of salinity. A survey of 390 freshwater gel-chem drilling mud solids demonstrated an average chloride concentration of 1,115 mg/L, ranging as high as 45,400 mg/L, and with a mean and maximum electrical conductivity (EC) of 8.5 and 98 dS/m, respectively (Macyk et al 1992). In addition, relatively high sulfate concentrations can occur naturally in some soils (e. g. Solonchic soils), and can be as high as 10,000 mg/kg (as sulfate), and occasionally higher. Formation of

insoluble barium sulfate during soil preparation, digestion and analysis from excessive sulfate concentrations may reduce the recovery of soluble barium for both total acid methods and soluble barium extractions. Alternatively, high chloride concentrations may potentially increase the mobility of soluble barium in soil. Alternatively, since there is evidence in the literature that barite aqueous solubilities increase with increasing NaCl concentrations (Kuhn et al 1995, Templeton 1960), high chloride concentrations could potentially increase levels of soluble barium in soil. Increased calcium concentrations may increase concentration of soluble (free) barium in soils where cation exchange is a significant controlling variable. Accordingly, the objective of this study was to examine the impact of a range of soil sulfate and chloride concentrations on the recovery of total and free barium from soil using a variety of analytical methods.

Magnesium chloride and magnesium sulfate were selected to be used in the experiment as the salts added (spiked) to the soil, rather than other possible salt species such as calcium salts. It was thought that calcium salts could potentially confound the study interpretation due to the similar behaviors of barium and calcium with charged clay sites, and could therefore result in difficulty in isolating the effects caused purely by the anion pair in terms of the cation-clay interactions.

Sand and clay-textured soils were spiked with laboratory grade magnesium sulfate or magnesium chloride at concentrations of 1,000, 3,000, 10,000 and 30,000 mg/kg as the sulfate or chloride ion. Soils were homogenized by end-over-end tumbling overnight, and then each was split into 4 aliquots. The salt-amended soils were then spiked with barite at concentrations of 1,000, 3,000 and 10,000 mg/kg as barite-barium. The soils were hydrated to a saturated paste and allowed to equilibrate for 24 hours. The treated soils were then dried and disaggregated. The resulting experimental design comprised 40 samples for each of: 1) chloride in sand; 2) sulfate in sand, 3) chloride in clay; and, 4) sulfate in clay. Each of the resultant 160 test samples were each then individually extracted and analyzed using the draft BC 1.0 M CaCl₂ soluble barium extraction method, as well as the BC SALM method (Version 1.0) and the EPA 3050B strong acid digest performance-based method for total barium.

4.0 RESULTS AND DISCUSSION

4.1 PHASE 2A - OPTIMIZATION OF CALCIUM CHLORIDE EXTRACTION METHOD

Analytical results for Phase 2a calcium chloride extractions, strong acid and total barium methods are provided in Appendix 2, Tables 2a-1 to 2a-4. Percent recoveries were calculated for all methods by including the recovery of barium in the unspiked control soils (0 mg/kg Ba) using that particular method, as well as the nominal spiked barium concentration.

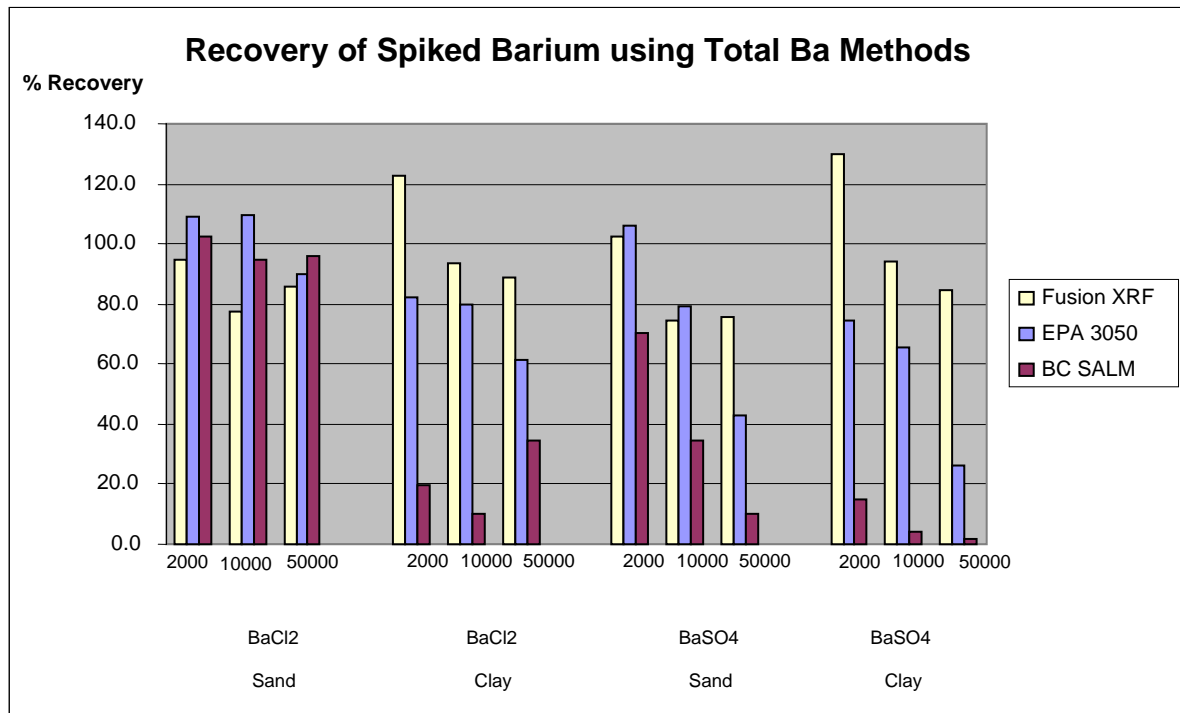
Recovery of spiked barium using total barium methods for Phase 2a are presented in Figure 1.0. Fusion-XRF was clearly the most aggressive method, recovering all barium present in both sand and clay spiked with either barium chloride or barium sulfate (within

experimental error). Recoveries ranged from 76 to 130% of barium spiked to soil. Both acid digest methods were able to capture all of the barium spiked as soluble barium chloride to sand. As expected, the low sulfate concentration and low cation exchange capacity of sand allowed barium to remain soluble and available.

The EPA 3050B acid digest method was able to capture barium from barium chloride spiked clay at 80% recovery or better, up to the 10,000 mg/kg treatment. Recovery of barium was reduced to 61% in the highest treatment, likely due to reaching the limit of solubility of barium salts. Similarly, recoveries were reduced in the 50,000 mg/kg treatment to 43 and 26% respectively, in barium sulfate spiked sand and clay.

The BC SALM method was clearly far weaker than the 3050B digestion in terms of barium recovery. Recoveries were substantially lower than the EPA method for both barium chloride and barium sulfate spiked sand and clay. Recovery of barium from barium sulfate spiked clay was only 15% in the 2000 mg/kg treatment for barium sulfate spiked clay, in contrast to the 75% recovery demonstrated by the EPA 3050B method for the same treatment. It appears that the BC SALM method is only capable of solubilizing barium sulfate to a relatively low concentration, as demonstrated by the 70% recovery of barium in the 2,000 mg/kg barium sulfate spiked sand treatment, compared to a 35% recovery in the corresponding 10,000 mg/kg treatment. Note that Study 2b-2 indicated that in the absence of the pre-digestion dilution step applied in this study, barium results were similar or even lower.

Figure 1. Recovery of Spiked Barium Using Total Ba Methods

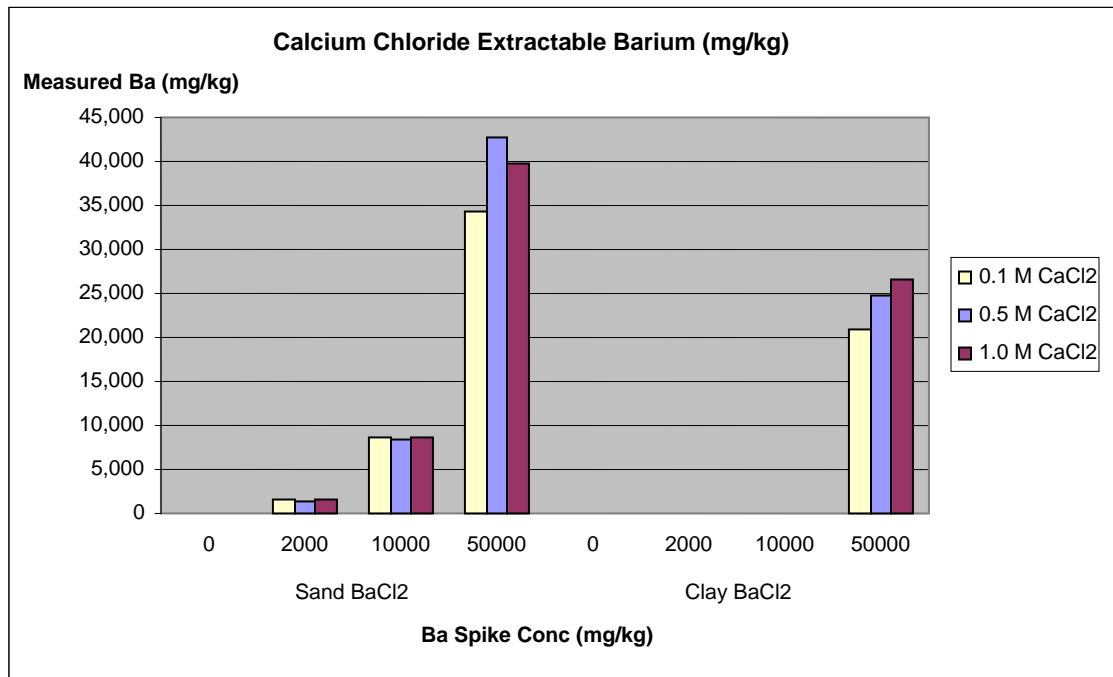


The results of the Phase 2a calcium chloride extraction of barium spiked soils are presented in tables 2a-1 to 2a-4 in Appendix 1. Barium chloride spiked sand and clay results are pictured in Figure 2. It would be expected that most of the barium chloride spiked to sand would remain as soluble and available barium. The calcium chloride

method was able to extract all or most barium present in this sand, for all treatments tested. Recoveries ranged from 68% to 102% for all extraction strengths. Therefore, it is clear that both the Alberta Environment method (0.1 M calcium chloride) and the candidate 1.0 M method perform as required in that all soluble and available barium is detected.

Available barium in clay spiked with barium chloride would be expected to have reduced concentrations, as sulfate salts present in the clay sample and the relatively high cation exchange capacity may immobilize the barium. This is also demonstrated in Figure 2 where barium concentrations in all calcium chloride strengths are reduced to near background concentrations up to 10,000 mg/kg barium spike. Somewhere between 10,000 and 50,000 mg/kg, the sulfate and CEC become saturated, and excess barium is extracted by all three calcium chloride extraction methods. This again demonstrates that both the AENV and proposed BC soluble barium methods perform as required, capturing soluble barium, but not insoluble or bound and immobile barium.

Figure 2. Calcium Chloride Extractable Barium



The extraction of soluble barium by calcium chloride methods in sand and clay spiked with barium sulfate is presented in Fig 3. In this Figure, the differences between extraction solvent strength are demonstrated. Barium concentrations recovered by calcium chloride extraction were all low relative to the concentration of barium sulfate spiked to both sand and clay, but substantially greater than background barium concentrations for the sand. It appears that barium sulfate has a greater solubility in calcium chloride, to a maximum of about 380 mg/kg (or 38 mg/L in solution) as demonstrated in the barium sulfate spiked sand at 10,000 mg/kg barium spike treatment. The 50,000 mg/kg barium spike treatment showed similar results to the 10,000 mg/kg treatment. The recovery of barium from barium sulfate spiked sand ranged from approximately 0.3% to 10%, depending on spike concentration and extracting solution. The recovery of barium sulfate in sand with calcium chloride to concentrations well

above background are interesting in that barite is insoluble and would be expected to remain separate from the soil matrix. This suggests that barium sulfate solubility is substantially increased in a calcium chloride solution, compared to its insolubility in water. These results were confirmed under laboratory conditions for barite alone in section 2b-5. Drilling waste sites are frequently associated with high chloride or sulfate concentrations, and therefore, the potential implications of high background salt concentrations should be examined.

As expected, little barium was extracted from barium sulfate spiked clay by any of the CaCl_2 extractions. The highest concentration extracted was approximately 20 mg/kg in the 50,000 mg/kg spiked clay using 1.0 M calcium chloride method, which corresponds to a recovery of approximately 0.04%. Results for all barium spike concentrations were the same as that extracted from unspiked clay for the same method, indicating that all the barium sulfates spiked, regardless of amount, remained insoluble and/or sequestered. However, it is possible that a saturation point exists at some concentration greater than 50,000 mg/kg.

With the exception of barium chloride spiked sand, where all the barium was recovered, for all treated soils at all concentrations, for both barium chloride and barium sulfate spiked soil, increasing the concentration of calcium chloride increased the amount of barium extracted from soil. This is also true for unspiked background soils. The increase appears to be roughly doubling the concentration of measured soluble barium for each increase from 0.1 M to 0.5 and 1.0 M. Barium recovery in fine textured soils appears to be increasing because of both increased barite solubility and stronger cation exchange effects. The results indicate that the proposed 1.0 M calcium chloride method provides a slightly more aggressive extraction than the AENV 0.1 M CaCl_2 method. However, the proposed higher strength method does not appear to extract unavailable and immobile barium.

The effects of holding calcium chloride extracts under room temperature and refrigeration for 3 and 7 days suggest a slight upward trend consistent with loss of sample volume due to evaporation during storage. The trend is very small however; generally speaking there seems to be no significant change in extract Ba concentrations in storage.

Figure 3. Calcium Chloride Extractable Barium

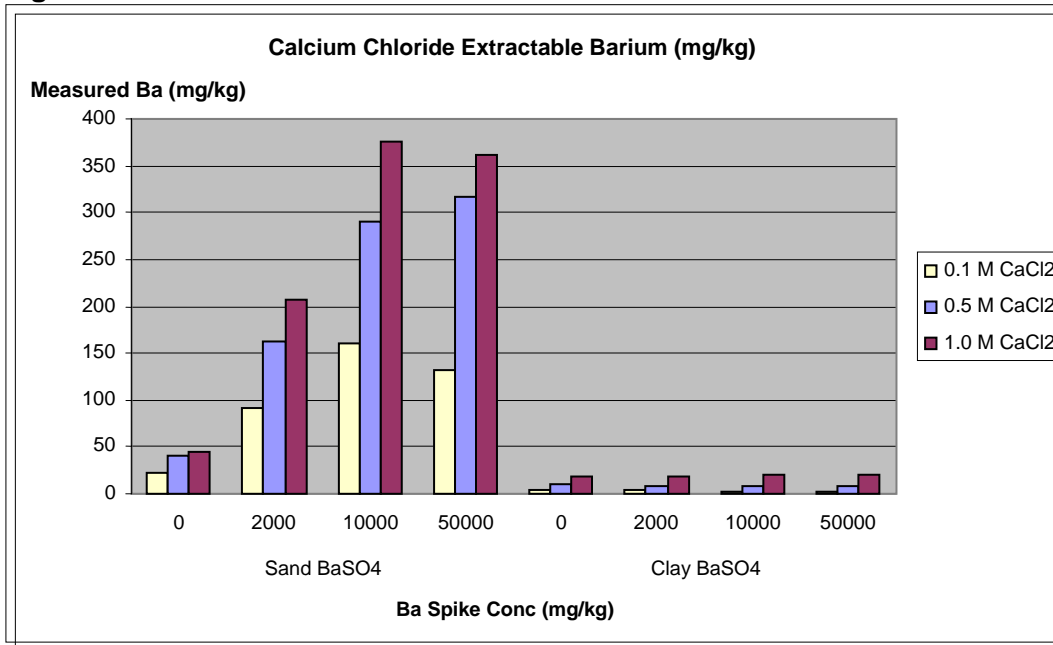
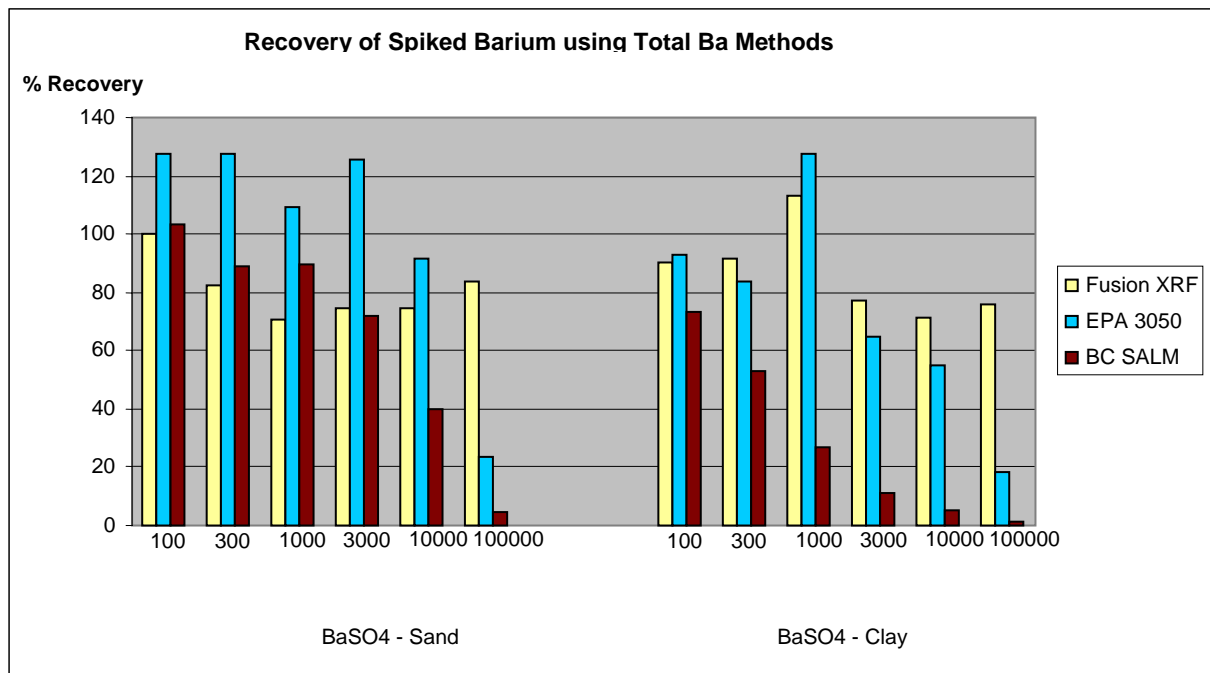


Figure 4. Phase 2b Recovery of Spiked Barium Using Total Barium Methods



The barium results for the barium sulfate spiked clay treatments were interesting in that there did not appear to be a maximum concentration to which the BC SALM method was capable of complete recovery, as had been originally predicted from Phase 1 results. It was thought that at some barite concentration ceiling, the solubility of barium sulfate under acid digest conditions would be reached, after which no further increases would

be seen. Rather, the relative recovery of barium in this study was low even for moderately contaminated concentrations that may be typical of drilling waste sites, and declined steadily with increasing true barium concentration. Only 53%, 27% and 11% of applied barium was recovered from the 300, 1,000 and 3,000 mg/kg treatments. The EPA 3050B method was considerably more aggressive, demonstrating quantitative recovery for treatments up to 1,000 mg/kg (93% to 128%), and recoveries of greater than 50% for all concentrations of 10,000 mg/kg or less. BC SALM recoveries of barium sulfate were reduced more dramatically by the clay matrix than were the 3050B recoveries.

The results for the total barium acid digest methods demonstrated in both Phase 2a and 2b indicate that the EPA 3050B method achieved good recoveries of barium up to 10,000 mg/kg in sand, but only to 2000 mg/kg in clay. The BC SALM method recoveries were quantitative only to about 1,000 mg/kg in sand, and were biased low at all levels in clay. Therefore, neither method could be relied on to provide a true measure of total barium concentration in soil, even at moderately low contaminant levels in typical subsoils. The results also suggest that for typical field subsoils, there doesn't appear to be a cap or maximum concentration at which the methods could be used reliably to provide an accurate measure of barite content. However, both methods will provide much more aggressive and higher results than any of the considered soluble barium methods.

4.2 PHASE 2B – RESULTS OF BARIUM METHOD SIDE STUDIES

Results for the seven side studies which investigated several methodology variables for the acid digestion and calcium chloride extractable barium methods are presented in Appendix 4. Recovery of barium by acid digestion methods was significantly affected by lab-specific variables within the selected digestion techniques.

The impact of key sample digestion variables (from studies 2b-1, 2b-2, and 2b-6), including the volume of acid digest, acid strength and the weight of sample digested, as compared to barium recovery using mandatory method elements are presented in Figures 5 (US EPA 3050) and 6 (SALM).

2b-1. Acid Volume

Barium recoveries from barium sulfate spiked sand were not impacted by doubling the acid volume used to digest soil using the US EPA 3050B method. This was also the case for EPA 3050B in barium sulfate spiked clay. However, the BC SALM method demonstrated a moderate increase for all test concentrations of barium sulfate spiked in either sand or clay using 10 mL of acid, compared to the minimum requirement of 5 mL of nitric and hydrochloric acid mix. Even the amount of background barium extracted from the unspiked clay was increased in the double acid test.

2b-2. Acid Strength

Acid strength had a marked impact on barium sulfate recoveries for both methods in barium sulfate spiked clay. Sample weight and volume were maintained in this test series, however, the acid was not diluted with deionized water during digestion. Therefore, acid strength was increased relative to the original tests conducted with

dilution (10 mL for EPA 3050B and 50 mL total volume for BC SALM). For both methods, barium recovery was reduced for all test treatments, including the unspiked background soil. For EPA 3050, results were roughly one third of the unmodified test recoveries in treatment of 10,000 and greater, with recoveries of 22%, 7% and 5% in the undiluted test compared to 55%, 26% and 18% in test treatments of 10,000, 50,000 and 100,000 mg/kg. For the BC SALM undiluted method, recoveries for all test treatments were essentially the same as the barium concentration recovered from unspiked clay, at approximately 116 to 230 mg/kg. This effect may be a result of a combination of decreased solubility of insoluble barium sulfate with lower dilution volume, formation of barium nitrate from the presence of concentrated nitric acid, which also has a relatively low water solubility, and a decreased soil:acid volume ratio resulting in a lower potential for exposure to the surface area of soil particles.

It should be noted that the BC SALM method requires a mandatory use of the minimum soil:concentrated acid volume ratio (1 g soil:5 mL conc. acid). However, acid strength may be changed by the laboratory as a performance based variable. It was noted in Phase 1 that the BC SALM method results performed by ALS-Vancouver were consistently lower than those completed by NWL. It was recognized mid-way through the Phase 2 studies that this variable differed between the two labs, with ALS-Vancouver digesting without any dilution of the acid:soil mix. The Phase 1 differences may be explained by this method variable, which tends to increase recoveries for barium.

Figure 5. Barium Recovery in Sulfate Spiked Soils with EPA 3050B

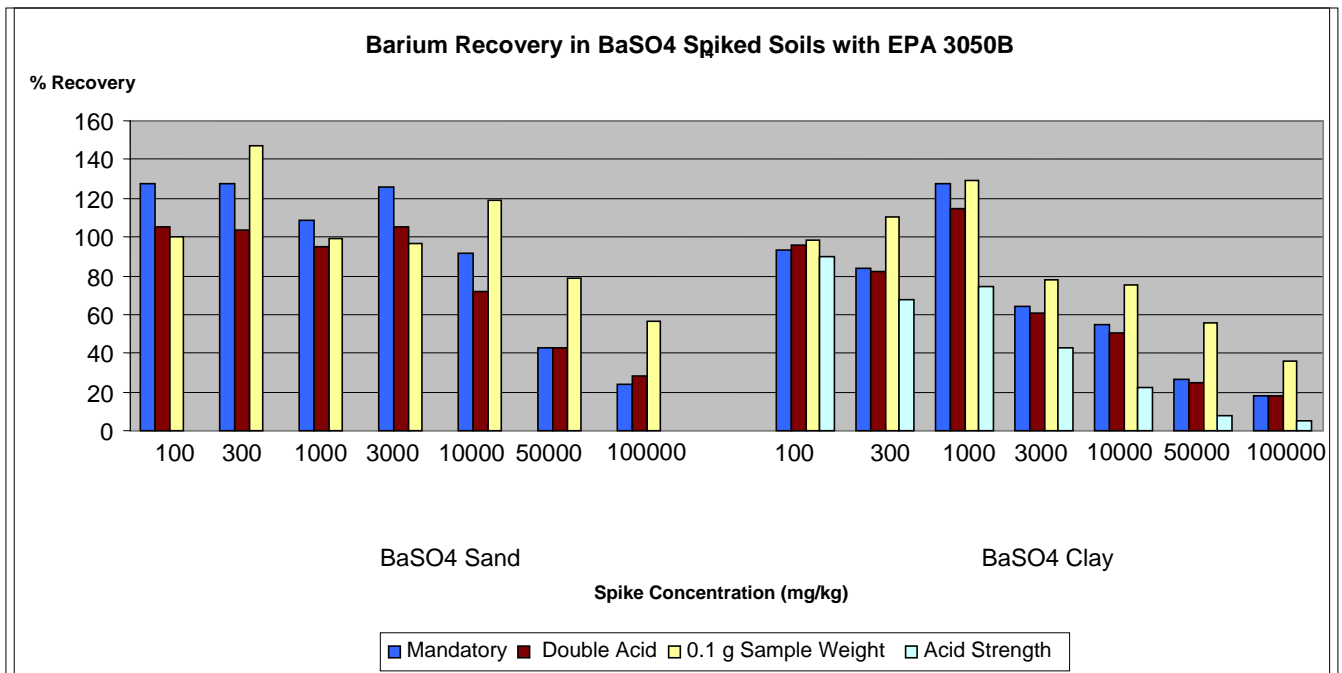
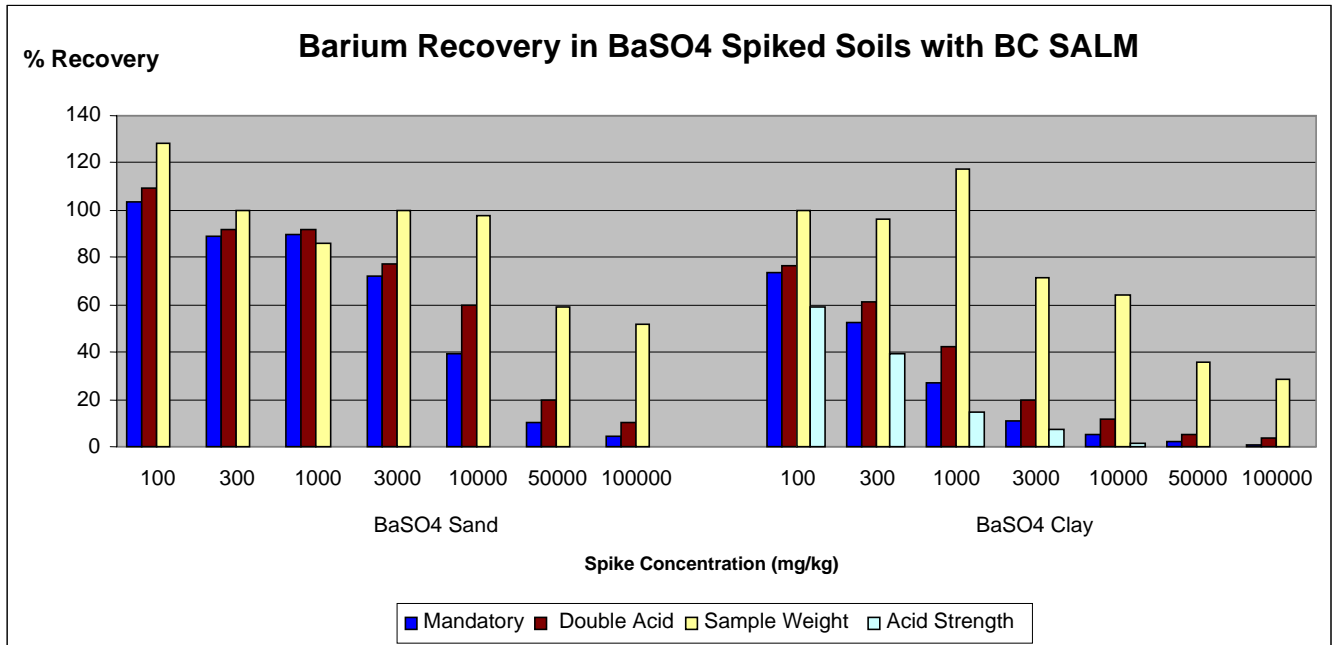


Figure 6. Barium Recovery in Sulfate Spiked Soils with BC SALM

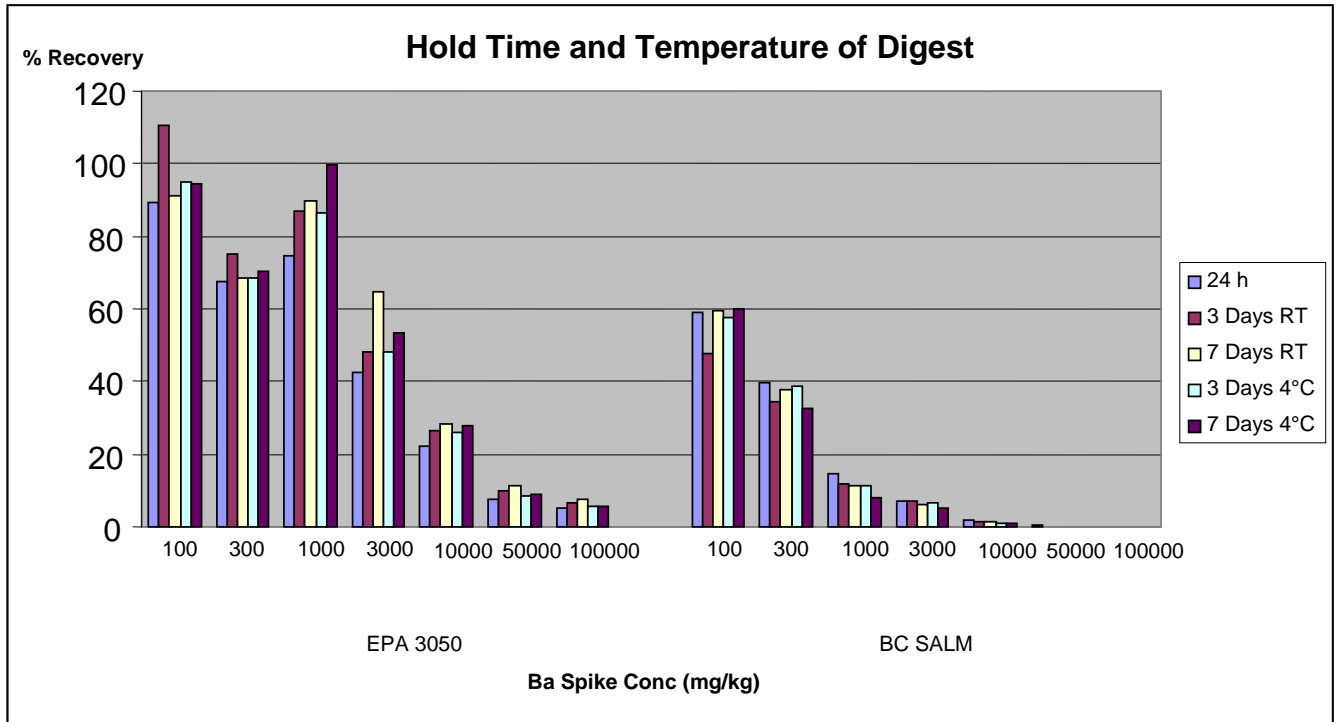


These results suggest that the acid strength used for the BC SALM digestion must be designated as a mandatory element. Although the use of a more dilute acid appeared to enhance barium recoveries, additional work would be required to determine the effect of this variable on other metals.

2b-3. Digest Hold Time and Temperature

The effect of holding the acid digest prior to analysis at both room temperature and refrigeration is presented in Figure 7 and in Table 2b-3 in Appendix 4. Overall, the effect of holding the digest prior to analysis either at 4°C or at room temperature is minor for both methods. Careful examination of Figure 7 indicates a possible slight increase in recovery with holding time for the US EPA 3050B method, and a possible slight decrease for SALM, but the changes are relatively minor, and likely within the analytical uncertainty of these measurements. This study was not designed to assess statistical significance, and it is not possible to determine whether these apparent changes are significant. Note that all 2b-3 data was determined using the reference BC SALM technique, without the deionized water dilution step prior to digestion.

Figure 7. Effect of Hold Time and Temperature of Digest on Barium Recovery



2b-4. Effect of Final Dilution of Digest

Table 2b-4 in Appendix 4 presents the results of the final dilution volume study. Increasing the final volume of the completed digest from 50 mL, to 100 or 200 mL, prior to analysis by ICP had no impact on a 3000 mg/kg barium sulfate spiked sand or clay. This is in contrast to the results demonstrated when altering the acid volume or strength during digestion. This suggests that exchange of barium from charged clay sites occurs mainly during digestion, and that digestion conditions, rather than the conditions during post digestion dilution, have the primary control over barium recovery, and that the potentially increased barium solubility in the final dilution volume is of only secondary importance. However, this result would need to be confirmed using higher concentrations of barium spiked soil. This is certainly a positive outcome, as it would be difficult if not impossible to mandate the final dilution volume of digests due to its dependency on sample concentration and laboratory instrumentation.

The results of Phase 2 total barium methods clearly indicate the significance of minor alterations of digestion techniques on the recovery of barium using either BC SALM or EPA 3050. If a regulatory numeric standard is used under various jurisdictions, enhanced definition of these methodologies is necessary. Further investigation into differences between EPA 3050B Nitric/Peroxide, EPA 3050B Nitric/Peroxide/HCL, EPA 3051, and BC SALM is a recommended course of action for future studies concerning assessment of total barium techniques. Future studies could examine effect of acid type (nitric or HCL, or a combination of both), temperature of digestion, the duration of digestion, and use of microwave digestion methods.

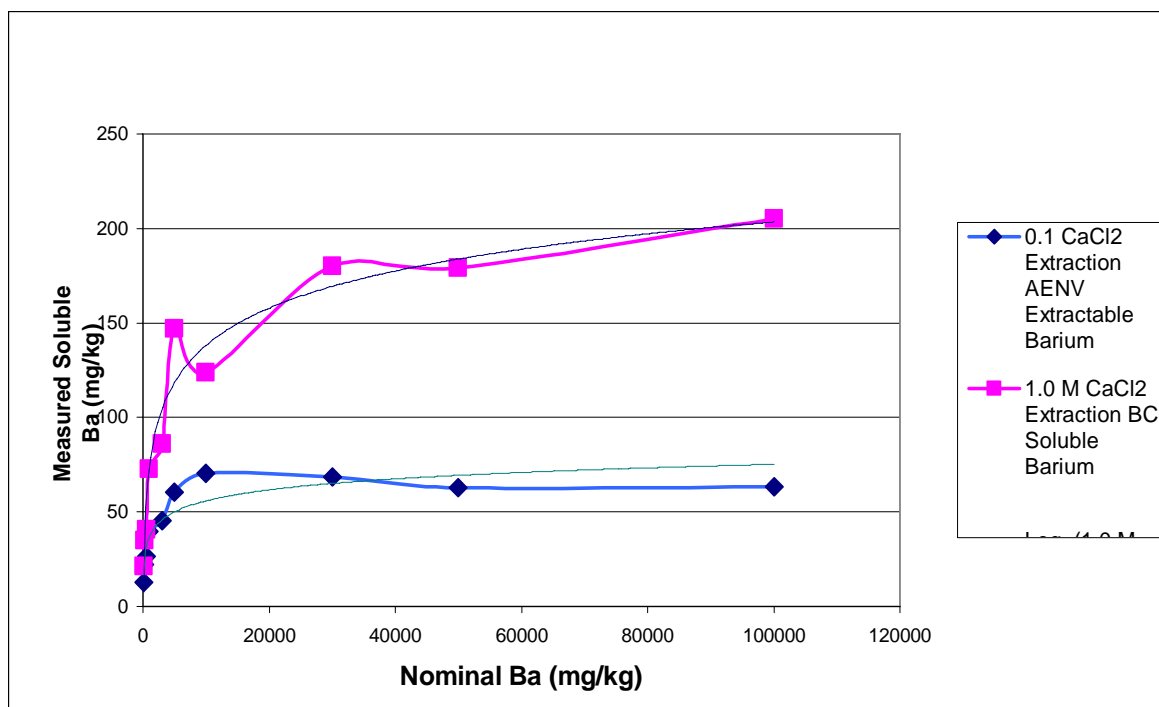
2b-5. Solubility of Barite in CaCl₂ and Strong Acid

The solubility of barite in the calcium chloride extraction solvent for the proposed BC Soluble Barium method and in the strong acids used for the total barium acid digest methods was investigated in order to ascertain if there was a maximum concentration that could be recovered from soils, based on solubility alone under specified conditions. These studies clearly demonstrated that barium sulfate solubility under these method conditions is a key constraint variable in recovery of barium from barite, and that these methods have a maximum concentration of barium that can be recovered from soils, regardless of soil physical and chemical characteristics.

2b-5a. Solubility of Barite in Calcium Chloride

The concentrations of barium measured in treatments of barite extracted with either the AENV Extractable Barium Method (0.1 M CaCl₂) or the draft BC Soluble Barium Method (1.0 M CaCl₂) are presented in Figure 8 and in Table A5-1 of Appendix 5.

Figure 8. Barite Solubility in Calcium Chloride Extractions



The results indicate that the barium sulfate solubility is greater in a calcium chloride solution relative to barite solubility in a water solution (2.4 mg/L barium in deionized water), and that barium sulfate solubility increases with increasing calcium chloride concentration. In both the 0.1 M and 1.0 M calcium chloride extraction solutions, the measured barium (dissolved) increased with an increasing spiked barium concentration, to a maximum observed at about the nominal 5,000 mg/kg barium-spiked treatment. Using the average of measured barium concentrations at this plateau to estimate the degree of solubility (5,000 to 100,000 mg/kg treatments); the solubility of barium sulfate

is estimated as 6.5 mg/L in 0.1 M CaCl₂, and 17 mg/L in 1.0 mg/L CaCl₂. In other words, based on barium sulfate solubility alone, the BC Soluble Barium Method (1.0 M CaCl₂) is capable of extracting a maximum concentration of 170 mg/kg of barium from a barium sulfate spiked soil compared to a maximum of around 65 mg/kg by the AENV (0.1M CaCl₂,) method. Kuhn (et al 1995) also demonstrated that barite solubility is increased in brine solutions. Barite solubility was increased to approximately 13.7 mg/L and 27 mg/L as barium, in 100,000 and 200,000 mg/L NaCl solutions. Similarly, Templeton (1960) showed solubility coefficients for barite increasing almost 20-fold in a 300,000 mg/L NaCl solution.

The higher concentrations of soluble barium demonstrated in the Phase 2a results for the proposed BC Soluble Barium method, compared to the AENV 0.1 M CaCl₂ procedure, appear to be a result of increased solubility of barium sulfate in the increased calcium chloride extraction solution strength. The results of this barite solubility study confirms that the BC Soluble Barium method recovers a higher concentration of barium from soils than the AENV method because barite solubility increases with increasing extraction solution concentrations. It also demonstrates that the soluble barium measured in soil using the calcium chloride 1.0M CaCl₂ method is moderate (about 2.5x greater) and is still limited by a maximum aqueous barium concentration (see Table A5-1). This indicates that it is an appropriate method in terms of the determination of soluble barium in soils.

2b-5b. Maximum Recovery of Barium from Pure Barite in Strong Acid Digests

Digestion of pure barite product was conducted for both acid digest methods, in order to better understand the ability of these methods to recover barium from soil and to evaluate the significance of barium sulfate solubility compared with soil physical interactions during digestion. The results of barite product digestion are presented in Appendix 4, Table 2b-5. It is apparent that based strictly on barium sulfate solubility, both methods do exhibit a maximum concentration ceiling for complete digestion. This ceiling appears to be slightly greater than 10,000 mg/kg for the EPA 3050B method, and slightly less than 5,000 mg/kg for the BC SALM method. Previous work in Louisiana (Deuel & Freeman 1989) also indicated an upper limit to barium in soil tested by acid digestion methods. The results suggest that barium sulfate solubility under acid digest conditions is not the only factor controlling barium extraction. Other complex factors likely include soil interactions such as cation exchange as well as the influence of background soil salt concentrations. Both methods were able to recover greater concentrations of barium in barium sulfate spiked clay, compared with what would be predicted based on barium sulfate digestion alone. This is particularly true for the EPA 3050B method. For example a maximum barium sulfate recovery around 16,000 mg/kg for a 50,000 mg/kg treatment was determined, compared to a measured barium concentration of around 21,000 in the same concentration spiked to sand. In this case, presence of additional salts may be causing the greater recovery of barium.

2b-6. Sample Weight

Results for study 2b-6 are presented in Figures 5 and 6. In contrast to the reduced recoveries demonstrated by increasing acid volume and strength, digesting a smaller amount of soil improved barium recoveries in both sand and clay. For the EPA 3050B method in sand for the 3 highest spike concentrations, using 0.1 g of soil resulted in recoveries of 119%, 79% and 56%, compared to 92%, 43% and 24% respectively where 0.5 g of sand was digested. This trend was similar for clay spiked barium, with barium concentrations approximately 30% higher in the 10,000 mg/kg treatment and higher for digestions performed on the smaller volume of soil.

The BC SALM method recoveries using 0.1 g of soil weight demonstrated dramatically improved recoveries in sand and clay treatments with greater improvements typically occurring at higher spike concentrations. The use of the smaller sample size enabled quantitative recovery of barium from barite samples at concentrations up to 1000 mg/kg barium in sand or clay, and close to quantitative recovery up to a spike concentration of 10000 mg/kg barium (64% in clay, contrasting with only 5% when the standard sample size was used).

2b-7. Salt Concentrations in Soil

The effect on barium recovery in barium spiked soils co-contaminated with high sulfate and chloride salts was investigated. Total barium acid digest methods and the draft BC soluble barium method was used in the experiment. Results are summarized in Tables 2 to 4, as well as the overall data presented in Appendix 5.

2b-7a. BC Soluble Barium

The impact of co-contamination of barium and chloride in sand is shown in Table 2 and Figure 9. There was a small increase in the measured soluble barium with increasing chloride concentrations in the 0 mg/kg barium treatment. Addition of nominal 1,000 and 3,000 mg/kg chloride concentrations appear to approximately double the measurable background soluble barium concentration. This would imply that natural, ambient barium is being mobilized from the soil as a result of magnesium chloride addition. This result is consistent with a soil study which demonstrated an increase of soluble barium released from soils with addition of sodium chloride. Barium extracted by the AENV 0.1 M calcium chloride method was 0.02 mg/L in background soil. Addition of 30,000 mg/kg sodium chloride resulted in a 3.4 mg/L measured soluble barium (AENV 2005). Addition of barite to the same salt-applied soils at up to 10,000 mg/kg did not increase the soluble barium concentration, suggesting that the soluble barium was released from the soil, rather than from solubilization of barite.

Relatively high chloride concentrations appeared to reduce the soluble barium measured in the chloride spiked coarse-textured soil. A small decrease in soluble barium was observed in the highest treatment (30,000 mg/kg chloride, 10,000 mg/kg Ba treatment – measured soluble barium = 216 mg/kg) compared to the same barite treatment without added chloride (soluble barium = 330 mg/kg).

Addition of sulfate in barite spiked sand resulted in a significant decrease in the measured soluble barium (Figure 10). In the highest barite: sulfate treatment, the measured amount of soluble barium was reduced to 20 mg/kg, compared to 191 mg/kg

in sand with no sulfate addition. The reduction in soluble barium is directly correlated with the amount of sulfate added to sand, for each barite treatment. The reduction in soluble barium in sand with added sulfate is obviously a result of formation of insoluble barium sulfate.

The addition of chloride or sulfate salt had essentially little impact on the measured amount of soluble barium in clay-textured soil (Figures 11 and 12). Soluble barium measured in barite spiked clay, treated with either chloride or sulfate for all treatments, were low and near background concentrations. Soluble barium concentrations ranged from 9.6 to 21.3 mg/kg. There was observed to be a very small increase in the measured soluble barium concentration in the highest chloride spiked barite clay series, however, the increase is relatively small and potentially due to measurement variability, and is therefore likely insignificant.

Since these concentrations of soluble barium are much lower than the barium concentrations obtained from barite solubility in 1.0 M CaCl₂ alone (Figure 8), these results indicate that sorption of barium to clay cation exchange sites is the primary controlling variable in this soil type, and barium sulfate solubility in salt solutions plays a secondary role in the barium solubility in clay soils.

Table 2. Measured Barium by BC Soluble Barium (1.0 M CaCl₂) in Chloride and Sulfate Spiked Sand and Clay

		Chloride Addition to Barium Spiked Soils - BC Soluble Barium							
		Sand				Clay			
		Nominal Barium Conc.				Nominal Barium Conc.			
		A	B	C	D	A	B	C	D
		0	1,000	3,000	10,000	0	1,000	3,000	10,000
		Mean Measured Soluble Barium (mg/kg)				Mean Measured Soluble Barium (mg/kg)			
Chloride Concentration (mg/kg)	0 Cl	23	155	190	330	13.8	14.6	16.2	15.7
	1,000 Cl	55	145	226	258	14.3	15.2	14.9	16.5
	3,000 Cl	57	191	199	274	14.0	15.0	15.2	16.9
	10,000 Cl	44	150	214	265	14.4	15.5	17.6	21.3
	30,000 Cl	31	130	184	216	14.5	14.9	16.4	19.5
		Sulfate Addition to Barium Spiked Soils - BC Soluble Barium							
		Sand				Clay			
		Nominal Barium Conc.				Nominal Barium Conc.			
		A	B	C	D	A	B	C	D
		0	1,000	3,000	10,000	0	1,000	3,000	10,000
		Mean Measured Soluble Barium (mg/kg)				Mean Measured Soluble Barium (mg/kg)			
Sulfate Concentration (mg/kg)	0 SO₄	24	130	160	191	13.8	13.4	13.7	12.2
	1,000 SO₄	32	53	64	76	13.0	12.5	13.1	12.7
	3,000 SO₄	25	29	33	34	12.7	12.1	11.6	12.4
	10,000 SO₄	15	18	19	18	9.6	11.4	12.0	12.8
	30,000 SO₄	14	17	17	20	10.1	9.7	10.5	11.0

Figure 9. BC Soluble Barium in Chloride and Barium Spiked Sand

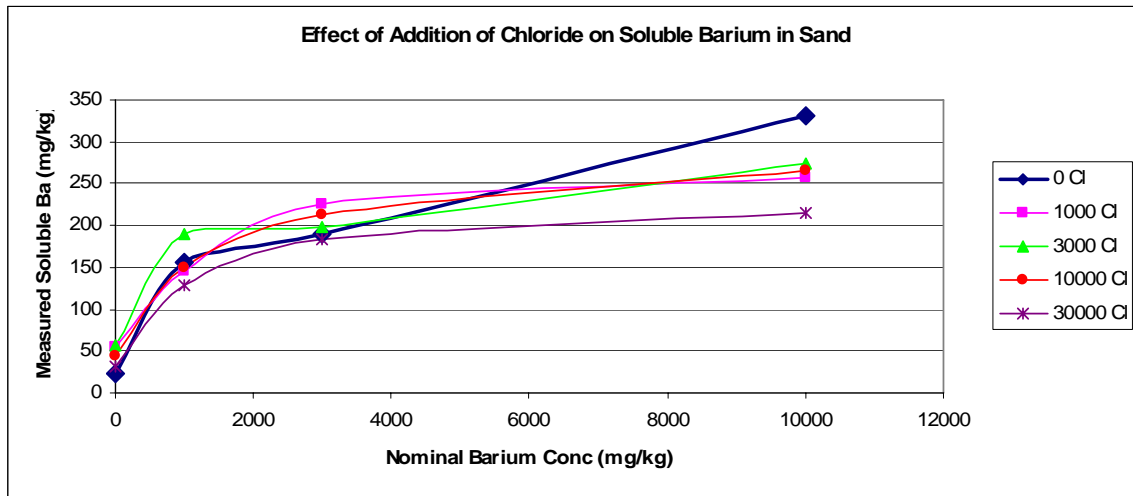


Figure 10. BC Soluble Barium in Sulfate and Barium Spiked Sand

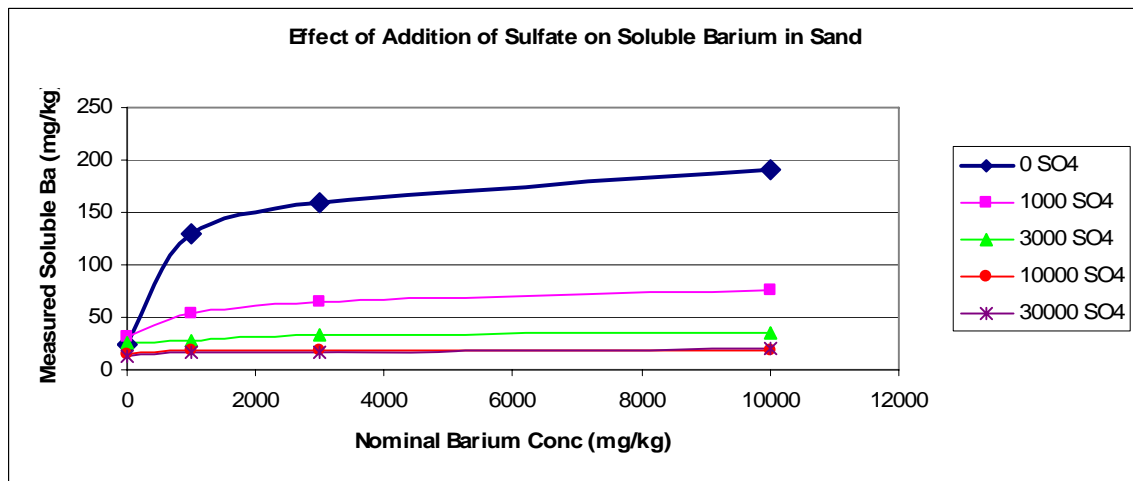


Figure 11. BC Soluble Barium in Chloride and Barium Spiked Clay

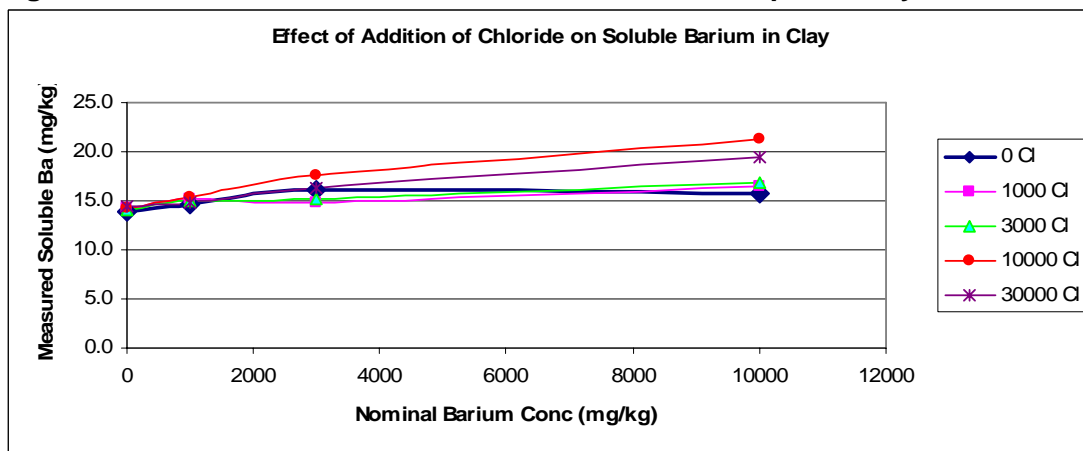
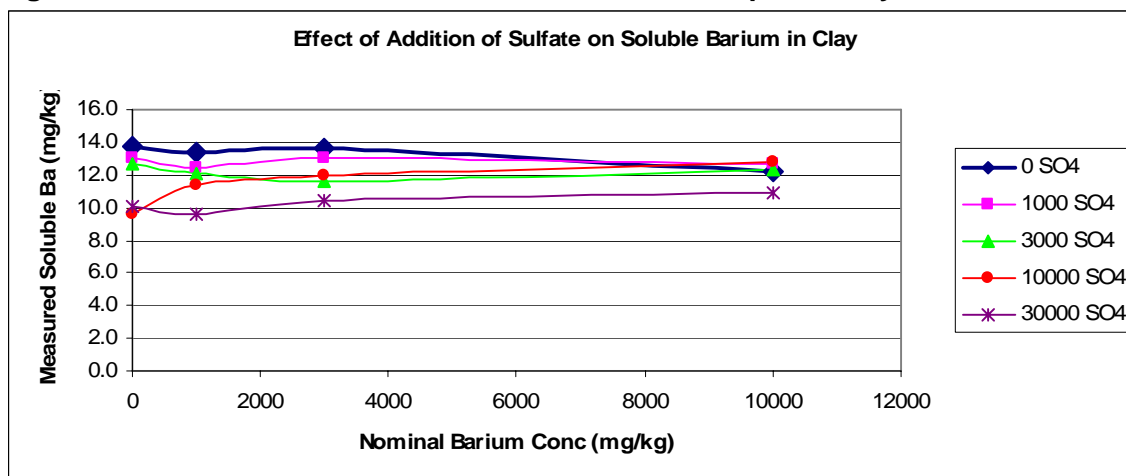


Figure 12. BC Soluble Barium in Sulfate and Barium Spiked Clay



2b-7b. BC SALM Barium

Analysis of barium using the BC SALM total barium method for sulfate or chloride amended and spiked barite soils generally provided consistent results with those determined using the BC soluble barium extract (1.0 M CaCl₂) methodology. BC SALM method experimental results are summarized in Table 3, and Figures 13 to 16.

As expected, the barium measured by the BC SALM method was higher for all corresponding treatments in the sandy soil compared to the clay (discounting background barium content). For the sand series, an increasing barium concentration was measured across the nominal 0 to 10,000 mg/kg barium spiked soil series (Table 3). In contrast to the sand series observations, all clay series treatments were observed to be similar to the background barium soil concentration soil (i.e., soil not spiked with barium), suggesting a maximum acid extractable barium concentration of around 150 mg/kg in clay soil, using the BC SALM method (Figure 13).

Addition of chloride to barite spiked sand had no significant effect on barium measured by the BC SALM method, except a possible decrease in barium measured in the highest chloride treatment (Figure 13). Similar to the BC Soluble Barium results, the BC SALM barium measured in the 30,000 mg/kg chloride treatment was lower than that measured in the highest nominal barite spiked sand without addition of chloride (i.e., 10,000 mg/kg barite treatment). However, no other trend is apparent.

Increasing the sulfate soil content in barite spiked sand clearly decreased the barium concentration measured using BC SALM method (Figure 14).

The results for the effect of chloride and sulfate addition in clay on the measured barium concentration using the BC SALM method are presented in Figures 15 and 16. The barium concentrations in clay measured using the BC SALM method are very similar across all barium and chloride treatments, suggesting that a maximum SALM extractable barium concentration in clay soil had been reached. Addition of chloride to the clay soil did not have a significant effect on the barium concentrations measured, and therefore on the barium recovery. Unlike the BC Soluble Barium method results for the corresponding soil spiked series, sulfate addition to barite spiked clay resulted in a decreased measurable BC SALM barium in the three higher sulfate treatments, for each respective barium concentration.

Table 3. Measured Barium by BC SALM Total Barium in Chloride and Sulfate Spiked Sand and Clay

		Chloride Addition to Barium Spiked Soils - BC SALM Barium							
		Sand				Clay			
		Nominal Barium Conc.				Nominal Barium Conc.			
		A	B	C	D	A	B	C	D
		0	1,000	3,000	10,000	0	1,000	3,000	10,000
		Mean Measured BC SALM Barium (mg/kg)				Mean Measured BC SALM Barium (mg/kg)			
Chloride Concentration (mg/kg)	0 Cl	51	428	777	1410	154	160	147	140
	1,000 Cl	77	417	758	1090	136	163	158	140
	3,000 Cl	78	431	758	1300	146	162	142	140
	10,000 Cl	80	433	687	1165	155	158	161	135
	30,000 Cl	53	434	775	1057	158	169	173	165

		Sulfate Addition to Barium Spiked Soils - BC SALM Barium							
		Sand				Clay			
		Nominal Barium Conc.				Nominal Barium Conc.			
		A	B	C	D	A	B	C	D
		0	1,000	3,000	10,000	0	1,000	3,000	10,000
		Mean Measured BC SALM Barium (mg/kg)				Mean Measured BC SALM Barium (mg/kg)			
Sulfate Concentration (mg/kg)	0 SO4	71	381	668	1225	153	136	149	130
	1,000 SO4	263	409	716	879	139	138	147	135
	3,000 SO4	242	343	524	518	128	128	125	145
	10,000 SO4	90	223	254	225	104	96	105	100
	30,000 SO4	59	92	136	170	60	61	65	69

Figure 13. BC SALM Barium in Chloride and Barium Spiked Sand

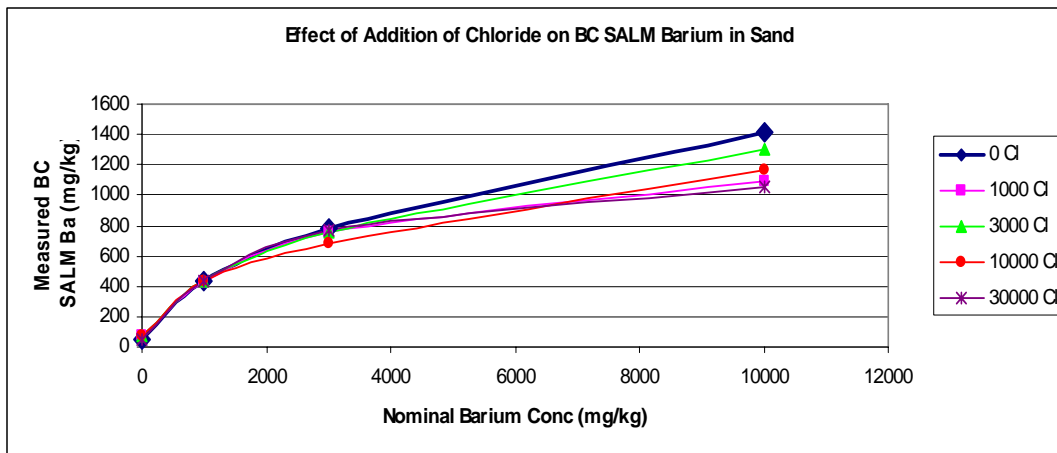


Figure 14. BC SALM Barium in Sulfate and Barium Spiked Sand

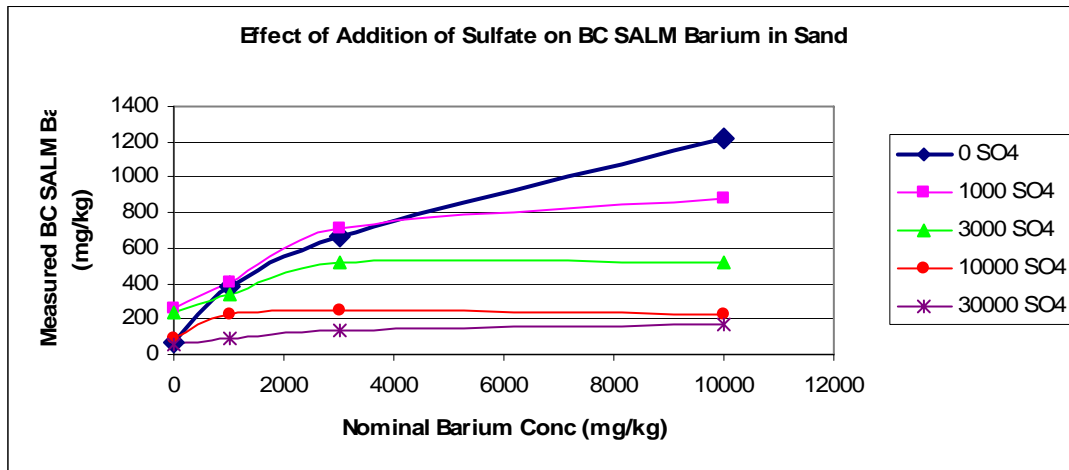


Figure 15. BC SALM Barium in Chloride and Barium Spiked Clay

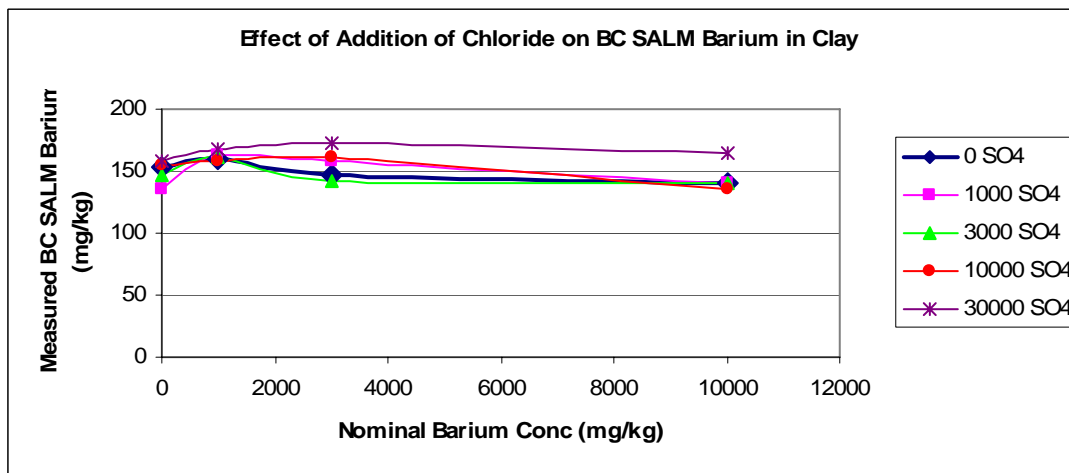
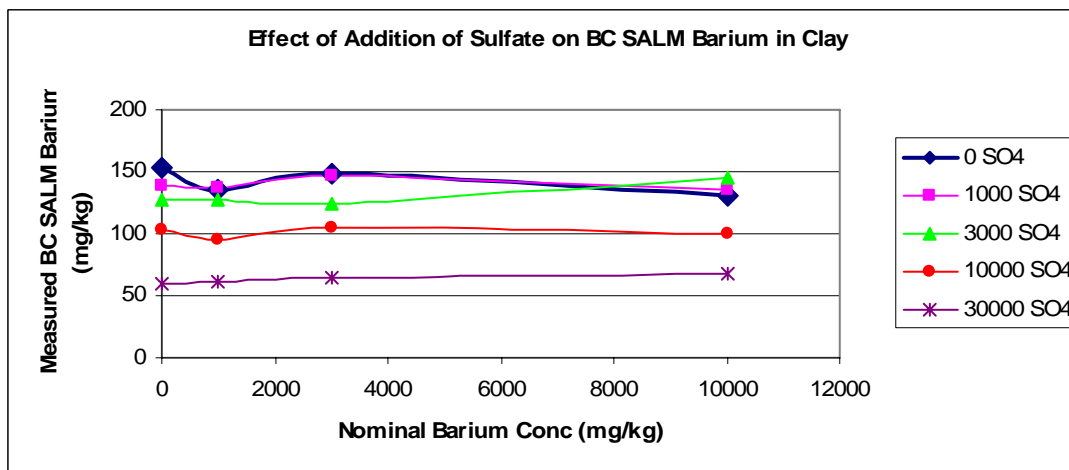


Figure 16. BC SALM Barium in Sulfate and Barium Spiked Clay



2b-7c. EPA 3050B Barium

The results for the concentration of barium using the EPA 3050B Strong Acid Digest method for total barium in spiked barite soil amended with sulfate or chloride, are summarized in Table 4 and Figures 17 to 20.

Recovery of spiked barium in both sand and clay are substantially greater for the EPA 3050B method compared to the BC SALM method, as also demonstrated throughout the previous Phase 1 and other parts of the current Phase 2 work.

Barium recovery from chloride spiked sand or clay as measured by EPA 3050B did not demonstrate any clearly significant trends.

Like the other two methods, there is a decrease in measurable barium in the highest barite treatment in sand and clay spiked with sulfate, however, it is not as clear and proportional as that shown with the less aggressive methods (Figures 18 and 20).

Although less impacted than the BC SALM method by an increasing soil chloride or sulfate concentration, the results suggest that the EPA 3050B acid digest method may be unable to give a true measure of total soil barium concentration, based on the recovered concentration compared to the spiked (nominal) concentration.

Table 4. Measured Barium by EPA 3050B Total Barium in Chloride and Sulfate Spiked Sand and Clay

		Chloride Addition to Barium Spiked Soils - EPA 3050B Barium							
		Sand				Clay			
		Nominal Barium Conc.				Nominal Barium Conc.			
		A	B	C	D	A	B	C	D
		0	1,000	3,000	10,000	0	1,000	3,000	10,000
		Mean Measured EPA 3050B Barium (mg/kg)				Mean Measured EPA 3050B Barium (mg/kg)			
		Chloride Concentration (mg/kg)	0 Cl	64	901	1865	4890	283	939
1,000 Cl	125		581	2315	7015	369	1065	2175	4540
3,000 Cl	104		768	2005	7005	308	1060	2105	4410
10,000 Cl	101		665	1675	5375	373	1023	2085	4240
30,000 Cl	68		660	1780	6275	330	1003	1905	4195
		Sulfate Addition to Barium Spiked Soils - EPA 3050B Barium							
		Sand				Clay			
		Nominal Barium Conc.				Nominal Barium Conc.			
		A	B	C	D	A	B	C	D
		0	1,000	3,000	10,000	0	1,000	3,000	10,000
		Mean Measured EPA 3050B Barium (mg/kg)				Mean Measured EPA 3050B Barium (mg/kg)			
		Sulfate Concentration (mg/kg)	0 SO4	103	773	2335	7130	300	1235
1,000 SO4	367		863	2915	4825	325	1120	2205	4790
3,000 SO4	443		1006	2300	7220	285	1100	2030	3725
10,000 SO4	124		1380	1765	5645	300	1060	2005	3795
30,000 SO4	184		650	2195	5595	300	1110	1880	3440

Figure 17. EPA 3050B Barium in Chloride and Barium Spiked Sand

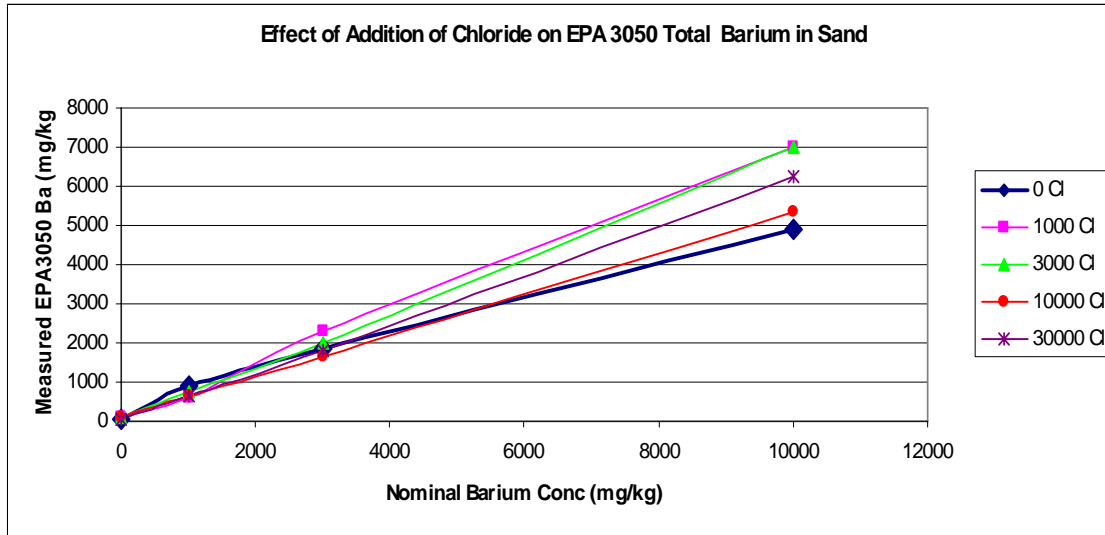


Figure 18. EPA 3050B Barium in Sulfate and Barium Spiked Sand

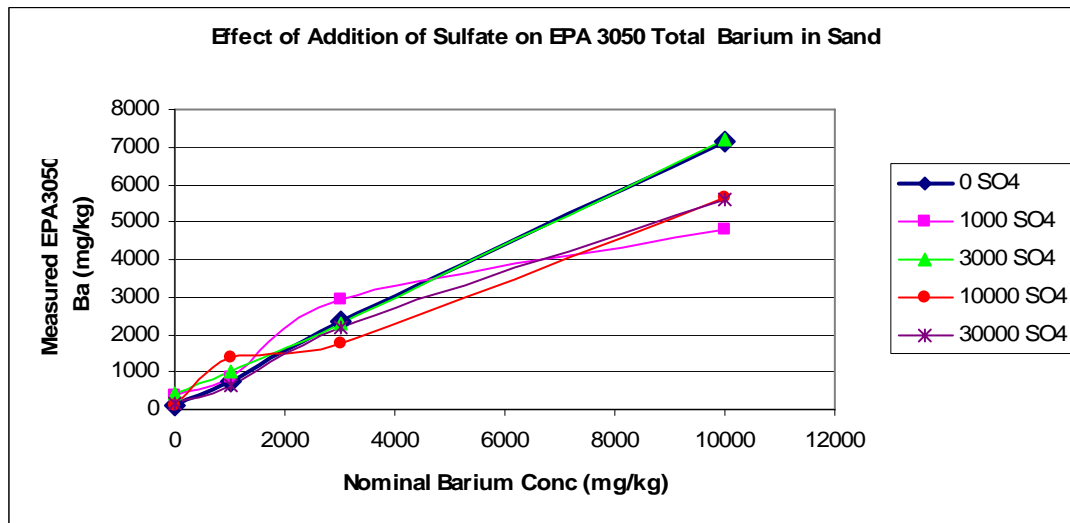


Figure 19. EPA 3050B Barium in Chloride and Barium Spiked Clay

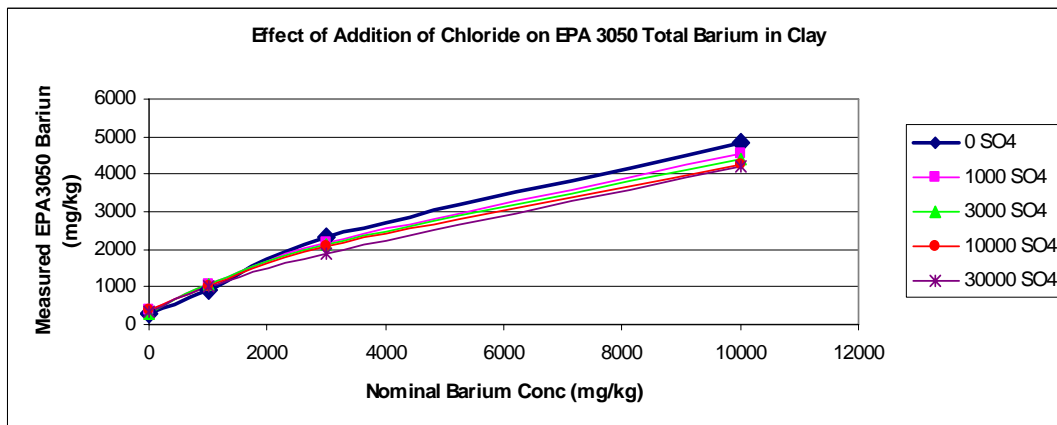
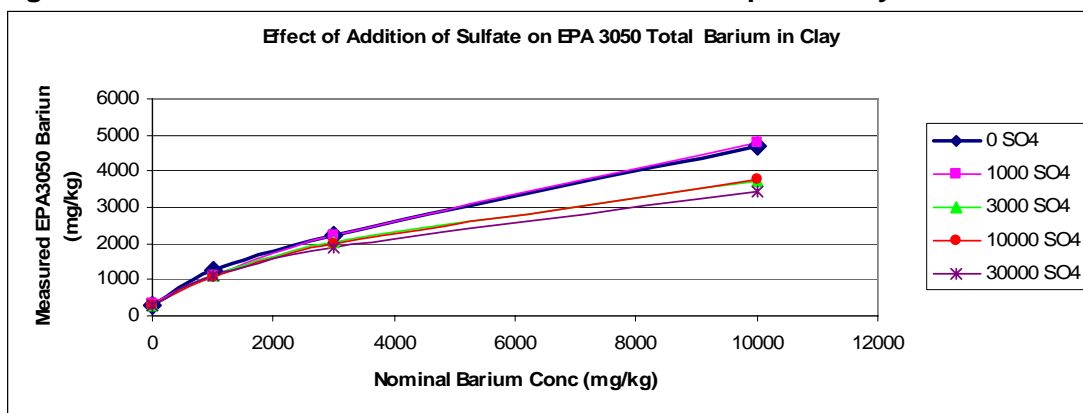


Figure 20. EPA 3050B Barium in Sulfate and Barium Spiked Clay



5.0 RECOMMENDATIONS AND CONCLUSIONS

The calcium chloride soluble barium extraction procedure proved to be a reliable method for measuring the available and potentially mobile and toxic forms of barium from differing soil types and contaminant concentrations. Both the AENV 0.1 M method, and the candidate 1.0 M CaCl_2 method for BC capture soluble and unbound barium, yet still allow bound and immobile barium to be sequestered in clay soil types or as barium sulfate.

Increased CaCl_2 concentrations increase the solubility of barite in laboratory solutions, which at least partially explains the increased soluble barium recovery from soils using the extraction solution. Increased CaCl_2 concentrations could simulate the effect of brines from produced water that may be present in some drilling waste sites.

Increasing the calcium chloride extract concentration from 0.1 M to 1.0 M was effective in increasing the recoveries of barium from spiked soils. This result confirms results determined in Phase 1, which showed improved recovery with a range of spiked and real-world soils. This indicates that the candidate method would be an appropriate recommended method as it should provide a worst-case estimate of the concentration of barium adsorbed to cation exchange sites that may be environmentally available. The candidate method did not appear to be overly aggressive for the liberation of barite.

Modifications to CaCl_2 concentration is simple and effective, yet the extraction method remains essentially the same as the standard Alberta Environment method for soluble barium, and is therefore unlikely to cause undue practical limitations at participating laboratories.

The total acid digest methods of EPA 3050B and BC SALM proved to be unreliable measures of total barium concentrations in both soil types. Poor recoveries were demonstrated at barium contaminant concentrations that are likely typical of many barite field sites. Decreasing the soil sample size by a factor of 5 dramatically increased the recovery of barium. The dependency of both methods on true barium concentrations, sulfate concentrations, soil texture (clay content, cation exchange capacity), and on method variables such as acid digest volumes, acid strength, and sample size remains a

significant concern. The EPA 3050B proved considerably more aggressive than the BC SALM, but small differences in either method can have significant impacts on barium results, and these differences may not be identified during performance based validations of methods unless barite soils are specifically addressed. Furthermore, the lack of a concentration ceiling, below which quantitatively accurate total barium results would be achieved, prevents use of a staged analysis that had been originally considered (i.e. analysis by BC SALM to 10,000 mg/kg Ba, analysis by fusion for greater barium contamination levels). Therefore, a regulatory numeric standard for total barium at contaminated sites is not recommended due to the inability to rely on obtaining an accurate estimate of real concentrations of total barium in a variety of soil types and contaminant conditions using the BC SALM method.

However, although not capable of generating quantitative total barium results even at low levels, the BC SALM method is consistently much more aggressive than the calcium chloride method, and may be appropriate to generate analytical results for environmentally available forms of barium. BC SALM would produce more conservative (higher) barium measures than the calcium chloride method, but less conservative (lower) barium measures than 3050B or fusion techniques. Increased standardization of the BC SALM method would be required to ensure reproducible barium results are generated across laboratories.

Concern for solubilization of barium in soils with relatively elevated levels of salinity, such as those originating from brine (chloride) or sulfate salts, was the rationale for investigating the effect of high salt concentrations on barium solubility, and therefore potential mobilization. In sand textured soils, increasing concentrations of soil chloride resulted in only a marginal (and perhaps insignificant) increase in the measured soluble barium. In fact, at the highest soil chloride treatment, there appear to be an overall decrease in the measured barium. Sulfate addition resulted in an overall significant reduction in the measured soluble barium in all barite spiked soil treatments.

In fine textured (clay) soils, barium binding to cation exchange sites appears to be the predominant mechanism controlling the measured concentration of soluble barium. Chloride and sulfate addition to barite spiked clay had no overall effect on the measured soluble barium. Since availability of barium in fine soils is controlled primarily by barium's affinity to soil cation exchange sites rather than limited by barite solubility, it is unlikely that barite soils exposed to high concentrations of chloride or sulfate will result in any significant increase in the mobility of barium.

The ability to measure total barium by either of the strong acid digestion methods was proven to be adversely affected at increasing barite spiked soil levels and also reduced by increasing sulfate content. The BC SALM method yielded significantly lower barium concentrations when higher concentrations of sulfate were present. The US EPA 3050B method showed a greater degree of total barium recovery, and was less impacted by sulfate soil content than the BC SALM method. However, the US EPA method also appears to be generally unable to provide a quantitative measure of total barium content in clay textured soil. Barium concentration measured by either method was typically found to be a significant underestimation of the true total barium concentration, particularly in situations in which the sulfate concentration is relatively high.

Overall, the addition of sulfate to barite-spiked soil tends to reduce the concentration of barium measured by the soluble barium or either of the "total" barium methods, however,

the magnitude of the effect is a function of soil properties and varies between the different extractions. A potential co-contaminant which tends to reduce the availability of barium will not be a concern in the overall management of barium-contaminated sites.

The addition of chloride to barite-spiked soil did not appear to have a consistent or significant effect on the results of either the soluble or "total" barium methods. If high levels of chloride were ever found to influence these methods, it would only occur at such high levels that direct management of salinity issues would be required, such that any minor effects on measured barium concentrations would be unlikely to affect overall site management decisions.

6.0 REFERENCES

Alberta Environment. Soil Quality Guidelines for Barite (2004). Publication #T/738. 6.6.2 *Analytical Method for Extractable Barium*.

BC SALM. British Columbia Ministry of Environment, Lands and Parks. Contaminated Sites Regulation Analytical Method 8, Version Date: February, 2001. *Strong Acid Leachable Metals (SALM) in Soil, Version 1.0*.

Carter, M.R., 1993. Soil Sampling and Methods of Analysis. Canadian Society of Soil Science. Lewis Publishers, 1993.

Deuel, L.E. and Freeman, B.D. 1989. Amendment to Louisiana Statewide Order 29-B Suggested Modifications for Barium Criteria. In SPE/IADC Drilling Conference, New Orleans.

EPA 3050. Test Methods for Evaluating Solid Waste, SW-846 Vol. 1A. Method 3050B revision 2, Dec 1996, *Acid Digestion of Sediments, Sludges, and Soils*.

Kuhn, M., Bartels, J., Pape, H., Schneider, W. and Clauser C. 1995. Modeling chemical brine-rock interaction in geothermal reservoirs. University of Technology Aachen (RWTH). Applied Geophysics, Lochnerstr. 4-20, D-52056 Aachen, Germany.

Lindsay, W.L., and Norvell, W.A., 1969. Equilibrium relationships of Zn²⁺, Fe³⁺, Ca²⁺. And H⁺ with EDTA and DTPA in soils. Soil. Sci. Soc. Am. Proc. **33**:62-68.

Lindsay, W.L., and Norvell, W.A., 1978. Development of a DTPA test for zinc, iron, manganese, and copper. Soil. Sci. Soc. Am. J. **42**:421-428.

Macyk, T.M., Abboud S.A. and Nikiforuk, F.I. 1995. Alberta Drilling Waste Sump Chemistry Study. Alberta Research Council. Prepared for Alberta Land Conservation and Reclamation Council. Report RRTAC 92-6.

Merry, R.H., and Tiller, K.G., 1978. The contamination of pasture by a lead smelter in a semi-arid environment. Aust. J. Exp. Agric. Anim. Husb. **18**:89-96.

Williams, C., and Thornton, I., 1973. The use of soil extractants to estimate plant-available molybdenum and selenium in potentially toxic soils. Plant Soil. **39**:149-159.

Appendix 1.

Table A1-1. Detailed Characterization of Background Soils

Method	Parameter Name	Unit	Detection Limit	Sand	Clay	Silty Clay Loam	
Cation Exchange Capacity (CEC) for General Soil	Calcium	mg/kg	4	1970	7720	8130	
	Magnesium	mg/kg	2	34	1910	301	
	Potassium	mg/kg	20	<20	260	80	
	Sodium	mg/kg	12	<10	213	30	
	Base saturation	%	1	780	227	345	
	Calcium	meq/100g	0.0003	9.81	38.5	40.6	
	Magnesium	meq/100g	0.0008	0.28	15.7	2.48	
	Sodium	meq/100g	0.003	<0.05	0.925	0.13	
	Potassium	meq/100g	0.003	<0.05	0.68	0.2	
	ESP	%	0.2	<4	3.76	1	
	TEC	meq/100g	2	10	56	43	
	CEC	meq/100g		1.3	24.6	12.6	
Carbon and Nitrogen in soil (FSJ)	Organic Matter	%	1	<1	2	<1	
	Carbon	%	0.05	<0.05	1.13	0.43	
Hot Water Soluble	Boron	ug/g	0.1	<0.1	1	0.7	
Metals Strong Acid Digestion	Mercury (Hot Block) in Soil	Mercury	ug/g	0.01	0.01	0.08	0.04
	Metals ICP-MS (Hot Block) in soil	Antimony	ug/g	0.2	<0.1	<0.2	<0.2
		Arsenic	ug/g	0.2	2.4	10.5	8.4
		Barium	ug/g	1	64	333	195
		Beryllium	ug/g	0.1	0.1	1.2	0.7
		Cadmium	ug/g	0.01	0.06	0.42	0.28
		Chromium	ug/g	0.5	3.4	34.4	21.4
		Cobalt	ug/g	0.1	2.2	12.8	10.7
		Copper	ug/g	1	3	32	19
		Lead	ug/g	0.1	2.3	14.1	9.9
		Molybdenum	ug/g	1	<1	<1	<1
		Nickel	ug/g	0.5	6.1	38.3	29.6
		Selenium	ug/g	0.3	<0.2	1.4	0.4
		Silver	ug/g	0.1	<0.1	0.2	0.2
		Thallium	ug/g	0.05	0.06	0.3	0.26
		Tin	ug/g	1	1	<1	<1
		Vanadium	ug/g	0.1	6	65.4	43.5
		Zinc	ug/g	1	12	111	65

Appendix 1.

Table A1-1. Detailed Characterization of Background Soils (cont'd).

Method		Parameter Name	Unit	Detection Limit	Sand	Clay	Silty Clay Loam
Physical and Aggregate Properties	Moisture	Moisture	%	0.1	1.6	23	12.1
	Particle Size Analysis - GS	Texture			Sand	Clay	Sandy Clay Loam
		Sand	%		96.4	14.4	45.7
		Silt	%		1.2	26.2	25.3
		Clay	%		2.4	59.4	29
Salinity	Saturated Paste in General Soil	pH	pH		8.4	7.7	7.8
		EC	dS/m	0.01	0.21	4.05	2.53
		SAR			0.2	1	0.2
		% Saturation	%		35	108	55
		Calcium	meq/L	0.01	1.89	26.9	32.5
		Calcium	mg/kg		13.1	583	358
		Magnesium	meq/L	0.02	0.38	36.9	7.43
		Magnesium	mg/kg		1.6	484	49.5
		Sodium	meq/L	0.04	0.19	5.89	0.9
		Sodium	mg/kg		2	147	11
		Potassium	meq/L	0.03	0.06	0.69	<0.2
		Potassium	mg/kg		<1	29	<6
		Chloride	meq/L	0.03	0.07	1.31	0.14
		Chloride	mg/kg		1	50	3
		Sulfate-S	meq/L	0.06	0.61	64.9	37
Sulfate-S	mg/kg		3.4	1120	326		
TGR	T/ac		<0.1	<0.1	<0.1		
CaCl ₂ Extractable Barium			mg/kg	0.05	9.4	1.1	2.7

Appendix 2. Phase 2a Results: Calcium Chloride/Total Barium Methods

Table 2a-1. Barium Chloride in Sand				Total Barium Methods (mg/kg)			CaCL ₂ Extractable Barium (mg/kg)		
Soil Type	Spike Chemical	Soil Spike Concentration (mg/kg)	Data Type	EPA 3050	BC SALM	Fusion XRF	CaCL ₂ Extractable Barium (mg/kg)		
				NWL	NWL	ALS-CHEMEX	0.1 M	0.5 M	1.0 M
Sand	Barium Chloride	0	Rep. A	128	57	400	14	20	26
			Rep. B	163	74	500	14	29	54
			Mean	146	66	450	14	25	40
			% Recovery	n/a	n/a	n/a	n/a	n/a	n/a
Sand	Barium Chloride	2000	Rep. A	2250	1930	2000	1,540	1500	1,400
			Rep. B	2420	2300	1800	1740	1440	1620
			Mean	2335	2115	1900	1640	1470	1510
			% Recovery	109	102	95	76	69	70
Sand	Barium Chloride	10000	Rep. A	10200	9050	8600	8,610	7,800	7,600
			Rep. B	12100	9960	6900	8500	9100	9460
			Mean	11150	9505	7750	8555	8450	8530
			% Recovery	110	94	78	84	83	84
Sand	Barium Chloride	50000	Rep. A	42100	49000	41300	39,500	46,200	41,200
			Rep. B	48400	47000	44700	29100	39100	38500
			Mean	45250	48000	43000	34300	42650	39850
			% Recovery	90	96	86	68	85	79

Appendix 2 Continued. Phase 2a Results: Calcium Chloride/Total Barium Methods

Table 2a-2. Barium Chloride in Clay				Total Barium Methods (mg/kg)			CaCL ₂ Extractable Barium (mg/kg)		
Soil Type	Spike Chemical	Soil Spike Concentration (mg/kg)	Data Type	EPA 3050	BC SALM	Fusion XRF			
				NWL	NWL	ALS-CHEMEX	0.1 M	0.5 M	1.0 M
Clay	Barium Chloride	0	Rep. A	347	150	1,000	2	7	10
			Rep. B	362	153	1,000	<5	10	22
			Mean	355	152	1000	2	8	16
			% Recovery	n/a	n/a	n/a	n/a	n/a	n/a
Clay	Barium Chloride	2000	Rep. A	1920	416	2500	6	23	53
			Rep. B	1940	440	2400	6	29	64
			Mean	1930	428	2450	6	26	59
			% Recovery	82	20	123	0.3	1.1	2.5
Clay	Barium Chloride	10000	Rep. A	8100	985	9400	6	17	40
			Rep. B	8400	1070	9300	<5	14	38
			Mean	8250	1028	9350	6	15	39
			% Recovery	80	10	94	0.1	0.1	0.4
Clay	Barium Chloride	50000	Rep. A	33800	20900	45300	24100	30100	29100
			Rep. B	28000	13900	43700	17800	19400	24300
			Mean	30900	17400	44500	20950	24750	26700
			% Recovery	61	35	89	42	49	53

Appendix 2 Continued. Phase 2a Results: Calcium Chloride/Total Barium Methods

Table 2a-3. Barium Sulfate in Sand				Total Barium Methods (mg/kg)			CaCL ₂ Extractable Barium (mg/kg)		
Soil Type	Spike Chemical	Soil Spike Concentration (mg/kg)	Data Type	EPA 3050	BC SALM	Fusion XRF			
				NWL	NWL	ALS-CHEMEX	0.1 M	0.5 M	1.0 M
Sand	Barium Sulfate	0	Rep. A	104	86	2,800	28	30	35
			Rep. B	116	72	2,900	16	52	54
			Mean	110	79	2850	22	41	45
			% Recovery	n/a	n/a	n/a	n/a	n/a	n/a
Sand	Barium Sulfate	2000	Rep. A	2320	1270	1700	93	163	197
			Rep. B	2160	1650	2400	89	162	218
			Mean	2240	1460	2050	91	163	208
			% Recovery	106	70	103	4	8	10
Sand	Barium Sulfate	10000	Rep. A	7600	3300	6700	155	300	356
			Rep. B	8400	3700	8200	164	280	395
			Mean	8000	3500	7450	160	290	376
			% Recovery	79	35	75	2	3	4
Sand	Barium Sulfate	50000	Rep. A	20000	5220	37700	132	394	336
			Rep. B	22900	4700	38100	133	240	385
			Mean	21450	4960	37900	133	317	361
			% Recovery	43	10	76	0.3	0.6	0.7

Appendix 2 Continued. Phase 2a Results: Calcium Chloride/Total Barium Methods

Table 2a-4. Barium Sulfate in Clay

Soil Type	Spike Chemical	Soil Spike Concentration (mg/kg)	Data Type	Total Barium Methods (mg/kg)			CaCL ₂ Extractable Barium (mg/kg)		
				EPA 3050	BC SALM	Fusion XRF	0.1 M	0.5 M	1.0 M
				NWL	NWL	ALS-CHEMEX			
Clay	Barium Sulfate	0	Rep. A	292	178	800	4	8	13
			Rep. B	292	168	800	<5	13	24
			Mean	292	173	800	4	10	19
			% Recovery	n/a	n/a	n/a	n/a	n/a	n/a
Clay	Barium Sulfate	2000	Rep. A	1720	334	2600	3	7	12
			Rep. B	1700	314	2600	<5	10	23
			Mean	1710	324	2600	3	8	18
			% Recovery	75	15	130	0.1	0.4	1
Clay	Barium Sulfate	10000	Rep. A	6700	420	9200	3	8	16
			Rep. B	6800	402	9600	<5	10	23
			Mean	6750	411	9400	3	9	19
			% Recovery	66	4	94	0.0	0.1	0.2
Clay	Barium Sulfate	50000	Rep. A	14600	785	41800	2	8	21
			Rep. B	12000	1060	42500	<5	8	20
			Mean	13300	923	42150	2	8	20.4
			% Recovery	26	2	84	0.0	0.0	0.0

Appendix 3. Phase 2b Data Tables

Table 2b-1. Barium Sulfate in Sand				Total Barium Methods (mg/kg)		
				EPA 3050	BC SALM	Fusion XRF
Soil Type	Spike Chemical	Soil Spike Concentration (mg/kg)	Data Type	NWL	NWL	ALS- CHEMEX
Sand	Barium Sulfate	0	Rep. A	123	89	1600
			Rep. B	88	74	1600
			Mean	106	82	1600
			% Recovery	n/a	n/a	n/a
Sand	Barium Sulfate	100	Rep. A	236	196	600
			Rep. B	332	179	500
			Mean	284	188	550
			% Recovery	127	103	100*
Sand	Barium Sulfate	300	Rep. A	451	340	700
			Rep. B	582	340	700
			Mean	517	340	82
			% Recovery	127	89	233
Sand	Barium Sulfate	1000	Rep. A	1040	906	1000
			Rep. B	1370	1030	1200
			Mean	1,205	968	1100
			% Recovery	109	90	71
Sand	Barium Sulfate	3000	Rep. A	4000	2110	2500
			Rep. B	3820	2320	2800
			Mean	3,910	2215	2650
			% Recovery	126	72	75
Sand	Barium Sulfate	10000	Rep. A	9400	4000	7300
			Rep. B	9100	4000	8400
			Mean	9,250	4000	7850
			% Recovery	92	40	74
Sand	Barium Sulfate	100000	Rep. A	24200	4390	79400
			Rep. B	23600	4840	89600
			Mean	23,900	4615	84500
			% Recovery	24	5	84

Appendix 3 (cont'd). Phase 2b Data Tables

Table 2b-2. Barium Sulfate in Clay				Total Barium Methods (mg/kg)		
				EPA 3050	BC SALM	Fusion XRF
Soil Type	Spike Chemical	Soil Spike Concentration (mg/kg)	Data Type	NWL	NWL	ALS- CHEMEX
Clay	Barium Sulfate	0	Rep. A	391	181	900
			Rep. B	348	171	900
			Mean	370	176	900
			% Recovery	n/a	n/a	n/a
Clay	Barium Sulfate	100	Rep. A	442	214	900
			Rep. B	430	191	900
			Mean	436	203	900
			% Recovery	93	73	90
Clay	Barium Sulfate	300	Rep. A	560	261	1100
			Rep. B	560	242	1100
			Mean	560	252	1100
			% Recovery	84	53	92
Clay	Barium Sulfate	1000	Rep. A	1860	313	2200
			Rep. B	1640	323	2100
			Mean	1,750	318	2150
			% Recovery	128	27	113
Clay	Barium Sulfate	3000	Rep. A	2070	365	3000
			Rep. B	2280	346	3000
			Mean	2,175	356	3000
			% Recovery	65	11	77
Clay	Barium Sulfate	10000	Rep. A	5600	541	7900
			Rep. B	5800	547	7700
			Mean	5,700	544	7800
			% Recovery	55	5	72
Clay	Barium Sulfate	100000	Rep. A	19500	1040	78000
			Rep. B	17200	1060	74600
			Mean	18,350	1,050	76300
			% Recovery	18	1	76

Appendix 4. Phase 2b Side Study Data Tables (mg/kg)

Soil Type	Spike Chemical	Soil Spike (mg/kg)	Data Type	2b-0. Total Barium Methods using Reference Method Mandatory Requirements (from Table 2b)		Total Barium Methods 2b-1. Double Acid Volume Ratio Study		Total Barium Methods 2b-6. Sample Weight Study	
				EPA 3050	BCSALM	EPA 3050B Acid Volume 20 mL	BC SALM Acid Volume 10 mL	EPA 3050	BC SALM
Sand	Barium Sulfate	0	Rep. A	123	89	127	75	220	58
			Rep. B	88	74	98	64	180	62
			Mean	106	82	113	70	200	60
			% Recovery	n/a	n/a	n/a	n/a	n/a	n/a
Sand	Barium Sulfate	100	Rep. A	236	196	201	159	420	200
			Rep. B	332	179	275	225	180	210
			Mean	284	188	238	192	300	205
			% Recovery	127	103	105	110	100	128
Sand	Barium Sulfate	300	Rep. A	451	340	386	340	546	360
			Rep. B	582	340	496	350	929	360
			Mean	517	340	441	345	738	360
			% Recovery	127	89	103	92	148	100
Sand	Barium Sulfate	1000	Rep. A	1040	906	940	1030	1140	915
			Rep. B	1370	1030	1200	946	1250	911
			Mean	1,205	968	1,070	988	1,195	913
			% Recovery	109	90	95	92	100	86
Sand	Barium Sulfate	3000	Rep. A	4000	2110	3250	2330	3400	3480
			Rep. B	3820	2320	3310	2430	2800	2620
			Mean	3,910	2,215	3,280	2,380	3,100	3,050
			% Recovery	126	72	105	77	97	100
Sand	Barium Sulfate	10000	Rep. A	9400	4000	6700	6240	11500	9730
			Rep. B	9100	4000	7900	5760	12800	9940
			Mean	9,250	4,000	7,300	6,000	12,150	9,835
			% Recovery	92	40	72	60	119	98
Sand	Barium Sulfate	50000	Rep. A	20000	5220	20900	10000	37000	36000
			Rep. B	22900	4700	21800	10000	42000	23000
			Mean	21,450	4,960	21,350	10,000	39,500	29,500
			% Recovery	43	10	43	20	79	59
Sand	Barium Sulfate	100000	Rep. A	24200	4390	27400	10400	60500	53700
			Rep. B	23600	4840	28500	9800	52500	50200
			Mean	23,900	4,615	27,950	10,100	56,500	51,950
			% Recovery	24	5	28	10	56	52

Appendix 4 (Cont'd). Phase 2b Side Study Data Tables (mg/kg)

Soil Type	Spike Chemical	Soil Spike (mg/kg)	Data Type	2b-0. Total Barium Methods using Reference Method Mandatory Requirements (from Table 2b)		Total Barium Methods 2b-1. Double Acid Volume Ratio Study		Total Barium Methods 2b-6. Sample Weight Study		Total Barium Methods 2b-2. Acid Strength Study	
				EPA 3050	BCSALM	EPA 3050B Acid Volume 20 mL	BC SALM Acid Volume 10 mL	EPA 3050	BC SALM	EPA 3050	BC SALM
Clay	Barium Sulfate	0	Rep. A	391	181	406	241	400	340	370	203
			Rep. B	348	171	389	236	440	330	320	199
			Mean	370	176	398	239	420	335	345	201
			% Recovery	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Clay	Barium Sulfate	100	Rep. A	442	214	463	270	493	430	400	188
			Rep. B	430	191	494	250	533	440	396	168
			Mean	436	203	479	260	513	435	398	178
			% Recovery	93	73	96	77	99	100	89	59
Clay	Barium Sulfate	300	Rep. A	560	261	560	310	831	683	481	200
			Rep. B	560	242	580	350	761	539	392	196
			Mean	560	252	570	330	796	611	437	198
			% Recovery	84	53	82	61	111	96	68	40
Clay	Barium Sulfate	1000	Rep. A	1860	313	1610	527	1900	1520	970	175
			Rep. B	1640	323	1590	526	1780	1620	1040	178
			Mean	1,750	318	1,600	527	1,840	1,570	1,005	177
			% Recovery	128	27	114	43	130	118	75	15
Clay	Barium Sulfate	3000	Rep. A	2070	365	2070	632	2600	2370	1380	230
			Rep. B	2280	346	2070	637	2700	2400	1460	230
			Mean	2,175	356	2,070	635	2,650	2,385	1,420	230
			% Recovery	65	11	61	20	77	72	42	7
Clay	Barium Sulfate	10000	Rep. A	5600	541	5200	1170	7940	6700	2920	182
			Rep. B	5800	547	5300	1150	7720	6530	1690	187
			Mean	5,700	544	5250	1,160	7,830	6,615	2,305	185
			% Recovery	55	5	50	11	75	64	22	2
Clay	Barium Sulfate	50000	Rep. A	14600	785	12300	2440	28000	18500	3470	122
			Rep. B	12000	1060	13000	2500	28000	17400	4080	116
			Mean	13,300	923	12,650	2,470	28,000	17,950	3,775	119
			% Recovery	26	2	25	5	56	36	7	0
Clay	Barium Sulfate	100000	Rep. A	19500	1040	17800	4000	37000	29000	4380	181
			Rep. B	17200	1060	18400	3800	36000	28000	5800	175
			Mean	18,350	1,050	18,100	3,900	36,500	28,500	5,090	178
			% Recovery	18	1	18	4	36	28	5	0

Appendix 4 (Cont'd). Phase 2b Side Study Data Tables (mg/kg)

Soil Type	Spike Chemical	Soil Spike (mg/kg)	Data Type	Total Barium Methods 2b-3. Hold Time/Temp Study: Immediate		Total Barium Methods 2b-3. Hold Time Study Day 3 RT		Total Barium Methods 2b-3. Hold Temp Study Day 3 Fridge		Total Barium Methods 2b-3. Hold Time Study Day 7 RT		Total Barium Methods 2b-3. Hold Temp Study Day 7 Fridge	
				EPA 3050	BC SALM	EPA 3050	BC SALM	EPA 3050	BC SALM	EPA 3050	BC SALM	EPA 3050	BC SALM
Clay	Barium Sulfate	0	Rep. A	370	203	372	306	335	186	382	194	358	167
			Rep. B	320	199	192	190	293	166	332	184	319	130
			Mean	345	201	282	248	314	176	357	189	339	149
			% Recovery	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Clay	Barium Sulfate	100	Rep. A	400	188	407	169	396	166	414	183	413	159
			Rep. B	396	168	439	163	390	152	421	161	416	140
			Mean	398	178	423	166	393	159	418	172	415	150
			% Recovery	89	59	111	48	95	58	91	60	95	60
Clay	Barium Sulfate	300	Rep. A	481	200	487	195	461	191	495	195	495	154
			Rep. B	392	196	386	182	379	179	404	174	404	138
			Mean	437	198	437	189	420	185	450	185	450	146
			% Recovery	68	40	75	34	68	39	68	38	70	33
Clay	Barium Sulfate	1000	Rep. A	970	175	1080	146	1070	127	1180	131	1300	86
			Rep. B	1040	178	1150	152	1200	136	1250	138	1370	95
			Mean	1,005	177	1,115	149	1,135	132	1,215	135	1,335	91
			% Recovery	75	15	87	12	86	11	90	11	100	8
Clay	Barium Sulfate	3000	Rep. A	1380	230	1550	229	1530	203	2630	178	1670	165
			Rep. B	1460	230	1620	244	1650	210	1710	228	1900	158
			Mean	1,420	230	1,585	237	1,590	207	2,170	203	1,785	162
			% Recovery	42	7	48	7	48	7	65	6	53	5
Clay	Barium Sulfate	10000	Rep. A	2920	182	3120	137	3100	109	3410	123	3130	72
			Rep. B	1690	187	2280	146	2300	119	2450	126	2600	75
			Mean	2,305	185	2,700	142	2,700	114	2,930	125	2,865	74
			% Recovery	22	2	26	1	26	1	28	1	28	1
Clay	Barium Sulfate	50000	Rep. A	3470	122	4740	112	3941	67	5600	106	4150	55
			Rep. B	4080	116	5100	100	4570	59	5700	91	4690	46
			Mean	3,775	119	4,920	106	4,256	63	5,650	99	4,420	51
			% Recovery	7	0	10	0	8	0	11	0	9	0
Clay	Barium Sulfate	100000	Rep. A	4380	181	5900	150	4770	97	6500	161	4980	88
			Rep. B	5800	175	7600	156	6400	100	8600	126	6400	84
			Mean	5,090	178	6,750	153	5,585	99	7,550	144	5,690	86
			% Recovery	5	0	7	0	6	0	8	0	6	0

Appendix 4 (Cont'd). Phase 2b Side Study Data Tables

2b-4. Final Dilution Volume of Digest Solution Prior to ICP Analysis

Soil Type	Spike Chemical	Soil Spike (mg/kg)	Data Type	Total Barium Methods 2b-4. Final Dilution Volume Study (mg/kg)		Total Barium Methods 2b-4. Final Dilution Volume Study (mg/kg)		Total Barium Methods 2b-4. Final Dilution Volume Study (mg/kg)	
				EPA 3050B 50 mL	BC SALM 50 mL	EPA 3050B 100mL	BC SALM 100mL	EPA 3050B 200 mL	BC SALM 200 mL
Sand	Barium Sulfate	3000	Rep. A	3060	2060	2780	1866	2560	2148
			Rep. B	2490	2000	3100	2100	2800	1800
			Mean	2775	2,030	2940	1,983	2680	1,974
			% Recovery	89	66	95	64	86	64
Clay	Barium Sulfate	3000	Rep. A	2070	370	2000	344	2000	328
			Rep. B	2170	300	2100	374	2040	344
			Mean	2120	335	2050	359	2020	336
			% Recovery	63	11	61	11	60	11

Appendix 4 (Cont'd). Phase 2b Side Study Data Tables

2b-5 Comparison of Barite Product Solubility to Barium Sulfate Spiked in Soil and Sand (mg/kg)			2b-0. Total Barium Methods using Reference Method Mandatory Requirements (from Table 2b)		2b-0. Total Barium Methods using Reference Method Mandatory Requirements (from Table 2b)		Barite Product Nominal(mg/kg)	Total Barium Methods 2b-5. Barite Product		
Soil Type	Soil Spike (mg/kg)	Data Type	EPA 3050	BCSALM	Soil Type	EPA 3050		BCSALM	EPA 3050	BC SALM
Clay	10000	Rep. A	5600	541	Sand	9400	4000	10000	7800	5500
		Rep. B	5800	547		9100	4000		7500	5200
		Mean	5,700	544		9,250	4,000		7,650	5,350
		% Recovery	55	5		92	40		77	54
								11000	7110	
								12000	6930	
								11,500	7,020	
								38	23	
Clay	50000	Rep. A	14600	785	Sand	20000	5220	50000	13800	7780
		Rep. B	12000	1060		22900	4700		12900	8040
		Mean	13,300	923		21,450	4,960		13,350	7,910
		% Recovery	26	2		43	10		27	16
Clay	100000	Rep. A	19500	1040	Sand	24200	4390	100000	14100	7000
		Rep. B	17200	1060		23600	4840		15000	6500
		Mean	18,350	1,050		23,900	4,615		14,550	6,750
		% Recovery	18	1		24	5		15	7
								16200	6120	
								17100	6540	
								16,650	6,330	
								6	2	
								15300	6150	
								16100	5960	
								15,700	6,055	
								31	12	

Appendix 5. Phase 2b-7SS Data Tables

Table A5-1. Barite Solubility in CaCl₂

Nominal Barium from Barium Sulfate (mg/kg)	Measured Barium			
	0.1 M CaCl ₂		1.0 M CaCl ₂	
	mg/kg	mg/L	mg/kg	mg/L
100	13	1.3	21	2.1
300	22	2.2	35	3.5
500	26	2.6	41	4.1
1,000	40	4.0	73	7.3
3,000	45	4.5	86	8.6
5,000	60	6.0	147	14.7
10,000	71	7.1	124	12.4
30,000	69	6.9	180	18
50,000	63	6.3	179	17.9
100,000	64	6.4	205	20.5
Average from 5,000 to 100,000	65	6.5	167	17

Appendix 5. Phase 2b-7SS Data Tables (cont'd)

Table A5-2. Chloride Spiked Sand

			Nominal Barium Spiked to Soils (mg/kg)											
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
BC Soluble Barium			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Chloride Concentration (mg/kg)	1	0	24	23	23	154	156	155	192	188	190	351	309	330
	2	1,000	67	42	55	147	142	145	202	249	226	255	261	258
	3	3,000	63	52	57	205	176	191	198	199	199	286	262	274
	4	10,000	50	37	44	152	148	150	210	217	214	253	277	265
	5	30,000	32	30	31	124	135	130	183	184	184	214	217	216
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
Modified BC SALM			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Chloride Concentration (mg/kg)	1	0 CI	52	50	51	413	443	428	839	715	777	1400	1420	1410
	2	1,000 CI	79	74	77	390	444	417	800	715	758	1160	1020	1090
	3	3,000 CI	80	76	78	414	448	431	716	799	758	1320	1280	1300
	4	10,000 CI	90	69	80	428	437	433	684	689	687	1190	1140	1165
	5	30,000 CI	46	60	53	376	491	434	807	743	775	984	1130	1057
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
EPA 3050B Total Barium			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Chloride Concentration (mg/kg)	1	0 CI	56	71	64	936	866	901	1940	1790	1865	3780	6000	4890
	2	1,000 CI	144	105	125	645	517	581	2300	2330	2315	6920	7110	7015
	3	3,000 CI	111	96	104	789	746	768	1960	2050	2005	6480	7530	7005
	4	10,000 CI	101	100	101	541	788	665	1700	1650	1675	5610	5140	5375
	5	30,000 CI	61	75	68	708	612	660	1780	1780	1780	6470	6080	6275

Appendix 5. Phase 2b-7SS Data Tables (cont'd)

Table A5-3. Sulfate Spiked Sand

			Nominal Barium Spiked to Soils (mg/kg)											
			A			B			C			D		
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
BC Soluble Barium														
Sulfate Concentration (mg/kg)	1	0	26	23	24	132	128	130	157	162	160	192	189	191
	2	1,000	32	33	32	54	52	53	63	65	64	73	79	76
	3	3,000	24	27	25	32	26	29	34	32	33	35	34	34
	4	10,000	15	16	15	18	19	18	20	19	19	18	18	18
	5	30,000	14	14	14	18	17	17	17	17	17	20	20	20
			Nominal Barium Spiked to Soils (mg/kg)											
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Modified BC SALM														
Sulfate Concentration (mg/kg)	1	0 SO4	67	75	71	352	409	381	650	686	668	1160	1290	1225
	2	1,000 SO4	247	278	263	411	406	409	748	684	716	922	835	879
	3	3,000 SO4	235	249	242	343	343	343	557	491	524	486	550	518
	4	10,000 SO4	91	89	90	236	209	223	253	254	254	200	250	225
	5	30,000 SO4	58	60	59	84	100	92	135	136	136	140	200	170
			Nominal Barium Spiked to Soils (mg/kg)											
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
EPA 3050B Total Barium														
Sulfate Concentration (mg/kg)	1	0 SO4	65	141	103	757	788	773	1380	3290	2335	7220	7040	7130
	2	1,000 SO4	314	420	367	1020	706	863	3350	2480	2915	5310	4340	4825
	3	3,000 SO4	607	278	443	1120	891	1006	2630	1970	2300	8120	6320	7220
	4	10,000 SO4	104	143	124	1010	1750	1380	2040	1490	1765	5090	6200	5645
	5	30,000 SO4	195	172	184	662	638	650	2030	2360	2195	5990	5200	5595

Appendix 5. Phase 2b-7SS Data Tables (cont'd)

Table A5-4. Chloride Spiked Clay

			Nominal Barium Spiked to Soils (mg/kg)											
			A			B			C			D		
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
BC Soluble Barium			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Chloride Concentration (mg/kg)	1	0 CI	14.2	13.4	13.8	14.6	14.6	14.6	16.8	15.5	16.2	15.4	16.0	15.7
	2	1,000 CI	14.3	14.2	14.3	14.3	16.1	15.2	14.7	15.1	14.9	16.7	16.2	16.5
	3	3,000 CI	13.9	14.1	14.0	15.6	14.3	15.0	15.4	14.9	15.2	17.2	16.6	16.9
	4	10,000 CI	14.4	14.3	14.4	15.1	15.8	15.5	18.0	17.1	17.6	22.8	19.8	21.3
	5	30,000 CI	13.7	15.3	14.5	14.6	15.1	14.9	15.8	16.9	16.4	19.0	19.9	19.5
			Nominal Barium Spiked to Soils (mg/kg)											
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Modified BC SALM Chloride Concentration (mg/kg)	1	0 CI	142	166	154	159	160	160	163	130	147	140	140	140
	2	1,000 CI	144	128	136	158	167	163	147	168	158	130	150	140
	3	3,000 CI	138	154	146	147	177	162	149	134	142	140	140	140
	4	10,000 CI	163	146	155	157	159	158	168	154	161	140	130	135
	5	30,000 CI	161	154	158	173	164	169	172	173	173	160	170	165
			Nominal Barium Spiked to Soils (mg/kg)											
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
EPA 3050B Total Barium Chloride Concentration (mg/kg)	1	0 CI	272	293	283	1010	867	939	2260	2370	2315	4940	4710	4825
	2	1,000 CI	364	374	369	1080	1050	1065	2110	2240	2175	4920	4160	4540
	3	3,000 CI	315	300	308	1080	1040	1060	2170	2040	2105	4360	4460	4410
	4	10,000 CI	377	369	373	965	1080	1023	1990	2180	2085	4280	4200	4240
	5	30,000 CI	325	334	330	945	1060	1003	1920	1890	1905	4230	4160	4195

Appendix 5. Phase 2b-7SS Data Tables (cont'd)

Table A5-5. Sulfate Spiked Clay

			Nominal Barium Spiked to Soils (mg/kg)											
			A			B			C			D		
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
BC Soluble Barium			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Sulfate Concentration (mg/kg)	1	0	14.0	13.5	13.8	13.2	13.6	13.4	13.7	13.6	13.7	12.5	11.8	12.2
	2	1,000	12.6	13.4	13.0	12.2	12.7	12.5	12.7	13.4	13.1	11.9	13.4	12.7
	3	3,000	12.9	12.4	12.7	11.6	12.5	12.1	11.1	12.1	11.6	12.6	12.1	12.4
	4	10,000	9.6	9.5	9.6	11.4	11.3	11.4	12.7	11.2	12.0	12.4	13.2	12.8
	5	30,000	9.3	10.9	10.1	9.4	9.9	9.7	10.4	10.5	10.5	11.1	10.8	11.0
			Nominal Barium Spiked to Soils (mg/kg)											
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
Modified BC SALM			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Sulfate Concentration (mg/kg)	1	0 SO4	161	144	153	139	132	136	157	140	149	130	130	130
	2	1,000 SO4	149	128	139	138	137	138	151	142	147	130	140	135
	3	3,000 SO4	128	128	128	130	125	128	124	125	125	150	140	145
	4	10,000 SO4	105	102	104	95	96	96	103	107	105	99	100	100
	5	30,000 SO4	63	56	60	60	61	61	65	64	65	65	72	69
			Nominal Barium Spiked to Soils (mg/kg)											
			0			1,000			3,000			10,000		
			Measured Barium Concentration (mg/kg)											
EPA 3050B Total Barium			Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean	Rep A	Rep B	Mean
Sulfate Concentration (mg/kg)	1	0 SO4	310	290	300	1210	1260	1235	2260	2200	2230	4800	4590	4695
	2	1,000 SO4	330	320	325	1070	1170	1120	2140	2270	2205	5150	4430	4790
	3	3,000 SO4	290	280	285	1120	1080	1100	2000	2060	2030	3790	3660	3725
	4	10,000 SO4	310	290	300	1070	1050	1060	2010	2000	2005	3830	3760	3795
	5	30,000 SO4	300	300	300	1070	1150	1110	1700	2060	1880	3680	3200	3440