Equilibrium Environmental Inc.

SULFATE ADSORPTION AND DESORPTION PROPERTIES OF ALBERTA SOILS AND THEIR RELEVANCE TO TRANSPORT PROPERTIES AND LEACHING / REDISTRIBUTION RATES

FINAL REPORT

Prepared for:

Alberta Upstream Petroleum Research Fund (AUPRF)
Petroleum Technology Alliance of Canada (PTAC)

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April 2012

ACKNOWLEDGEMENTS

The authors would like to acknowledge and thank the following organizations and individuals for their valuable contributions to this research project:

- Petroleum Technology Alliance of Canada (PTAC)- research funding
- Alberta Upstream Petroleum Research Fund (AUPRF) – research funding
- Program of Energy Research and Development (PERD) - research funding
- Suncor (Petro-Canada) - supplying soil cores
- Husky Oil Operations - supplying soil cores
- Exova - in-kind analytical contributions

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1 INTRODUCTION

Sulfur is a relatively abundant element that occurs in a variety of forms in the environment. One of the most important forms is sulfate - a fully oxidized inorganic anion derived from sulphur. Calcium sulfate (gypsum) and sodium sulfate are soluble salts which contribute to soil salinity, reduced vegetative growth, and impaired groundwater quality. Both these salts can originate from natural or anthropogenic sources, and both occur naturally in Western Sedimentary Basin soils.

The energy sector is a source of potentially deleterious sulfate impacts in surface soils. Various practices in the up-stream oil and gas industry can result in subsoil sulfate salts being brought to the surface where increased salinity can cause impairment of vegetative growth. Sulfate redistribution occurs after site remediation activities such as excavation of produced-water impacted soil followed by soil replacement, when excavation depths or the quality of backfill are inadequate. Commonly, calcium sulfate is used as an amendment to soil to reduce high sodium levels at produced water releases, or as part of the oilsands consolidated tailings process, increasing sulfate concentrations. Drilling muds can contain high levels of soluble sulfate salts and historical applications of large quantities at drill sumps have resulted in many sites experiencing deteriorated soil quality and reductions in vegetation growth. Another example is the blocks of elemental sulfur from processing natural gas, crude oil, or bitumen. These sulphur blocks are typically stored outdoors where they are exposed to rainfall and erosion from wind.

There is a need to provide guidance tools and land management recommendations for evaluating, managing, or remediating the risks of sulfate to surface soils and groundwater. Consequently, the objective of the project is to increase the level of knowledge of the environmental mobility of sulfates (particularly calcium and sodium salts) in soil and groundwater. The knowledge gained on sulfate mobility will provide an initial framework for recommendations for sulfate soil guidelines and land management practices. An additional goal of the project is to evaluate the remediation potential of sulfate salts for SAR-impacted soils.

Pursuant to these goals, the following activities have been performed in previous stages of this project. The year shown refers to the date of the referenced report (Equilibrium Environmental 2010 or Equilibrium Environmental 2011), summarizing research from 2009-2010 and 2010-2011 project phases respectively.

- Review of naturally occurring sulfate (2010)
- Review of sulfur and sulfate emissions by oil and gas industry (2010)
- Review of sulfate toxicity toward plants (2010)
- Review of sulfate isotope methods for natural vs anthropogenic source (2010)
- Literature review for sulfate adsorption was performed (2010 and 2011)
- Review of gypsum solubility (2010 and 2011)
- Preliminary leaching column work at relatively low sulfate concentrations (2011)
- Preliminary soil extraction experiments (2011)
- Evaluation of the remediation potential of sulfate salts (2011)

As a follow-up to this previous work, the following activities were performed in this stage of the project (2011-2012) and are summarized herein:

- Field reference soils (fine and coarse) were collected from two locations in Alberta to serve as standards for leaching and adsorption experiments

- Continued leaching column work was performed to evaluate the relative mobility of sulfate relative to a chloride tracer at higher sulphate concentrations.

- Additional sulfate adsorption experiments were performed on the fine and coarse reference soils using a known sorptive compound (boron) for comparison

- Preliminary transport modeling was performed to further evaluate the theoretical potential for sulphate retardation relative to chloride

- Based on this research, an analysis of potential pathways and receptors for sulphate was performed in support of guideline development. Potential mechanisms to derive guidelines for each of the pathways were evaluated, especially in the context of the proposed Subsoil Salinity Tool (SST) environment for guideline implementation. This also included an analysis of regulatory and policy issues to be further investigated and discussed as this SST implementation proceeds.

2 REFERENCE SOIL COLLECTION

Reference soils are valuable for both guideline development and method development work, and provide a standardized means to evaluate the behavior of various environmental chemicals in soil and groundwater. Reference soils are typically chosen to be representative of broad, important soil types and are often targeted toward particular textures. “Fine” versus “coarse” textured soils is one common division, with fine soils typically higher in clay content and often with more pronounced sorptive behavior toward various soil chemicals compared to coarse soils with lower clay content.

2.1 FINE SOIL

Clay loam soil previously collected from near Delacour, Alberta in 1995 had been used by Environment Canada for method development work for many years. Soil maps indicated the original soil collection location from 1995 to be within the ‘Delacour’ soil group, with the soil described as an Orthic Black Chernozem showing a clay content of approximately 30.1% and texture of clay loam.

This 1995 location was located on an undeveloped road allowance which has subsequently been developed into a highway during the intervening years making it no longer suitable for reference soil collection. Several potential alternative locations within the Delacour region were evaluated by Equilibrium Environmental in November 2010 based on soil maps, with one location in particular located on a suitable undeveloped road allowance and showing a comparable clay loam texture.

Laboratory chemistry and texture results for this soil location are summarized in Table 2.1 below. Salinity was low (0.5 dS/m), with chloride and sulfate both below 15 mg/kg. Clay content was 32%, with the soil classified as a fine ‘clay loam’. Organic matter was 3.9%, lower than the 12.8% reported for the 1995 clay loam collection but similar to the coarse soil described in the next section. Hydrocarbons, pesticides, and herbicides were all below detection limits.

Table 2.1. Fine reference soil properties

Parameter	**Value**	**Unit**
EC	0.51	dS/m
SAR	<0.1	
Chloride	7	mg/kg
Sulfate SO_4	12	mg/kg
CEC	19	meq/100g
Organic matter	3.9	%
Saturation %	79	%
pH	7.4	
HWS Boron	0.5	mg/kg
% sand	33.0	%
% silt	35.0	%
% clay	32.0	%
Texture	Clay loam	
% retained 75 µm mesh	32.0	%
Coarse vs fine	Fine	

The initial soil collection was performed on November 19, 2010, with the collected soil pails used for a variety of toxicity and transport testing in Alberta. The soil collection process involved stripping back the sod layer with sharp shovels, followed by removing soil to approximately 30 cm depth with a shovel and placing into pails after removing large rocks, stones, and aggregates. Photos of this initial collection are shown in Figure 2.1, showing snow cover on the ground but not-yet frozen soil collected into 5-gallon pails. An additional round of soil collection was later performed on September 30, 2011, with photos before and after collection shown in Figures 2.2 and 2.3, followed by subsequent backfilling with clean fill.

Figure 2.1. 2010 fine soil collection (November 2010)

Figure 2.2. 2011 fine soil location (pre-collection) - facing west

Note: location of 2010 collection event shown in foreground. Fenceline denotes undeveloped road allowance

Figure 2.3. 2011 fine soil location (post-collection) – facing northwest

2.2 COARSE SOIL

A standard coarse field soil had not yet been sourced from within Alberta prior to 2011, though such a soil would be beneficial for a wide range of guideline-development and method-development activities. Consequently, potential locations for coarse, sandy loam chernozems were identified using soil maps, with a set of possible locations identified south of Vulcan, Alberta. Initial field reconnaissance was performed in October 2011, with samples from six distinct locations obtained with apparent loam/sandy loam texture and submitted for laboratory analysis. Of these locations, one was selected as most suitable for larger-scale collection based on laboratory ‘sandy loam’ texture analysis.

The collection location was located approximately 40 km southeast of Vulcan, Alberta and near Travers Reservoir. Based on soil maps, the soil was likely an Orthic Dark Brown Chernozem from the Kessler or Carmangay soil series.

Selected analytical data from this coarse soil collection is shown in Table 2.2. Salinity was low, with EC of 0.26 dS/m and chloride and sulfate both below 15 mg/kg. Clay content was 18.0%, with soil texture classified as a coarse ‘sandy loam’. Organic matter was 3.0%, similar to the 2010-2011 clay loam. Hydrocarbons, pesticides, and herbicides were all below detection limits.

Table 2.2. Coarse reference soil properties

Parameter	Value	Unit
EC	0.26	dS/m
SAR	<0.1	
Chloride	7	mg/kg
Sulfate SO4	11.4	mg/kg
CEC	16	meq/100g
Organic matter	3.02	%
Saturation %	51	%
pH	5.8	
HWS Boron	0.6	mg/kg
% sand	61.6	%
% silt	20.4	%
% clay	18.0	%
Texture	Sandy loam	
% retained 75 um mesh	60.1	%
Coarse vs fine	Coarse	

The soil collection process involved stripping back the sod layer with sharp shovels, followed by removing soil to approximately 30 cm depth with a shovel and placing into pails after removing large rocks, stones, and aggregates. Overall, the soil texture was visibly less clayey and cohesive than the clay loam, as expected for a coarser, sandy loam. Photos of this soil collection location are shown in Figures 2.4 to 2.5, prior to back-filling.

Figure 2.4. Coarse soil location (pre-collection) - facing west

Note: fence-line denotes undeveloped road allowance

Figure 2.5. Coarse soil location (after soil collection) – facing southeast

3 LEACHING EXPERIMENTS

Additional leaching column experiments were conducted in the current project year to expand on results from previous years. For context, a review of relevant experiments from previous years is provided below in Section 3.1 followed by a description of the current experiments in Section 3.2.

3.1 REVIEW OF PREVIOUS EXPERIMENTS

One method of examining the fate and transport of sulfate salts is to directly measure their movement using leaching experiments. To perform these experiments, field soils and cores were collected from a variety of sites with varying soil texture and sulfate concentrations. Field cores were often collected in clear plastic tubes to allow easier inspection of soil type and sample integrity, though some samples were also collected in traditional metal Shelby tubes. The soils thus collected ranged from dry, coarse, light-colored sandy soils to dark, saturated clayey soils.

Samples without apparent channels could be tested as ‘undisturbed’ cores in customized shelby-tube permeameters (leaching columns). Other cores with significant voids or channels were emptied, homogenized, dried and ground, and sieved through #10 (2 mm) mesh. These soil samples were then be tested as ‘repacked’ samples using one or more layers of soil in clear permeameters. In general, the benefits of repacked soil include greater soil homogeneity combined with the ability to do multiple replicates or tests on the same soil provided sufficient quantities are available for testing. Potential drawbacks include a disruption of the natural soil structure which is likely altered during the grinding and screening stages, though this may have more relevance for absolute moisture transport rates and less relevance for relative ion transport rate comparisons. Further details about leaching column experimental design setup can be found in Equilibrium Environmental, 2011.

The leaching of sulfate salts from soil is highly relevant to many situations, including cases where sulfates from deeper depths have been brought to the root-zone such as through pipeline construction practices. Understanding the potential effects of these relocated sulfate salts on plant growth over time requires an understanding of the rate that the salts may leach to below the root-zone under irrigated or natural precipitation scenarios. To help understand this type of scenario, two experiments were performed whereby existing salts were leached from soil and are described below.

3.1.1 Leaching existing salts from soil: Experiment #1

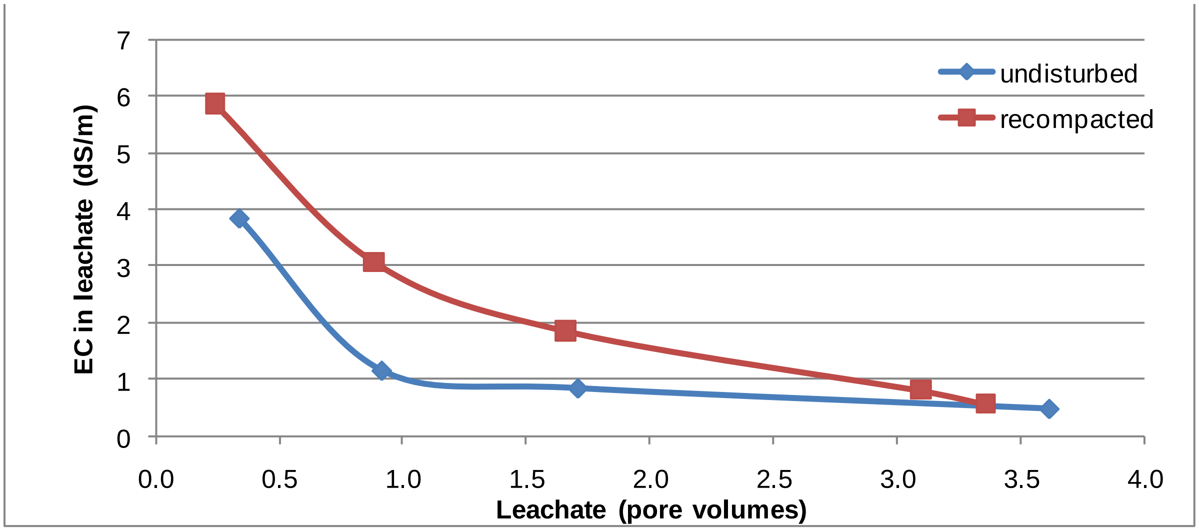
The goal of this experiment was to examine the rate of sulfate leaching from southern Alberta soils. A clear plastic soil core from near Medicine Hat (Alberta) was tested in an undisturbed configuration in a modified Shelby-tube permeameter (cores generously supplied by Petro-Canada/Suncor). The core was first cut to length and lightly compacted to reduce chances for significant side-wall leakage. A second sample from the same core was removed from the core, homogenized, screened, and tested in a recompacted configuration. The initial soil chemistry via standard saturated paste extraction is shown below, with overall salinity primarily due to sulfate rather than chloride and differences between the two samples due to natural variability in soil salinity:

– Sulfate:	270 – 550 mg/kg (mix of Na/Mg/Ca)
– Chloride:	38 – 50 mg/kg
– EC:	1.7 – 2.8 dS/m

The results from leaching clean tap water through the soils are shown in Figure 3.1 below, showing the change in leachate EC over time. It was observed that initial leachate EC was approximately 2-fold higher than the saturated paste EC in both cases, a typical ratio between saturated paste and pore water concentrations due to differences in moisture content.

As per common procedures witih leaching column experiments, the time scale is often expressed in terms of pore volumes to allow comparison between samples with potentially different hydraulic conductivities. EC was observed to drop toward approximately 10% of the initial value in 3 to 4 pore volumes. Though the absolute rate would depend on soil hydraulic conductivity and moisture drainage rate, these results suggest that soluble sulfate salts are capable of relatively rapid leaching from surface soils given sufficient moisture. This is relevant to scenarios such as the leaching of sulfate salts brought to near the root-zone by construction activities. This salt leaching rate could likely be increased further by irrigation to increase the moisture flow through the soil, thus providing an additional option for sulfate management practices in some cases.

Figure 3.1. Leaching sulfate from undisturbed and recompacted cores



3.1.2 Leaching existing salts from soil: Experiment #2

Though the above experiment provided an indication of the overall rate of sulfate leaching, it did not investigate potential differences in the leaching rates of sulfate compared to chloride. To further investigate this issue, this experiment compared the leaching rates of $CaSO_4$, Na_2SO_4, and NaCl from artificially impacted (spiked) soil. A loam soil (approximately 22% clay) was homogenized, screened, and split into three equal portions. Each soil portion was then spiked with an equivalent amount of cations (matching milliequivalents) for each of the three salts. The soils were lightly repacked into three fixed wall permeameters, and the columns leached from top to bottom with clean tap water. Initial properties of the three spiked soils along with unspiked soil properties are shown in Table 3.1. The initial EC of the leachate is also shown for comparison to initial saturated paste soil concentrations.

Table 3.1. Initial chemistry from soil spiking and leaching experiments

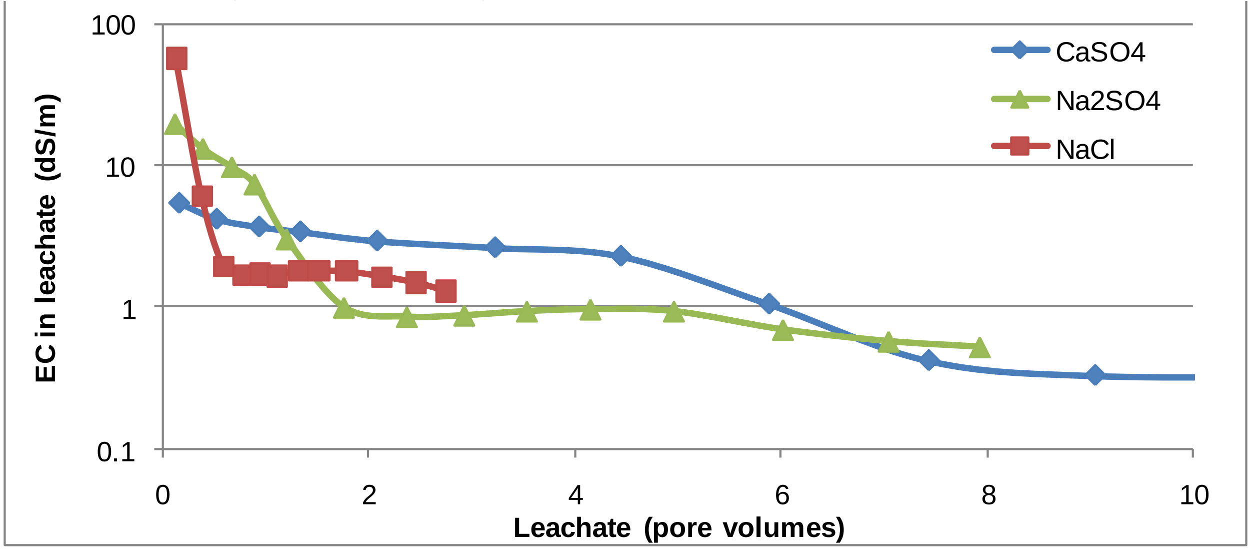
Soil	Soil EC / cation ratio	Initial soil EC (dS/m)	Initial leachate EC (dS/m)
Original soil	0.09	1.7	-
$CaSO_4$ spiked	0.08	4.0	6.4
Na_2SO_4 spiked	0.09	11	22
NaCl spiked	0.11	16	55

It is noteworthy from the above results that the EC / cation ratio is higher for chloride than sulfate, implying that sulfate may have a relatively lower influence on EC than chloride in some situations. This EC/cation ratio ratio is often taken to be relatively constant regardless of the ion type, but this suggests the potential for differences depending on the type and quantity of ion.

It is also noteworthy that the initial leachate EC was 1.6- to 3.4-fold higher than saturated paste soil EC, comparable to the ratio observed in the previous experiment. This ratio was highest for sodium chloride (3.4-fold) compared to sodium sulfate (2-fold) despite both salts having high solubility in tap water. The lowest ratio was observed for gypsum (1.6-fold), suggesting the influence of solubility limits under these leaching conditions.

Figure 3.2 shows the leaching behavior over time, with different leaching behavior observed for the three salts. NaCl was initially the fastest to leach (in terms of pore volumes), and then slowing after approximately 2 pore volumes. Na_2SO_4 overtook NaCl after approx 1.5 pore volumes, and the two reached a relatively similar state after 3 pore volumes. $CaSO_4$ was the slowest to leach, with a relatively flat plateau apparent up to 4 pore volumes. This is likely due to the continuous dissolution of precipitated gypsum, and demonstrates one potential effect of sorption / precipitation on sulfate transport.

Figure 3.2. Leaching of spiked salts from recompacted soils



Overall, it is noteworthy that Na_2SO_4 behaved differently than NaCl during early leaching, though this effect may be more common at high salt concentrations. This may be due to EC vs cation non-linearities for sulfate, or column wetting effects and their possible interaction with dissolution / adsorption kinetics for sulfate.

3.1.3 Leaching salt solutions through clean soil: low sulfate concentrations

While the above experiments examined the leaching of salts from soil with clean water, examining an alternative scenario whereby salt-containing solutions are leached through clean soil are also highly relevant. The goal of this initial experiment was to leach chloride, sulfate, and boron solution through clean (pre-leached) loam and evaluate the relative transport rates between the three species. Chloride is assumed to behave as essentially an inert tracer, whereas boron is known to have measurable sorption properties in many soils.

An initial leaching solution was first prepared using a multi-component mixture of calcium chloride, sodium sulfate, and boric acid. This cation mixture was chosen to have relatively similar concentrations of sodium and calcium, and be unlikely to be influenced by sulfate precipitation effects based on the relatively low sulfate concentration of 1,000 mg/L (comparable to approximately 200-300 mg/kg on a soil basis). Nominal properties of this inlet solution are shown in Table 3.2 below, with chloride concentrations also a nominal 1,000 mg/L.

Table 3.2. Nominal concentrations of multi-component leaching solution

Parameter	Value
EC	4.6 dS/m
Chloride	1000 mg/L
Sulfate	1000 mg/L
Boron	3.9 mg/L
Calcium	560 mg/L
Sodium	500 mg/L
SAR	5.9

Figure 3.3 shows the evolution of chloride, sulfate, and boron concentrations over time with the horizontal axis expressed in pore volumes. It can be seen that the outlet leachate concentrations approach the inlet concentrations over time, at which point the column can be considered to have reached steady-state. Reaching this steady-state requires approximately 2-3 pore volumes for sulfate and chloride, and approximately 12-15 pore volumes for boron. This latter result is consistent with literature which suggests the leaching boron to an equivalent level as chloride often requires several-fold more water.

Figure 3.3. Relative leaching rates of chloride, sulfate, and boron

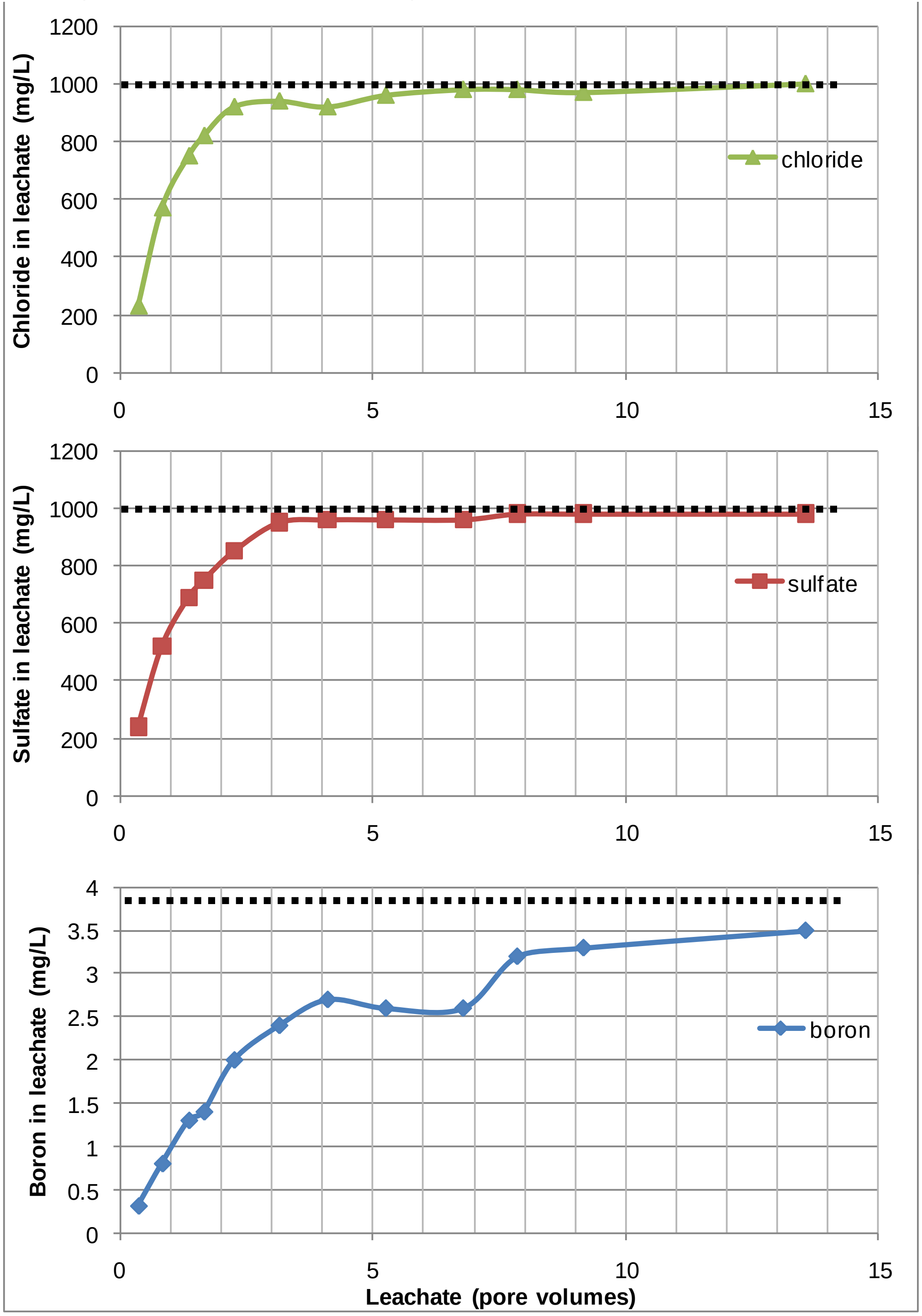
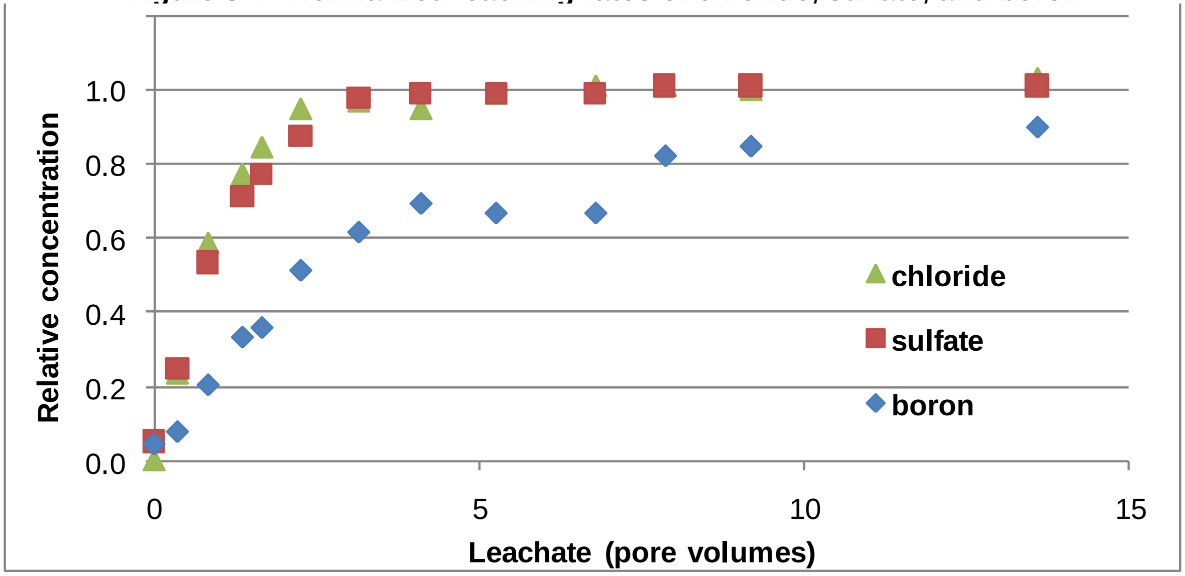


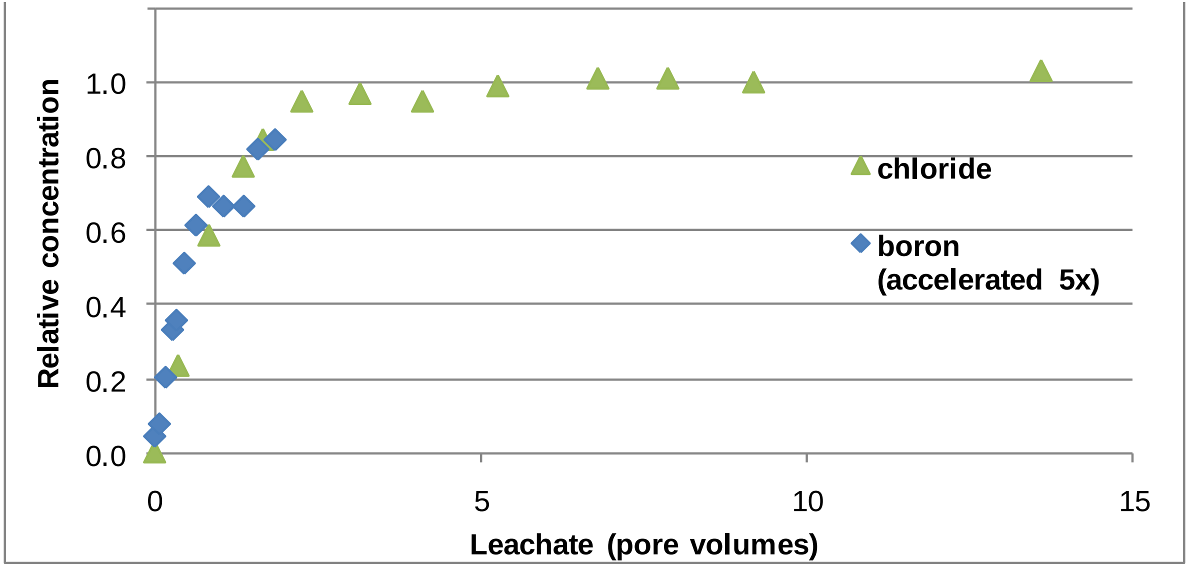
Figure 3.4 presents the same results but with concentrations normalized relative to the inlet to allow for comparisons on the same vertical axis. While boron appears significantly slower than chloride or sulfate, chloride and sulfate leached at similar rates at these concentrations and soil / ionic conditions. The sulfate concentration of 1,000 mg/L is lower than is often observed in saline prairie siols, and it is uncertain whether differences between chloride and sulfate may occur at higher sulfate concentrations or lower chloride concentrations.

Figure 3.4. Normalized leaching rates of chloride, sulfate, and boron



To provide an example of a technique for estimating retardation rates caused by sorption, Figure 3.5 shows the boron leaching curve after manually adjusting the boron time scale to match that of chloride. Boron matches chloride closely if hypothetically accelerated by 5-fold, implying a retardation factor of approximately 5 and a K_d of approximately 1 L/kg. Such a technique could theoretically also be used for sulfate if cases are found where leaching curves differ between sulfate and chloride.

Figure 3.5. Estimated retardation for boron transport

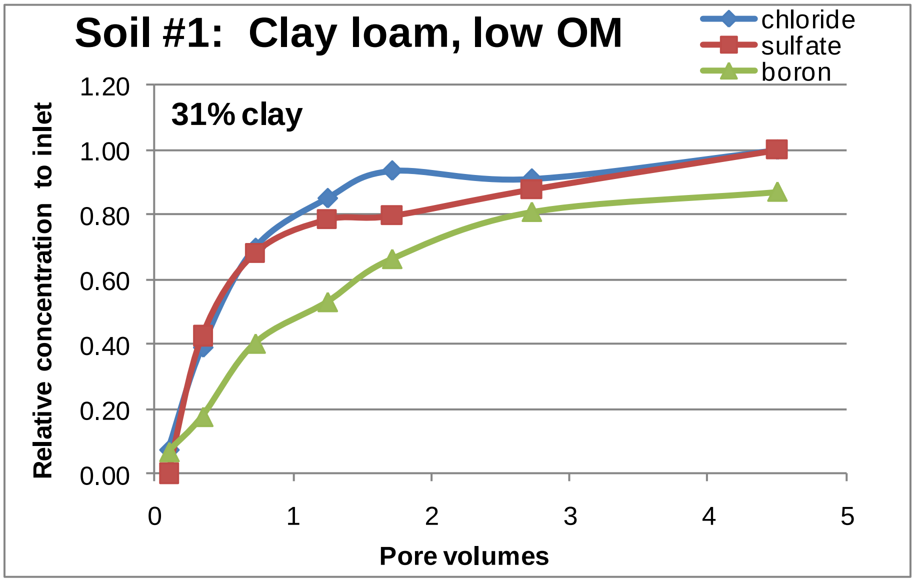


3.1.4 Phase 1: Low sulfate concentrations

To expand on previous leaching results, a similar leaching solution was created and evaluated for three different soil types. The leaching solution included sodium sulfate (1,000 mg/L nominal sulfate concentration) calcium chloride (nominal 1,000 mg/L chloride concentration) and boron (2.5 mg/L). The resulting calcium (600 mg/L) and sodium (460 mg/L) concentrations were thus an approximate 57:43 ratio. It should be noted that this 1,000 mg/L leachate sulfate concentration is equivalent to approximately 200-300 mg/kg on a soil basis assuming full pore-water equilibration without adsorption. This fairly low concentration was chosen to match literature data and the previous experiment.

Figure 3.6 shows leaching results from Soil #1, a clay loam (31% clay) with low organic matter. Outlet concentrations are normalized relative to inlet concentrations to allow comparisons, with no visible difference noted between sulfate and chloride. Visible retardation of transport is apparent for boron, providing some method validation due to the known sorptive qualities of boron.

Figure 3.6. Phase 1 leaching column results for Soil #1



Figures 3.7 and 3.8 provide corresponding curves for a clay loam (29% clay) with moderate organic matter and a loam soil (19% clay) with high organic matter. In each case, sulfate transport was comparable to chloride with no significant retardation observed. In contrast, boron transport was significantly slower than the chloride or sulfate salts in both soil #2 and soil #3.

Figure 3.7. Phase 1 leaching column results for Soil #2

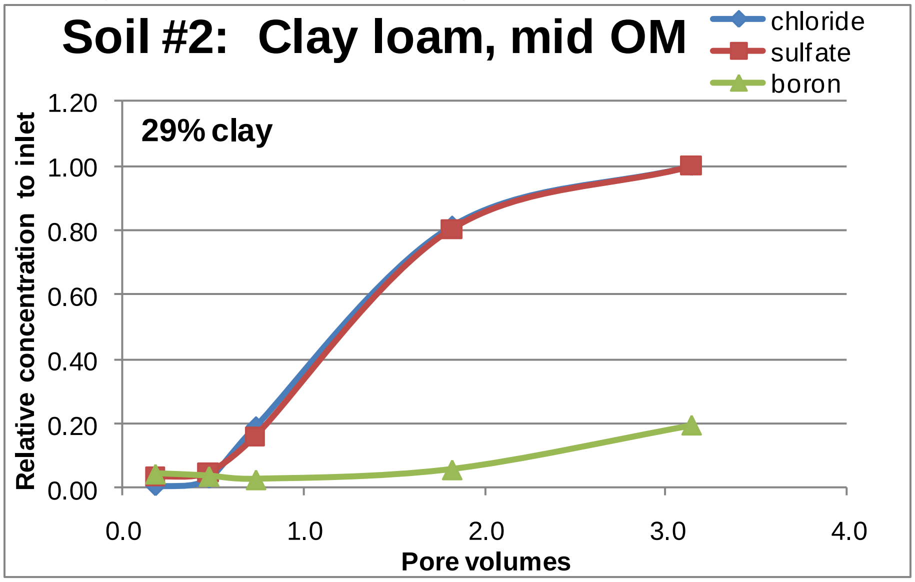
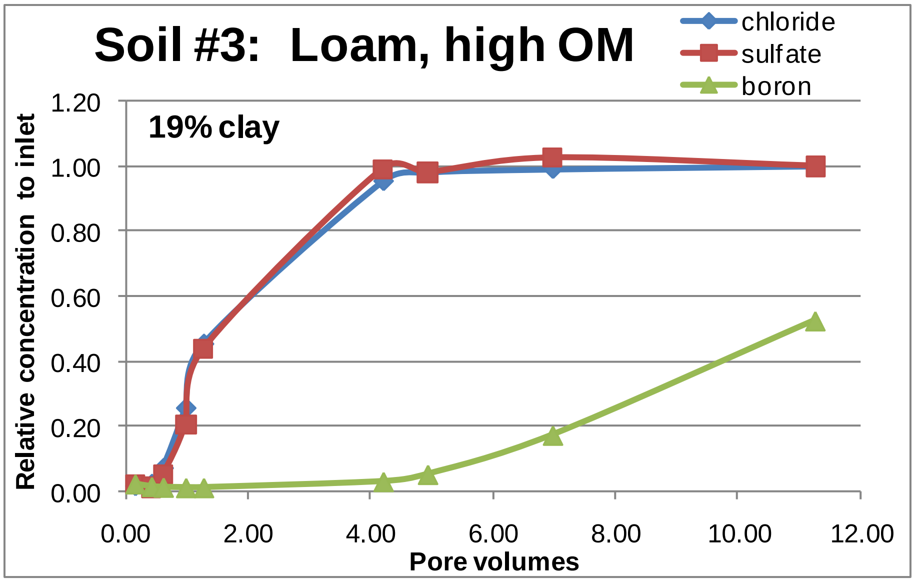


Figure 3.8. Phase 1 leaching column results for Soil #3



It should be emphasized that these transport experiments examined the specific situation of relatively low sulfate concentrations (equivalent to 200-300 mg/kg on a soil basis) in the presence of similar chloride concentrations. There is the potential for results to differ under scenarios with higher sulfate concentrations and/or lower chloride concentrations, with future experiments targeted in this direction. The influence of precipitation reactions that may retard sulfate flow relative to chloride has also not been tested nor the influence of wetting/drying cycles. These experiments were also performed under relatively high flow rates (approximately 30 mL per hour), potentially not providing sufficient time for adsorption or precipitation reactions to fully occur. The experiments described in the next section address several of these issues by leaching higher sulfate concentrations at slower flow-rates in a low-chloride environment.

3.2 CURRENT LEACHING COLUMN EXPERIMENTS

The previous leaching column experiments were expanded in the current (2011-2012) experimental phase in order to evaluate conditions which may be more likely to be influenced by sulfate precipitation reactions and show sulfate retardation relative to chloride. Based on theoretical considerations and previous research, such conditions could include higher sulfate concentrations, higher calcium concentrations, and lower flow-rates. Each of these conditions is relevant to practical field scenarios with sulfate impacts, some of which may be co-mingled with chloride and others which may not be. The current leaching experiments consist of Phase 2, Phase 3, and Phase 4 which are described below and show generally increasing sulfate concentrations in subsequent phases.

3.2.1 Phase 2: moderate sulfate concentrations

Phase two experiments Phase 2 experiments evaluated moderate sulfate concentrations (~5000mg/L), sourced primarily from sodium sulfate to ensure solubility plus a smaller amount (0.2%) of calcium sulfate. Chloride concentrations of 100 to 5,000 mg/L were also leached as high and low-concentration references, which could also be representative of chloride co-impacts at higher concentrations. All Phase 2 experiments used clay loam soils, with column 21.2 using the clay loam reference soil described in Section 2 and the other three experiments using soil from near Medicine Hat. Both soils had very similar clay contents of 31-32%. Flow rates for Phase 2 ranged from approximately 40-80 mL/day, substantially lower than the flow-rates used in Phase 1.

Figure 3.9 and 3.10 show results from leaching the 5,000 mg/L sulfate solutions along with the high-chloride solutions (approximately 5000mg/L chloride). Note that the leaching solution from Figure 3.10 has a higher sodium content than in Figure 3.9 to represent different initial SAR values and solubilities. Some signs of sulfate retardation were observed in each of these two experiments, with Figure 3.10 showing more visible retardation and Figure 3.9 more subtle.

Figure 3.9. Phase 2 leaching experiment using moderate sulfate and high chloride

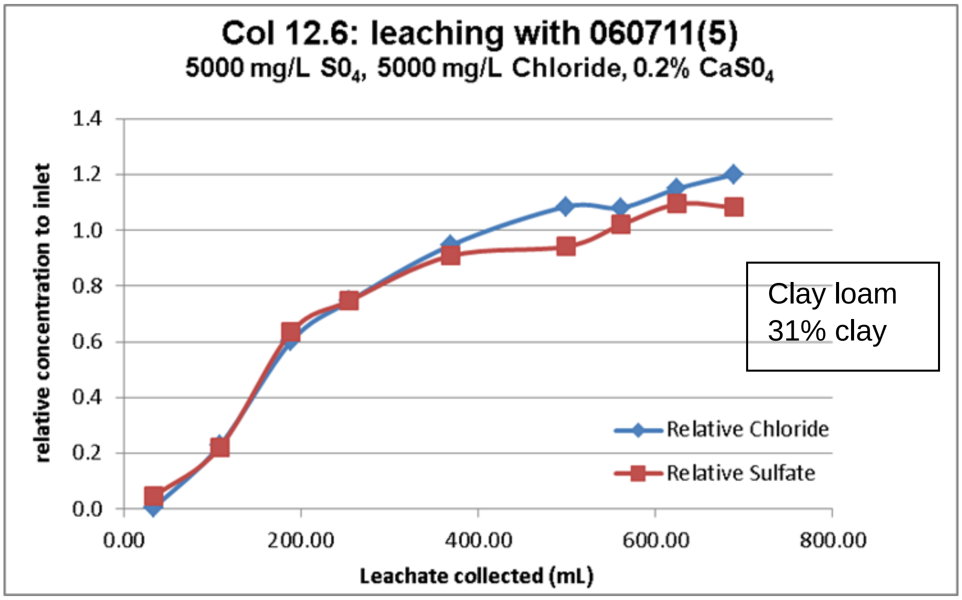
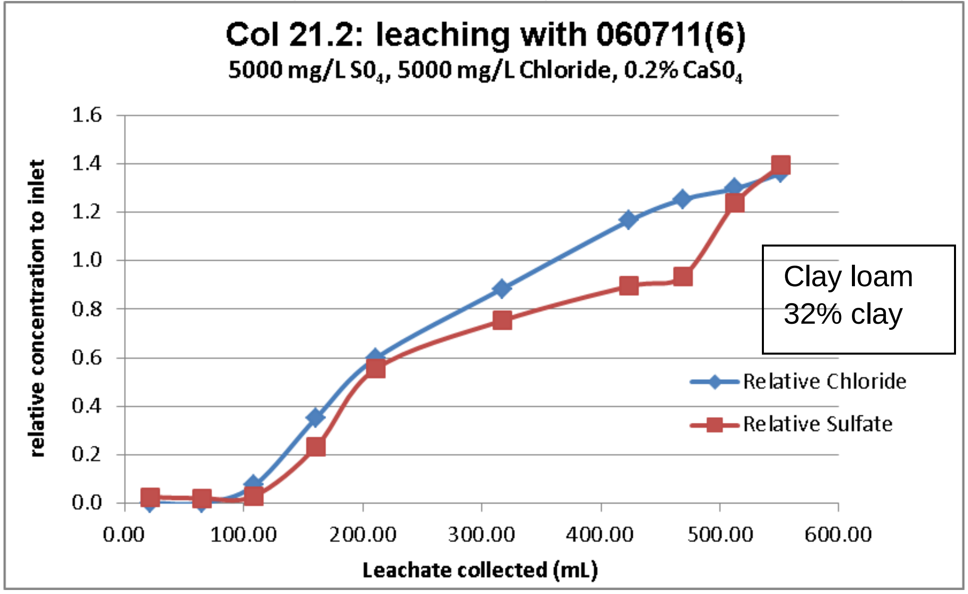


Figure 3.10. Phase 2 leaching experiment using moderate sulfate and high chloride



The next Phase 2 experiments tested lower chloride concentrations (100 – 1,000 mg/L) leached alongside moderate sulfate concentrations (5000 mg/L). These chloride concentrations are intended to function more as tracers and be less representative of chloride co-impacts. There were some signs of sulfate retardation in the 1,000 mg/L chloride experiment (Figure 3.11), but not in the experiment using 100 mg/L chloride (Figures 3.12). It is unclear whether this difference is related to chloride concentrations, or other unrelated factors such as experimental and/or analytical variability. It should be noted that lower chloride concentrations provide a more ‘invisible’ tracer with less potential sulfate interactions but more prone to analytical variability.

Figure 3.11. Phase 2 leaching experiment using moderate sulfate and low chloride

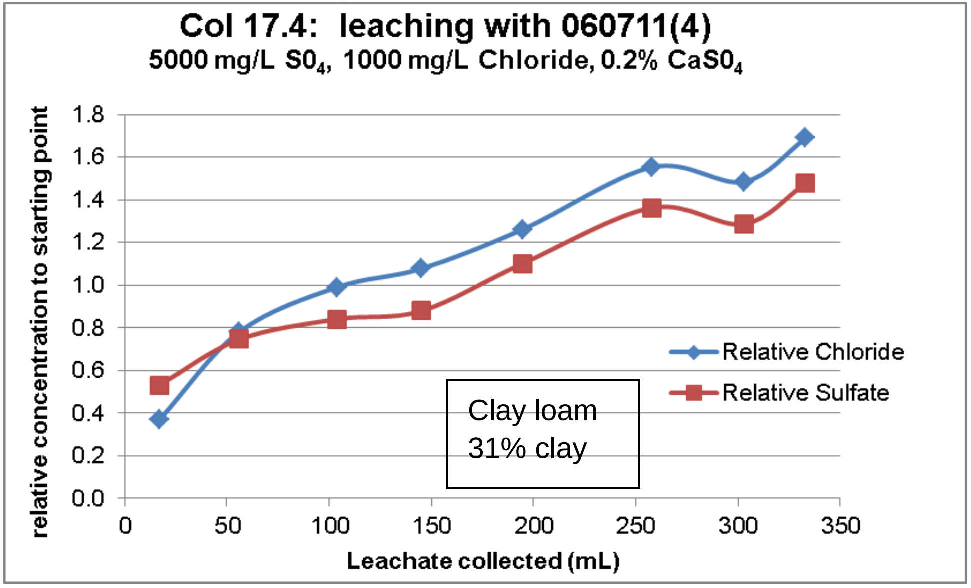
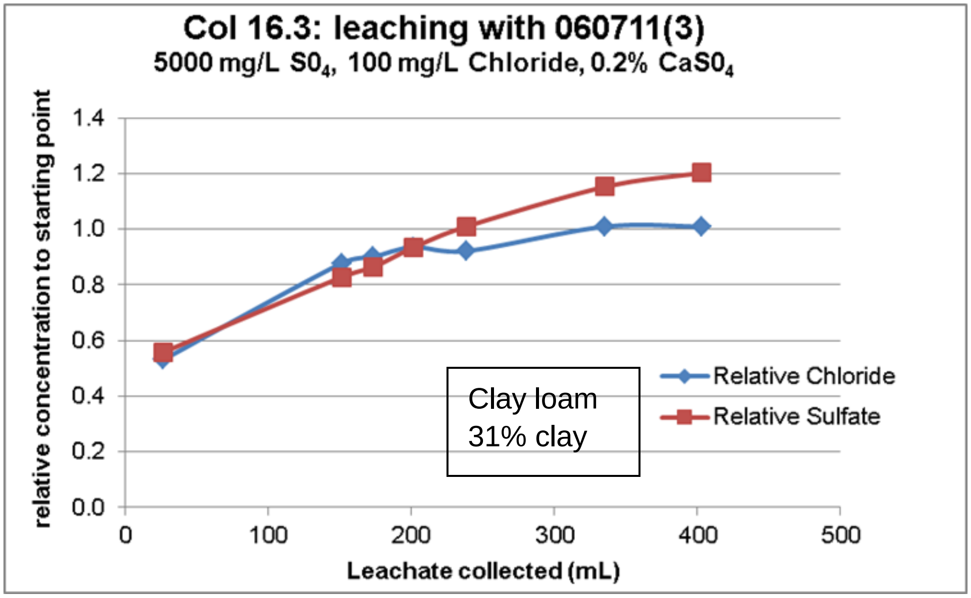


Figure 3.12. Phase 2 leaching experiment using moderate sulfate and low chloride



3.2.2 Phase 3: high sulfate concentrations

Based on the results of the lower concentration sulfate leaching experiments, a further set of follow-up experiments were performed using significantly increased sulfate concentrations of approximately 11,000 mg/L. This is likely comparable to approximately 2,000-3,000 mg/kg sulfate on a soil basis, and is highly relevant to conditions with high background salinity. Since this high sulfate concentration is beyond the solubility limit of gypsum, sodium sulfate was used as the primary sulfate salt along with varying amounts of calcium sulfate (gypsum) depending on the experiment. These experiments were performed in a low-chloride environment, using approximately 100 mg/L chloride to provide a minimal concentration for tracer purposes. They were also performed at a lower flow rate, averaging approximately 40 mL per day. The initial results from this experiment were reported in Equilibrium Environmental (2011), with updated results shown here including additional results at higher pore volumes as well as results for cations.

Table 3.3 shows three high-sulfate leaching solutions, the first of which obtained by mixing sodium sulfate and calcium chloride in the absence of calcium sulfate to obtain approximately 100 mg/L chloride and 11,000 mg/L sulfate. The second leaching solution had additionally 0.14% calcium sulfate added, which was on the cusp of the solubility limit under these conditions based on the initial appearance of turbidity (precipitate) during stepwise addition. The third leaching solution had a significant excess of calcium sulfate (1%), which is substantially beyond the solubility limit and thus exhibited significant turbidity due to undissovled gypsum. Other parameters such as EC, SAR, pH, and other cations such as calcium are also shown in Table 3.3.

Table 3.3. High-sulfate leaching solutions

		Leaching solution #1	**Leaching solution #2**	**Leaching solution #3**
Parameter	**Units**	**Na_2SO_4 + $CaCl_2$ + 0% $CaSO_4$**	**Na_2SO_4 + $CaCl_2$ + 0.14% $CaSO_4$**	**Na_2SO_4 + $CaCl_2$ + 1% $CaSO_4$**
Chloride	mg/L	129	102	101
Sulfate	mg/L	11,160	11,430	11,850
Calcium	mg/L	58	385	384
Sodium	mg/L	5,540	5,300	5,520
EC	dS/m	17.4	17.3	17.8
SAR		190	74	77
pH		6.0	6.3	6.9

The minimum calcium concentration occurred in the first leaching solution, showing 58 mg/L calcium due solely to calcium chloride. It is noteworthy that the maximum amount of additional calcium dissolved from calcium sulfate was approximately 327 mg/L (385 – 58 mg/L), which corresponds to an additional 785 mg/L sulfate. This is approximately 45% lower than the 590 mg/L calcium and 1,400 mg/L sulfate obtained when gypsum was dissolved in distilled water. This demonstrates a reduced solubility of gypsum in the presence of other sulfate ions, typically referred to as the ‘common ion’ effect. This has the opposite effect of non-common ions such as chloride, which serves to increase gypsum solubility. A review of gypsum solubility and its effects can be found in Equilibrium Environmental, 2011.

Since scenarios with high salinity due to sulfate often have calcium concentrations above 100 mg/L, the second and third leaching solutions were chosen for additional leaching experiments using the clay loam reference soil. Three separate experiments were performed, two of which used leaching solution #2 (0.14% calcium sulfate) with two different levels of soil compaction (‘high’ and ‘medium’). The third experiment used leaching solution #3 (1% calcium sulfate) also at the ‘medium’ level of soil compaction. All experiments were performed at a slower overall leaching rate than the previous experiments (approximately 40 mL/day) to allow additional time for sorption and/or precipitation reactors to occur. For all experiments, results are plotted with both sulfate and chloride concentrations normalized relative to the inlet solution concentrations to allow plotting on the same vertical axis. All experiments in Phase 3 were performed with the clay loam reference soil described in Section 2.

Figure 3.13 shows the results of the high compaction, high-sulfate leaching experiment with 0.14% calcium sulfate (experiment #1). Chloride concentrations are observed to increase faster than sulfate concentrations, with sulfate reaching approximately 70% of the inlet concentration by the time chloride has reached 100% of the inlet concentration. This suggests some retardation of sulfate relative to chloride, and may be due to sorption, precipitation, or some combination of the two.

Figure 3.13. Phase 3 high sulfate leaching experiment #1

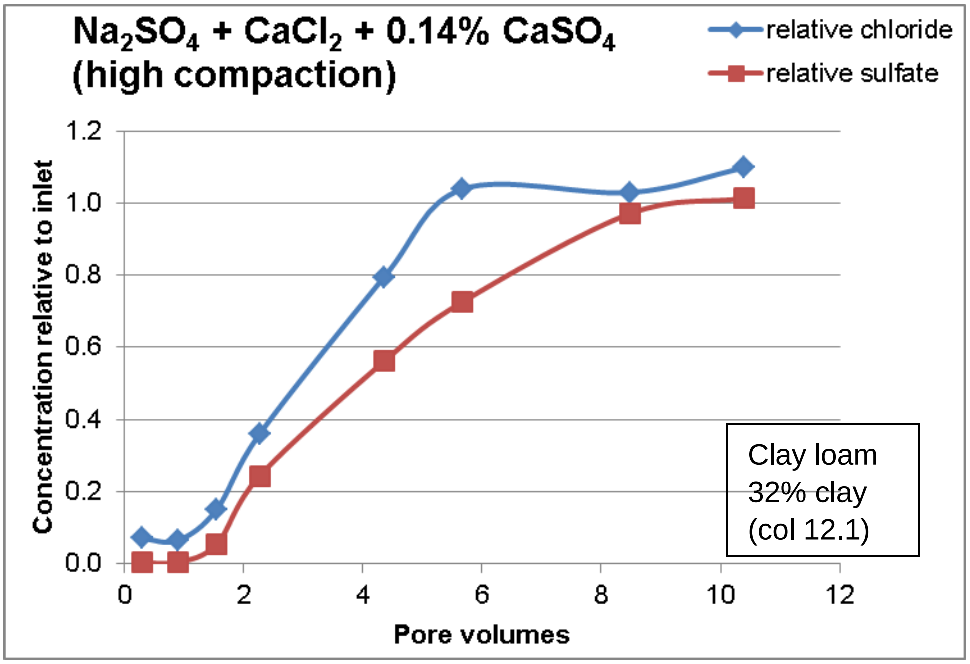


Figure 3.14 shows the second high-sulfate leaching experiment (experiment #2), which used the same leaching solution and clay loam soil as experiment #1 but with medium compaction rather than high compaction. As in the first experiment, a slower sulfate transport rate was observed relative to chloride. The relative chloride concentration approached 1.0 (inlet) after 2-3 pore volumes, whereas the relative sulfate concentration reached the inlet value after approximately 5 pore volumes. This again suggests some retardation of sulfate relative to chloride due to factors such as adsorption or precipitation.

Figure 3.14. Phase 3 high sulfate leaching experiment #2

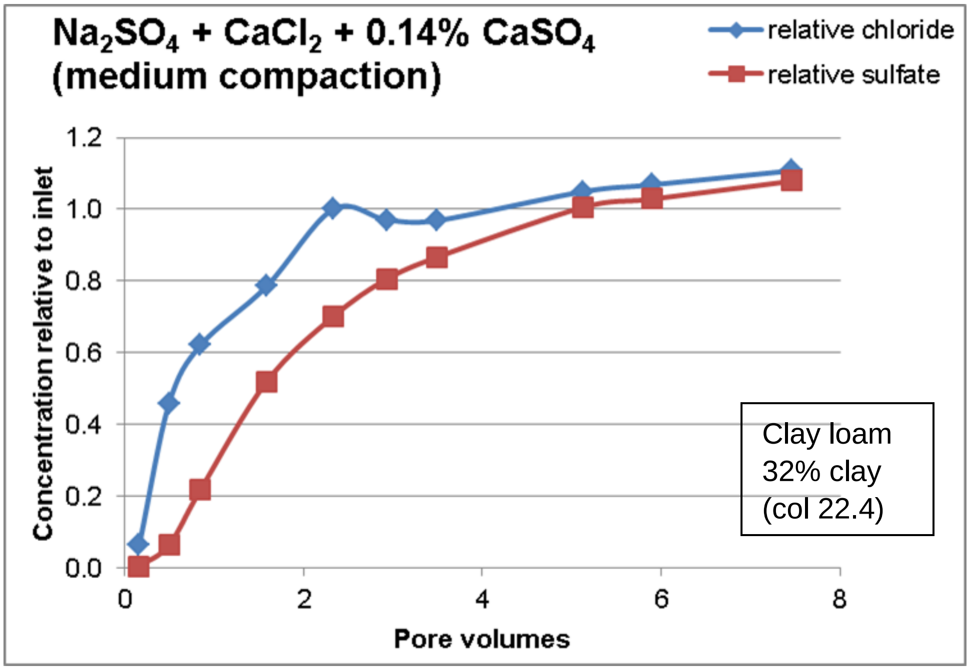
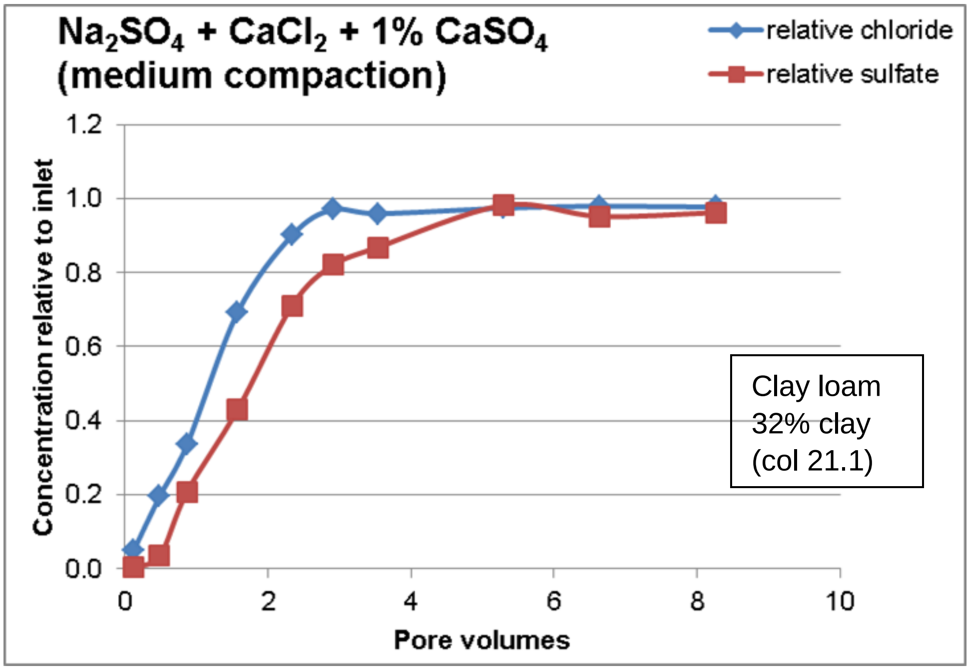


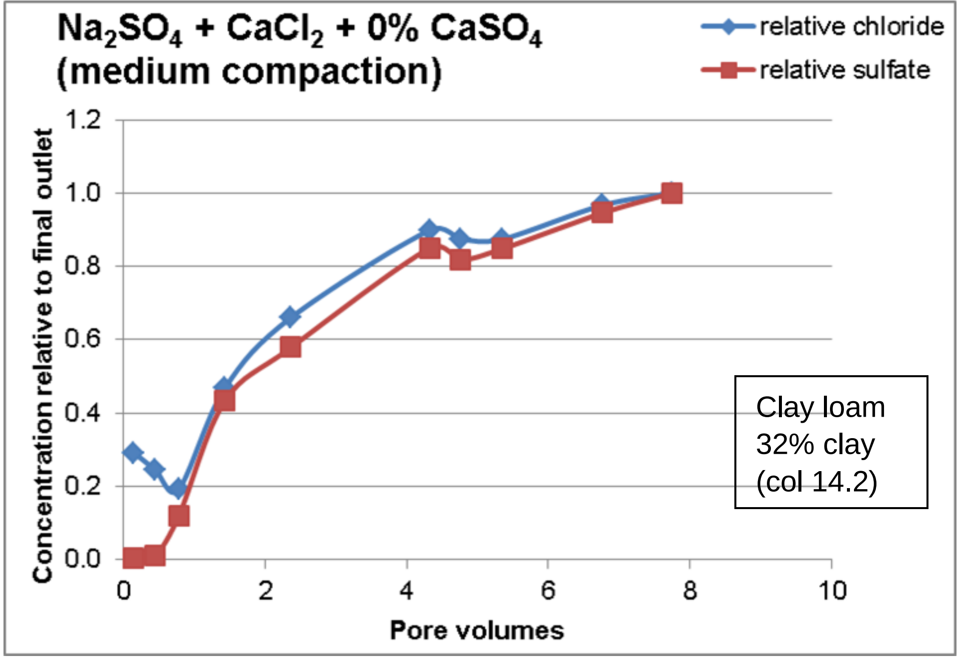
Figure 3.15 shows the third high-sulfate leaching experiment (experiment #3), which used the high (1%) calcium sulfate addition rate in the same moderately compacted clay loam. Similar behaviour is observed as for the first two experiments whereby sulfate concentrations are observed to transport more slowly than chloride. Relative sulfate concentrations are approximately 0.8 after three pore volumes, whereas relative chloride concentrations are similar to the inlet (1.0).

Figure 3.15. Phase 3 high sulfate leaching experiment #3 (with 1% gypsum)



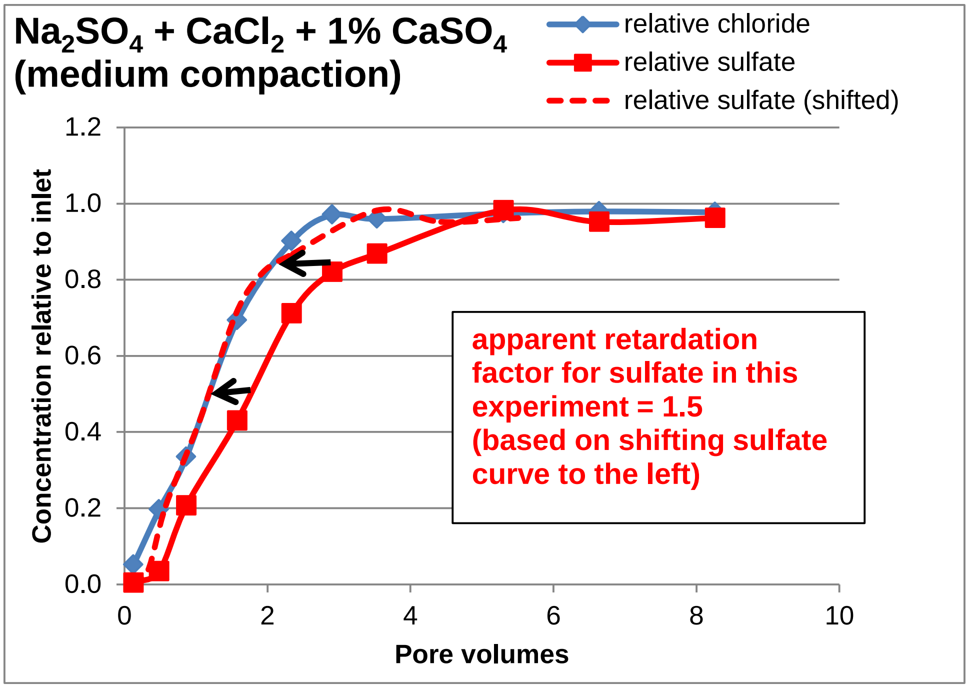
While the above three figures how some signs of sulphate retardation, results were not always conclusive as shown in Figure 3.16. No significant sings of sulphate retardation were observed, with some variability in chloride concentrations observed during the initial leaching stages. This may be partially a function of the low chloride concentrations used in the context of the inherent variability of practical leaching columh experiments.

Figure 3.16. Phase 3 high sulfate leaching experiment #4 (with 0% gypsum)



Experiments such as the high-sulfate experiments described above can be used to estimate apparent retardation factors for sulfate. Figure 3.17 shows an example of such a technique, showing the sulfate leaching curve shifted by an empirically-determined factor of 1.5 to approximately match the leaching rate of chloride. Assuming chloride to be essentially an inert tracer, this corresponds to a retardation factor of 1.5 for sulfate in this instance. Additional data collected and analyzed in this manner could allow a refined estimate of sulfate retardation under various scenarios, with additional high-sulfate experiments under reduced leaching rates likely good candidates to further examine these effects. While this technique does not directly distinguish between sorption and precipitation effects, it could potentially yield highly relevant transport information for sulfate relative to chloride and could also allow the estimation of apparent distribution coefficient (K_d) values for sulfate.

Figure 3.17. Phase 3 estimation of sulfate retardation for high-sulfate experiment #3



While the above graphs consider primarily anions, it is also useful to consider cations such as calcium and sodium since they tend to have more complex transport behavior than chloride or sulfate. They also have potential to influence sulfate mobility due to precipitation reactions. The phase 3 graphs below show that outlet calcium concentrations are higher than the inlet concentrations, an observation likely due to the leaching sodium sulfate knocking calcium off the cation exchange complex resulting in temporary precipitation of gypsum (Figures 3.18 and 3.19). This is considered to be a primary mechanism for the observed retardation of sulfate relative to chloride in several of these leaching column experiments.

Figure 3.18. Phase 3 experiment showing cations: example #1

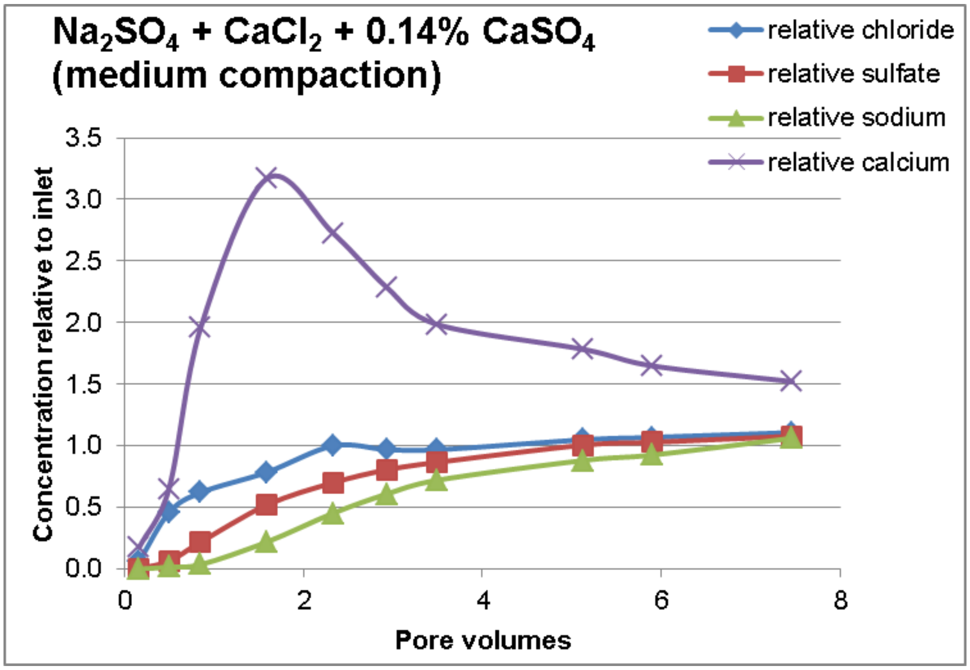
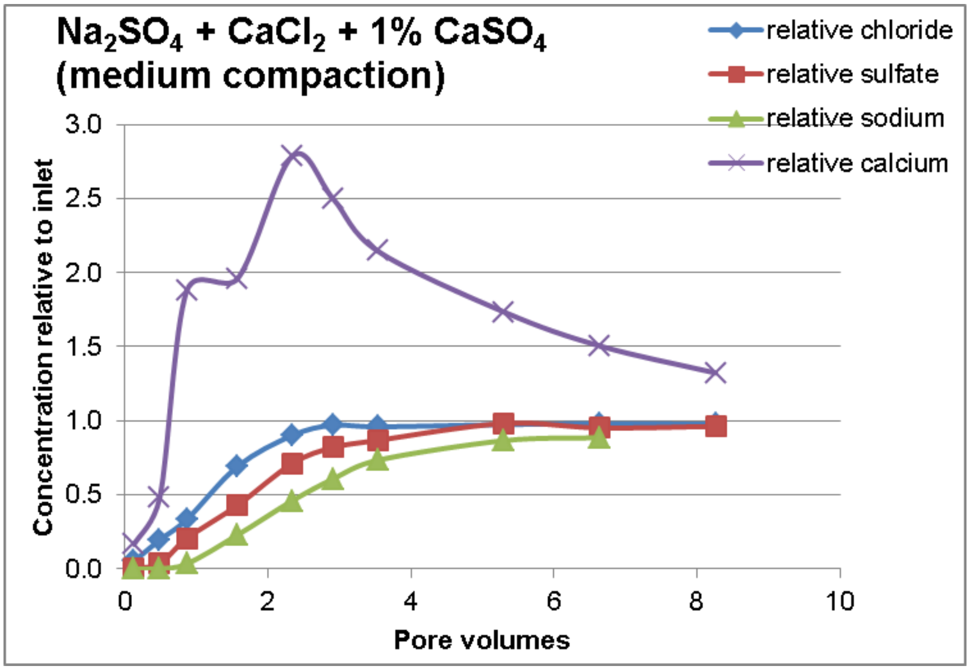


Figure 3.19. Phase 3 experiment showing cations: example #2



Overall, phase 3 experiments show that precipitation of gypsum during transport through the soil column is likely due to ion-exchange reactions with the calcium initially sorbed to the low-sodium cation exchange complex. Of the four experiments, three showed visible retardation of sulfate relative to chloride, with the following table showing retardation factors estimated using the same shifting method as shown in Figure 3.17. Retardation factors ranged from 1.0 for experiment #4 (no apparent retardation) to 1.35, 2.3, and 1.50 (visible retardation) for experiments #1, #2, and #3 respectively. These estimated retardation factors are shown in Table 3.4 (average of approximately 1.5), along with approximate values for apparent K_d's estimated using the formula below from Alberta Environment (2010) based on the measured bulk density and calculated porosity of the soil columns..

$$R = 1 + \frac{\rho_b * K_d}{\theta_t}$$

Where:

R = retardation factor (unitless)
ρ_b = dry soil bulk density (kg/L)
K_d = distribution coefficient (L/kg)
θ_t = total soil porosity (dimensionless)

Table 3.4 Estimated sulfate retardation factors and K_d's from Phase 3 experiments

Phase 3 experiment	Apparent retardation factor, R	Estimated dry bulk density (kg/L)	Estimated total porosity	Estimated Kd (L/kg)
#1 (col 12.1)	1.35	2.01	0.243	**0.04**
#2 (col 22.4)	2.3	1.33	0.500	**0.49**
#3 (col 21.1)	1.5	1.33	0.500	**0.19**
#4 (col 14.2)	1.0	1.33	0.500	**0.00**
Average	**1.54**	1.50	0.44	**0.18**

Estimated K_d values for sulfate under these testing conditions ranged from 0 to 0.49 L/kg, with an average of 0.18 L/kg associated with the average retardation factor of 1.5. This demonstrates that the observed sulfate precipitation reactions can result in measurable decreases in sulfate transport speed relative to chloride depending on soil and groundwater conditions.

3.2.3 Phase 4: medium-to-high sulfate concentrations

Phase 4 leaching column experiments evaluated medium-to-high sulfate concentrations (5,000 – 10,000 mg/L) derived primarily from sodium sulfate with a smaller portion (0.2%) of calcium sulfate to ensure complete initial solubility. Figure 3.20 and 3.21 show examples using coarse field-collected soil with approximately 22% clay (sandy clay loam). Leached sulfate concentrations were 5,000 to 10,000 mg/L, with chloride also co-leached at 100 mg/L as a reference. Example #1 in Figure 3.20 does not show apparent sulfate retardation compared to chloride, with both salts showing very similar behavior while outlet concentrations approach the inlet concentrations. Example #2 in Figure 3.21 shows some apparent sulfate retardation for the initial portion of the leaching, though some of the variability inherent in typical soil experiments is visible based on one apparently anomalous reading for chloride.

Figure 3.20. Phase 4 leaching column experiment example #1 (coarse soil)

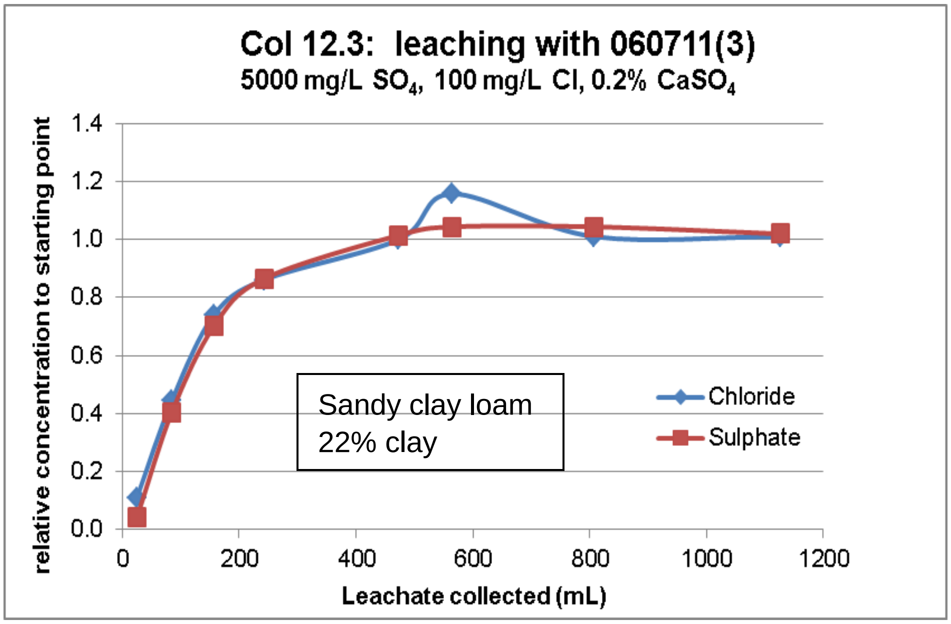
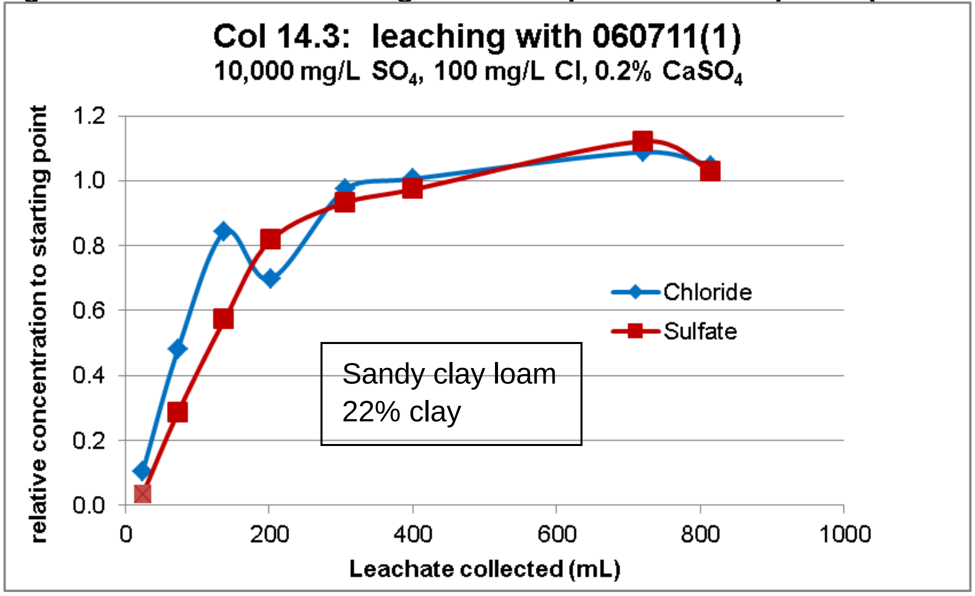


Figure 3.21. Phase 4 leaching column experiment example #2 (coarse soil)



Additional phase 4 experiments were also performed with fine soil, with Figures 3.22 and 3.23 showing leaching experiments with 10,000 mg/L sulfate using clay loam soil with approximately 32% clay. These were co-leached with either 1000 mg/L or 100 mg/L chloride for comparison. Clear signs of sulfate retardation were observed for both experiments, with experiment #3 in particular (with 100 mg/L chloride) showing notably slower sulfate transport compared to chloride. Experiment #4 also showed visible sulfate retardation, with estimates of retardation factors and apparent K_d's provided below.

Figure 3.22. Phase 4 leaching column experiment example #3 (fine soil)

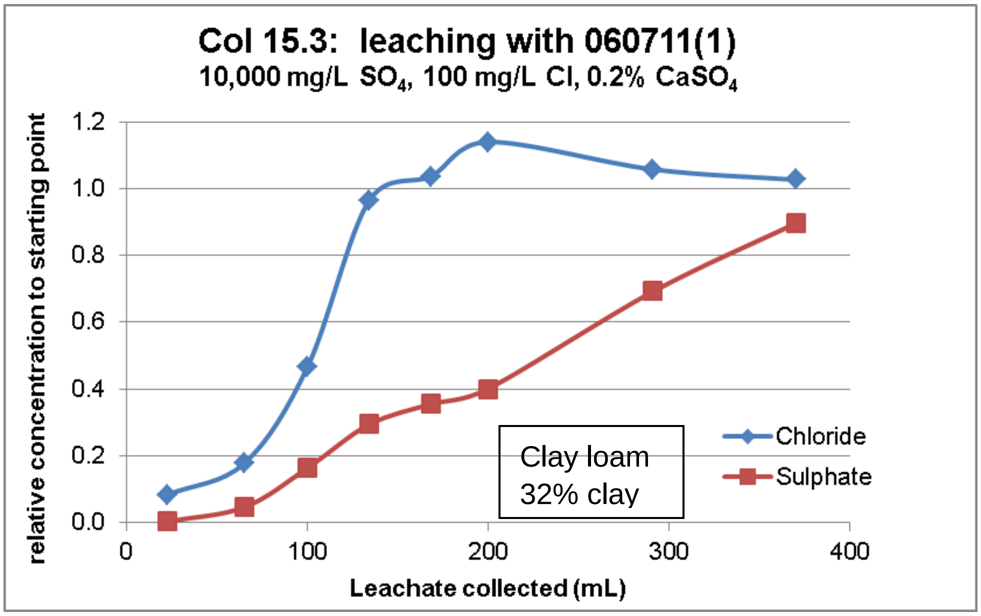
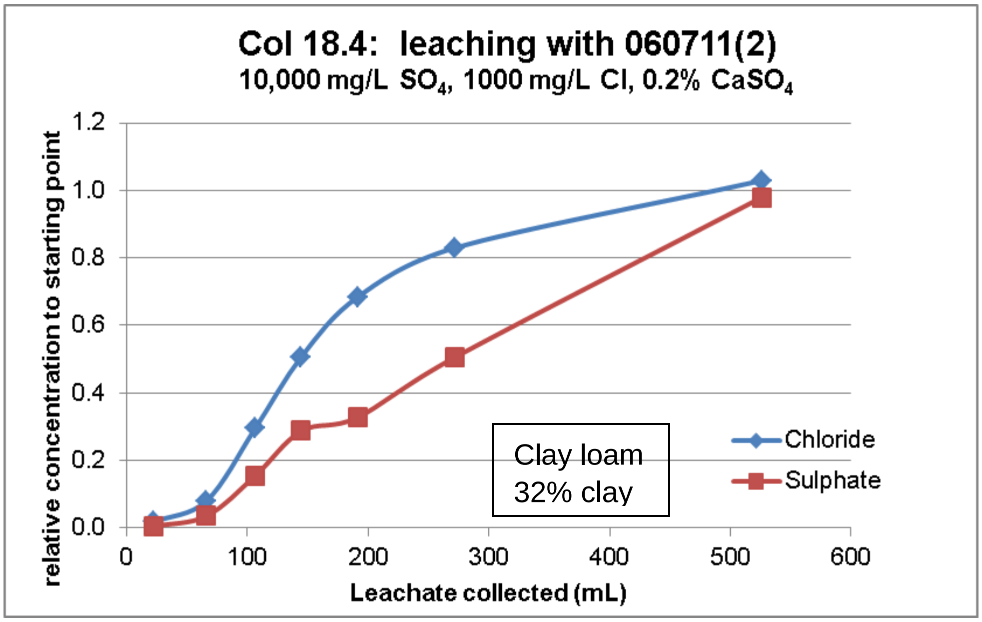


Figure 3.23. Phase 4 leaching column experiment example #4 (fine soil)



A summary of soil texture, bulk density, and estimated retardation factors is shown in Table 3.5 for the Phase 4 experiments. Retardation factors were estimated by shifting the sulfate leaching curves to match the chloride curves as closely as possible, and range from 1.0 to 2.22 (average 1.55). This corresponds to an estimated apparent K_d ranging from 0 to 0.35, averaging 0.15 L/kg and apparently dependent on a variety of test conditions.

Table 3.5. Estimated sulfate retardation factors and K_d's from Phase 4 experiments

Phase 4 column #	Soil type	% clay	Soil texture	Apparent retardation factor, R	dry bulk density (kg/L)	Estimated porosity	Estimated Kd (L/kg)
Col 12.3	sandy clay loam	21.6	coarse	1.0	1.62	0.389	0.00
Col 14.3	sandy clay loam	22.6	coarse	1.4	1.55	0.415	0.11
Col 15.3	clay loam	31.2	fine	2.2	1.50	0.434	0.35
Col 18.4	clay loam	32.6	fine	1.6	1.55	0.415	0.16
Average				**1.55**	**1.56**	**0.41**	**0.15**

3.3 LEACHING EXPERIMENT SUMMARY

Overall, clear signs of sulfate retardation / precipitation were observed in several leaching column experiments, particularly in Phases 3 and 4 with higher sulfate concentrations (5,000 – 10,000 mg/L) and finer, clayey soils. These results suggest that gypsum may be precipitated while initially soluble sulfates travel through the calcium-rich cation exchange complex of the clean soil. Both Phase 3 and Phase 4 showed average apparent sulfate retardation values ('R') of approximately 1.5, suggesting that chloride may move 50% higher than sulfate under these conditions. This represents an average apparent K_d of approximately 0.15 to 0.2 L/kg, which is likely a strong function of various soil and groundwater conditions.

These sulfate concentrations at which sulfate retardation was observed (5,000 – 10,000 mg/L in solution) are still in a reasonable range for soil, and represent approximately 1,250 – 2,500 mg/kg sulfate on a dry soil basis. This suggests that even higher sulfate concentrations (e.g., 15,000 – 20,000 mg/L) may show additional gypsum precipitation and sulfate retardation.

Table 3.6. Summary table of the four phases of leaching column experiments

	Leaching Solution Concentrations			
	Sulfate (from Na_2SO_4)	Gypsum ($CaSO_4$)	Chloride (from NaCl or $CaCl_2$)	Results
Units	**(mg/L)**	**(%)**	**(mg/L)**	
Phase 1*	1000	0	1000	No apparent difference in the rates of sulfate and chloride transport
Phase 2	5000	0.2	100 - 5000	Subtle yet visible signs of sulfate retardation in most of the Phase 2 experiments
Phase 3	10000	0, 0.14, 1	100	Clear sulfate retardation, especially at higher calcium concentrations. Average retardation factor of approximately 1.5, and an average Kd of approximately 0.18 L/kg
Phase 4	5000 - 10000	0.2	100	Clear signs of sulfate retardation, especially for the fine (clayey) soils. Average retardation factor of approximately 1.55, and an average Kd of approximately 0.15 L/kg

Phase 1 also included 2.5 mg/L Boron

To further verify the mechanism of sulfate retardation, additional batch adsorption and desorption (extraction) experiments were also performed, with preliminary experiments described in Equilibrium Environmental (2011) and current follow-up results described in the section below.

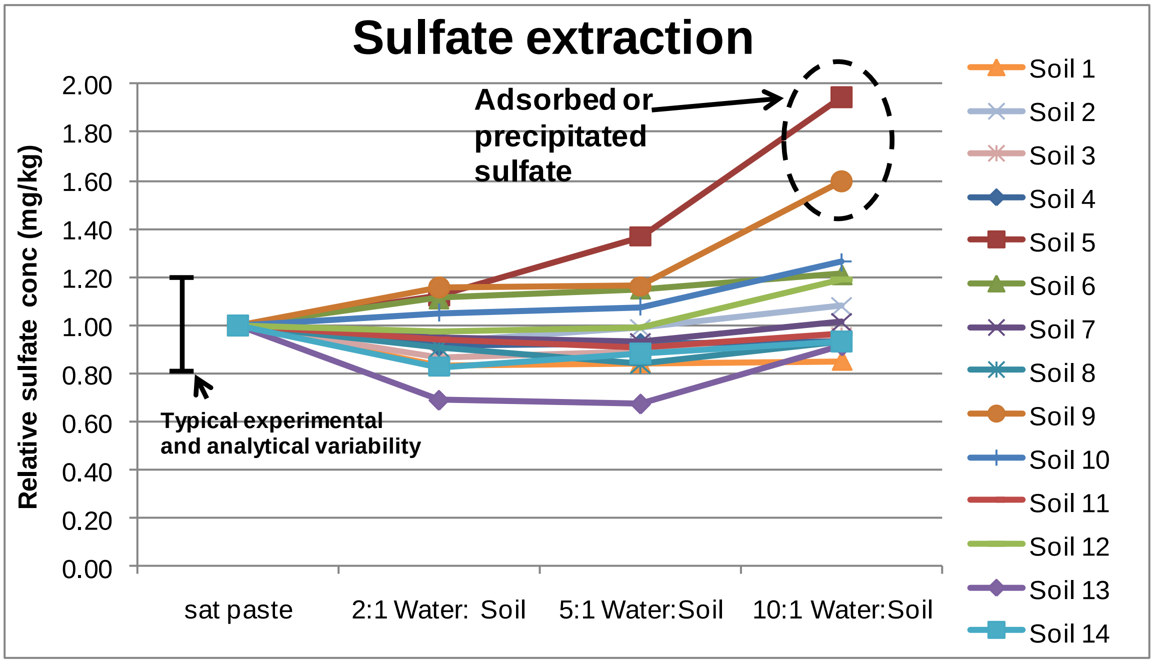
4 EXTRACTION / ADSORPTION EXPERIMENTS

Since sulfate could potentially have either adsorbed and/or precipitated portions along with the dissolved portion in wetted soil, alternative extraction methods were evaluated to compare the ability to desorb / dissolve / extract sulfate from soil. These experiments have relevance for the leaching / transport of sulfate through soils. Although leaching column work described above found evidence of sulfate retardation relative to chloride, additional extraction and adsorption experiments were also performed to further investigate this phenomenon, particularly at higher sulfate levels where sorption / precipitation effects may become more significant. Refer to Equilibrium Environmental 2011 for details of experimental design and preliminary extraction experiments.

4.1 EXTRACTION EXPERIMENTS

Soil extraction experiments described in Equilibrium (2011) were performed on various soils with a variety of textures. Overall, early sulfate extraction experiments showed clear signs of recovering precipitated sulfate in some samples, reinforcing the conclusion that precipitation is a key process for sulfate transport (Figure 4.1).

Figure 4.1. Sulfate concentrations for 14 Alberta soils under 4 different extractions

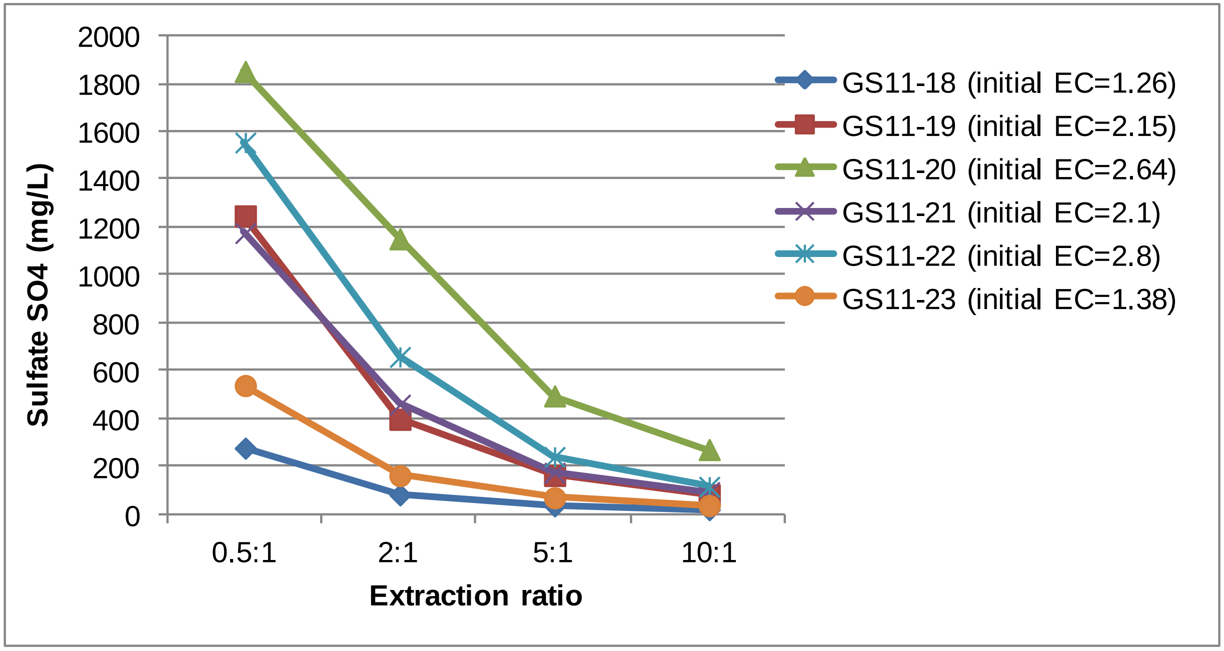


The preliminary extraction experiments described above suggest that this technique of increasing extraction ratios is a simple and useful method for evaluating the presence of precipitated gypsum.

To further study this methodology, surficial samples were obtained from a site in central Alberta which was known to have historical gypsum amendments used to treat elevated soil SAR due to a produced water spill. The gypsum applications were performed more than 20 years ago based on historical records, and spanned at least three years. Six grab-samples (GS11-18 through GS11-12) were obtained from the top 30 cm of soil within the former spill path area.

The same four extraction ratios were used, including firstly a saturated paste extraction showing saturation percentages of approximately 50% (approximately 0.5:1 water-to-soil ratio), as well as the higher fixed-ratio extractions of 2:1, 5:1, and 10:1. Extracts were analyzed for various cations and anions on a mg/L basis, and also converted to a mg/kg basis to allow a variety of comparisons. Initial EC of the saturated paste extracts ranged from 1.26 to 2.8 dS/m, with initial saturated paste EC's and sulfate concentrations (mg/L at the given extraction ratios) shown in Figure 4.2. Sulfate concentrations ranged from approximately 300 mg/L up to 1,800 mg/L in the saturated paste extracts and then decreased substantially at the higher extraction ratios.

Figure 4.2. Sulfate concentrations (mg/L) for different extraction ratios at former spill site



When expressed on a mg/kg basis in Figure 4.3, most samples showed some minor increases in sulfate concentrations with the higher extraction ratios, but with one sample in particular showing substantially increasing sulfate concentrations (GS11-20). This sample also had one of the highest initial saturated paste EC's (2.64 dS/m), suggesting that precipitated sulfate remained in the saturated paste extract which became further solubilized with additional water. Figure 4.4 shows these sulfate concentrations expressed relative to the initial saturated paste concentrations, with the clearest increase visible for GS11-20 showing a near 2.5-fold increase in sulfate concentrations at the higher extraction ratios. Thus suggests that more than half the total amount of gypsum was precipitated within the saturated paste extract, and likely substantially more than that would be precipitated at the lower moisture content present in field conditions.

Figure 4.3. Sulfate concentrations (mg/kg) for different extraction ratios

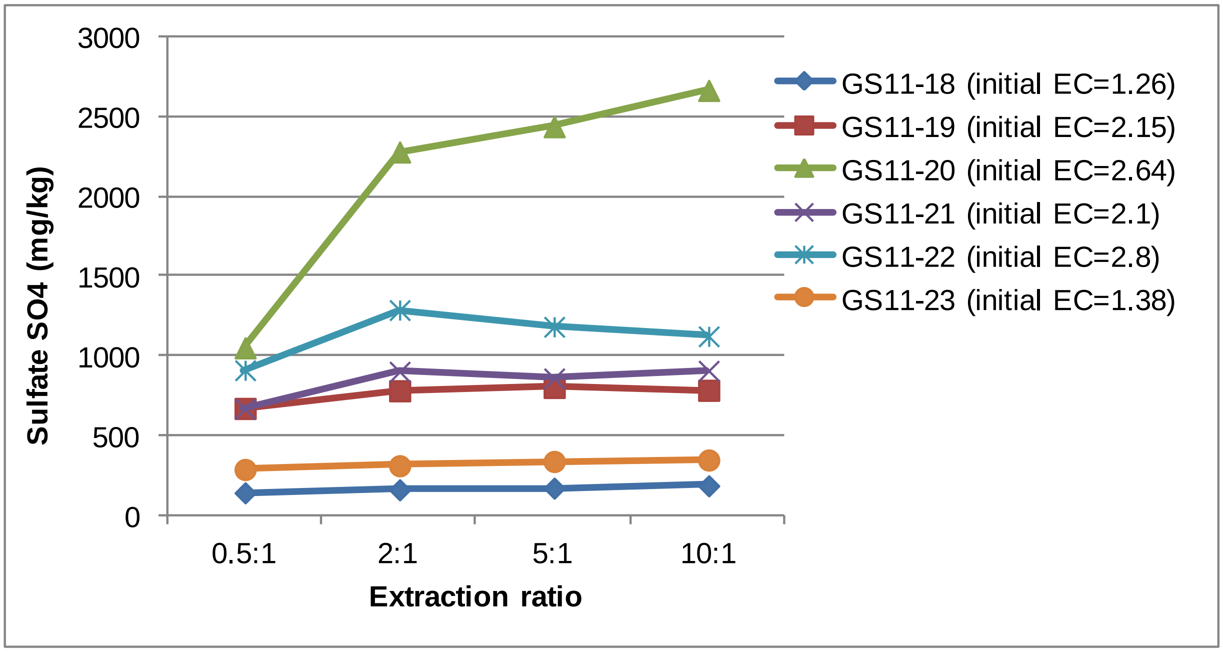
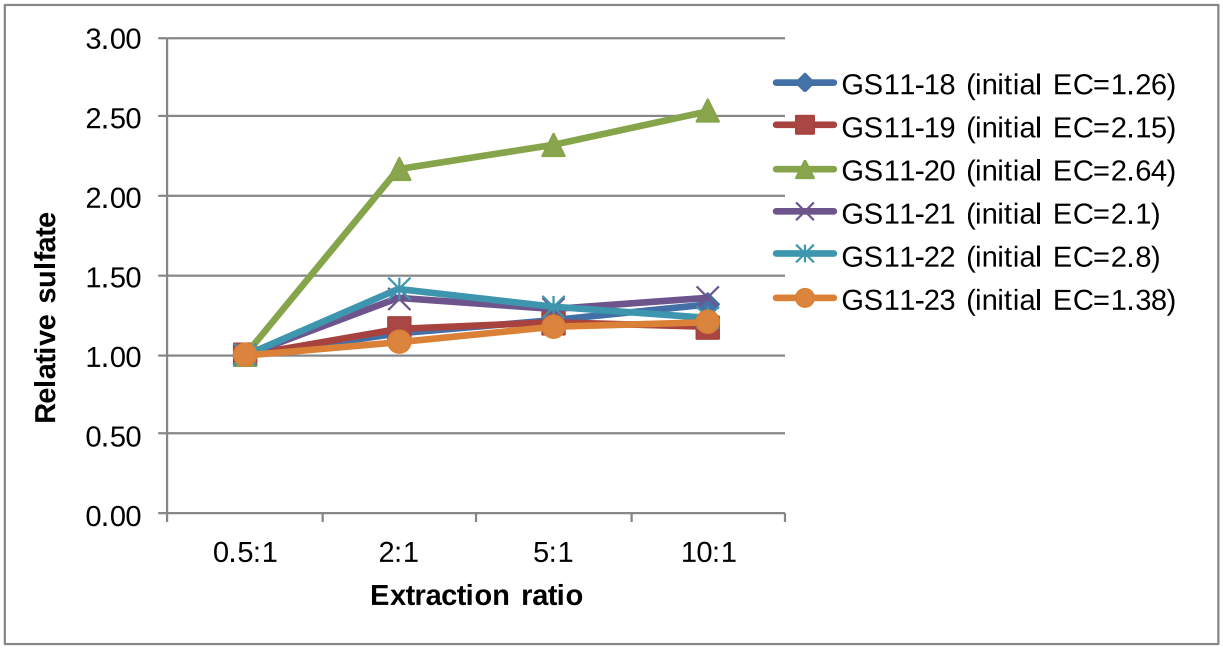
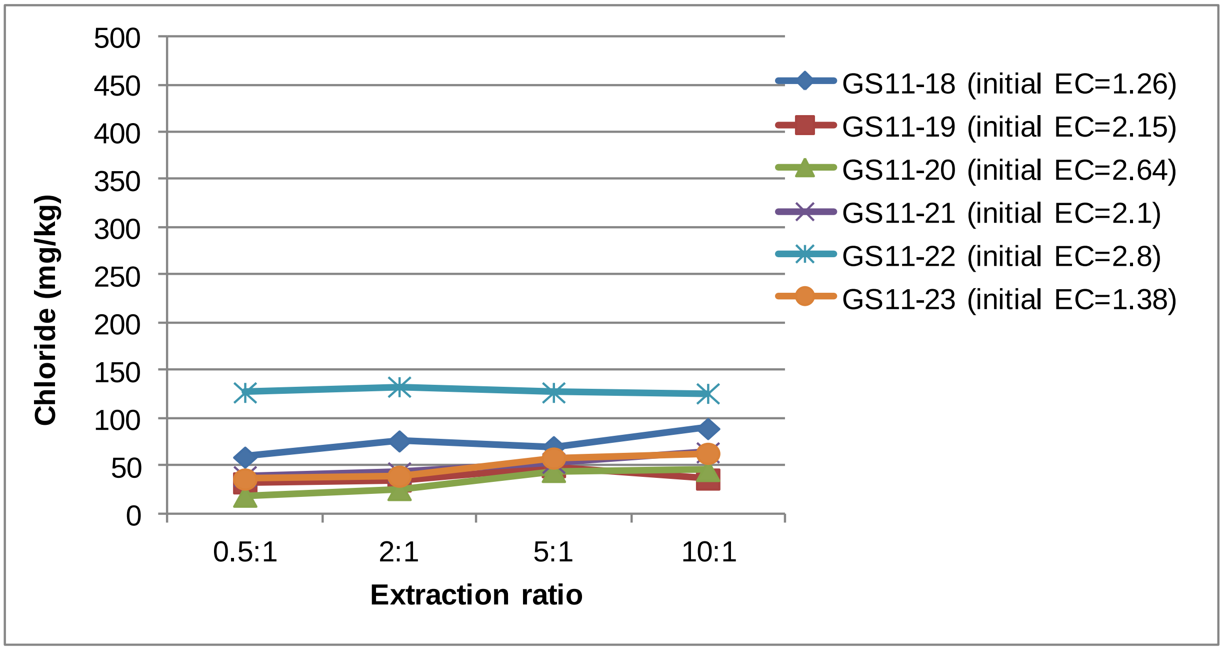


Figure 4.4. Relative sulfate concentrations (mg/kg basis) for different extraction ratios



Chloride concentrations were observed to be significantly lower than sulfate in these samples, with Figure 4.5 showing chloride concentrations below 150 mg/kg for all samples regardless of extraction ratio. This suggests that sulfate is contributing more to soil EC than chloride in these soils, and that chloride from the historical spill has largely leached out of shallow surficial soils in the intervening years since the spill and soil amendments.

Figure 4.5. Chloride concentrations (mg/kg) for different extraction ratios



Cations were also measured in the extractions, with Figure 4.6 showing calcium concentrations increasing by more than 2-fold (approaching 1,000 mg/kg) in the sample with highest precipitated gypsum (GS11-20). Figure 4.7 shows calcium concentrations relative to the saturated paste extracts (mg/kg basis), with the similar shape and magnitude compared to the relative sulfate concentrations further suggesting that the precipitated sulfate salts were predominantly gypsum.

Figure 4.8 shows sodium concentrations, with sodium generally less than 100 mg/kg and also showing some trends of increasing with extraction ratio. Magnesium concentrations were generally low (less than 50 mg/kg), though with some minor increases potentially observed with higher extraction ratios in Figure 4.9. These concentration increases do not necessarily imply that sodium or magnesium were initially precipitated (sodium and magnesium sulfate are both highly soluble), but the concentration increases could be related to cation exchange reactions which could occur after the dissolution of gypsum. This could result in some sodium and magnesium which were initially adsorbed on the cation exchange complex being displaced by newly-dissolved calcium and released into solution. This process is similar to what could be expected when SAR (sodium) impacts are remediated by the addition of calcium-containing compounds such as gypsum.

Figure 4.6. Calcium concentrations (mg/kg) for different extraction ratios

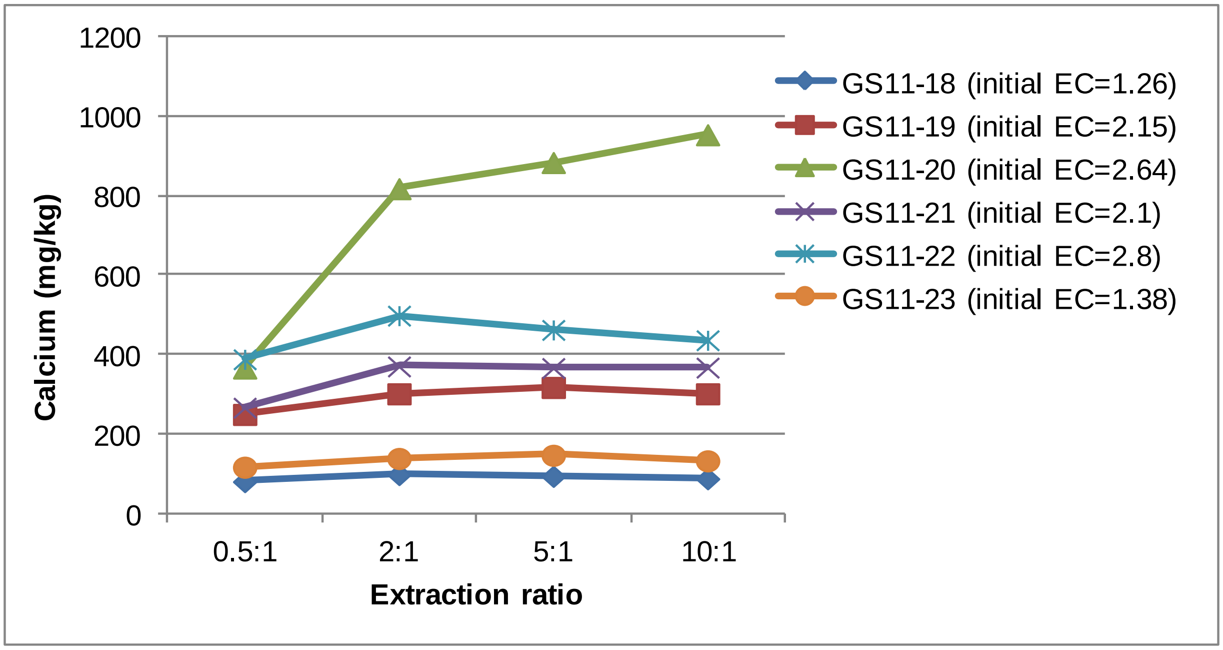


Figure 4.7. Relative calcium concentrations (mg/kg basis) for different extraction ratios

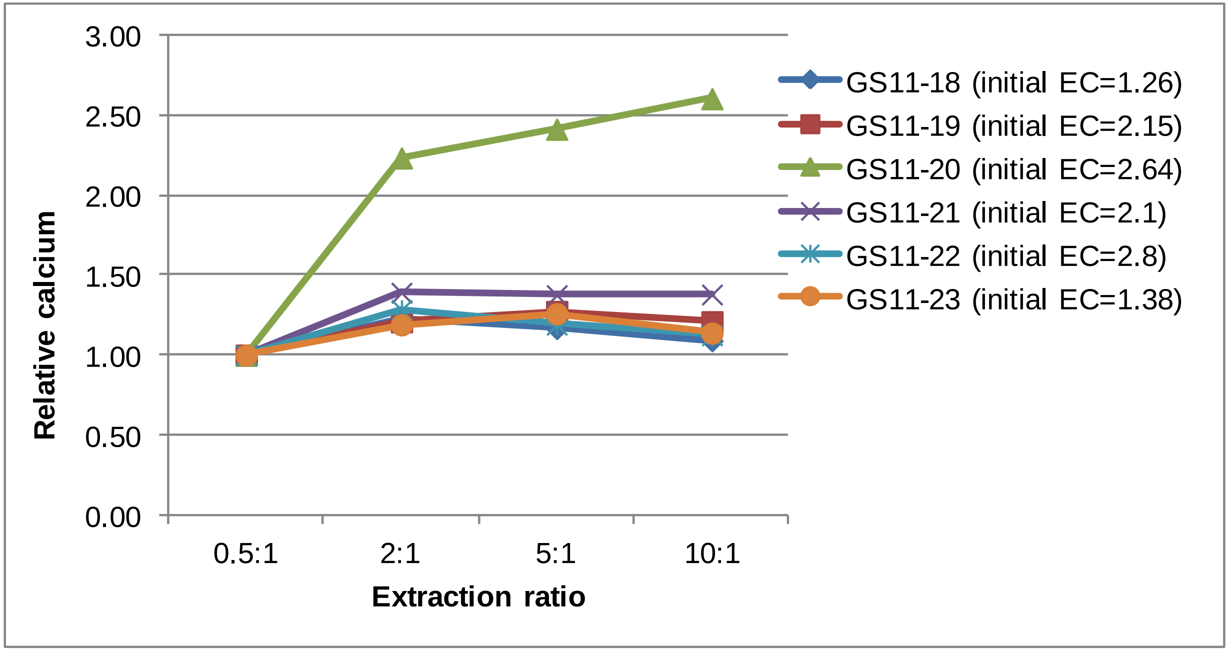


Figure 4.8. Sodium concentrations (mg/kg) for different extraction ratios

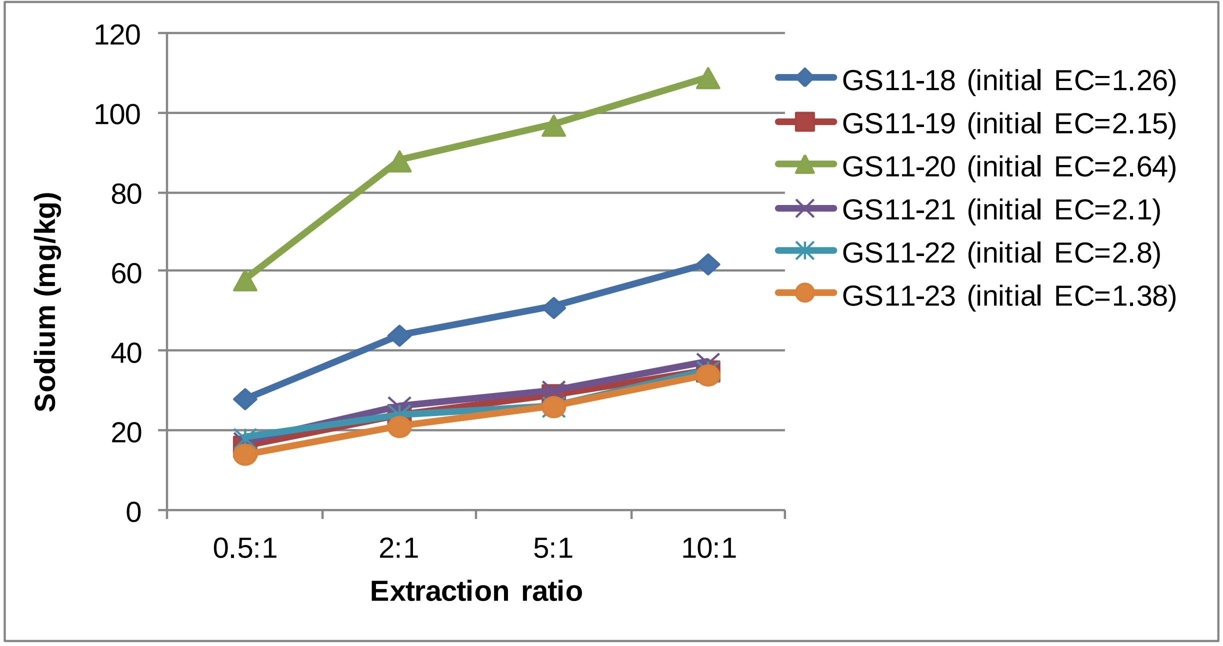
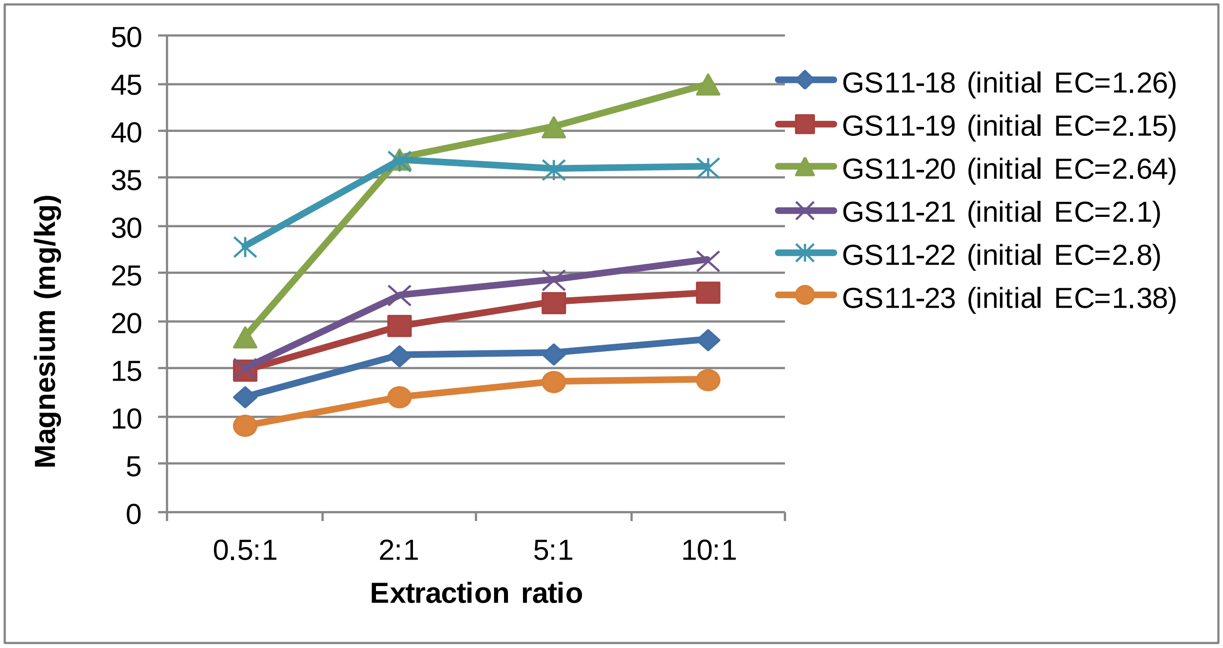


Figure 4.9. Magnesium concentrations (mg/kg) for different extraction ratios



The overall success of these historical gypsum amendments can be partially evaluated by observing SAR and EC values for the surficial grab samples. Figure 4.10 shows SAR values consistently below 2 on a saturated paste basis, or in the ‘Good’ SCARG category. EC values in Figure 4.11 are consistently below 3 dS/m (saturated paste), suggesting any residual effects of the gypsum application on EC do not appear excessive. It is thus likely that these historical gypsum applications sufficiently reduced SAR (and increased surface soil permeability) such that the likely initially high chloride concentrations were reduced substantially by leaching to the relatively low levels observed in these present-day surface samples.

Figure 4.10. Surficial SAR values for historical spill area previously treated with gypsum

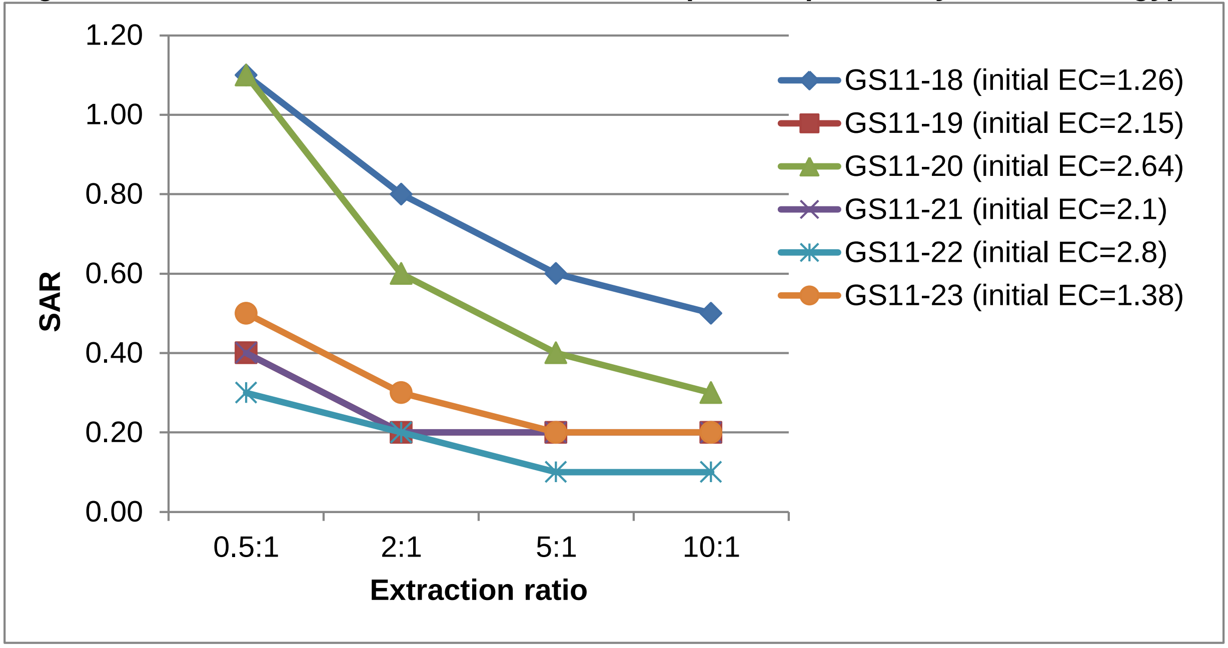
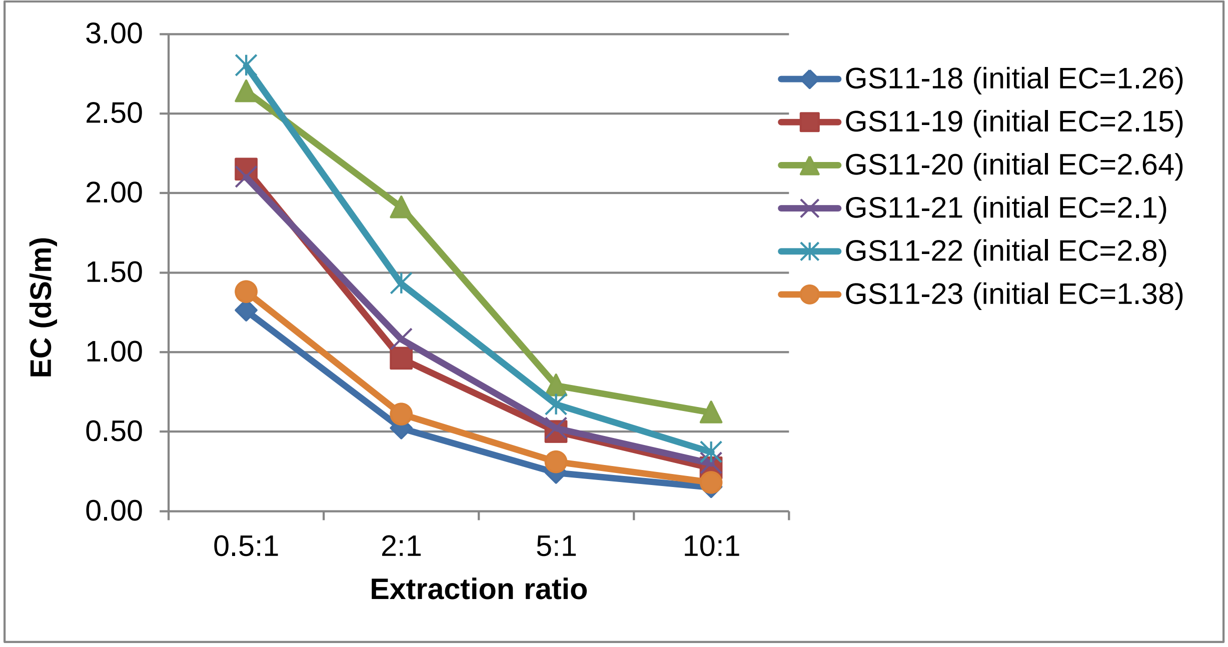


Figure 4.11. Surficial EC values for historical spill area previously treated with gypsum



4.2 ADSORPTION EXPERIMENTS

Batch adsorption experiments were performed to investigate the possibility that sulfate adsorption occurs from solution onto soil. Preliminary results from last year were inconclusive, finding no significant decreases in solution sulfate concentrations after exposure to soil and suggesting that there may be relatively minor effects of adsorption of sulfate occurring at typical Alberta sulfate levels. This research was expanded on in 2011-2012 using an altered methodology and testing the newer clay and sandy loam reference soils. For details on the experimental design of sulfate adsorption experiments and preliminary results, refer to Equilibrium Environmental 2011.

Sulfate adsorption was assessed by comparing final and initial solution concentrations as background reference soils were added to solutions with known (spiked) sulfate concentrations. Figure 4.12 shows the initial sulfate concentrations in absolute terms plus the final concentrations after addition of either clay loam or sandy loam reference soils. Due to the large range of initial sulfate concentrations (1,000 to 10,000 mg/L), the same results expressed as relative sulfate concentrations are shown in Figure 4.13. In both cases, reductions in final concentrations relative to initial concentrations were observed though the differences tended to be minor (generally less than 5%). This suggests a fairly limited adsorption effect beyond the initial (and fairly low) concentrations of sulfate present in the reference soils.

Figure 4.12. Sulfate adsorption for clay loam and sandy soils (absolute concentrations)

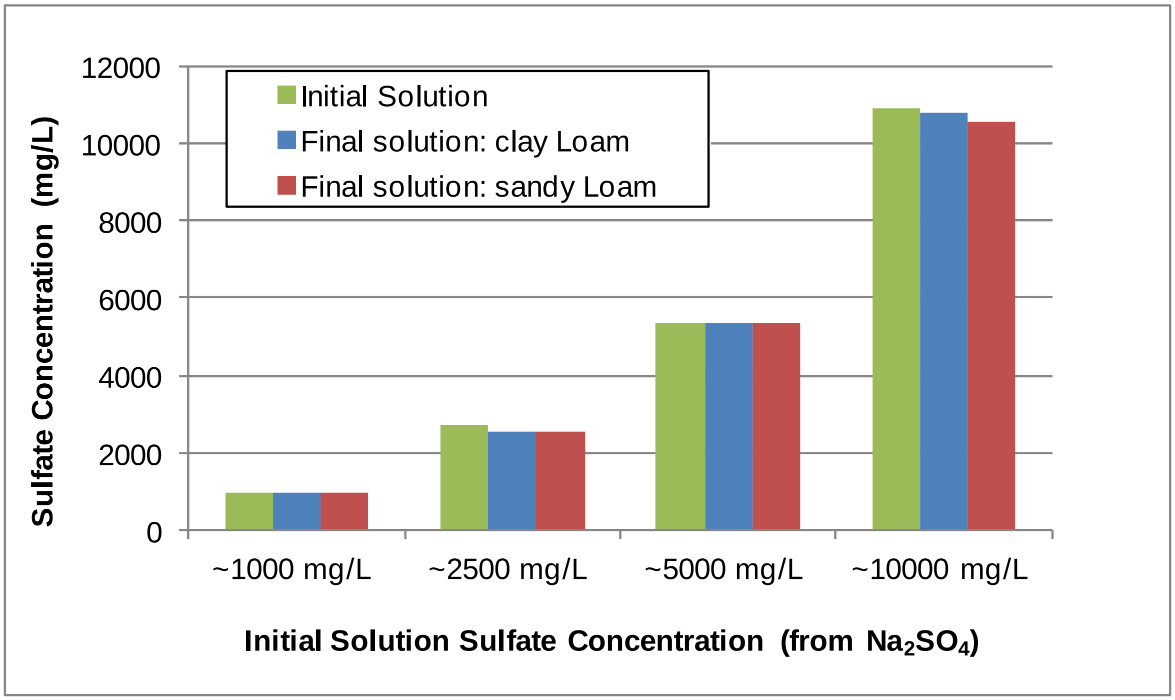
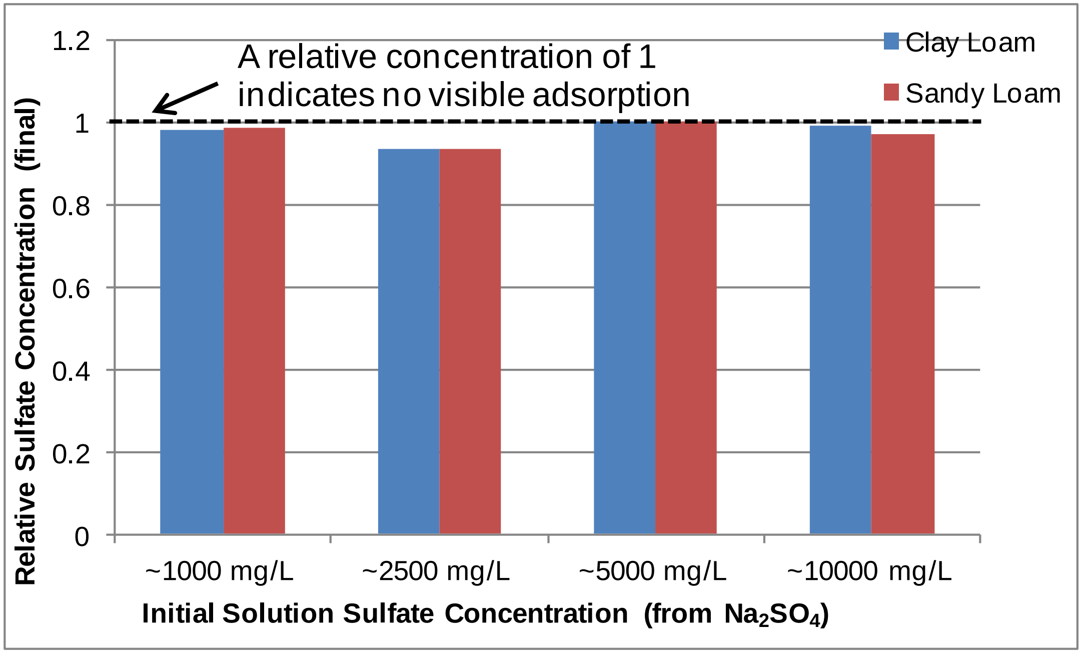
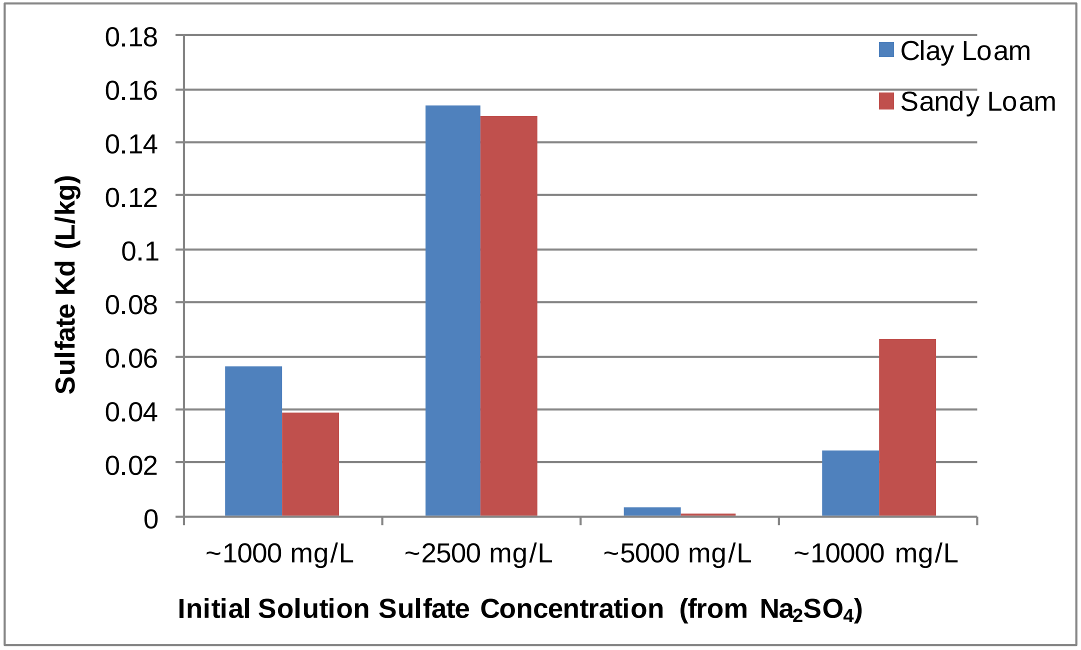


Figure 4.13. Sulfate adsorption for clay loam and sandy soils (relative concentrations)



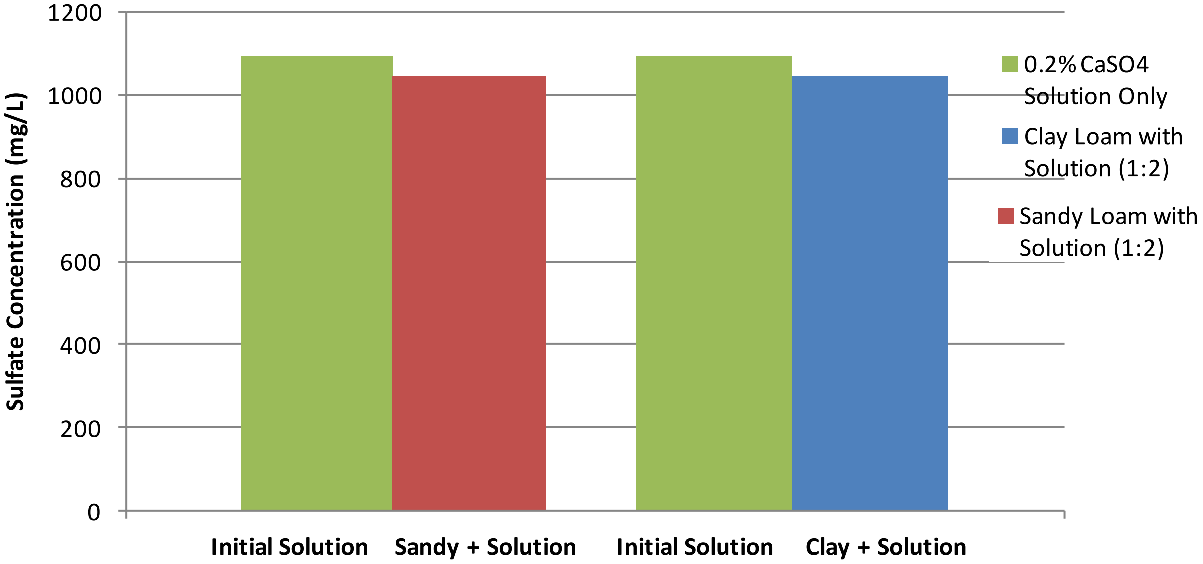
These changes in sulfate concentration after soil addition can be used to estimate apparent distribution coefficients (K_d's) by assuming the sulfate lost by solution was sorbed onto soil surfaces. This calculation also includes a correction for the initial minor background sulfate concentration in the reference soils. These apparent K_d values range from less than 0.01 to 0.15 L/kg, with Figure 4.14 showing no significant pattern of adsorption based on either soil type or initial solution sulfate concentration.

Figure 4.14. Sulfate adsorption for clay loam and sandy soils (apparent Kd)



Sulfate adsorption was further explored in the two reference soils using a gypsum solution of 0.2% $CaSO4 \cdot 2H_20$ (near its solubility limit). Figure 4.15 shows similar adsorption responses for the clay loam and sandy loam reference soils. The initial sulfate concentration of 1,095 mg/L was reduced to 1,044 mg/L for both the clay loam and sandy loam when the reference soils were mixed with the solution at a 1:2 soil:solution ratio. This represents relatively minor (~5%) reductions in final sulfate concentrations relative to initial solution concentrations, though as discussed earlier the reference soils themselves also have some small background concentrations of sulfate which is contributed to the system but nonetheless shows a minor reduction in final concentration.

Figure 4.15. Sulfate adsorption experiment using a 0.2% $CaSO_4$ (gypsum) solution



For context and method verification, the adsorption of boron was also tested using the same reference clay loam and sandy loam soils since boron is known to be a sorptive species. Figure 4.16 compares the absolute concentration of boron in various initial solutions with the final concentrations after combining in a 2:1 ratio with the two reference soils. A clear trend of sorption is apparent, with final solution concentrations measurably lower than initial concentrations. Figure 4.17 shows the same data in terms of relative boron concentrations, showing the final solution concentrations ranging from 40-80% of the initial solutions.

Figure 4.16. Boron adsorption for clay loam and sandy soils (absolute concentrations)

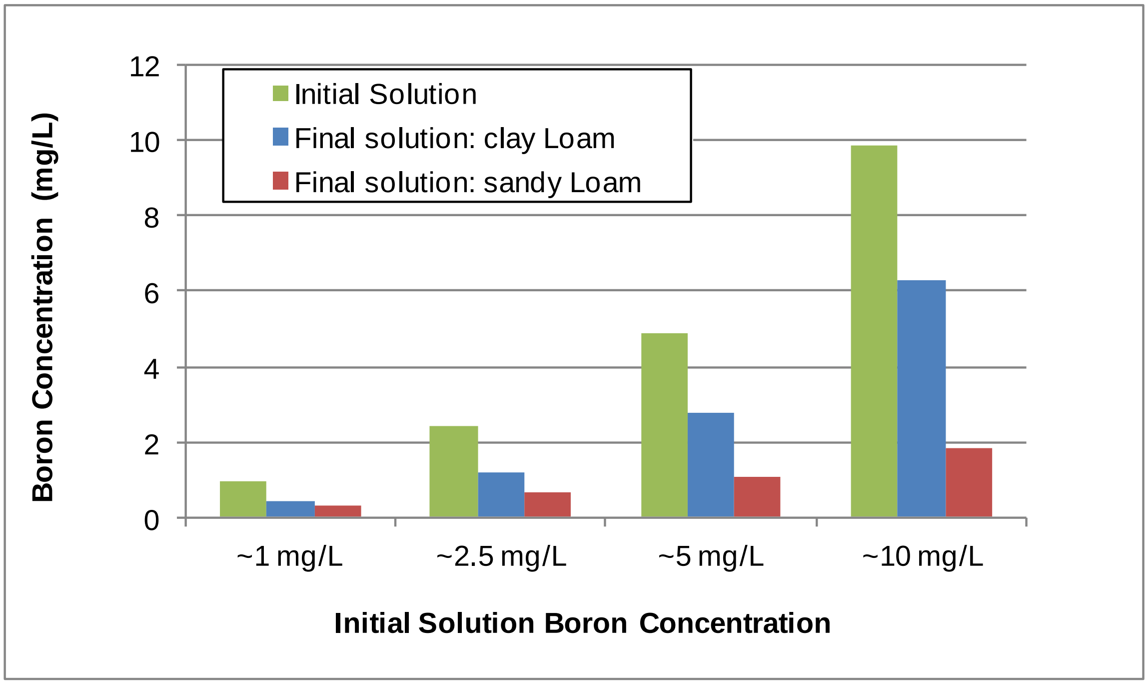
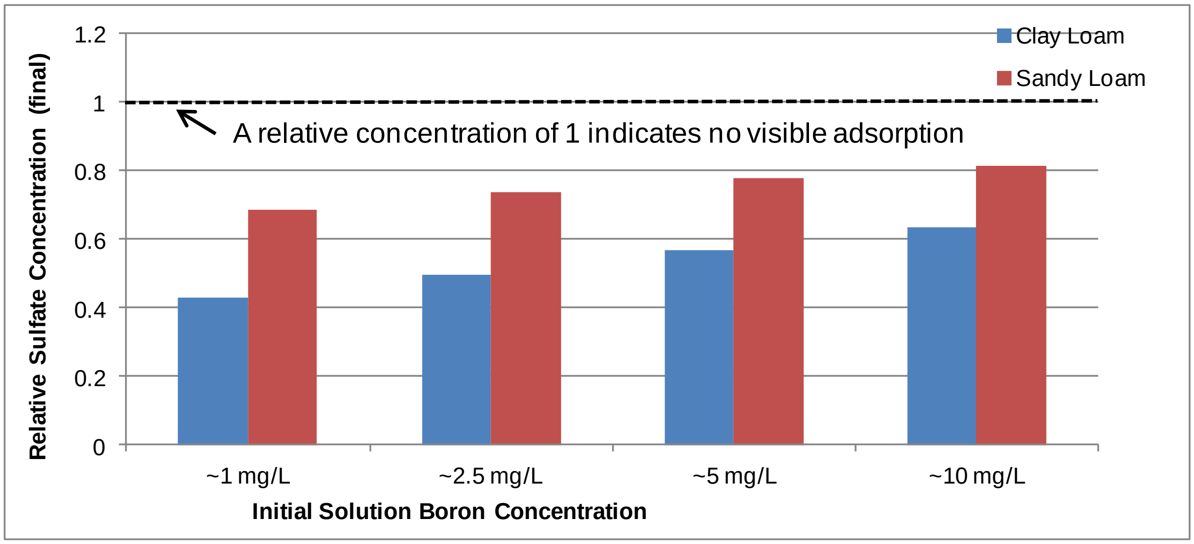
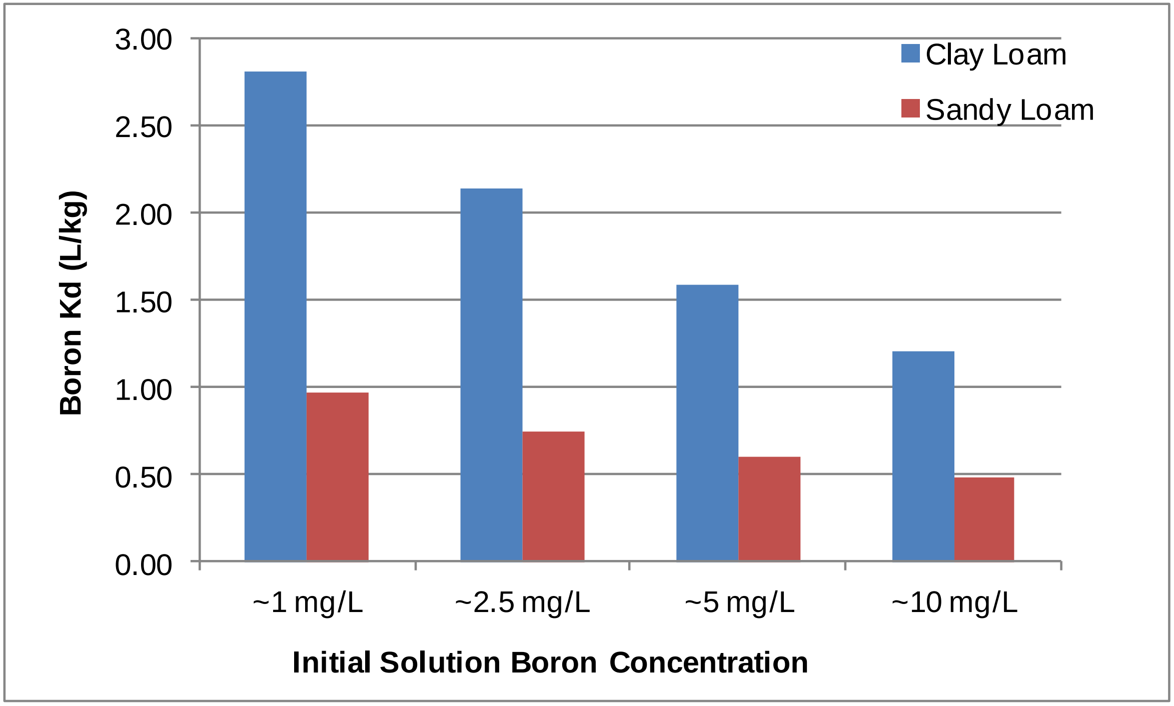


Figure 4.17. Boron adsorption for clay loam and sandy soils (relative concentrations)



Boron adsorption for clay and sandy soils is represented as apparent K_d values in Figure 4.18 using the same technique as sulphate (a ratio of estimated sorbed divided by dissolved concentrations). These results clearly show that the extent of boron adsorption varies as a function of soil type as well as initial solution concentrations. Measured K_d values range from 0.5 to 2.7 L/kg, similar to values estimated through other means through research by the PTAC Boron Working Group. This suggests that the sorption methodology used for sulphate is appropriate, and that the K_d values for sulphate are substantially below those measured for boron. It should be noted that these adsorption experiments do not evaluate precipitation effects which appear likely to have more significant effects on sulphate transport than sorption.

Figure 4.18. Boron adsorption for clay loam and sandy soils (apparent Kd)



5 TRANSPORT MODELING

Transport of sulfate through soil was modeled using the program 'LEACHC' to evaluate the theoretical potential for retardation and precipitation compared to chloride. In making their predictions, these models consider water and solute transport, Gapon selectivity coefficients, cation exchange, dissolution of bicarbonates into water from CO_2 in air, and they also consider dissolution / precipitation of gypsum as well as of soil carbonate salts including calcite. Initial conditions such as cation concentrations, water content, and other factors are evaluated to determine the solubility of sulfate.

5.1 TRANSPORT MODELING – SOLUBILITY

The solubility of sulfate under different concentrations and calcium:sulfate ratios was modeled, where sodium was used to make up the remainder of cations. The solution concentration (solubility) of pure sodium sulfate solution (near 0.01 calcium:sulfate ratio) is modeled in Figure 5.1 which exhibited a linear trend for solubility limits across the range of sulfate concentrations tested (behaviour similar to chloride). The slope of approximately 2 represents the 50% saturation percentage simulated, suggesting 1000 mg/kg sulphate would be equivalent to approximately 2000 mg/L sulphate on a saturated paste basis assuming a sodium sulphate source. For comparison, Figure 5.2 shows the solubility limits for a pure calcium sulfate solution (0.99 calcium:sulfate ratio), which shows a linear phase before plateauing at a maximum threshold of approximately 1,400 mg/L. This is fairly similar to the gypsum solubility limits described in Equilibrium, 2010 and 2011. These extreme cases are shown overlain with intermediate calium:sulfate ratios of 0.1, 0.25, and 0.5, in order to better illustrate the effect of cations on sulfate solubility (Figure 5.3). The different ratios assessed showed distinct solubility limits, with higher calcium contents showing the strongest deviation from the chloride-like behaviour of sodium sulphate in terms of solubility.

Figure 5.1. Solubility limits of sodium sulfate on a sat paste basis

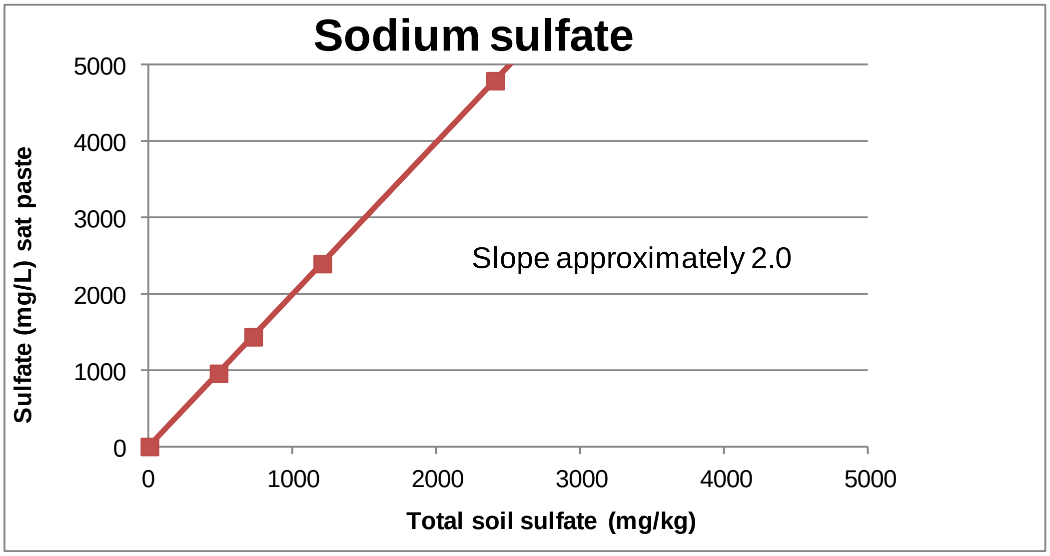


Figure 5.2. Solubility limits of calcium sulfate (gypsum) on a sat paste basis

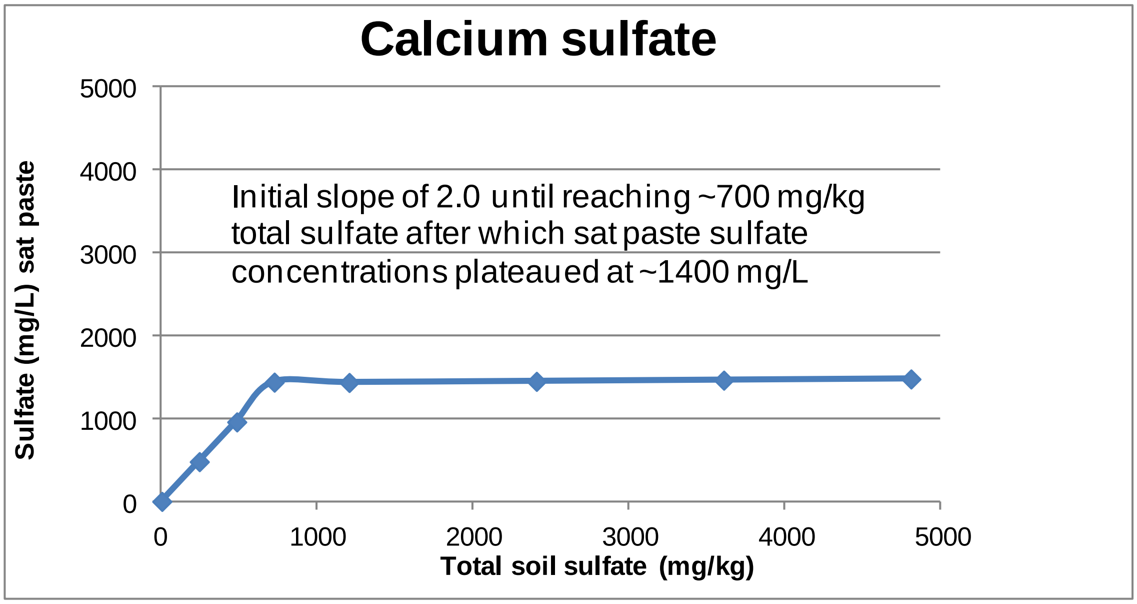
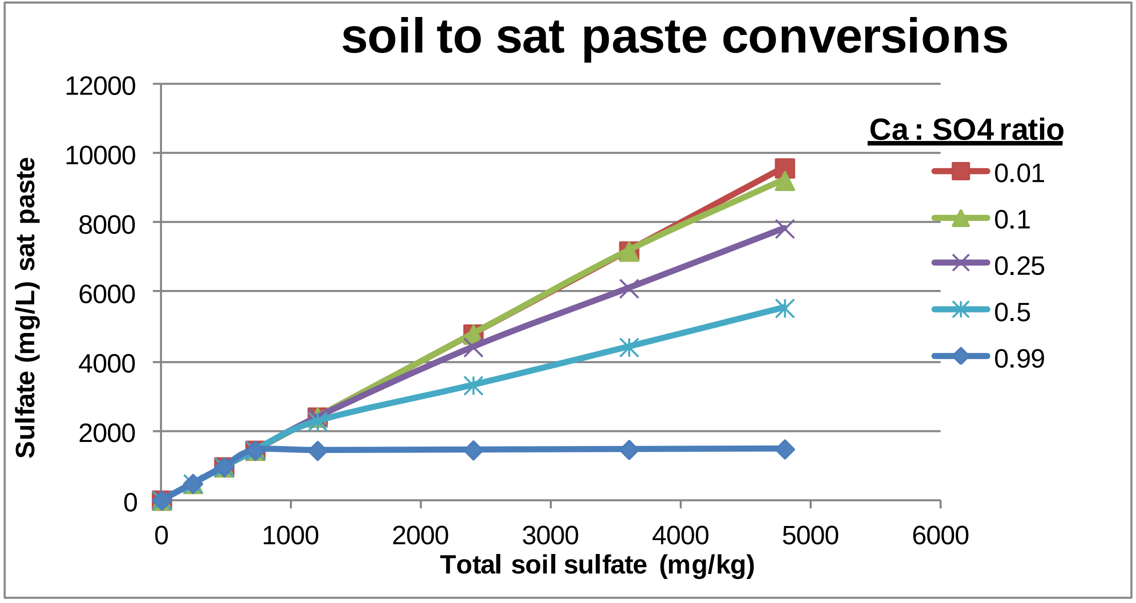


Figure 5.3. Solubility limits of sulfate as a function of calcium on a sat paste basis



The solubility limits of sulfate were also calculated and expressed on a pore water basis in order to evaluate the increase in concentrations due to conversion from saturated paste to pore water conditions. Figure 5.4 shows a pure sodium sulfate solution (near 0.01 calcium:sulfate ratio) exhibiting a linear relationship for solubility limits across the range of sulfate concentrations tested. In contrast, the solubility limits for a pure calcium sulfate solution (0.99 calcium:sulphate ratio) appear to experience a brief initial linear phase before plateauing at a maximum threshold of again near 1,400 mg/L – the apparent modeled solubility limit (Figure 5.5).

Figure 5.4. Solubility limits of sodium sulfate on a pore water basis

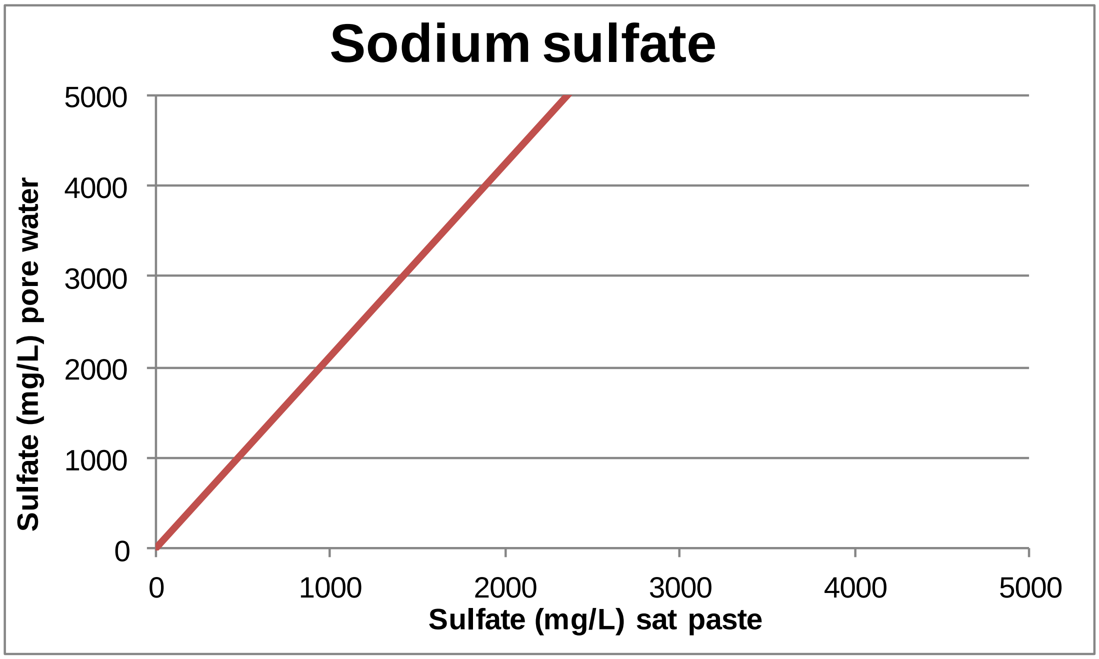
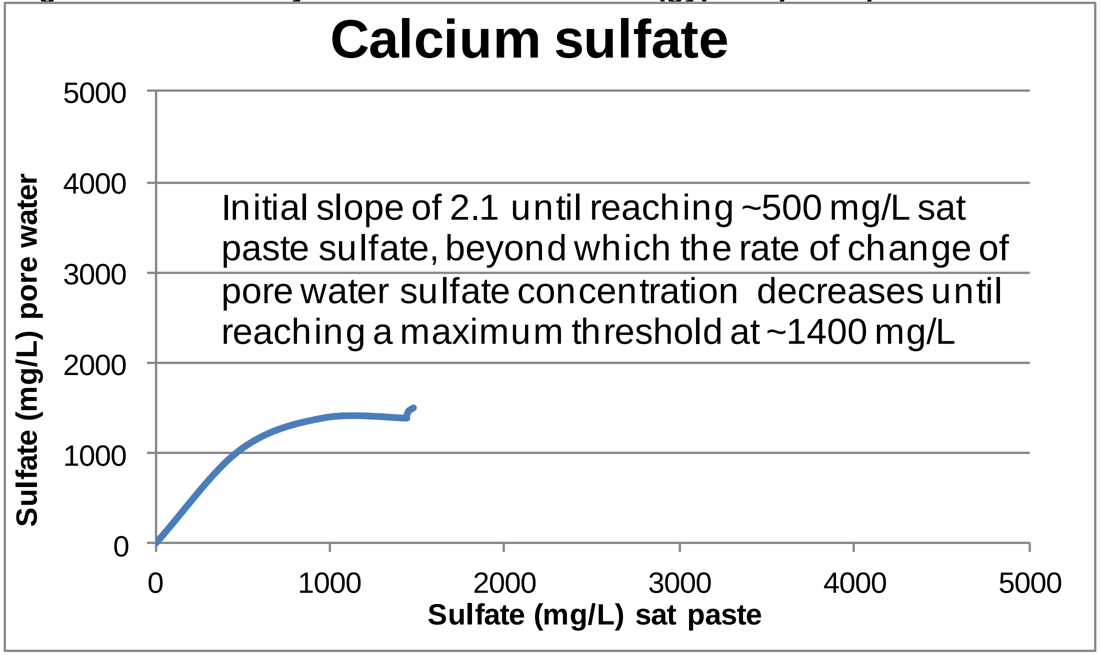


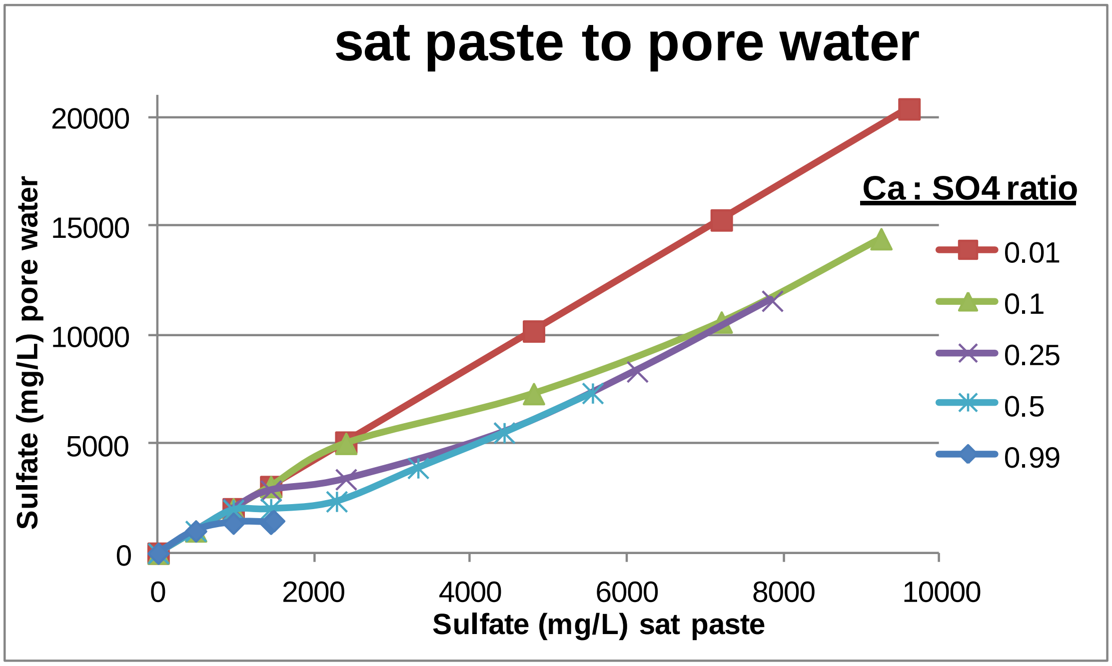
Figure 5.5. Solubility limits of calcium sulfate (gypsum) on a pore water basis



Initial slope of 2.1 until reaching ~500 mg/L sat paste sulfate, beyond which the rate of change of pore water sulfate concentration decreases until reaching a maximum threshold at ~1400 mg/L

Figure 5.6 shows the extreme cases described above (0.01 and 0.99) overlain with intermediate calcium:sulfate ratios of 0.1, 0.25, and 0.5, in order to better illustrate the effect of cation ratios on sulfate solubility. Overall, the same trend was observed regarding the solubility limits of sulfate on a pore water basis as was found with the saturated paste series. In general, higher calcium concentrations resulted in stronger deviations in sulfate behaviour from chloride. Again, the different cation ratios showed distinct solubility limits – presumably as a function of their unique calcium contents (Figure 5.6).

Figure 5.6. Solubility limits of sulfate as a function of calcium on a pore water basis



5.2 TRANSPORT MODELING - LEACHING

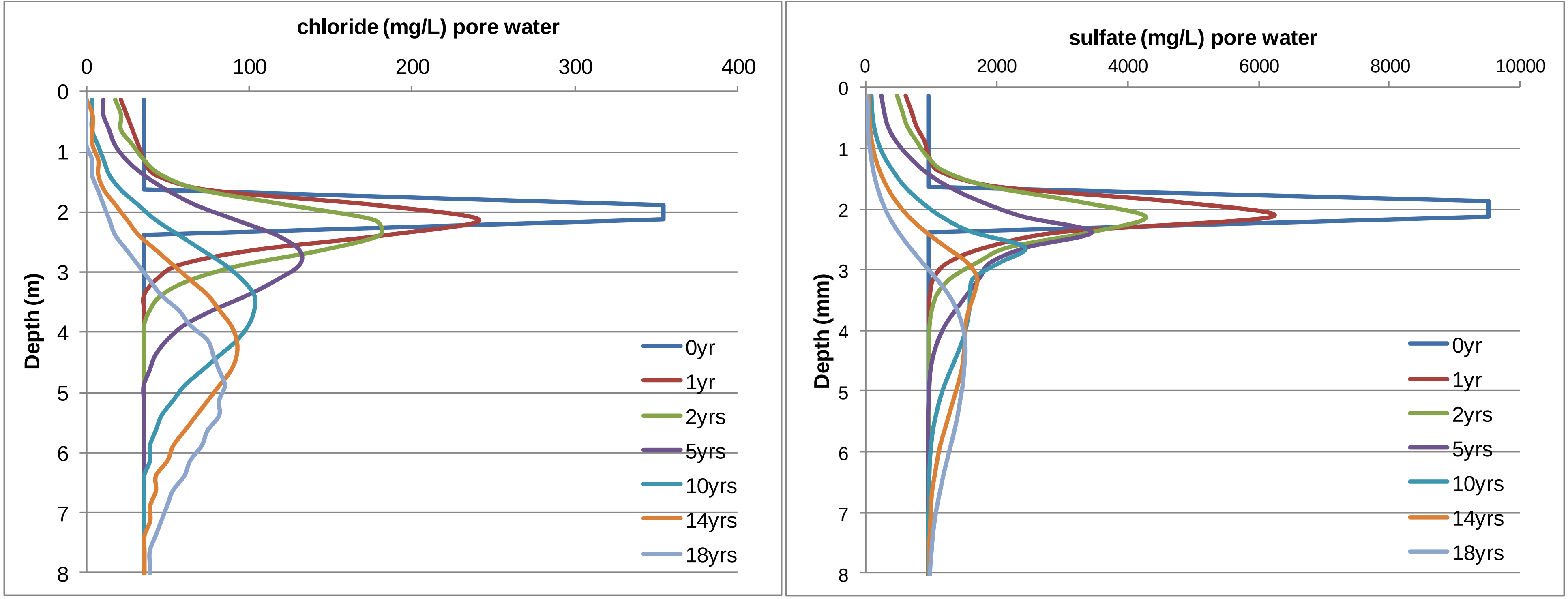
Models were then further advanced to evaluate the leaching of sulfate relative to chloride using relatively high initial sulfate concentrations (10,000 mg/L in soil solution) and high initial sodium (SAR ~ 60) to ensure complete initial solubility. Other details of the model parameters are shown in Table 5.1 below, including a relatively fast drainage rate (60 mm/year, equivalent to the Alberta Environment Tier 1 default drainage rate for coarse soils) to provide a rate potentially relevant to lateral transport as well as the modeled vertical transport. Chloride was used as a conservative tracer for comparison purposes, with substantially lower initial chloride impact concentrations (350 mg/L) to keep interaction effects to a minimum. Sulfate and chloride background concentrations were approximately 1,000 and 35 mg/L respectively, with impact concentrations thus 10-fold above background in each case. This allows for direct comparisons of ‘relative’ chloride and sulfate concentrations (relative to the initial impacts) without disproportionate influence of background conditions in either case.

Table 5.1. Example LEACHC model parameters for evaluating sulfate transport

Parameter	**Value**
Drainage rate	60 mm/year
Water table depth	~ 2 m
Soil dry bulk density	1.62 kg/m^3
Soil total porosity	0.381
Cation exchange capacity	240 meq/kg
Gapon selectivity coefficient: Mg/Ca	1.1
Gapon selectivity coefficient: Ca/Na	2.2
Gapon selectivity coefficient: Ca/K	0.15
Sulfate impact composition	Sodium sulfate
Initial sulfate impact depth	~ 1.8 – 2.3 m
Initial sulfate impact concentration	~10,000 mg/L (in soil solution)
Initial sulfate background concentration	~ 1,000 mg/L (in soil solution)
Initial impact SAR	59 (in soil solution)
Initial impact EC	16 (in soil solution)
Initial chloride impact concentration	~350 mg/L (in soil solution)
Initial chloride background concentration	~35 mg/L (in sol solution)

Transport was modeled for 18 years, with the evolution of chloride and sulfate concentrations over time shown in Figure 5.7. Results show a visible retardation of sulfate relative to chloride, likely primarily due to precipitation as soluble sulfate salts travel through calcium-rich unimpacted soils and undergo cation exchange / precipitation reactions. The initial reduction in peak sulfate concentrations is also greater than that of chloride due to the temporary precipitation of sulfate as gypsum. There is also some visible upward migration of both sulfate and chloride into the root-zone, with less apparent differences between the salts visible in this model scenario. Additional insight is also obtained by comparing relative concentrations of chloride and sulfate in the sections below.

Figure 5.7. Modeling the rate of sulfate leaching relative to chloride



Additional comparisons between the modeled sulfate and chloride transport may be performed by expressing concentrations relative to the initial peak impact concentrations. These normalized, relative concentrations can then be directly compared to evaluate differences in transport. For example, Figure 5.8 shows the relative breakthrough concentrations for both sulfate and chloride into the root-zone, with a peak 21% of the initial impacts (or approximately an additional 11% above background) reaching the root-zone after approximately 1 year. The apparent similarity between sulfate and chloride for this aspect is potentially due to the interplay between the upward diffusion of sulfate/chloride compared to the rapid downward leaching of salts due to the fast drainage rate. In this sense, there may be some potential for a faster-leaching salt such as chloride to show similar or lower breakthrough concentrations than a slower-leaching salt in an upgradient direction. Results may be different in a downward (down-gradient) direction, as discussed below.

Figure 5.8. Relative root-zone (upgradient) break-through of sulfate vs chloride

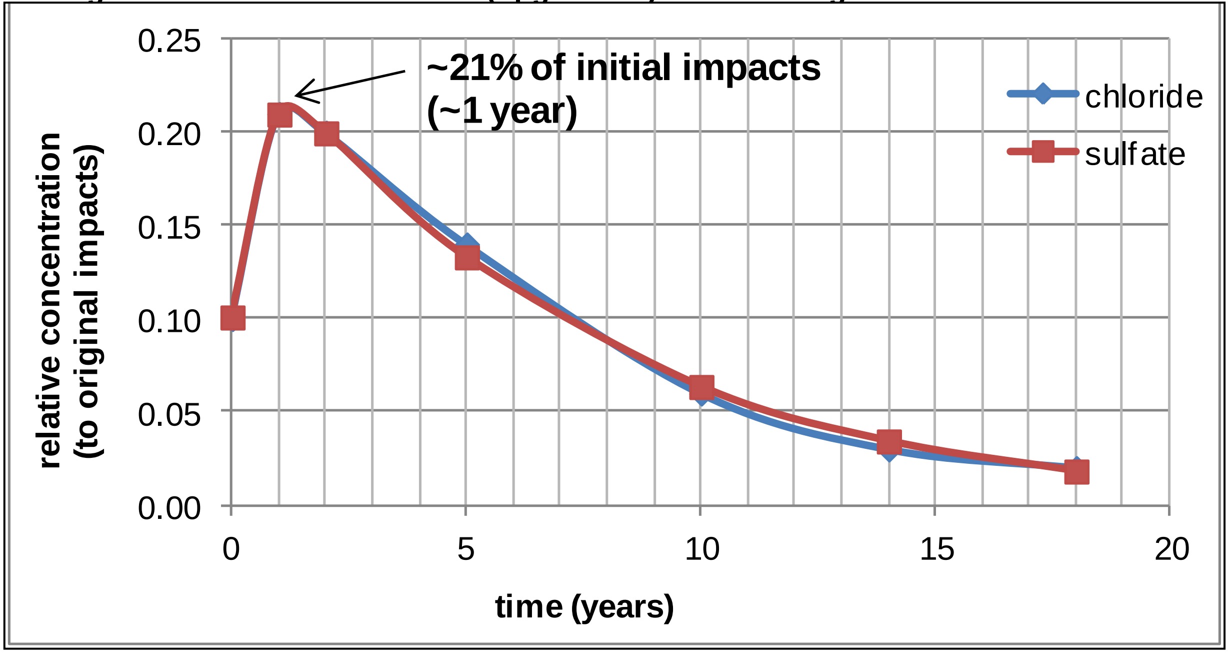


Figure 5.9 shows relative down-gradient breakthrough of sulfate compared to chloride at a depth of 2.5 m (thus, directly below the initial impacts). Chloride reaches a peak of 52% of the initial impacts after approximately 1.2 years, whereas sulfate reaches a peak of approximately 36% of the initial impacts after approximately 3.5 years. Similarly, Figure 5.10 shows peak breakthrough concentrations further downgradient (5 m depth), with chloride reaching a peak of 26% of the initial impacts after approximately 12 years whereas sulfate reaches a lower peak of 16% of the initial impacts after approximately 16 years.

Overall, this model scenario thus shows an apparent attenuation as well as retardation of sulfate transport compared to chloride, with relative differences in peak time and concentration a complex function of numerous model parameters. This attenuation and retardation is modelled to be due primarily to precipitation reactions since the LEACHC model does not consider potential sulfate adsorption. Sulfate adsorption, if present and significant under certain situations, could potentially slow sulfate transport further.

Figure 5.9. Relative down-gradient break-through of sulfate vs chloride (2.5 m depth)

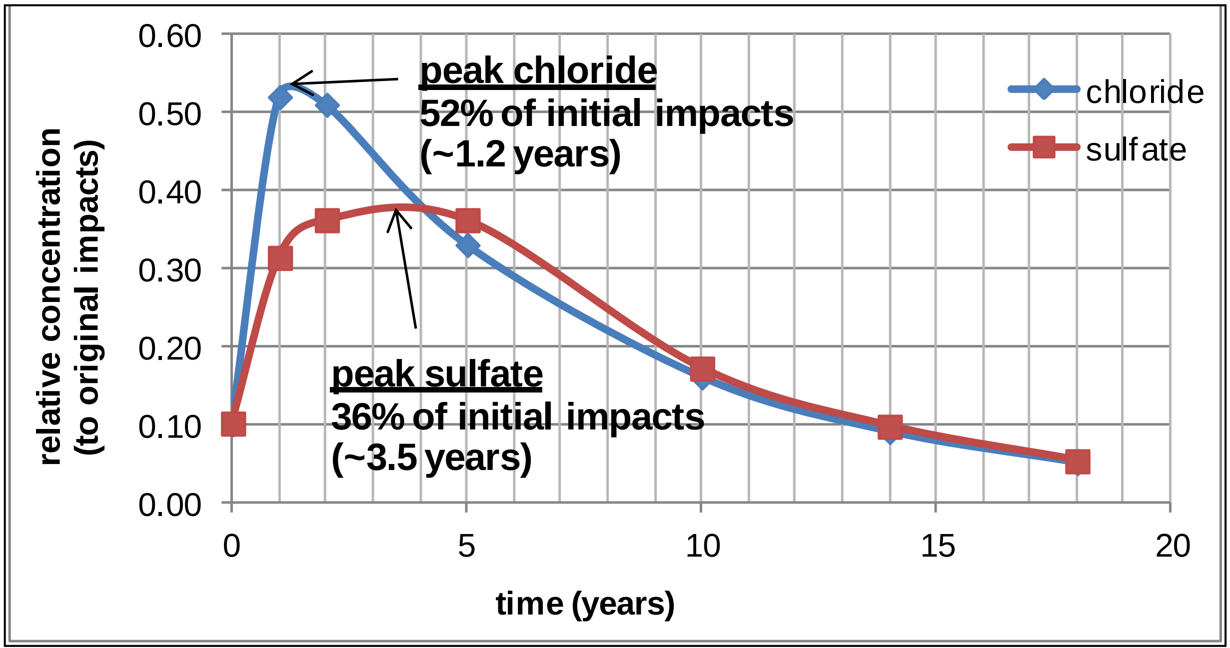
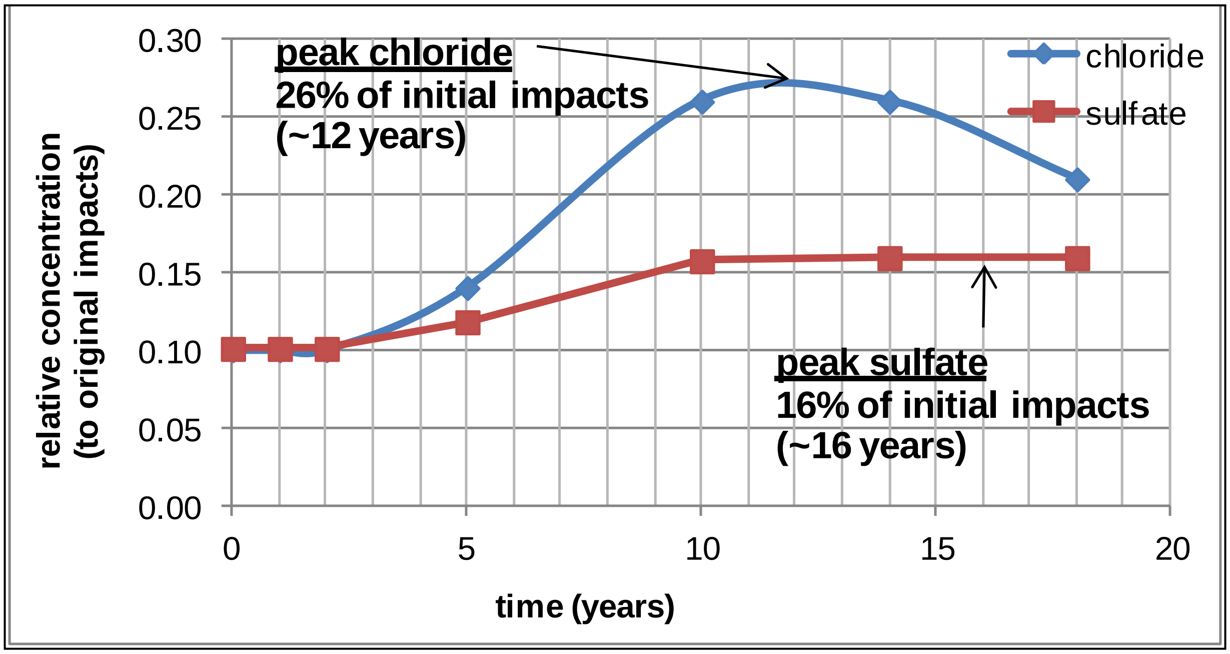


Figure 5.10. Relative down-gradient break-through of sulfate vs chloride (4 m depth)



6 SUBSOIL SULFATE GUIDELINE RECOMMENDATIONS AND POLICY ISSUES

Due to the large number of variables identified which influence sulfate fate and transport, it is recommended that subsoil sulfate guidelines be implemented within the context of the Alberta Environment 'Subsoil Salinity Tool' (SST). This allows tailoring of guidelines to site-specific conditions while maintaining a consistency of analysis from site-to-site without the need for a complex, data-intensive site-specific risk assessment for each site.

Subsoil sulfate guidelines generated in this manner would generally apply to subsoils below the root-zone, and not the root-zone itself where SCARG (Alberta Environment, 2001) typically applies. Subsoil chloride protocols from the SST could be modified as appropriate to generate site-specific guidelines for subsoil sulfate for various receptors outlined below.

6.1 PATHWAYS FOR SUBSOIL SULFATE GUIDELINE DEVELOPMENT

Five potential pathways could be considered during the implementation of subsoil sulfate guidelines into the SST:

a) Upward migration of subsoil sulfate into root-zone (potential for future SCARG exceedance)
b) Dugout pathway: irrigation water
c) Dugout pathway: livestock water
d) Aquatic life pathway (lateral transport)
e) DUA pathway (vertical transport)

Each of these five key pathways for subsoil sulfate could be considered based on meeting appropriate Tier 1 guidelines at each receptor. Though each of the above five pathways are consistent with the current SST chloride pathways, each of them tends to have differences in how they may be implemented in the SST for sulfate instead of chloride. These differences generally result from differences in contribution to electrical conductivity (EC), differences in toxicity (to livestock, human, or aquatic life), differences in transport speed, or differences in peak concentrations estimated at receptors. The transport-related factors are generally related to a combination of precipitation and/or cation exchange factors.

Each of these pathways is discussed below, including a discussion of potential ways to implement guidelines in the SST. Key policy issues are also identified in each case which require further discussion with various stakeholders such as Alberta Environment and the PTAC Salinity Working Group in order to clarify aspects of the guideline implementation.

6.1.1 Upward migration into root-zone

The potential for upward migration into the root-zone is one possible pathway to consider for SST implementation. As per chloride, elevated sulfate (above-background levels) may potentially transport back upwards into the root-zone and cause potential future Tier 1 (SCARG) exceedances. Transport of high concentrations of sulfate may be slower than chloride due to factors such as precipitation reactions converting soluble sodium sulfates into less soluble calcium sulfates as sulfates travel through background (calcium-rich on the cation exchange complex) soils. These precipitations reactions influence sulfate soil concentrations and therefore pore water concentrations, saturated paste concentrations, and EC conversions differently for sulfate than chloride.

One approach would be to calculate a root-zone EC buffer in a similar way as for chloride, but with appropriate adjustments for the relative solubility and equivalent weight of sulfate relative to chloride. Sulfate influences EC less than chloride on a mg/L basis. The potential for measured (saturated paste) sulfate concentrations to result in lower pore water concentrations than expected for chloride should also be considered due to sulfate solubility limits. This approach may require providing additional input data such as calcium concentrations. Appropriate adjustments may also be useful to ensure that sulfate concentrations above background are considered.

6.1.2 Dugout pathway: irrigation water

Another possible pathway consistent with existing SST policy is considering the mixing of sulfate-containing groundwater with surface water being collected in a dugout for irrigation purposes. The dugout irrigation pathway for sulfate could function similarly to chloride in the SST and the same adjustment factors for mixing into collected surface water could be used. Dugouts are primarily intended to collect surface water, but some groundwater may also infiltrate and mix with the surface water. The dugout irrigation pathway is currently screened in SST using background TDS and a similar method could be used for calculating irrigation 'buffer.' However, an adjustment should be considered to account for the different equivalent weight of sulfate (less EC influence) since risk from irrigation water is primarily a function of EC. For example, a given TDS due to sulfate contributes approximately 1/3 less than the equivalent TDS due to chloride and thus poses a lesser risk.

6.1.3 Dugout pathway: livestock water

Dugout water can also be used to supply drinking water for livestock. Standard SST protocol for mixing with surface water could be used as per the irrigation pathway based on soil texture. The current livestock watering guidelines in the SST are based on TDS in categories shown below, with the pathway screened based on the background TDS in shallow groundwater.

- Background TDS <3,000 mg/L "Good"
- Background TDS 3,000 – 7000 mg/L "Marginal"
- Background TDS >7000 mg/L "Unusable" (pathway excluded)

Beyond these TDS guidelines, there is also an Alberta Environment Tier 1 livestock watering guideline of 1,000 mg/L which could potentially be used instead of the TDS guideline. This livestock guideline may be less conservative than the TDS guideline in some cases but more conservative in other cases depending on background salinity and how the pathway is screened. As an example of this pathway screening issue, 1000 mg/L pore water sulfate is equivalent to approximately 200-250 mg/kg soil, and would often be exceeded (thus potentially ruled out) using existing protocol based on background soil concentrations. On the other hand, the livestock TDS-based guidelines would rule out the pathway less often. CCME may be updating their sulfate water guidelines in the near future which could have relevance to this pathway.

6.1.4 **Aquatic life pathway**

Alberta Environment currently does not have an aquatic life sulfate guideline, possibly partially because high background sulfate conditions are common in many parts of the prairies. British Columbia has an aquatic life guideline of 100 mg/L, although there is some debate about some aspects of the toxicity studies available at the time (~2000). These concerns included the limited number of species used, the fact that hardness (a mitigating factor) was not considered, as well as the possible use of potassium sulfate for some studies (potassium is more toxic to aquatic life). Updated guidelines have been proposed that considers hardness (Elphick, 2011):

- 'Soft' (10-40 mg/L hardness) → 129 mg/L SO4
- 'Moderately hard' (80-100 mg/L hardness) → 644 mg/L SO4
- 'Hard' (160-250 mg/L hardness) → 725 mg/L SO4

Transport time and peak breakthrough could also be adjusted for sulfate precipitation / retardation effects. Regardless of which aquatic life guideline and transport parameters are used, background concentrations at the receptor may often exceed guidelines. 1,000 mg/L sulfate at the discharge point is equivalent to ~200-250 mg/kg, which would often be exceeded by background conditions. This issue of background concentrations often being near or above relevant toxicity thresholds is more prevalent for sulfate than chloride, and is a significant policy issue for both aquatic life an DUA pathways.

An 'Incremental Risk' is potentially appropriate in these cases, and can be useful when background concentrations are elevated above guidelines or toxicity thresholds such for lead or various hydrocarbon fractions in peat soils. This approach results in guidelines being applied "on-top" of background conditions thus providing a limit on incremental risk. One major benefit of an incremental risk approach is that it avoids flagging background concentrations as exceedances.

With such an approach, a further issue is whether background should be considered at the site only or also at the aquatic receptor. Background conditions at a site will generally be well characterized, but it may be possible for background at the aquatic life receptor to be different. For example, a highly saline slough may be the nearest receptor for sulfate impacts at a 'good' quality site, making the risk from moderate sulfate impacts at the site relatively less important to that receptor. Note that background conditions at the actual receptor are often not known. Another possible option would be to investigate background salinity at the receptor, using that data as appropriate.

Other options and alternatives to incremental risk include ruling out the pathway, allowing a certain percent increase above background, or calculating a buffer to an alternative threshold.

6.1.5 DUA pathway

For the DUA pathway, Alberta Environment has a sulfate drinking water guideline for humans of 500 mg/L. Some aspects of this guideline calculation could be the same as for chloride including general transport to DUA concepts and dilution into DUA via DF3. One aspect that could be different includes the potential for slowed vertical transport and additional peak attenuation of sulfate compared to chloride.

An incremental risk approach is also possible for this pathway due to the significant sulfate concentrations frequently in background. Similar to the aquatic life pathway, it could essentially calculate a guideline and apply it ‘on-top’ of background conditions. This approach essentially sets the incremental risk for the site impacts (above background) to be less than the Tier 1 guidelines at the receptor. An additional issue is that the Alberta Environment drinking water TDS guideline is also 500 mg/L, although this is more conservative than the sulfate guideline since cations also need to be considered. This raises the question as to whether the sulfate guideline be used preferentially over the TDS guideline since it is more targeted.

A potential alternative to this incremental approach would be to exclude the DUA pathway in conditions where background sulfate concentrations would be expected to exceed the DUA guideline for sulfate. This could potentially happen in large numbers of scenarios due to elevated background sulfate concentrations within shallow or deep tills, or within the DUA itself.

7 CONCLUSIONS AND NEXT STEPS

Previous conclusions from this research project include:

- Calcium sulfate (gypsum) and sodium sulfate are soluble salts which contribute to soil salinity, reduced vegetative growth, and impaired groundwater quality. Both these salts can originate from natural or anthropogenic sources, and may be introduced into shallow soil through oil and gas activities such as drilling waste disposal, pipeline construction, or elemental sulfur storage.

- Sulfate behavior may differ from chloride behavior in terms of EC response, especially at high sulfate concentrations or with calcium ions (gypsum, $CaSO_4$). In particular, Na_2SO4 potentially has less effects on EC than sodium chloride at high concentrations.

- Preliminary soil-spiking experiments suggest Na_2SO4 may be potentially less mobile than NaCl at high concentrations, though this mobility may change over time as the initially-high concentrations are reduced by leaching.

- Gypsum EC in saturated paste and pore water is limited to approx 2-4 dS/m depending factors such as the presence of other ions. This limit may cause the saturated paste methodology to over-estimate plant risk from gypsum in some cases.

- Soluble sulfates may be approximately 90% leached from soil after 3-5 pore volumes, with similar results observed for chloride. This has relevance to sulfates brought to the surface by construction practices, and their potential rate of leaching out of the root-zone into subsoil. In contrast, boron which has known sorptive qualities may require significantly more time for comparable leaching.

- Along with leaching column experiments, adsorption and extraction experiments provide alternative methods to evaluate the transport and sorption / precipitation behavior of sulfate salts such as calcium or sodium sulfate.

- Preliminary leaching column experiments at fast leaching rates and 1,000 mg/L sulfate show similar sulfate and chloride transport rates, though this corresponds to relatively low sulfate concentrations on a soil basis (near 200 mg/kg) and relatively balanced calcium and sodium concentrations (57/43 ratio). Other conditions may be more likely to show differences between sulfate and chloride transport rates and include higher sulfate concentrations, different cation ratios, lower chloride concentrations, and slower leaching rates.

- Preliminary sulfate desorption experiments showed some instances of sulfate desorption / solubilization which may differ from chloride under certain circumstances. These experiments point to the possibility of a pool of either adsorbed or precipated sulfate which may be present in some scenarios, though desorption experiments cannot necessarily distinguish between the two. This sulfate may be extracted in batch experiments with varying amounts of water or by groundwater in the field given sufficient time.

- Calcium sulfate (gypsum) solutions were effective in remediating SAR-impacted soils when the EC of the soil was relatively low. Due to the higher solubility compared to gypsum, magnesium sulfate was more effective in some cases when the EC of the SAR-impacted soils was higher.

- An SST-like framework is one promising possibility for implementing sulfate guidelines and thus providing an improved ability to manage sulfate impacts more effectively. Such a framework could provide the ability to generate subsoil sulfate guidelines which would be unlikely to cause potential exceedances in the future due to upward, downward, or lateral transport to various receptors.

Updated conclusions from this stage of the project include:

- Based on the low-sulfate leaching experiments from previous years, follow-up leaching experiments at higher (5,000 - 10,000 mg/L) sulfate were performed at slower overall leaching rates (Phase 2, 3, and 4). Solubility limits for calcium sulfate were clearly observed, and evidence of sulfate retardation relative to chloride apparent in several experiments with various gypsum concentrations and soil compaction rates.

- The observation of sulphate retardation under some circumstances (especially high sulphate concentrations) suggests the presence of sorption and/or precipitation reactions for sulphate. Both of these would have the effect of slowing sulfate transport relative to an in inert tracer such as chloride, and also potentially reduce the peak concentrations observed at relevant receptors compared to chloride. Both of these factors would influence risk estimations and guideline development.

- Observed sulfate retardation in Phases 3 and 4 was likely due to precipitation reactions, and showed an average apparent retardation factor of approximately 1.5. This suggests chloride moving approximately 50% faster than sulfate under these conditions, a factor which is likely a function of several soil and groundwater parameters. This observed retardation corresponds to apparent K_d’s for sulfate ranging from approximately 0 to 0.49 L/kg (average 0.15 – 0.2 L/kg), and is also likely highly dependent on soil texture, soil salinity, leaching solution compositions, and several other factors.

- Sulfate adsorption experiments were performed using newly-collected coarse and fine reference soils. Some relatively minor signs of sulfate adsorption were observed, though at levels significantly below those observed for a known sorptive species such as boron which was tested for comparison. This suggests that direct sorption may play a more minor role in overall sulfate transport than the potentially more significant precipitation effects.

- Transport modeling for sulfate was performed using the LEACHC program for salinity, allowing the modeling of cation exchange processes and gypsum precipitation as well as non-reactive water and solute transport. Various model scenarios were identified whereby sulfate transport may be slower than chloride, typically due to precipitation of calcium sulfate rather than any sorption mechanism. This precipitation could potentially occur in the initial source area where saturated paste concentrations may over-represent the total amount of sulfate dissolved in pore water. Additional precipitation may also occur as soluble sulfate salts are transported through clean soil with significant background calcium on the cation exchange complex (eg, background soils with low SAR). Such precipitation reactions may result in both a slowing and attenuating of sulfate concentrations relative to chloride, both of which would have influence on relative risk and developed guidelines.

- Due to the large number variables identified which influence sulfate fate and transport, it is recommended that subsoil sulfate guidelines be implemented within the context of the Alberta Environment 'Subsoil Salinity Tool' (SST). This allows tailoring of guidelines to site-specific conditions while maintaining a consistency of analysis from site-to-site without the need for a complex, data-intensive site-specific risk assessment for each site.

- It is recommended that the following five key pathways be considered during the implementation of subsoil sulfate guidelines into the SST: 1) upward migration of sulfate into the root-zone; 2) risk to irrigation water sourced from a dugout; 3) risk to livestock water sourced from a dugout; 4) risk to an aquatic life receptor from sulfate transported laterally; and 5) risk to the DUA (domestic use aquifer) for human drinking water from sulfate transported vertically

- Though each of the above five pathways are consistent with the current SST chloride pathways, each of them tends to have differences in how they may be implemented in the SST for sulfate instead of chloride. These differences generally result from differences in contribution to electrical conductivity (EC), differences in toxicity (to livestock, human, or aquatic life), differences in transport speed, or differences in peak concentrations estimated at receptors. The transport-related factors are generally related to a combination of precipitation and/or cation exchange factors.

- Subsoil sulfate guidelines to protect the root-zone may be handled in a similar way as chloride, but likely with some adjustment for the reduced contribution of EC from sulfate compared to chloride (a higher equivalent weight). Additional analysis may also be needed to distinguish between natural (background) vs anthropogenic sulfate, a factor which is typically not required for chloride.

- Irrigation water from a dugout could be protected in a similar manner as for chloride, but potentially with additional consideration of the reduced contribution to EC of sulfate versus chloride. This has relevance for whether irrigation guidelines are based on EC or TDS, with the correlations between the two somewhat different for sulfate and chloride.

- Livestock water from a dugout could also be protected in a similar manner as for chloride, but some additional consideration may be required of the potentially higher toxicity of sulfate to cattle compared to chloride. This is reflected in the Alberta

Environment drinking water guideline of 1,000 mg/L for sulfate which is more conservative than the 3,000 mg/L TDS guideline.

- The aquatic life pathway requires some estimate of the transport properties of sulfate compared to chloride in order to estimate the peak future sulfate concentration at the point of discharge to the aquatic life receptor. One complicating factor to be addressed is the lack of an aquatic life guideline for sulfate, though some science-based proposals are available from literature which potentially include hardness as a modifying factor.

- The DUA pathway also requires some estimate of the transport properties of sulfate in order to estimate the peak future sulfate concentrations within a DUA. The difference between the human drinking water guideline of 500 mg/L for sulfate compared to 250 mg/L for chloride would also need to be considered.

- An additional complication for several of these pathways (especially aquatic life and DUA) is the potential presence of highly elevated sulfate in background conditions which may already be near or above relevant toxicity thresholds or guidelines. In such cases, techniques such as pathway elimination or an incremental risk approach may be considered.

Recommended next steps for sulfate guideline development include additional discussions through the PTAC Salinity Working Group to refine various policy and regulatory issues surrounding the implementation of subsoil sulfate guidelines in the Subsoil Salinity Tool (SST). This may involve additional algorithm refinement and/or sulfate transport modeling depending on the key issues identified and implementation methods chosen.

8 CLOSURE

This document was prepared by Equilibrium Environmental Inc. under contract to Environment Canada solely for the purpose of providing information relevant to the fate and transport of sulfate salts. Equilibrium does not accept responsibility for the use of this report for any purpose other than intended or to any third party unless otherwise stated, in whole or in part, and we exercise no duty of care in relation to this report to any third party. Any questions regarding this document should be direct to Greg Huber or Anthony Knafla at (403) 286 7706.

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9 REFERENCES

Alberta Environment. 2010. Alberta Tier 1 Soil and Groundwater Remediation Guidelines. Edmonton: Air, Land and Waste Policy Branch Environmental Assurance Division.

Alberta Environment, 2001. Salt Contamination Assessment & Remediation Guidelines. Environmental Sciences Division. Environmental Service. Pub No. T/606

Aylmore, L., Mesbahul, K., Quirk, J.,1967. Adsorption and Desorption of Sulfate Ions by Soil Constituents. *Soil Science*, Vol 103, No.1, 10-15.

British Columbia Ministry of Environment, 2006. K_d (Chloride) Analytical Method Validation Interlab Study (CSR#12355). Prepared by JRD Consulting Company, June 28, 2006.

Elphick, J.R., M. Davies, G.Gilron, E.Canaria, B. Lo, H. Bailey, 2011. An aquatic toxicological evaluation of sulfate: the case for considering hardness as a modifying factor in setting water quality guidelines. Environmental Toxicology and Chemistry, Vol 30, No.1, pp 247-253.

Equilibrium Environmental, 2011. Study of the Fate and Transport of Calcium Sulfate (Gypsum) Concentrations in Shallow Soil. Final report, Prepared for Environment Canada April, 2011.

Equilibrium Environmental, 2010. Environmental Loading and Toxicity of Sulfate – a Literature Review. April, 2010.

Shaeffer, P., Stevens, D., 1991. Evaluation of Procedures for Aggregating Nonlinear Sulfate Adsorption Isotherm Data*.* *Soil Sci. Soc. Am. J*, **55**: 684-692.

Singh, B.R., 1984a. Sulfate Sorption by Acid Forest Soils: 2. Sulfate adsorption isotherms with and without organic matter and oxides of aluminum and iron. *Soil Science*, 138 (4), 294-297.

Singh, B.R., 1984b. Sulfate Sorption by Acid Forest Soils: 4. Kinetics and Effects of Temperature and Moisture. *Soil Science*, 138 (4), 440-447.

Sokolova, T.A., Alekseeva, S.A, 2008. Adsorption of Sulfate Ions by Soils (A Review*). Eurasian Soil Science*, Vol.41, **2**, 140-18.

US EPA, 1989. Direct/Delayed Response Project: Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in Northeast and Southern Blue Ridge Province. Document# EPA/600/3-89/061a, July 1989.