

DEVELOPMENT OF BC CSR ANALYTICAL METHOD FOR SOLUBLE BARIUM

PHASE 1: EVALUATION OF VIABLE ANALYTICAL METHODS FOR SOLUBLE BARIUM

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

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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, unless they are strongly sequestered onto soil cation exchange sites (e.g. barium chloride, barium acetate).

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 (Norwest Labs / Bodycote), 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

This report documents Phase 1 of the project.

2.0 PHASE 1 OUTLINE AND OBJECTIVES

Phase 1 of the project was divided into four components:

1. Identification of Potential Analytical Methods for Soluble Barium.
2. Preliminary Laboratory Testing of Candidate Methods for Soluble Barium.
3. Laboratory Optimization of Variables for Calcium Chloride Methods.
4. Cursory Evaluation of Methods for Total Barium.

For the first component, Miles Tindal prepared a summary of potential methods from the literature that were identified by the Barite-Barium Issues Committee and the BCLQAAC Barite Task Group. This summary is included in section 3 of this report.

The second component of the Phase 1 study consisted of a laboratory evaluation of all the proposed soluble barium methods using a barium carbonate field soil, a barite field soil, and three barite spiked background reference soils of differing soil textures.

The third component of the Phase 1 study involved laboratory optimizations of the calcium chloride extraction method that is prescribed by Alberta Environment for their regulation of soluble barium. This method was identified early on as a strong candidate for the BC method. Key variables associated with this method, including pH, calcium chloride concentration, and extraction ratio, were investigated in an attempt to characterize their effects on barite recovery from soils of varied textures.

The fourth component of Phase 1 was a preliminary evaluation of four different analytical methods for total and strong acid leachable barium. All samples analyzed by the targeted soluble barium methods were analyzed by these methods in order to determine the true total barium concentrations of the test samples, and also to assess the relative performance of these methods for total barium.

3.0 IDENTIFICATION OF POTENTIAL SOLUBLE BARIUM METHODS

There are a wide range of potential methods for the chemical analysis of barium in soil. Some of these methods may approximate the “total” barium concentration, and others may approximate the “soluble” barium concentration. A brief summary of five potential analytical methods for soluble barium is provided here, together with some discussion on the relevance and potential pros and cons of each.

Analytical methods for soils typically include an extraction step and a measurement step. In the case of determining soluble barium in soil, it is anticipated that the major difference between methods will be in the extraction, and that the measurement technique used (typically atomic absorption or inductively coupled plasma) will have relatively little effect on the outcome. Accordingly, this discussion focuses on extraction techniques. Extraction techniques reviewed here include the following:

- Alberta Barite Guidelines Calcium Chloride Extraction;
- DTPA extraction;
- EDTA extraction;
- Synthetic Precipitation Leaching Procedure (SPLP); and,
- Toxicity Characteristic Leaching Protocol (TCLP).

3.1 Alberta Barite Guidelines Calcium Chloride Extraction

This method uses excess calcium ions to displace barium from cation exchange sites, and measures the total amount of barium that is dissolved in the pore water together with the barium that can be released through cation exchange. The barium measured by this method has been shown to correlate well to the fraction of barium that is bioavailable to plants, while neither the fraction in a saturated paste extract, nor the strong acid leachable barium (by EPA 3051) in the soil yielded a satisfactory correlation with plant-bioavailable barium (Chevron Canada Ltd., unpublished data). The method was developed for the Alberta Barite Guidelines Project, and was shown to be rugged (not unduly sensitive to small variations in the extraction time, extraction methodology, or dilution ratio).

The extraction methodology may be summarized as follows. The sample is prepared by air drying and sieving to <2 mm. 10 g of prepared sample is added to 100 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.

Among other variables, this project investigated whether a modification of this method using acidified calcium chloride solution was likely to be effective. The rationale was to simulate the most acid conditions that might reasonably be encountered in the environment in an oilfield setting (drilling mud sump, etc) without generating the extremely acid conditions of one of the strong acid extractions. A pH of 5 was identified by CAPP as approximately the worst case pH that would apply for these conditions.

Two other key variables of the CaCl_2 (calcium chloride concentration and extraction solution : soil ratio) were also evaluated to assess their effects on barium recovery from barite and a barium carbonate field soil.

3.2 DTPA Extraction (Carter, 1993)

DTPA is diethylene triamine pentaacetic acid, and is a chelating agent used in the extraction of available micronutrient cations Fe, Mn, Cu, and Zn. The DTPA soil test has potential relevance to the ecological direct contact exposure pathway, since it attempts to extract the labile fraction of various trace element cations in soil, and the results have been correlated to the fraction that is bioavailable to plants. The DTPA method was first proposed by Lindsay and Norvell (1967), and has received extensive validation (ten published papers referenced in Lindsay and Norvell, 1978) as being a good indicator of plant-available Zn, Fe, Mn, and Cu. The DTPA methodology published by Lindsay and Norvell (1978) and repeated in Carter (1993) was optimized for the extraction of the trace elements Zn, Fe, Mn, and Cu in soil. DTPA is used in this extraction because it has a favourable combination of stability constants for forming complexes with the four above-noted ions (Lindsay and Norvell, 1978). The DTPA method is inexpensive, reproducible, and easily adaptable to routine operations (Carter, 1993). No record was found of the method having been used to estimate plant-available barium.

The DTPA soil test was based on sound principles of soil and chelation chemistry (Lindsay and Norvell, 1978), and the extraction fluid is buffered to pH 7.3. The applicability of the method at more acidic pH values may be limited due to the potential for the DTPA to become saturated by calcium freed from the dissolution of calcium carbonate and bicarbonate. Detailed chemical speciation modelling would likely be required before attempting to adapt the parameters of the extracting solution.

The standard (Carter, 1993) DTPA soil test uses the following procedure. 10 g of air-dry soil (2 mm) is placed in a 125 mL Erlenmeyer flask. 20 mL of the extracting solution (0.005 M DTPA, 0.01 M CaCl_2 , and 0.1 M triethanolamine) is added, and the covered flask is agitated for 2 hours on a horizontal shaker with a stroke of 8.0 cm, and a speed of 120 cycles/min. The resultant suspension is filtered through Whatman No. 42 filter paper prior to analysis. The purpose of the triethanolamine (TEA) is to buffer the extracting solution to pH 7.3. The purpose of the CaCl_2 is to enable the extract to attain equilibrium with CaCl_2 , and so minimize the dissolution of CaCO_3 .

Before using this method as a possible candidate to assess available barium, it would be necessary to ensure that there was sufficient chelation capacity for the maximum concentrations of total labile cations that were anticipated. It should be noted that with the standard DTPA method, the maximum theoretical concentration of total extracted cations would be 10 mM cations/kg soil, equivalent to 1,370mg/kg soluble barium, if barium was the only cation extracted. The concentration of soluble barium in soil may exceed this value in certain situations, and accordingly, it may be necessary to increase either the concentration of the DTPA in the extracting solution, or the volume of extracting solution. Using 5 g soil and 25 mL of extracting solution with 0.05M DTPA would allow a maximum theoretical concentration of 250 mM of cations to be extracted, equivalent to approximately 34,000 mg/kg soluble barium, if barium was the only cation extracted.

It would also be possible to buffer the extracting solution to a more acidic pH, but, in a calcareous soil, this would likely result in increased dissolution of CaCO_3 , with the potential for saturating the available DTPA molecules with Ca, rather than Ba. As noted above, chemical speciation modelling would be required to ensure that the theoretical basis of the DTPA soil test was still valid for the amended composition of the extracting solution.

3.3 EDTA Extraction (Carter, 1993)

EDTA is ethylene diamine tetraacetic acid, and is a chelating agent similar in structure to DTPA. Many of the comments made for the DTPA soil test above apply equally to the EDTA extraction. EDTA extractable Cd, Cu, Pb, and Zn has been shown to be a good measure of the labile fraction of these soils that is available to plants (Merry and Tiller, 1978). Williams and Thornton (1973) have also shown that EDTA-extractable Mo and Se give a good prediction of the plant-available fraction of these metals, while total Mo and Se correlated poorly with the plant-available fractions. As with the DTPA soil test, the EDTA method has potential relevance to the ecological direct contact exposure pathway.

Various extraction procedures using EDTA have been described. These vary in the concentration of EDTA used, and the buffered pH of the extracting solution. Carter (1993) describes the following procedure. 5 g of air-dry soil (2 mm) is placed in a 125 mL Erlenmeyer flask. 25 mL of the extracting solution (0.05 M EDTA, adjusted to pH 7.0 with NH_4OH) is added, and the covered flask is shaken for 1 hour at a speed of 120 cycles/min. The resultant suspension is filtered through Whatman No. 42 filter paper prior to analysis.

Using the Carter (1993) EDTA method, the maximum theoretical concentration of total extracted cations would be 250 mM cations/kg soil, equivalent to approximately 34,300 mg/kg soluble barium, if barium was the only cation extracted.

3.4 Synthetic Precipitation Leaching Procedure (SPLP) USEPA SW-846 Method 1312

This method is included as a possible option for measuring “soluble” barium. The extraction fluid is designed to be representative of acid rain in the western United States. This method would be expected to be significantly less aggressive than strong acid extractions.

The extraction methodology may be summarized as follows. The particle size of the soil phase is reduced, if necessary. A minimum sample of 100 g is extracted (18 hours on a rotary agitator) with an amount of extraction fluid equal to 20 times the weight of the solid phase. For sites west of the Mississippi, the extraction fluid used is a 60/40 weight percent mixture of sulfuric and nitric acids with a pH of 5.0. Following extraction, the sample is then filtered ready for analysis.

The SPLP method has potential relevance to calculating soil quality guidelines protective of groundwater exposure pathways, since it aims to simulate the leaching of soils by through the action of a mildly acidic synthetic precipitation.

3.5 Toxicity Characteristic Leaching Procedure (TCLP) USEPA SW-846 Method 1311

This method is included for completeness, since it is commonly used in the environmental field to determine “leachable” metals in soils and industrial wastes. The procedure is a requirement within many landfill disposal regulations, including the BC Hazardous Waste Regulation.

The methodology is similar to the SPLP, but the extraction fluid used is different (slightly more acidic). In the case of drilling waste sumps, this method may be less relevant than the SPLP, based on the extraction fluid.

The extraction methodology may be summarized as follows. The particle size of the soil phase is reduced, if necessary. A minimum sample of 100 g is extracted (18 hours on a rotary agitator) with an amount of extraction fluid equal to 20 times the weight of the solid phase. Depending on the characteristics of the sample, the extraction fluid used is either acetic acid with a pH of 2.88, or a mix of acetic acid and sodium hydroxide with a pH of 4.93 (most sample types require the pH 4.93 fluid). Following extraction, the sample is filtered prior to analysis.

The TCLP extraction has been suggested by some as possibly being relevant to determining the available fraction of a metal in a mammalian stomach, based on the pH of the extraction. However, while the pH may be close to the physiologically relevant range, the extraction ratio is not, since incidental soil ingestion in the human stomach likely results in an extraction ratio closer to 10,000:1. True physiologically-based extraction tests (PBETs) have shown that the fraction of barium extracted from a barite-contaminated soil is strongly dependant on the extraction ratio.

4.0 EXPERIMENTAL PLAN FOR LABORATORY STUDIES

The primary objective of the phase 1 laboratory studies was to assess the various candidate soluble barium methods for their efficacy and recovery when applied to barite impacted soils of various 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 recoveries of soluble and non-sequestered forms of barium, with far lesser recovery of barite barium.

Two field-collected barium-affected soils (a barium carbonate soil, and a barite soil) and three barite-spiked background reference soils were prepared for analysis by a series of analytical methods for soluble barium and total barium ranging widely in vigour. The background reference soils included a sand, a sandy clay loam, and a clay. These were freshly spiked with drilling-mud grade barite at a concentration of 2,000 mg/kg barium (above background levels).

4.1 PREPARATION OF TEST SOILS

Five test soils were included in the Phase 1 investigations. Two of the soils were field-collected soils provided by ALS Edmonton. Both soils were assumed to be contaminated with barium from their original drilling waste related field sites. The remaining three soils, provided by Husky, were collected from sites as background samples and have likely not been exposed to industrial contaminants. These field background soils, which had previously been dried and ground, were spiked with barite to achieve desired barium concentrations of 2,000 mg/kg.

The first field soil used in the study was a sandy loam, with a total barium concentration of 2,460 mg/kg (by Fusion-XRF and Direct-XRF). The site in question had used barium carbonate as a weighting agent (not a common practice). Hence, this soil was designated as "Barium Carbonate Field Soil". This soil provided a valuable opportunity to assess candidate soluble barium methods using a soil that had been impacted with a more soluble form of barium than barite. It is important to note that this soil may contain a mixture of barium carbonate and barite.

A second field soil was obtained that is representative of typical barite sites. The second field soil was also a sandy loam with approximately 2,600 mg/kg total barium (by both Fusion-XRF and Fusion-ICP methods). Soluble barium in this sample by the Alberta Environment CaCl₂ method was typical of barite contaminated soils associated with drilling wastes. This soil was designated as "Barite Field Soil".

In order to investigate the impact of soil texture on the soluble barium methods, three barite spiked background soils were included in this study. The background soils types included sand, clay, and a sandy clay loam. These soils were characterized extensively for physical and chemical parameters (presented in Appendix 1). Key characteristics of the three soils that are most pertinent to soluble barium methods are provided in Table 1.

Table 1. Primary Characteristics of Background Soils

Parameter Name	Units	“BaCO ₃ ” Soil (Sandy Loam)	“Barite” Soil (Sandy Loam)	Sand	Clay	Silty Clay Loam
Sand	%	69.4	55.6	96.4	14.4	45.7
Silt	%	14.8	24.8	1.2	26.2	25.3
Clay	%	15.8	19.6	2.4	59.4	29
CEC	meq/100g			1.3	24.6	12.6
Barium (EPA 3050B)	mg/kg			64	333	195
Extractable Barium	mg/kg			9.4	1.1	2.7
Sulfate-S	mg/kg			3.4	1,120	326

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) commonly used in drilling muds. Barite powder was added directly to the dry background soils to achieve a target concentration of 2,000 mg/kg (as barium) above background barium levels. The barium background levels in these soils are given in table 1. The first batch of barium spiked soils, used for replicate analysis 1 and 2 for all studies was mixed using end-over-end rotation for one hour. The batch was then split into two replicate samples and distributed for testing. A second batch of barite spiked soils was also prepared but was mixed by rotation for 24 h to ensure homogeneity. This batch was used as a third replicate for the extraction studies.

4.2 STRONG ACID AND TOTAL BARIUM TEST METHODS USED

Four methods for measuring total or strong acid leachable barium were included in this study. The USEPA 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 environmentally available metals in soils. 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 analysis method that combines the Fusion dissolution technique with XRF quantitation, resulting in a total metals assay with an extremely high analytical concentration range for barium and other major compositional elements.

These tests were included to give us true measures of the total barium in our test samples, and to examine the limitations of each method for measuring high concentrations of barite barium in soil. Previous work conducted on drilling waste contaminated soils by Norwest Labs has indicated that the strong acid digest methods have a maximum or upper limit of barium that can be extracted from soil (estimated between 5,000 to 8,000 mg/Kg Ba), but correlation of these maxima with true total barium

concentrations are not known. 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.

4.2.1 US EPA 3050B

Modified versions of the US EPA 3050B method were used by both 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 or ALS-EDM used hydrochloric acid in this digestion, which is an option within the 3050B method that might also be expected to influence recoveries. Digestion times and temperatures varied slightly between the two labs.

Both NWL and ALS digested 0.5 g soil weights, with dilution to a final volume of 50 mL. ALS used a digestion temperature of 95C. NWL used a digestion temperature of 120C. 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.

4.2.2 BC Strong Acid Leachable Metals (SALM)

Variations of the BC SALM strong acid digestion method were used by NWL, ALS Vancouver (ALS-VAN), and ALS-EDM for selected samples in the study. Samples are normally dried, ground, and sieved prior to digestion, with the >2mm fraction discarded (spiked samples in this study were not sieved).

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.

ALS-VAN digested approximately 1.5 gram sub-samples with 10 mL of concentrated 1:1 nitric:hydrochloric acids. Samples were digested for 2 hours at 90°C, as per the BC SALM reference digestion conditions. Digests were diluted to 50 mL prior to ICP analysis.

NWL digested 0.5 gram sub-samples with 5 mL of concentrated 1:1 nitric:hydrochloric acids. Samples were digested for 4 hours at 120°C (a performance based modification of the method). Digests were diluted to 50 mL prior to ICP analysis.

4.2.3 Fusion (Lithium Borate) - ICP

The Fusion - ICP method is applicable to whole rock analysis of soils, coal, ash and cement products, and was conducted by Norwest / Bodycote Laboratories in Surrey. Soils were prepared by drying and grinding to < 75 um, then ashing at 900 C. The ash is mixed with a borate flux (Lithium metaborate

and lithium tetraborate) in a graphite crucible and fused at 1050°C for 40 minutes. The melt is dissolved in HCl and HNO₃ for 1 hour with agitation. Barium is measured in the digest by ICP.

4.2.4 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 study, 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. The barium carbonate field sample was analyzed for total barium using a portable XRF instrument, and excellent confirmation was achieved versus the Fusion-XRF technique.

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.

4.3 CALCIUM CHLORIDE EXTRACTABLE BARIUM METHODS USED

4.3.1 Alberta Environment Extractable Barium Method

The standard Alberta Environment method employs 0.1 M CaCl₂ as the extraction fluid. The dried and disaggregated samples were extracted using 5 g of sample with 50 mL extraction fluid, with agitation for 2 hours. The extract was filtered through a paper filter and analyzed for barium by ICP. Extractable barium results by this standard Alberta method are referred to as AENV 10:1 0.1 M CaCl₂ in Table 3.

4.3.2 Acidic and Basic Calcium Chloride Extractions

A study was conducted to investigate whether modification of pH of the calcium chloride solution has an impact on measured soluble barium concentrations. Extractions for soluble barium were completed using the same standard AENV barium method as described above, but the 0.1M CaCl₂ extraction fluid was adjusted to pH 3 and pH 10 using dilute HCl or NaOH. The extraction solutions were allowed to settle overnight and the decanted supernatant was analyzed for barium. No attempts were made to buffer the pH of these extraction solutions, which was considered beyond the scope of this study.

4.3.3 Calcium Chloride Extractable Barium with Increased Extraction Ratio

Previous work with drilling waste contaminated soil has demonstrated that variation of sample size and extraction solution volume can have a major impact on the concentration of both total and soluble barium measurements. This effect is likely a result of the extremely low aqueous solubility of barium sulfate. The relative concentrations of anions present in solution, and sulfate in particular, tend to control the concentration of barium in solution. The impact of extraction volume was examined using the AENV soluble barium method, but doubling the volume of 0.1 M CaCl₂, to achieve a 20:1 extraction fluid to soil ratio. The results of these tests are referred to in Table 3 as 20:1 CaCl₂.

4.3.4 Extractable Barium with Modified Calcium Chloride Concentration

The 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).

The Methods Task Group speculated that increasing the concentration of calcium may increase the recoveries of soluble barium from soils with higher cation exchange potential. This possibility was investigated in a series of tests using the AENV Barite Method, but using variable calcium chloride concentrations for the extraction fluids. Extractions for the test soils (variable clay content and cation exchange capacity) were completed using 0.05 and 1.0M CaCl₂, in addition to the standard 0.1M concentration.

4.3.5 Extractable Barium with Increased CaCl₂ Concentration & Extraction Ratio

The combined effect of increased extraction volume and increased calcium chloride concentration was also examined by performing 20:1 CaCl₂:soil extracts with 1.0M CaCl₂.

4.4 ALTERNATIVE EXTRACTION METHODS USED

In addition to the calcium chloride methods, several alternative extraction methods were examined for their ability to capture soluble barium from soils. These methods were selected as they are commonly used for analysis of metals for other specific assessment or regulatory purposes.

4.4.1 EPA 1311 – Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP method (USEPA SW-846 Method 1311) was performed by weighing 10 g of test sample into 500 mL polypropylene bottles and adding 200 mL of extraction fluid to achieve a 20:1 extraction ratio. 10 gram sub-samples were used because the test samples were highly homogeneous and were limited in quantity. The extraction fluid was prepared by addition of acetic acid and sodium hydroxide to achieve a pH of 4.93. Samples were extracted for 18 h using a rotary agitator. The fluid was filtered with a Whatman #42 filter paper, and the final pH was recorded. Analysis for barium was conducted by ICP-MS.

4.4.2 EPA 1312 – Synthetic Precipitation Leaching Procedure (SPLP)

The SPLP extraction fluid was prepared by addition of a 60/40 mixture of sulfuric and nitric acids to deionized water to a pH of 4.2. The test soils were extracted at a leachate ratio of 20:1, using 10 g of soil and 200 mL of extraction fluid. 10 gram sub-samples were used because the test samples were highly homogeneous and were limited in quantity. The extraction was done for 18 h on a rotary agitator. The extraction fluid was then filtered with a Whatman paper filter, and the pH of the final solution was measured. Analysis for barium was conducted by ICP-MS.

4.4.3 Chelation Methods - DTPA and EDTA

The DTPA and EDTA solutions used for this study employed the standard chelation agent concentrations, as outlined in the Carter methods. The DTPA solution was 0.005 M DTPA in 0.01 M CaCl₂ and 0.1 M TEA. The EDTA solution was 0.05 M Na₂-EDTA, adjusted to pH 7 with an ammonia solution. Test soils by both methods were extracted using 5 g of soil with 25 mL of extraction solution in polyethylene vials, with end-to-end shaking for 1 hour. The vials were allowed to settle overnight, then the supernatants were analyzed for barium by ICP.

As indicated in section 3.3, the chelate concentrations used will limit the amount of barium that could potentially be complexed. In the absence of other competing cations, the theoretical maximum chelated barium concentrations by the methods as employed in this study would be 3,430 mg/kg for DTPA and 34,300 mg/kg for EDTA. Of course barium is not the only cation in competition for chelating agents, and other cations may form more stable complexes with EDTA, so the actual maxima will be lower.

5.0 RESULTS AND DISCUSSION

Analytical results for strong acid and total barium methods are provided below in Table 2. Results for calcium chloride extraction methods are presented in Table 3. Results for the alternative extraction methods are shown in Table 4.

Table 2. Strong Acid and Total Barium Methods

Test Sample	Data Type	EPA 3050 Ba	EPA 3050 Ba	BC SALM	BC SALM	BC SALM	Fusion-XRF Total Ba	Fusion-ICP Total Ba
		NWL Edm.	ALS Edm.	NWL Edm.	ALS Edm.	ALS Vanc.	ALS Chemex	NWL Surrey
BaCO ₃ Field Soil	Rep. 1	1,560	1,420	1,550	1,500	1,710	2,400	
	Rep. 2		1,510			1,720	2,075*	
	Rep. 3					1,680	2,900*	
	Mean	1,560	1,465	1,550	1,500	1,703	2,460	
Clay + Barite (2,000 mg/kg Ba spike)	Rep. 1	1,170	728	1,160		366	3,000	2,750
	Rep. 2	1,210	636	1,130		295	2,400	
	Rep. 3	1,760		540		285		
	Mean	1,380	682	943		315	2,700	2,750
Sandy Clay Loam + 2,000 mg/kg Barite	Rep. 1	1,680	1,050	1,640		608	2,600	2,740
	Rep. 2	1,970	1,090	1,770		412	2,700	
	Rep. 3	2,000		1,430		597		
	Mean	1,883	1,070	1,613		539	2,650	2,740

Test Sample	Data Type	EPA 3050 Ba	EPA 3050 Ba	BC SALM	BC SALM	BC SALM	Fusion-XRF Total Ba	Fusion-ICP Total Ba
		NWL Edm.	ALS Edm.	NWL Edm.	ALS Edm.	ALS Vanc.	ALS Chemex	NWL Surrey
Sand + Barite (2,000 mg/kg Ba spike)	Rep. 1	1,840	1,360	1,030		630	2,800	2,580
	Rep. 2	2,230	1,410	2,280		623	(1,500)**	
	Rep. 3	2,040		2,040		685		
	Mean	2,037	1,385	1,783		646	2,800	2,580
Barite Field Soil	Rep. 1	2,550	2,100	2,000		1870	2,600	2,530
	Rep. 2	2,190	1,810	2,390		1830	2,600	
	Rep. 3					1830		
	Mean	2,370	1,955	2,195		1843	2,600	2,530

All units in mg/kg. Red highlighted results are true total barium estimates.

* = Direct measurement XRF by a portable instrument (no fusion step) confirmed the 2,400 mg/kg fusion-XRF value.

**() = Outlier, excluded from averages.

Third replicate is an independently prepared barite spiked sample, equilibrated prior to digestion by rotation for 24h.

Table 3. Calcium Chloride Extraction Methods

Test Sample	Data Type	0.05 M CaCl ₂ 10:1 Extr. pH=3	0.05 M CaCl ₂ 10:1 Extr. pH=7	0.05 M CaCl ₂ 10:1 Extr. pH=10	0.1M CaCl ₂ 10:1 Extr. pH=7 AENV	0.1M CaCl ₂ 10:1 Extr. pH=7 AENV	0.1M CaCl ₂ 10:1 Extr. pH=3	0.1M CaCl ₂ 20:1 Extr. pH=7 18hr/2hr	1.0M CaCl ₂ 10:1 Extr. pH=7 2 hr	1.0M CaCl ₂ 20:1 Extr. pH=7 2hr
		ALS	ALS	ALS	ALS	NWL	ALS	NWL	ALS	NWL
BaCO ₃ Soil	Rep. 1				339	338	353	424	440	462
	Rep. 2				351		352	407		528
	Rep. 3				344		363	411		
	Mean				345	338	356	414	440	495
Clay + 2,000 mg/kg Barite	Rep. 1	0.7	0.7	0.7	1.2	2.0		5.2	14.6	41.0
	Rep. 2	0.7	0.7	0.7	1.1	1.4		3.6		30.8
	Rep. 3					2.4		4.6		35.3
	Mean	0.7	0.7	0.7	1.2	1.9		4.5	14.6	35.7
Sandy Clay Loam + 2,000 mg/kg Barite	Rep. 1	1.8	1.8	2.0	3.3	3.7		9.7	28.2	54.4
	Rep. 2	1.8	1.9	1.9	3.3	4.2		10		53.1
	Rep. 3					5.1		10		57.0
	Mean	1.8	1.9	1.9	3.3	4.3		9.9	28.2	54.8
Sand + 2,000 mg/kg Barite	Rep. 1	47.5	50.4	45.4	66.8	65.7		136	163	285
	Rep. 2	53.7	48.9	44.2	66.2	65.7		136		301
	Mean	50.6	49.7	44.8	66.5	65.7		136	163	293
Barite Field Soil	Rep. 1	21.0	19.9	19.9	37.8	34.5		66.9	106	189
	Rep. 2	20.9	20.2	19.8		31.7		67.0		189
	Rep. 3									
	Mean	21.0	20.1	19.9	37.8	33.1		67.0	106	189

All units in mg/kg.

ALS = ALS Edmonton

NWL = Norwest Labs / Bodycote Edmonton

Table 4. Alternative Extraction Methods

Test Sample	Data Type	Deionized Water 20:1 Extraction	TCLP 20:1 Leachate pH 4.93	SPLP 20:1 Leachate	EDTA Extraction 0.05M	DTPA Extraction 0.005M
		NWL Edm.	NWL Edm.	NWL Edm.	ALS Edm.	ALS Edm.
BaCO ₃ Soil	Rep. 1	2.0	108	6.2	484	19.2
	Rep. 2		104	6.0	482	18.8
	Rep. 3		98	5.0	496	19.3
	Mean	2.0	103	5.8	487	19.1
Clay + Barite (2,000 mg/kg Ba spike)	Rep. 1		1.8	0.6	0.99	0.04
	Rep. 2		0.8	0.4	0.98	0.03
	Mean		1.3	0.5	0.99	0.04
Sandy Clay Loam + Barite (2,000 mg/kg Ba spike)	Rep. 1		1.4	0.6	2.5	0.18
	Rep. 2		1.5	0.6	3.0	0.14
	Mean		1.5	0.6	2.8	0.16
Sand + Barite (2,000 mg/kg Ba spike)	Rep. 1		62.2	1.0	56.1	3.6
	Rep. 2		57.8	1.0	56.7	3.5
	Mean		60.0	1.0	56.4	3.6
Barite Field Soil	Rep. 1		42.8	0.6	9.83	0.80
	Rep. 2		44.0	0.6	9.81	0.77
	Mean		43.4	0.6	9.82	0.79

All units in mg/kg.

5.1 Results for Total Barium Methods

Both the Fusion-XRF and Fusion-ICP methods appeared to recover essentially 100% of the expected target concentrations of barium in all test samples. Exact recoveries for total barium in the field spiked samples could not be determined, because no Fusion-XRF or Fusion-ICP data was available for the unspiked soils (only strong acid barium data was available for background concentrations). Using the strong acid barium data as the background soil barium concentrations, average recoveries by the Fusion-XRF and Fusion-ICP methods were 117%, 122%, and 124% for the spiked clay, sandy clay loam, and sand samples respectively. This implies that the true total barium concentrations in these samples are likely about 400–500 mg/kg higher than the strong acid results (see Appendix 1) indicate.

The Fusion-XRF and Fusion-ICP methods were in very close agreement, except for one outlying Fusion-XRF replicate on the sand sample. It is suspected that this replicate may have been low due to settling and stratification of the heavy barite salts in the sand sample during transit.

As a check on recovery of barite barium by Fusion-XRF, we also conducted this analysis on the Barium Carbonate soil mixed 4:1 with pure barite. This gave a result of 11.55% barium, equal to 97% recovery.

The ALS Chemex Fusion-XRF method has an upper limit of approximately 50% barium. Pure barite is 59% barium by weight. Therefore this method should generate accurate total barium results up to a barite concentration of 85%. We did not verify the accuracy of the Fusion-ICP method at barium levels

above 3,000 mg/kg, but it is presumed that this method could also measure barium up to 100% purity if appropriate dilutions are employed prior to ICP analysis.

5.2 Results for Strong Acid Leachable Barium Methods

Recovery of barium by acid digestion methods was significantly affected by soil texture and by lab-specific variables within the selected digestion techniques.

Roughly speaking, recovery of the acid digestion results versus the Fusion-XRF or Fusion-ICP results ranged from 23-75% for the spiked sand, from 23-70% for the spiked sandy clay loam and from 13-55% for the spiked clay. Recovery for the barium carbonate soil and the barite field soil by all acid digestion methods was consistently higher, ranging from approximately 60-90%

Recovery tended to be lowest for the BC SALM method as used by ALS in Vancouver, even compared to BC SALM analyses by NWL-EDM. ALS Vancouver follows the reference BC SALM method conditions, whereas NWL-EDM utilizes performance-based digestion conditions. Differences in barium recoveries are likely due to inter-laboratory differences in either the temperature of digestion, the duration of digestion, the soil to acid ratios utilized, or other factors not yet understood. These differences reinforce our initial concerns that seemingly small differences in laboratory methods can have significant impacts on strong acid leachable barium results (at least in the case of barite), and that these differences may not be identified during performance based validations of methods unless barite soils are specifically addressed. Until these factors are better understood and controlled, little reliance should be placed on the results of strong acid methods for barite barium.

It is important to note that US EPA 3050B contains two options; one uses nitric acid with peroxide, and the other employs nitric acid, peroxide, and hydrochloric acid. In addition to potential differences due to sample weights and dilution volumes used, these two alternative digestion techniques may also influence total barium recoveries. US EPA 3051 is another commonly used method for digestion of total metals, which is often used interchangeably with 3050B. The major difference between 3050B and 3051 is the use of a microwave digestion technique, rather than the hot block digestion technique of 3050B. It is commonly assumed that the techniques provide comparable digestions for metals, but the correctness of this assumption for barite barium is not understood.

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. Close attention must be paid within future studies to digestion temperatures, times, acid:solid ratios, and other potentially significant method variables.

Correlation of strong acid digestion barium recoveries versus true total barium concentration is also an important relationship to investigate, since it is predicted that all acid digestion methods will experience a concentration ceiling for total barium.

5.3 Results for Calcium Chloride Extraction Methods

A wide range of concentrations and several different extraction ratios were tested. Barium recovery was extremely sensitive to soil texture. For the spiked soils, using the standard Alberta Environment method with neutral salt solution at 0.1M, a 1:10 soil : solution ratio, and a 2 hour extraction period, only about 1 mg/kg barium was recovered from the clay, about 3 mg/kg from the sandy clay loam, and about 70 mg/kg from the sand.

This finding had not been anticipated, on the grounds that barite is insoluble and would essentially remain separate from the soil matrix, so that barium availability would depend mainly on barite solubility in the extracting solution. The effect of cation exchange capacity on recoveries of extractable barium from barite is greater than had been anticipated.

For the field soils, about 40 mg/kg of standard calcium chloride extractable barium was found in the "barite soil", versus 350 mg/kg in the "BaCO₃" soil, whereas both soils have fairly comparable total barium concentrations (2,700 vs. 2,460 mg/kg). This difference in soluble barium recovery is probably not due to texture, since both soils are medium-coarse. Given the site history of the "barium carbonate" test sample, the increased soluble barium is likely due to at least some presence of BaCO₃ in the sample, which is consistent with the history of the site (barite may also be present).

Changing the initial pH of the 0.1M calcium chloride extract (by using small amounts of strong acid or alkali) had little or no effect on barium recovery. This lack of change may be partially due to the fact that by the end of the shaking period, extract pH had returned to within 0.5 of a pH unit lower or higher than in a neutral extract, due to the buffering action of the soil being extracted. An acid or alkaline extract pH could be maintained for longer, by using strong solutions of weak acids or bases, or with buffers such as phthalate or borax; however, the extraction method would thus in effect be changed. However, results achieved to date, including results for the pH 4.93 TCLP extraction, indicate that reducing the initial pH of extracting solutions to pH 5 or even pH 3 has little to no effect on soluble barium.

Increasing the calcium chloride concentration from 0.05M to 1.0M greatly increased barium recovery, as did using a 2-fold wider soil:solution extraction ratio. At the 10:1 extraction ratio, the increase in calcium chloride concentration from 0.05M to 1.0M increased barium recovery from the barite spiked clay and sandy clay loam soils by a factor of 21 and 15 times, respectively. For the spiked sand sample, the increase in CaCl₂ concentration produced a lesser, but still significant increase of 3.6 times. This suggests that the increased CaCl₂ concentration is promoting increased recovery of barite in coarse textured soils by increasing its solubility through an ionic co-solvency effect. Barium recovery in fine textured soils appears to be increasing because of both an increased barite solubility and stronger cation exchange effects. The increasing solubility of barite with increasing concentrations of sodium chloride in water has been documented in the literature (Templeton, 1960).

A deionized water extraction of the barium carbonate soil (20:1 ratio) was conducted to assess the relative importance of cation exchange on the extraction methods. This produced the lowest results by far of any extraction method, with soluble barium of only 2 mg/kg, or approximately 100-200 times less recovery than with the more aggressive calcium chloride and EDTA methods.

5.4 Results for Chelation Methods

The Lindsay & Norvell DTPA extraction procedure and the SPLP procedure gave generally much lower recoveries than the calcium chloride methods. The concentration of DTPA in the Lindsay & Norvell method is quite low; also the chelated complex with barium is likely to be much less stable than complexes of the micronutrient metals (Fe, Cu etc.) for which this test is routinely used. The DTPA method as employed achieves far lower recoveries of soluble barium than all versions of the calcium chloride extraction method, likely because the 0.005M DTPA concentration was too low for this application.

Extraction using Na₂-EDTA solution gave results that agreed quite well with the standard calcium chloride method for all the soils in the study. The EDTA concentration was ten times higher than the DTPA concentration, which is likely a factor in the increased recoveries of the EDTA method relative to the DTPA method. Further increases in the EDTA concentration of this method may result in higher

recoveries of barium. Because this method utilizes a 0.05M sodium salt of EDTA, there may also be cation exchange effects contributed from the presence of sodium.

Table 5. Comparison of All Soluble Barium Methods (Averages Shown)

Averages of Soluble Barium Methods	DI Water 20:1 Extr.	0.05 M CaCl2 10:1 Extr. pH=3	0.05 M CaCl2 10:1 Extr. pH=7	0.05 M CaCl2 10:1 Extr. pH=10	0.1M CaCl2 10:1 Extr. pH=7 AEnv	0.1M CaCl2 10:1 Extr. pH=3	0.1M CaCl2 20:1 Extr. pH=7	1.0M CaCl2 10:1 Extr. pH=7	1.0M CaCl2 20:1 Extr. pH=7	TCLP 20:1 Leach pH 4.93	SPLP 20:1 Leach	EDTA 0.05M 5:1 Extr.	DTPA 0.005 M 5:1 Extr.
BaCO3 soil	2.0				341	356	414	440	495	103	5.8	487	19.1
Spiked Clay		0.7	0.7	0.7	1.5		4.5	15	36	1.3	0.5	1.0	0.04
Spiked SCL		1.8	1.9	1.9	3.8		9.9	28	55	1.5	0.6	2.8	0.2
Spiked Sand		51	50	45	66		136	163	293	60	1.0	56	3.6
Barite Field Soil		21	20	20	38		67	106	189	43	0.60	9.8	0.8

5.5 Results for TCLP and SPLP Methods

The TCLP method also gave fairly similar recoveries to the Alberta Environment calcium chloride method. However, recoveries were very low for the clay and sandy clay loam soils. Without modification to incorporate a cation exchange process, these methods would not be expected to give reliable recoveries for soluble barium in fine-textured soils.

The SPLP method utilizes sulfuric acid in its extraction medium, which was immediately responsible for the precipitation of barium sulfate in all samples. For this reason, barium results in all samples were lowest by this method. SPLP was clearly not an appropriate technique for the determination of soluble barium.

5.6 Dilution Issues with ICP Analysis of Barium Digests / Extracts

Prior to barium analysis by ICP, sample extracts or digests may require dilution to within the linear range of the instrumentation. The degree of final dilution is dependent on the barium concentration as well as salinity, and on the actual instrument's upper limit of detection (usually higher for ICP-OES than ICP-MS). Because of the low solubility of barium, it is important to consider that final analytical results may potentially be influenced by variations in final solution volume. Large dilutions of the final digest may increase the measured barium concentration. This has not been investigated in detail, but should be considered when comparing test results among labs, and when designing analytical method schemes for general use.

6.0 RECOMMENDATIONS AND CONCLUSIONS

Refer to Figure 1 for a graphical comparison of most of the analytical results obtained for soluble barium methods. Methods involving pH change alone are excluded because they showed no effect.

The TCLP and SPLP methods can clearly be eliminated from further consideration. The SPLP method precipitates barium due to the presence of sulfuric acid, and the TCLP method does not adequately recover barium from cation exchange sites on fine textured soils.

Modifications to the pH of the calcium chloride extraction solutions produced no noticeable effect on barium recoveries of any test samples. Furthermore, the varied buffering potential of soil samples makes extraction pH a difficult variable to control. Achieving more effective pH buffering in a calcium chloride extraction method would require considerable further work and investigation, and is not merited given the effects observed thus far.

The standard 0.005M DTPA extraction was insufficiently vigorous for our purposes, with far less recoveries than any of the other techniques for all samples, including the relatively soluble form of barium from the barium carbonate soil. A significantly increased DTPA concentration may improve its performance, but the data available indicates that the EDTA chelation method would likely perform as well or better. No additional studies are recommended for this method.

The standard EDTA method performed similarly to the Alberta Environment calcium chloride method, and may have potential as a viable method for soluble barium. However, the mechanism of this extraction technique for barium is less understood than other techniques, particularly in terms of the chelation of barium, and how this may be affected by uncontrolled variables. To further pursue this method, considerably more investigation would be required into the effects of extraction ratio and EDTA concentration on barite recoveries, and on other factors that may affect chelation. We recommend that no further work is done on EDTA methods, unless the calcium chloride methods cannot meet the objectives of BC MOE. The calcium chloride methods are better understood, are known to be rugged and easy to use, and will give some consistency with the approach used in Alberta.

Increasing the calcium chloride extract concentration from 0.1 M to 1.0 M, combined with widening the extraction ratio from 10:1 to 20:1 were very effective in increasing the recoveries of barium from spiked and real-world soils. Optimization of these variables may be environmentally relevant for two reasons:

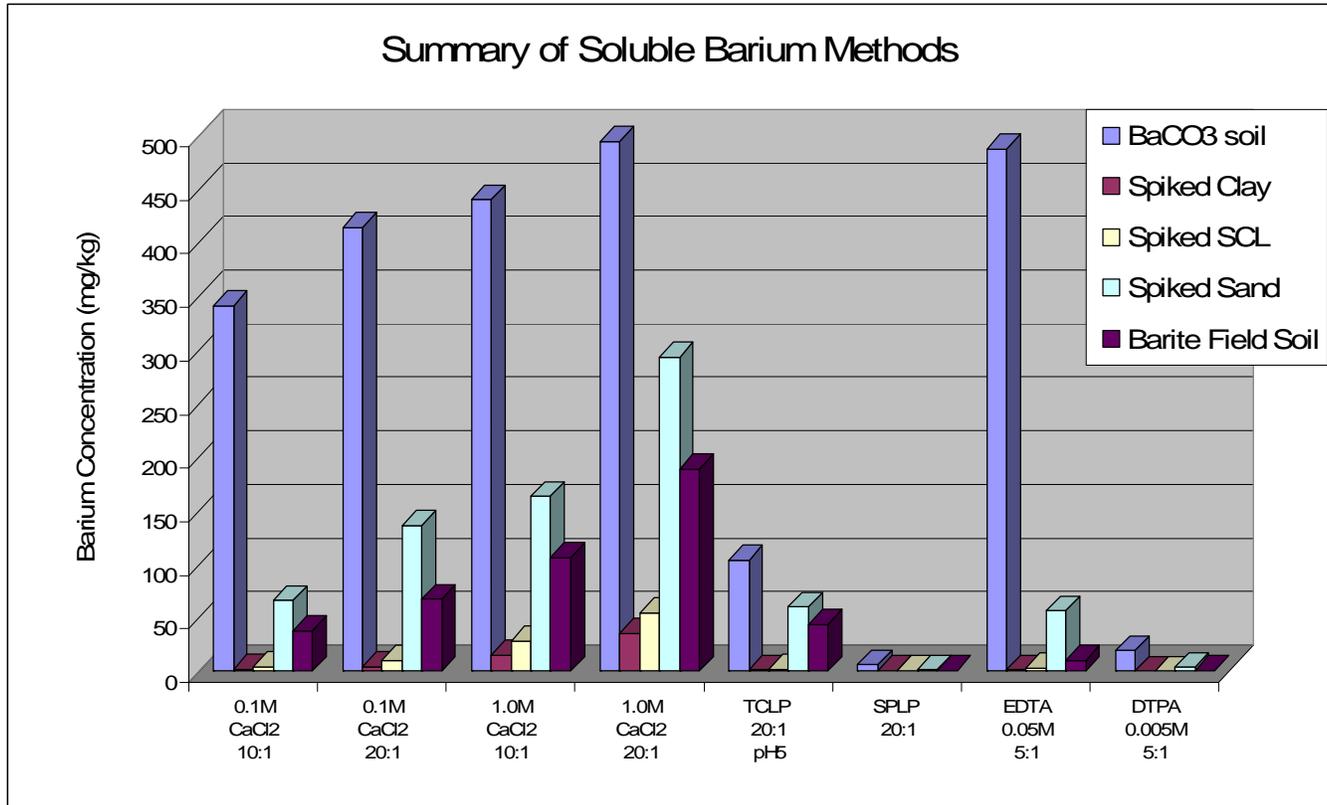
- i) Increased CaCl_2 concentration increases the recovery of barium from cation exchange sites on fine textured samples. Barium adsorbed to cation exchange sites may be environmentally available, as it is unlikely to be in the form of barite.
- ii) Increased CaCl_2 concentrations, which appear to increase the solubility of barite in laboratory solutions, could simulate the effect of brines from produced water that may be present in some drilling waste sites (Note however that brine solutions at drilling waste sites would likely never be found with salt concentrations as high as 1.0M).

Modifications to CaCl_2 concentration and extraction ratio would be simple and effective, yet the extraction method remains essentially the same as the standard Alberta Environment method for soluble barium. Inclusion of one or both of these modifications would seem to be the obvious changes to make the method more aggressive in terms of the recovery of soluble barium from fine-textured, retentive soils. These changes were much more effective than leaving the concentration of CaCl_2 unchanged at 0.01, and lengthening the extraction time.

However, soluble barium recoveries of these methods must first be evaluated 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 optimum method should not be overly aggressive for the liberation of barite.

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.

Figure 1. Graphical Comparison of Selected Soluble Barium Methods



REFERENCES

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

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.

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.

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

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*.

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*.

ASTM; American Society for Testing and Materials Volume 04.01 Method C114 Analysis of cement.

EPA 6200. Test Methods for Evaluating Solid Waste, SW-846 Vol. 1A. Method 6200, Revision 0, January 1998. *Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*.

Templeton, C. C. (1960). Solubility of Barium Sulfate in Sodium Chloride Solutions from 25° to 95°C. *Journal of Chemical and Engineering Data*, **5** (4), 514-516.

Appendix 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
		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. 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