Equilibrium Environmental Inc.

SULFATE ADSORPTION AND DESORPTION PROPERTIES

OF ALBERTA SOILS

AND THEIR RELEVANCE TO TRANSPORT PROPERTIES

AND REDISTRIBUTION RATES

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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 were performed in this stage of the project and summarized herein:

- Field soils and cores were collected from a variety of sites with varying soil texture and sulfate concentrations.

- Preliminary leaching column work was performed to evaluate the relative mobility of sulfate relative to a chloride tracer.

- Preliminary sulfate adsorption and desorption experiments were performed on a subset of field-collected soils

- Alternative extraction methods to the standard saturated-paste methodology were evaluated including fixed-ratio extractions ranging from 2:1 to 10:1 water-to-soil ratios

- Remediation potential of sulfate salts (particularly calcium and magnesium salts) evaluated

- The potential for developing subsoil sulfate guidelines using Subsoil Salinity Tool (SST)-like protocol modified for sulfate rather than chloride was investigated

2 LITERATURE REVIEW FOR SULFATE SORPTION

While the chloride anion is typically considered to have minimal sorption properties with soil (British Columbia Ministry of Environment, 2006), a preliminary literature review suggests that sulfate sorption may play a role in overall sulfate mobility (Sokolova, 2008). This paper reviews many years of experimental research regarding sulfate adsorption, and investigates some of the mechanisms influencing such sorption. For instance, mechanisms such as ligand exchange with the formation of outer- and innershphere complexes are discussed, along with Coulomb interaction with the surface of mineral particles such as clays other metal oxides. It also discusses the complex role of pH and buffering in sulfate-soil interactions, particularly in the context of deposition of acidic atmospheric sulphur-containing containing compounds such as sulphur oxides when may then oxidize to sulfate in soil. It identified several soil factors influencing the adsorption of sulfate, including factors such as pH, ionic strength of solution, initial concentration of sulfate ions, the content of non-silicate Fe and Al-containing compounds, the composition of clay minerals, soil age, temperature and water content of soil, calcium content, the presence of other anions, and organic matter content.

As an example of the complex interactions between sulfate and soil, some of the above factors (e.g., organic matter content) were reported to have contradictory results in literature. For example, Singh (1984a, 1984b) showed that organic matter had relatively little effect on sulfate adsorption in iron podzols, and reduced sulfate sorption in brown forest soils. It was speculated that these effects may sometimes be explained by the potential for certain types of organic matter to either cover surfaces capable of sorbing sulfates or directly compete for sorption sites in some cases. A reduction in sulfate adsorption onto iron oxides and hydroxides was also observed in the presence of humus acids, polyphenolic compounds, and low-molecular weight carboxylic acids in Inskeep, 1989.

One large EPA project ("Direct/Delayed Response Project") studied sulfate deposition/sorption on a broad range of soils from the United States (US EPA, 1989). This project was largely performed in the context of acid-rain sulphur deposition, where the transport of the resulting sulfate salts toward water bodies. It was of prime interest whether this transport would be expected to have an immediate (direct) or delayed response on the water bodies, primarily as a function of soils ability to sorb and hence buffer sulfate transport. In this project, sulfate adsorption isotherms were measured for several hundred U.S. soil samples by measuring the change in solutions of known sulfate concentration after mixing with soil at a fixed ratio. By performing such adsorption experiments with a variety of initial solution concentrations, curves known as 'adsorption isotherms' are obtained.

An example of such an isotherm is shown in Figure 2.1 below (Shaeffer, 1991), showing the mass of adsorbed sulfate on the vertical axis compared to the final concentration of dissolved solution sulfate on the horizontal axis. These units were originally expressed on a millimol cation basis (milliequivalents), with comparable concentrations in mg/kg and mg/L also shown at the maximum of each axis for comparison to typical soil test results. Many of the results resembled Freundlich or Langmuir isotherms, exhibiting non-linear initial behaviour with decreasing slope as solution concentrations increase. In contrast, the typical distribution coefficient (K_d) approach   assumes a linear isotherm where the soil does not reach states of decreasing or saturated sorption. Effective values of K_d can also be defined over smaller ranges of generally non-linear isotherms dividing the mass of adsorbed sulfate by the equilibrium solution concentration of sulfate, resulting in final units such as L/kg. For the graph shown in Figure 2.1, an effective K_d of approximately 4 L/kg is obtained in this manner, though the total amount of sulfate sorbed appears to be reaching a plateau by around 200 mg/kg and a solution concentration of around 50 mg/L. This solution concentration is lower than those typically observed in Alberta soils, and suggests the possibility of sulfate sorption sites potentially being fully occupied if similar soils are exposed to typical Alberta concentrations of sulfate. If sorption sites are already fully occupied (modeled best a Langmuir isotherm), transport properties may become similar to a non-sorptive species such as chloride above the sorption plateau.

Figure 2.1. Typical sulfate adsorption isotherm (Shaeffer, 1991)
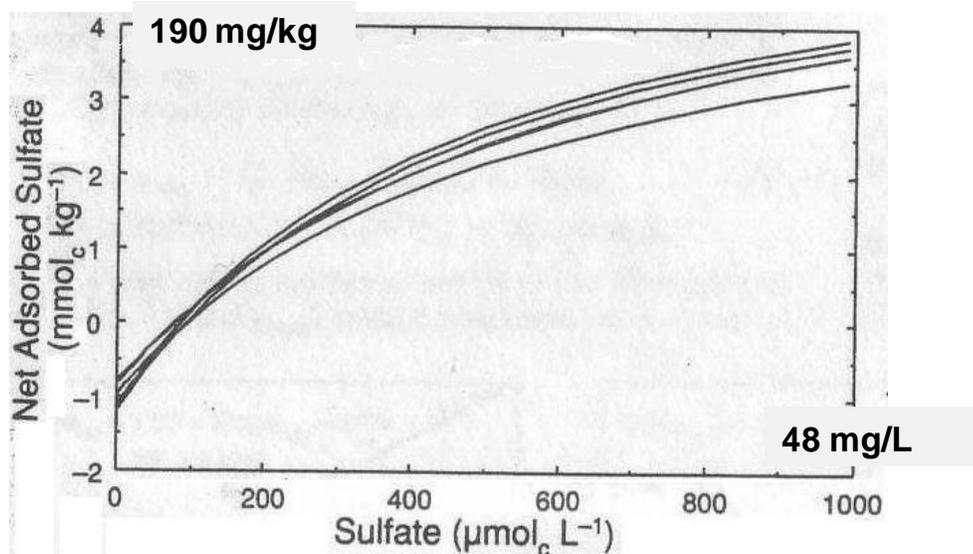
Other examples from literature provide mixed results regarding the potential magnitude of sulfate sorption properties, with soil texture and other parameters such as clay type, clay content, and pH likely playing a role. For example, Figure 2.2 shows an example of sulfate adsorption onto pure clay and provides some insight into possible interactions with practical soils which typically have lesser but still significant clay content (Aylmore, 1967). The total mass of adsorbed sulfate appears to plateau between 250 to 450 mg/kg depending on the type of clay, with the maximum adsorption corresponding to higher concentrations of up to 4,000 mg/L sulfate. Different values of apparent K_d (instantaneous slope of these curves) could be calculated depending on the interval of interest, though an effective value of near 0.1 L/kg could be estimated for this overall range. Significantly higher values of K_d would be estimated at low sulfate concentrations due to the high initial slopes, though the environmental relevance of low sulfate concentrations in some situations may be limited.

Figure 2.2. Sulfate adsorption isotherm onto clay (Aylmore, 1967)
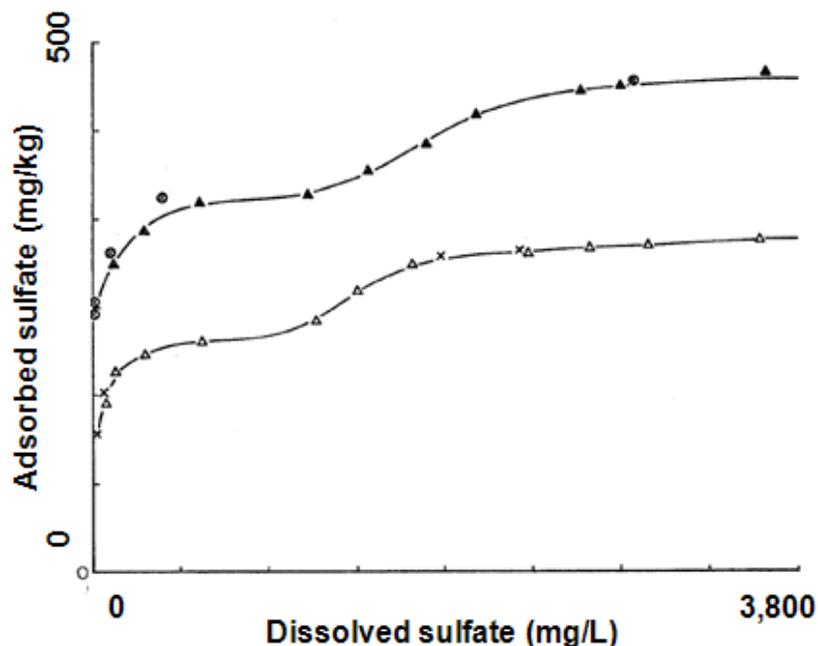
Overall, additional research is required to determine whether sulfate sorption may play a significant role in sulfate transport through soils such as those found in Alberta or other prairie provinces where naturally-occurring sulfate salts are relatively wide-spread. It would also be useful to increase understanding of what sulfate levels this sorption may be relevant at and what other soil factors influence this sorption.

3   GYPSUM SOLUBILITY

In addition to the sulfate sorption effects discussed in the previous literature review, the limited solubility of the common sulfate salt 'gypsum' ($CaSO_4 \cdot 2H_2O$, often simply referred to as $CaSO_4$) may also play a role and create the potential for precipitated gypsum to influence transport. Sulfates generally have lower solubility than chlorides, with gypsum solubility typically reported as approximately 2 g/L in literature (~2000 mg/L). This solubility can reportedly can almost double in presence of different ions (*e.g.*, chloride), and can reduce in the presence of other sulfate salts due to the common ion effect. It is thus relatively common to have saturated gypsum in solution plus undissolved, precipitated gypsum in soils which are naturally high in gypsum content.

To examine this effect, one experiment was performed to measure gypsum solubility in clean water followed by comparing this to the solubility in saline water. This is relevant to salt-impacted soils which also have naturally-occurring sulfate salts, a relatively common scenario where an improved understanding of the behavior of sulfate salts would be useful. Two different solubility scenarios were examined, the first involving dissolving excess gypsum in distilled water and the second dissolving excess gypsum in 10,000 mg/L sodium chloride. In each case, solution chemistry was measured with a particular emphasis on sulfate concentrations and total electrical conductivity (EC). Results are shown in Table 3.1, with the solubility of calcium sulfate in distilled water showing approximately 1,990 mg/L, of which 1,400 mg/L represented the contribution from the sulfate anion. This resulted in an EC of approximately 2.2 dS/m due to saturated gypsum in clean water. In contrast, when excess gypsum was dissolved in 10,000 mg/L NaCl, the total amount of dissolved sulfate increased to 2,400 mg/L and showed an approximate EC contribution of approximately 3.8 – 4.4 dS/m due to calcium sulfate. This experiment thus shows a typical range of approximately 2-4 dS/m total EC due to gypsum with results influenced strongly by the presence of other anions such as chloride.

Table 3.1. Gypsum solubility and the influence of elevated NaCl concentrations

Measured solution parameter	Scenario 1: Excess gypsum in distilled water	Scenario 2: Excess gypsum in 10,000 mg/L NaCl
Sulfate (mg/L)	1,400	1,200
Calcium (mg/L)	590	2,400
EC increase due to gypsum (dS/m)	2.2	3.8 – 4.4

It is important to note that this max gypsum EC applies to saturated paste as well as soil solution (pore water) concentrations. While soil tests typically measure saturated paste concentrations, plant roots are mainly affected by pore water salt concentrations and it is generally assumed that a consistent correlation exists between saturated paste and pore water concentrations. However, for substances such as gypsum where solubility limits can be significant, this relationship may be different and pore water concentrations may be essentially equivalent to saturated paste concentrations if precipitated gypsum is present in both cases. Thus, if two soils have equivalent saturated paste EC of approximately 3 dS/m due to either

gypsum or sodium chloride, the pore water concentration of the sodium chloride is likely to be approximately 6 dS/m whereas for gypsum it would remain saturated at the same 3 dS/m. The gypsum-containing sample would thus be expected to show less detrimental effects on plant growth, assuming differences in ion-specific toxicity to be minimal and the primary effects due to EC-induced osmotic stress. It thus appears that the saturated paste analytical methodology may thus overestimate toxicity due to gypsum in some cases, a point which may have relevance for sulfate guidelines or management practices.

4   **LEACHING 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 as shown in Figure 4.1.

Figure 4.1. Example of typical field-collected soil cores

Samples without apparent channels could be tested as 'undisturbed' cores in customized shelby-tube permeameters (leaching columns), with an example of such a configuration shown in Figure 4.2. Other cores with significant voids or channels were emptied, homogenized, dried and ground, and sieved through #10 (2 mm) mesh as shown in Figure 4.3. These soil samples can then be tested as 'repacked' samples using one or more layers of soil in clear permeameters such as shown in Figure 4.4.

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 soil 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.

Figure 4.2. Undisturbed column partially saturated in clear Shelby tube permeameter

Figure 4.3. Aggregated soil (right) passed through #2 and #10 screens (left)

Figure 4.4. Repacked column with two layers of #10 mesh soil

4.1 LEACHING EXISTING SALTS FROM SOIL

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.

4.1.1 **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 4.5 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 4.5. Leaching sulfate from undisturbed and recompacted cores
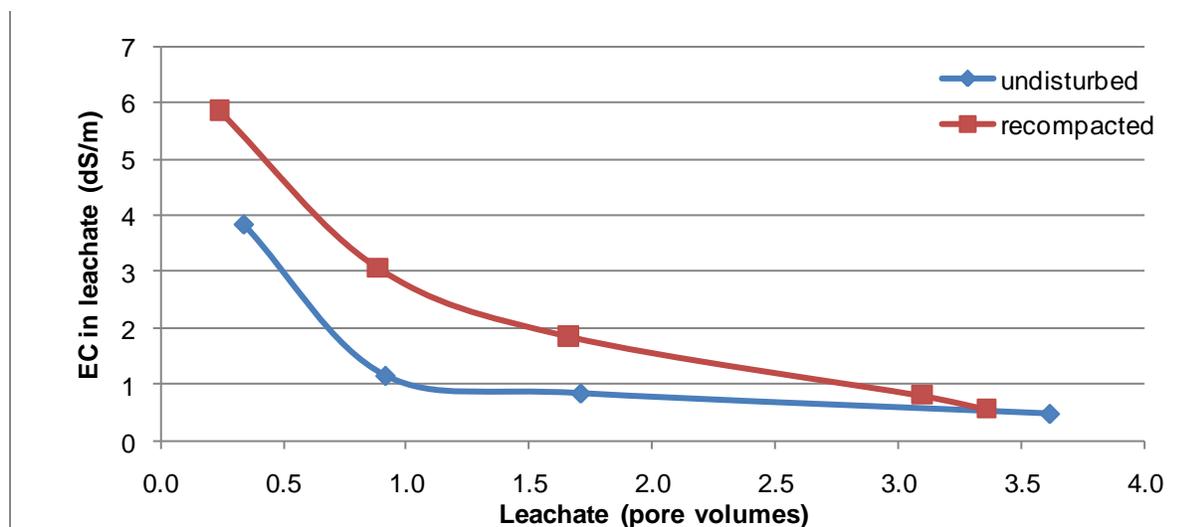
4.1.2 **Experiment #2**

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 4.1. The initial EC of the leachate is also shown for comparison to initial saturated paste soil concentrations.

Table 4.1. 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 4.6 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 4.6. Leaching of spiked salts from recompacted soils
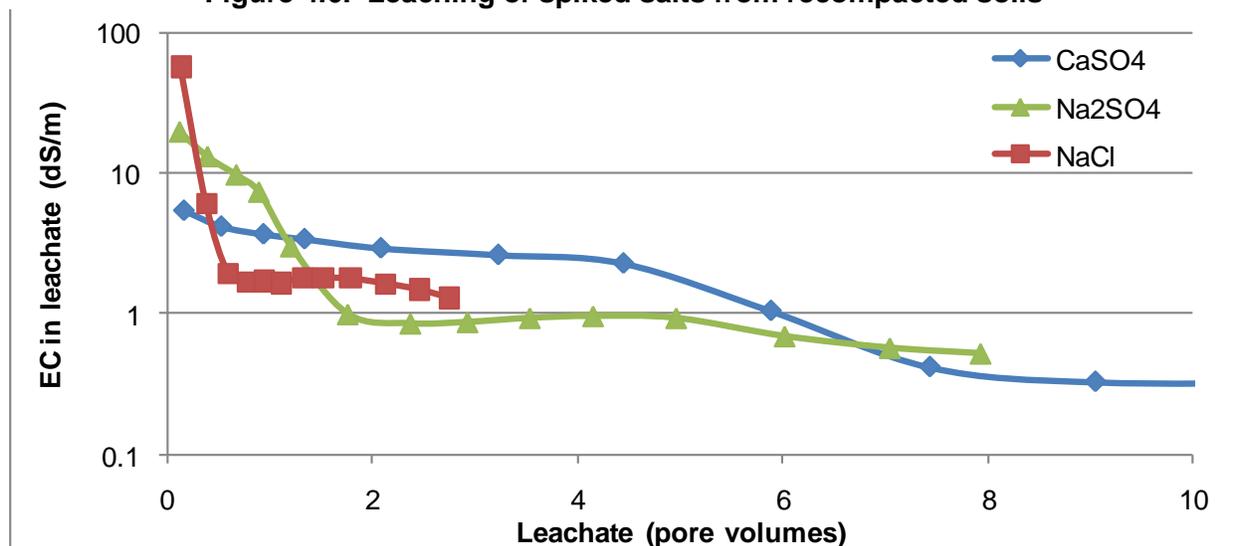
Overall, it is noteworthy that Na_2SO_4 behaved differently than NaCl during early leaching, though this effect may be more common at high salt concentrations. This may be due to EC vs cation non-linearities for sulfate, or column wetting effects and their possible interaction with dissolution / adsorption kinetics for sulfate.

4.2   LEACHING SALT SOLUTIONS THROUGH CLEAN SOIL

4.2.1   Initial experiments: 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 4.2 below, with chloride concentrations also a nominal 1,000 mg/L.

Table 4.2. 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 4.7 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 4.7. Relative leaching rates of chloride, sulfate, and boron
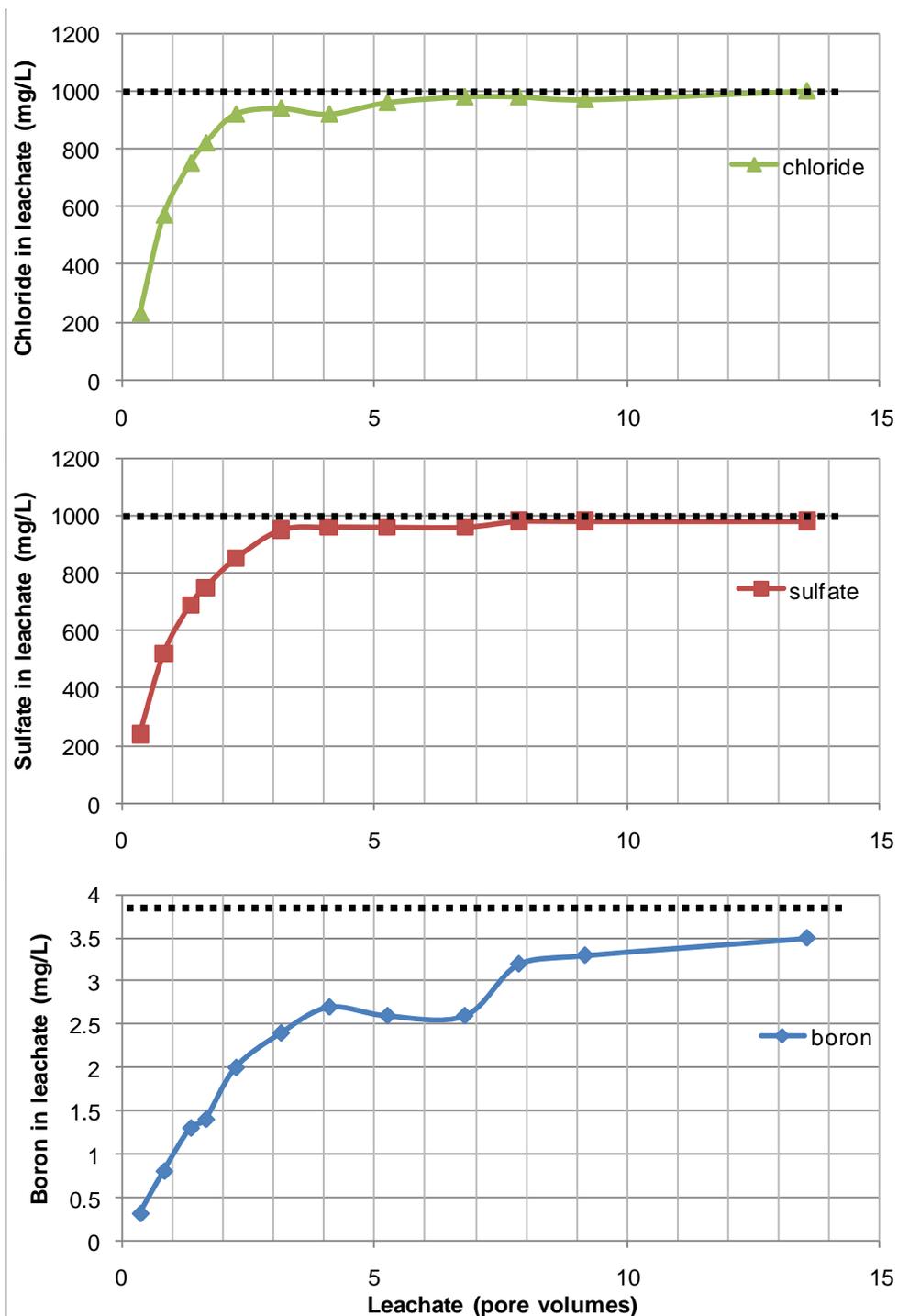
Figure 4.8 presents the same results but with concentrations normalized relative to the inlet to allow comparisons on the same vertical axis. While boron appears significantly slower than chloride or sulfate, it appears that chloride and sulfate leached at similar rates at these concentrations and soil / 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 4.8. Normalized leaching rates of chloride, sulfate, and boron
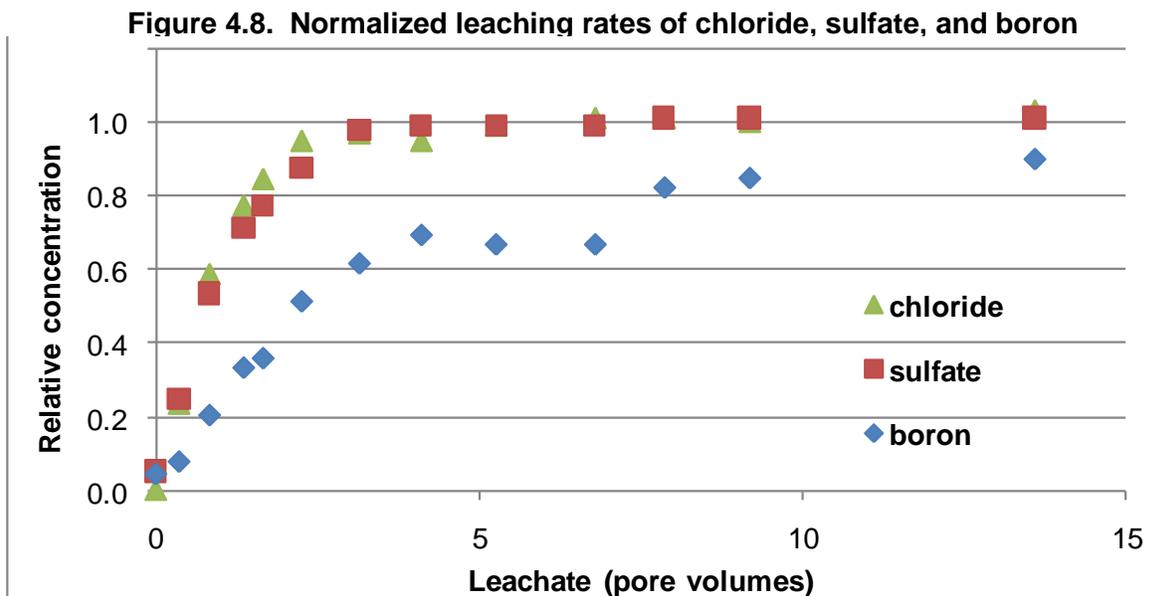
To provide an example of a technique for estimating retardation rates caused by sorption, Figure 4.9 shows the boron leaching curve after manually adjusting the boron time scale to match that of chloride. Boron matches chloride closely if hypothetically accelerated by 5-fold, implying a retardation factor 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 4.9. Estimated retardation for boron transport
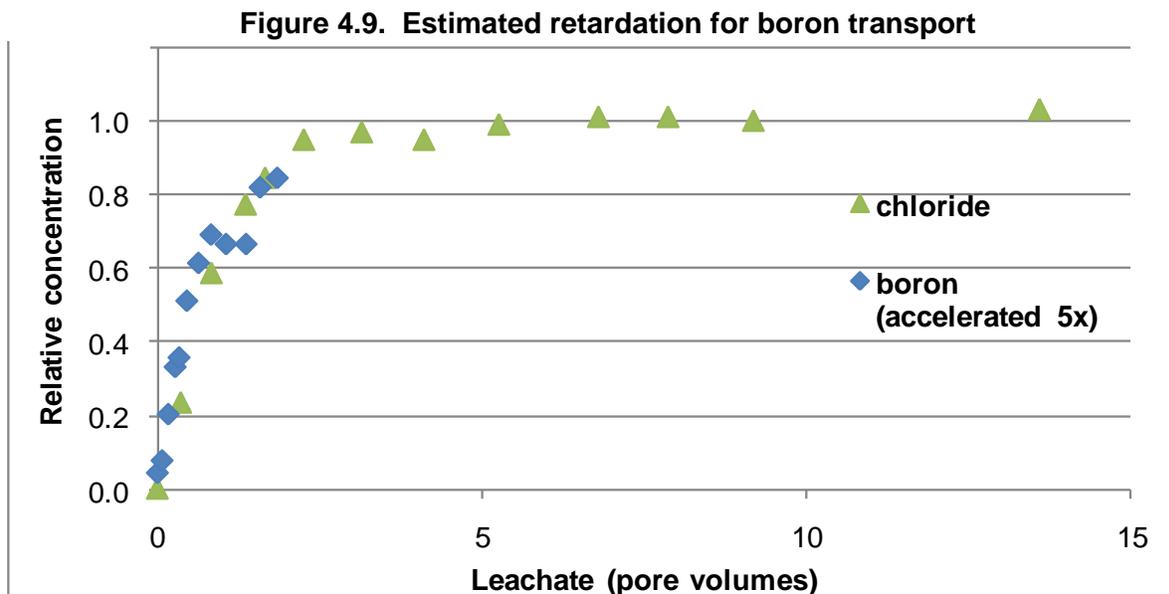
4.2.2   **Follow-up experiments: low sulfate concentrations**

To expand on leaching results from Section 4.2.1, 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 equilibriation without adsorption. This fairly low concentration was chosen to match literature data and experiment 4.2.1.

Figure 4.10 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 4.10. Leaching column results for Soil #1
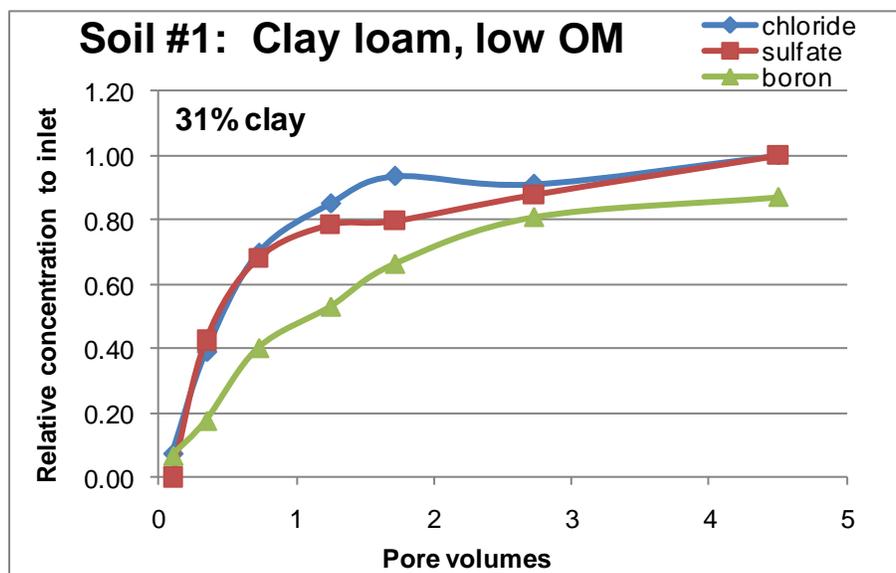
Figures 4.11 and 4.12 provide corresponding curves for a clay loam (29% clay) with moderate organic matter and a loam soil (19% clay) with high organic matter. In each case, sulfate transport was comparable to chloride with no significant retardation observed. In contrast, boron transport was significantly slower than the chloride or sulfate salts in both soil #2 and soil #2.

Figure 4.11. Leaching column results for Soil #2
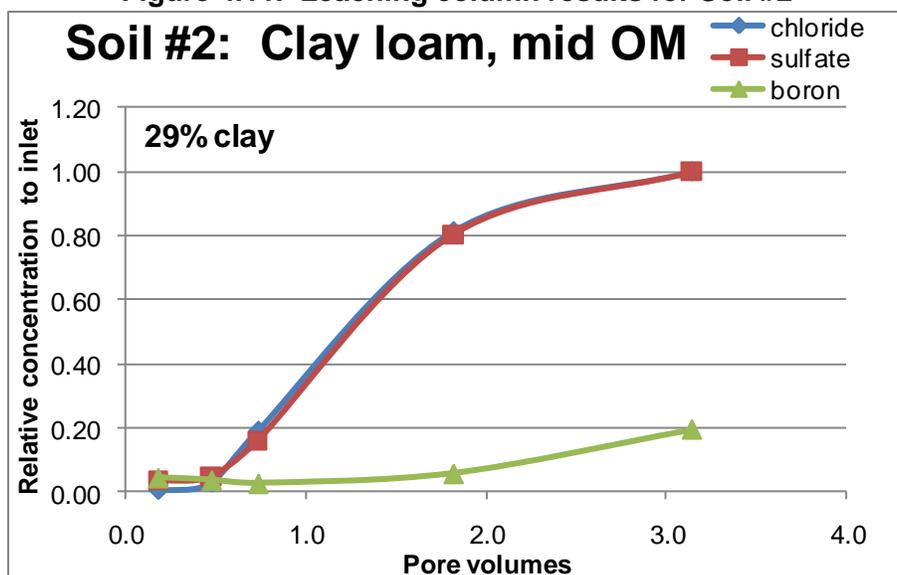
Figure 4.12. Leaching column results for Soil #3
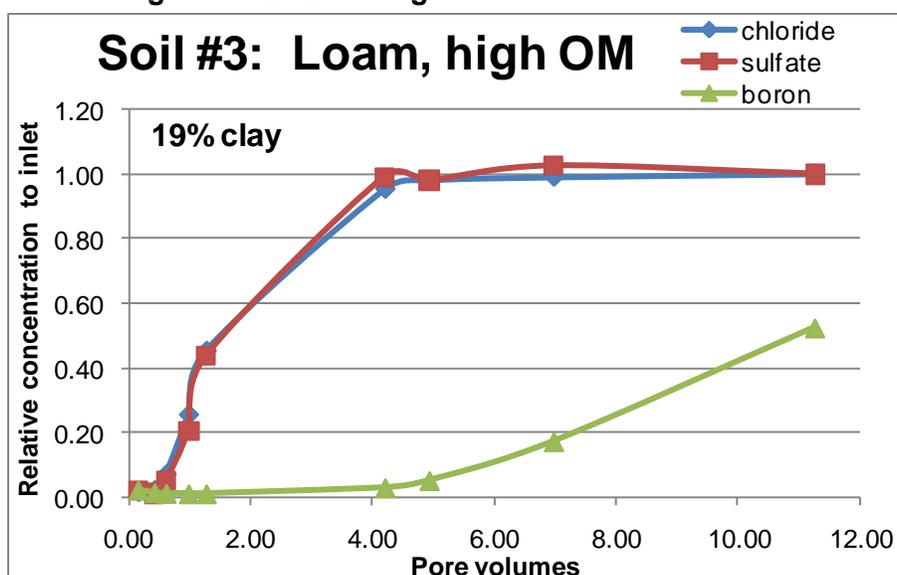
It should be emphasized that these transport experiments examined the specific situation of relatively low sulfate concentrations (equivalent to 200-300 mg/kg on a soil basis) in the presence of similar chloride concentrations. There is the potential for results to differ under scenarios with higher 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.

4.2.3   **Follow-up experiments: high sulfate concentrations**

Based on the results of the 1,000 mg/L 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 than Section 4.2.2, averaging approximately 40 mL per day.

Table 4.2 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 4.2.

Table 4.2. High-sulfate leaching solutions

Parameter	Units	Leaching solution #1 $Na_2SO_4 + CaCl_2$ + 0% $CaSO_4$	Leaching solution #2 $Na_2SO_4 + CaCl_2$ + 0.14% $CaSO_4$	Leaching solution #3 $Na_2SO_4 + CaCl_2$ + 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 in Section 3. 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 as shown in Section 3.

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 same clay loam soil as used in Figure 4.10. 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.

Figure 4.13 shows the results of the high compaction, high-sulfate leaching experiment with 0.14% calcium sulfate. 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 4.13. High sulfate leaching experiment #1
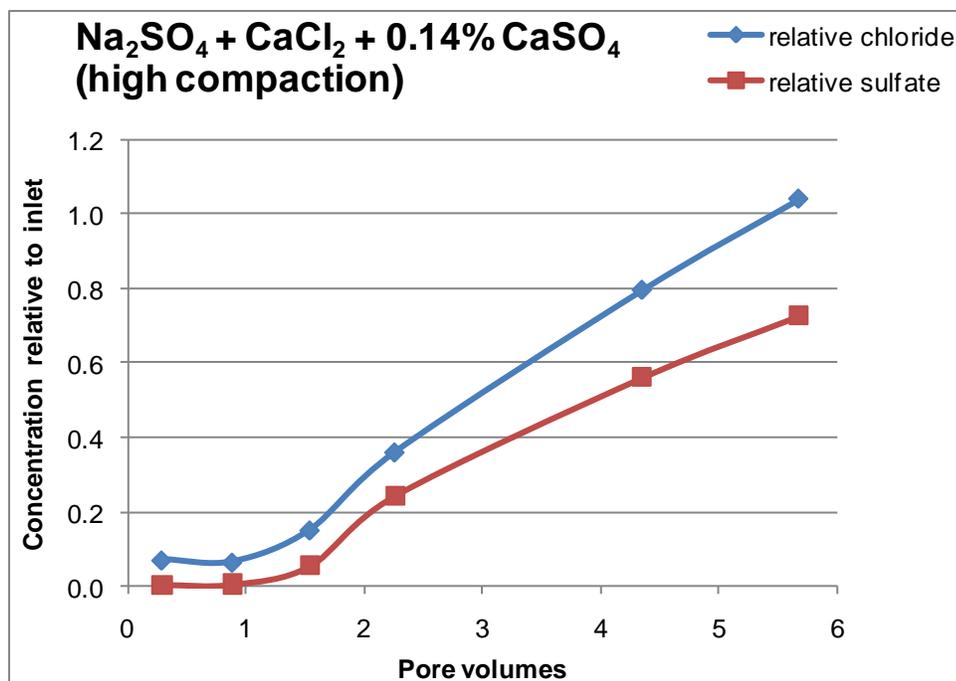
Figure 4.14 shows the second high-sulfate leaching experiment, which used the same leaching solution as experiment #1 but with medium compaction on the same clay loam soil as experiment #1. As in the first experiment, a slower sulfate transport rate was observed relative to chloride. The relative chloride concentration approached 1.0 (inlet) after 2-3 pore volumes, whereas the relative sulfate concentration reached 0.8 of the inlet after 3 pore volumes. This again suggests some retardation of sulfate relative to chloride due to factors such as adsorption or precipitation.

Figure 4.15 shows the third high-sulfate leaching experiment, 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 4.14. High sulfate leaching experiment #2
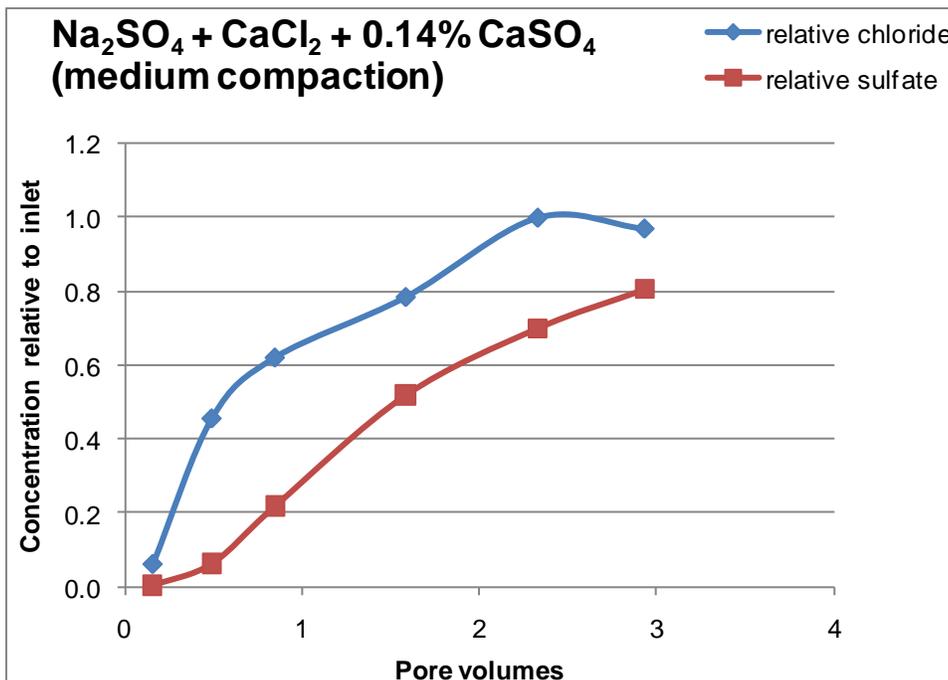
Figure 4.15. High sulfate leaching experiment #3
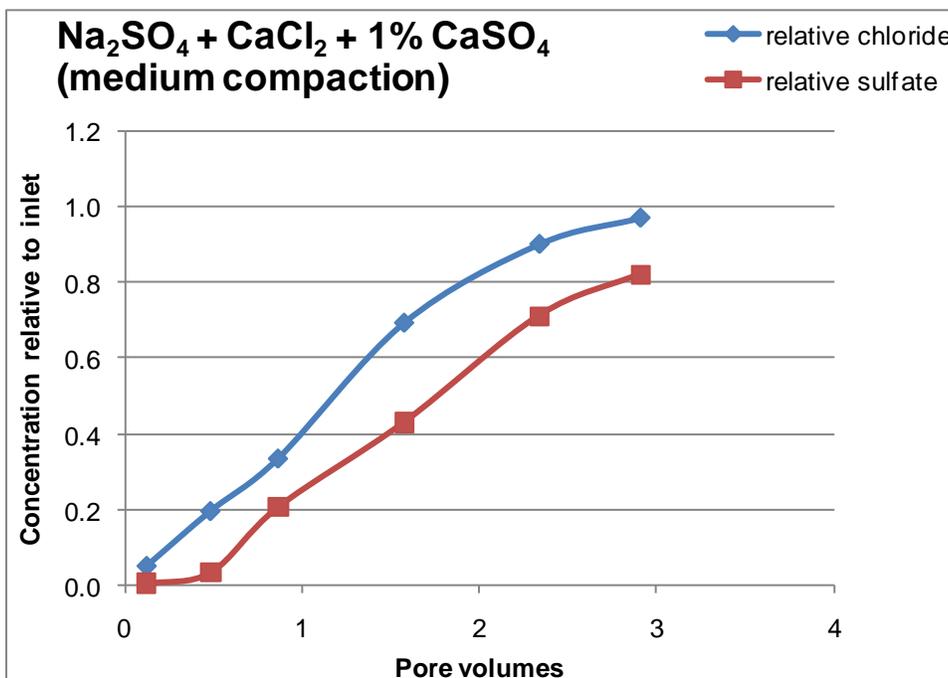
Experiments such as the three high-sulfate experiments described above can be used to estimate apparent retardation factors for sulfate. Figure 4.16 shows an example of such a technique, showing the sulfate leaching curve accelerated by an empirically-determined factor of 1.5 to approximately match the 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 4.16. Estimating sulfate retardation factor for high-sulfate experiment #3
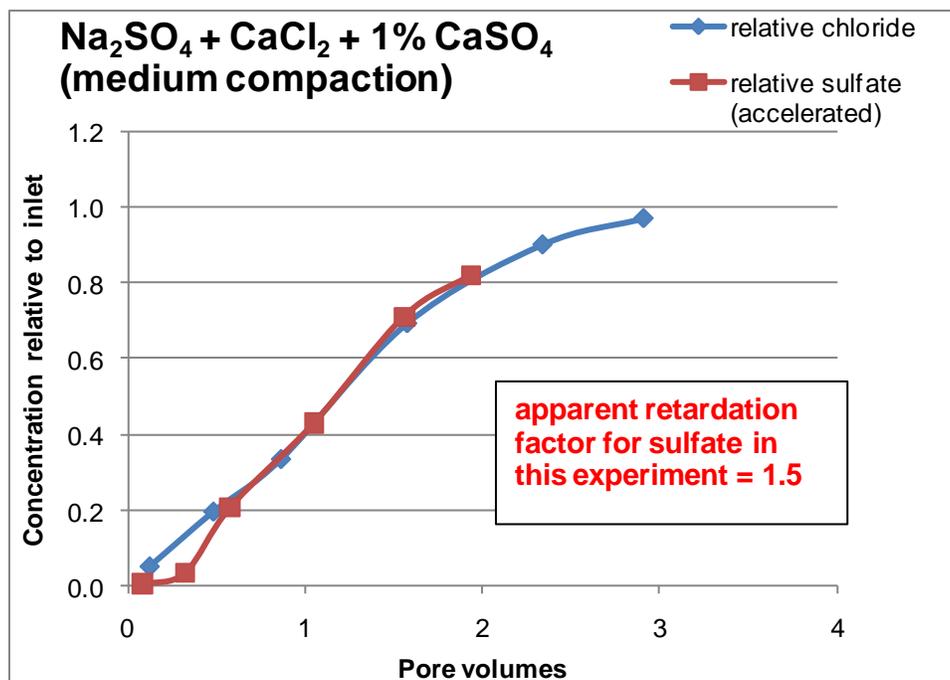
5   **SULFATE ADSORPTION EXPERIMENTS**

In this phase of the research, preliminary adsorption experiments were performed to determine if sulfate adsorption could be measured using a adsorption isotherm techniques. These techniques typically involve preparing a solution with a known concentrate of solute, adding a fixed amount of dry soil to this solution, mixing soil and solution and providing sufficient time to equilibriate, and finally measuring the equilibrium concentration of the solute in solution. Any reduction in solution concentration is interpreted as being sorbed onto the soil surface, and by varying the initial solution concentrations a series of experiments can be performed to result in an 'adsorption isotherm'.

As noted in British Columbia Ministry of Environment (2006), the measurement of partitioning coefficients for certain salts (e.g., chloride) may be associated with several difficulties due to the low expected adsorption. These difficulties may also apply to sulfate in varying degrees, and include difficulties in achieving sufficient measurement accuracy to observe the small changes in solution concentrations expected for poorly-sorbed solutes. Measurements are further complicated by the presence of background soil concentrations of the salt being investigated, and is likely to be a larger problem for sulfate than chloride.

Preliminary investigations were performed to investigate whether sulfate sorption was sufficiently strong to be observed with a relatively simple experimental protocol. In these experiments, clay loam soil (approximately 39% clay) was homogenized, dried and ground, passed through a #10 mesh screen (approximately 2 mm), and homogenized again. The soil used was chosen to be relatively low in initial sulfate concentrations to be representative of 'good' quality soils with EC < 2-3 dS/m. The characteristics of this soil when tested via standard saturated paste methodology are shown in Table 5.1.

Table 5.1. Initial soil characteristics for adsorption testing

Soil parameter	Value
Sulfate	132 mg/kg
Chloride	18 mg/kg
EC	18 mg/kg
Sodium	49 mg/kg
Calcium	38 mg/kg
Magnesium	8 mg/kg
Potassium	9.7 mg/kg
pH	7.8
Clay	39%
Silt	31%
Sand	30%
Texture	Clay loam

The initial solutions had nominal values of 1000, 500, and 250 mg/L for each of chloride and sulfate, prepared using mixtures of calcium chloride and sodium sulfate. This resulted in approximately 600 mg/L calcium and 460 mg/L sodium in the most concentrated solution (1,000 mg/L sulfate), with cations proportionally lower for the less concentrated solutions. Laboratory testing on the initial solutions showed measured initial values within 3% of the nominal values, with the difference likely due to factors such as reagent purity and analytical variability. Though sulfate was the ion of primary interest, the chloride was also included to function as a benchmark and additional control due to its known low-sorptive properties.

In these preliminary experiments, 1 part of soil was shaken into 5 parts solution (similar to the 1:6 ratio originally proposed in BC MOE, 2006), allowed to equilibrate overnight, and the final solution concentrations measured. Solution concentrations before and after soil addition are shown in Figure 5.1 for chloride, showing no apparent or consistent adsorption of chloride (as anticipated). Final chloride concentrations varied from 5% lower to 2% higher than initial concentrations, with this amount of analytical variability likely sufficient to obscure any minor sorption which was occurring.

Figure 5.1. Preliminary batch adsorption experiment results: chloride
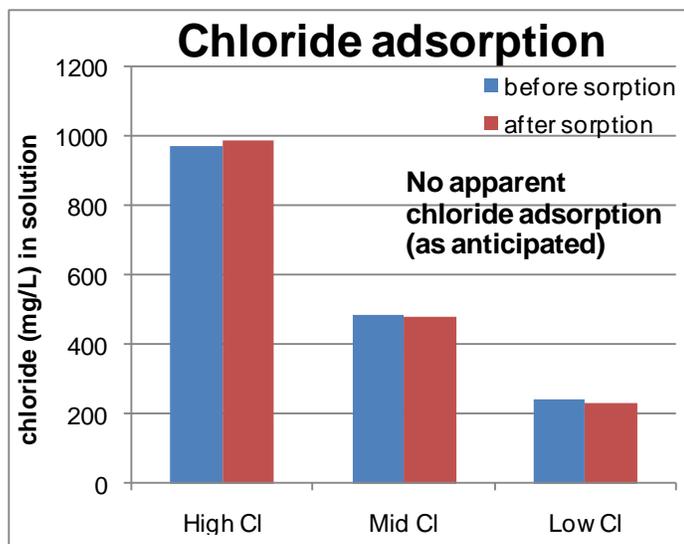
Similar results were observed for sulfate, with solution concentrations before and after soil addition shown in Figure 5.2. There was also no clear evidence of sulfate adsorption with this method, with solution concentrations after soil addition ranging from 0% to 4% higher than solution concentrations before addition. These results appear to be within the range of typical analytical variability, and may also be partially due to the dissolution of background sulfate. The influence of background sulfate could potentially be in the range of 28 mg/L, assuming the 132 mg/kg initially present in soil is fully solubilized at a 5:1 ratio.

Figure 5.2. Preliminary batch adsorption experiment results: sulfate
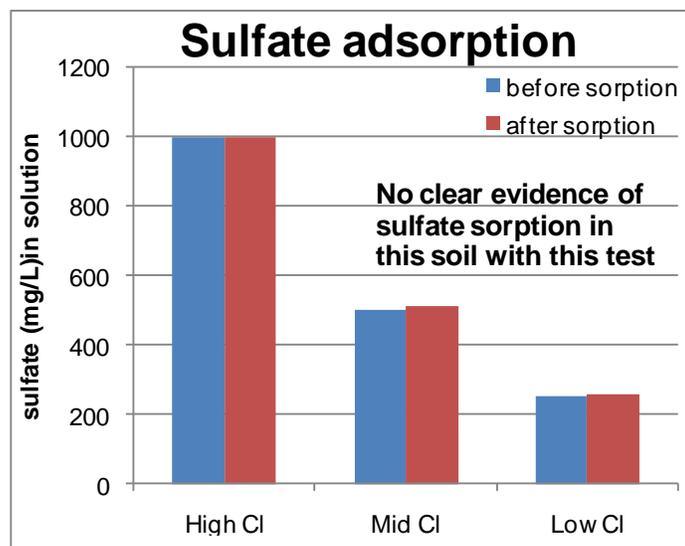
Though different soils may show different results, these preliminary batch adsorption results suggest that measuring adsorption isotherms for sulfate may have similar difficulties as chloride depending on the experimental procedure used.   Potential changes to the experimental procedure could include using a higher soil:water ratio, such as the 1:1 ratio suggested in BC MOE (2006) as a modification to their original 6:1 method in order to maximize the mass of salt sorbed and hence decrease the relative effect of analytical variability. Pre-leaching of the soil to remove background salt concentrations could also be useful (BC MOE, 2006), though the relevance to the many practical soils with measurable sulfate concentrations may be limited.

Additional modifications could also include using lower concentrations of the chloride benchmark, or potentially removing the chloride completely to limit the potential competition for sorption sites between anions. The use of different cation ratios may also influence sorption properties, though the reduced solubility of calcium sulfate (gypsum) compared to sodium sulfate or magnesium sulfate would limit the range of practical sulfate concentrations associated solely with calcium cations.   Before pursuing refinements to this adsorption isotherm methodology, other methods such as desorption experiments (Section 5) and leaching experiments (Section 6) were also evaluated for their ability to identify sulfate sorption phenomena.

6   SULFATE EXTRACTION EXPERIMENTS

6.1 PRELIMINARY EXTRACTION 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. To maintain maximum environmental relevance, initial experiments used water as the extractant but used variable soil:water ratios and evaluated their ability to extract sulfate. The use of additional water compared to the standard saturated paste methodology has some similarities to the prolonged leaching of sulfate-containing soils with low-sulfate groundwater or rainwater.

The two soils used for these initial desorption / extraction experiments were both sandy clay loams, with saturation percentages ranges from 60-70%. This indicates that a standard saturated paste extraction would use 100 parts of dry soil to 60-70 parts of water to perform the extraction. To complement this baseline extraction method, nominal water:soil ratios of 2:1, 5:1, and 10:1 were also evaluated to provide a wide range of water content differing by up 14-fold higher than used for the saturated paste.

Initial characteristics of the two test soils are shown in Table 6.1, with EC ranging up to 13-17 due to a combination of both sulfate and chloride. Sulfate concentrations range from approximately 1900 – 2800 mg/kg for the two soils, whereas chloride concentrations range from approximately 1,600 to 2,500 mg/kg. Sodium was the predominant cation in each case (1700 – 1900 mg/kg), with lesser but still-present calcium concentrations (320-380 mg/kg),

Table 6.1. Soil characteristics for extraction experiments via saturated paste

Soil parameter	Soil A	Soil B
Sulfate (mg/kg)	2828	1876
Chloride (mg/kg)	1626	2481
EC (dS/m)	13.0	17.0
Saturation percentage (%)	70.7	60.5
Sodium (mg/kg)	1768	1936
Calcium (mg/kg)	382	321
pH	7.9	8.3
Clay %	32	26
Silt %	23	17
Sand %	45	57
Texture	Sandy clay loam	Sandy clay loam

Results from the extraction experiments are shown in Figure 6.1 for chloride, with solution concentrations for each extraction ratio expressed in terms of mg/kg of the original soil for ease of comparison. As anticipated by the known low tendency for chloride to sorb to soils, the equivalent soil chloride concentrations did not change significantly using the various extraction ratio. Compared to the saturated paste baseline for soil A, the higher extraction ratios showed chloride concentrations ranging from 2-15% lower than the baseline. This trend is in the opposite direction of what would be expected if significant sorption were occurring, and is likely due to analytical variability. For Soil B, chloride concentrations ranged from 5% below baseline to 0.8% above baseline, and is also likely within the range of typical analytical variability.

Figure 6.1. Results from desorption / extraction experiments: Chloride
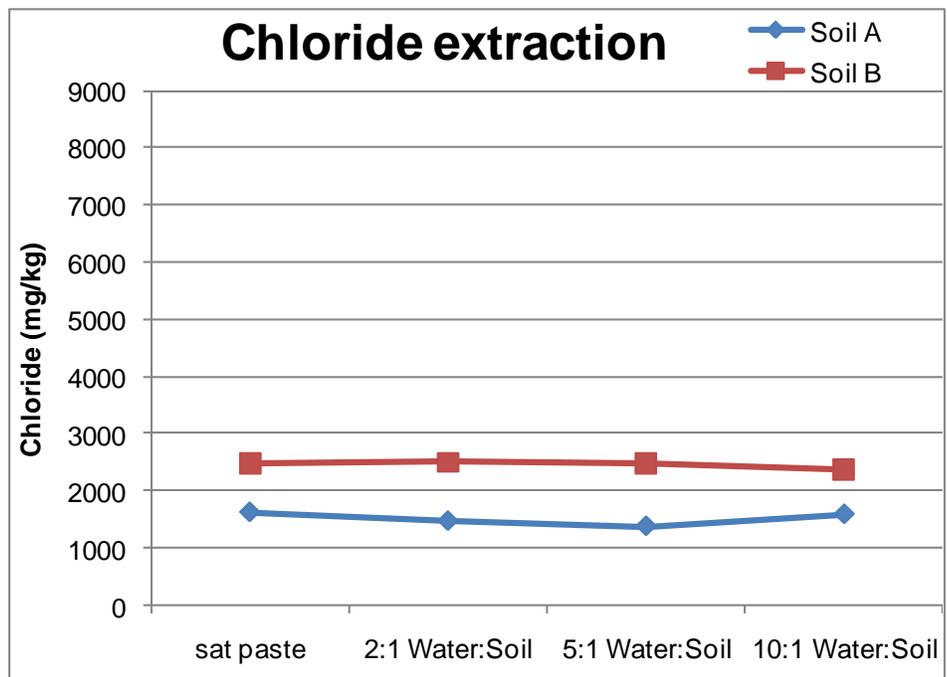
Sulfate extraction results are shown in Figure 6.2, with results visibly different from chloride. For both soils, the amount of sulfate extracted via saturated paste extraction was at least 2,000 mg/kg lower than the amounts extracted with the higher extraction ratios. In the case of Soil B, the maximum amount of sulfate extracted was approximately 5,000 mg/kg above baseline using the 5:1 extraction ratio. The lower amount of extracted sulfate at the 10:1 extraction (but still 3,500 mg/kg higher than baseline) is potentially due to difference in soil homogeneity and/or analytical variability.

Overall, the general trend of increased sulfate extraction with increasing extraction ratios for these two soils suggests the presence of sorbed or precipitated sulfate which was further desorbed and/or dissolved with increasing amounts of water. Though this test is not designed to distinguish between sorbed and precipitated sulfate, it also suggests that larger amounts of either may also be present at the further-reduced water content of saturated soil in the field.

Figure 6.2. Results from desorption / extraction experiments: Sulfate
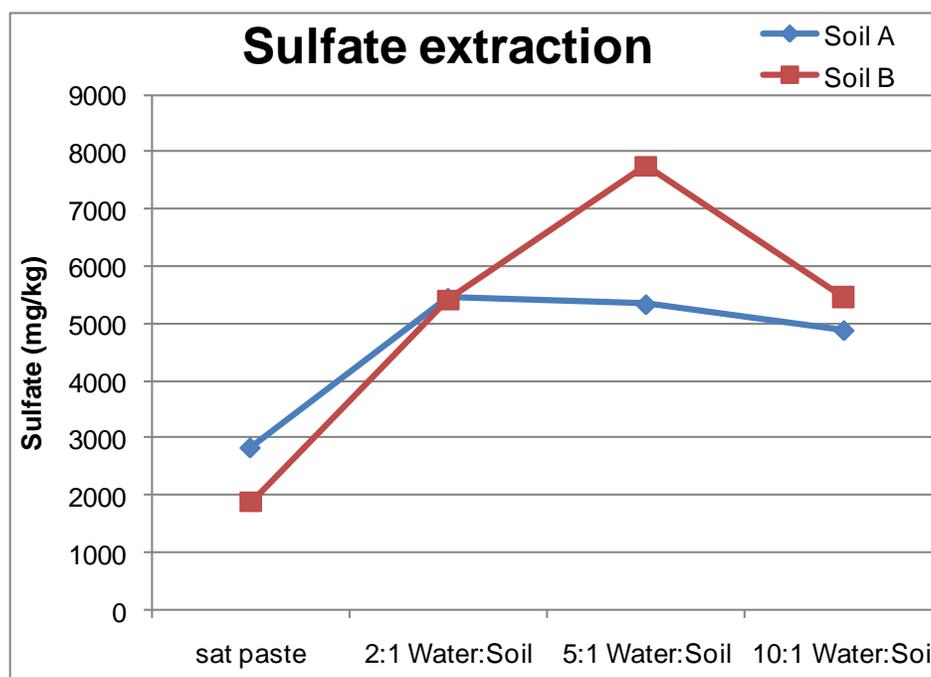
Useful information may also be obtained by examining the extracted cations from the above experiments.   Figure 6.3 shows the extracted sodium concentrations, increasing from approximately 2,000 mg/kg to approximately 3,000 mg/kg at increasing water content. Since sodium salts of both sulfate and chloride anions are generally highly soluble, it may be unlikely that this increase in sodium is due to the dissolution of precipitated sodium salts.   The desorption of sodium sulfate salts is thus one possible mechanism.

Figure 6.4 shows the corresponding results for extracted calcium, showing a significant increase from baseline to the higher extraction ratios. Due to the limited solubility of calcium sulfate (gypsum), there is potentially due to the dissolution of precipitated calcium sulfate with potential contributions from sorbed sulfate salts as well.

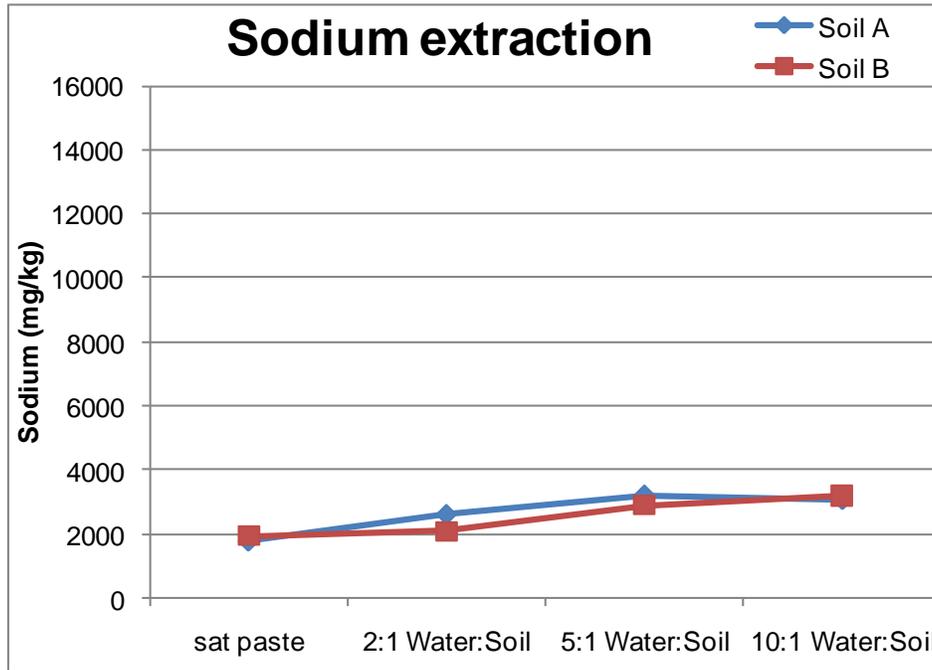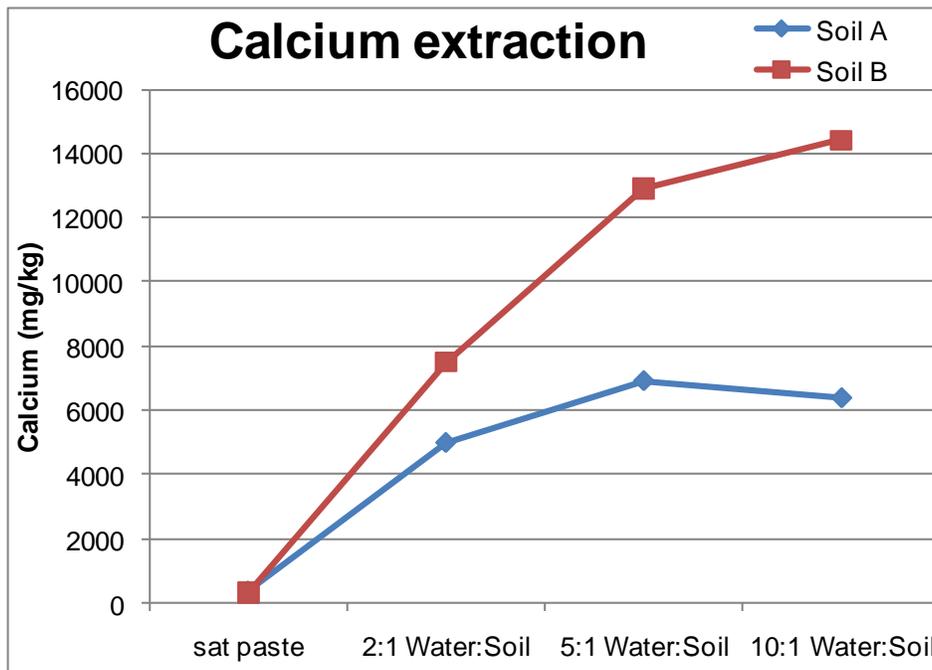**Figure 6.3. Results from desorption / extraction experiments: Sodium**

Figure 6.4. Results from desorption / extraction experiments: Calcium

6.2　FOLLOW-UP EXTRACTION EXPERIMENTS

Based on a similar methodology as the initial extraction experiments described in Section 6.1, follow-up extraction experiments were performed on fourteen Alberta soils from a variety of sites and with a variety of soil textures.　Soils were chosen to have measurable amounts of both chloride and sulfate in order allow the evaluation of sulfate extraction relative to the likely inert chloride tracer.

Chloride extraction results for the fourteen soils are shown in Figure 6.5, with chloride concentrations normalized to the saturated paste baseline in each case for ease of comparison. Results were observed to vary primarily within a plus-or-minus 20% range of baseline, likely due to typical analytical variability and limitations in soil homogeneity.　The relatively symmetrical distribution of these chloride extraction results both above and below baseline suggests a relative absence of significant sorption or precipitation effects for chloride.

Figure 6.5.　Chloride concentrations for 14 Alberta soils under 4 different extractions
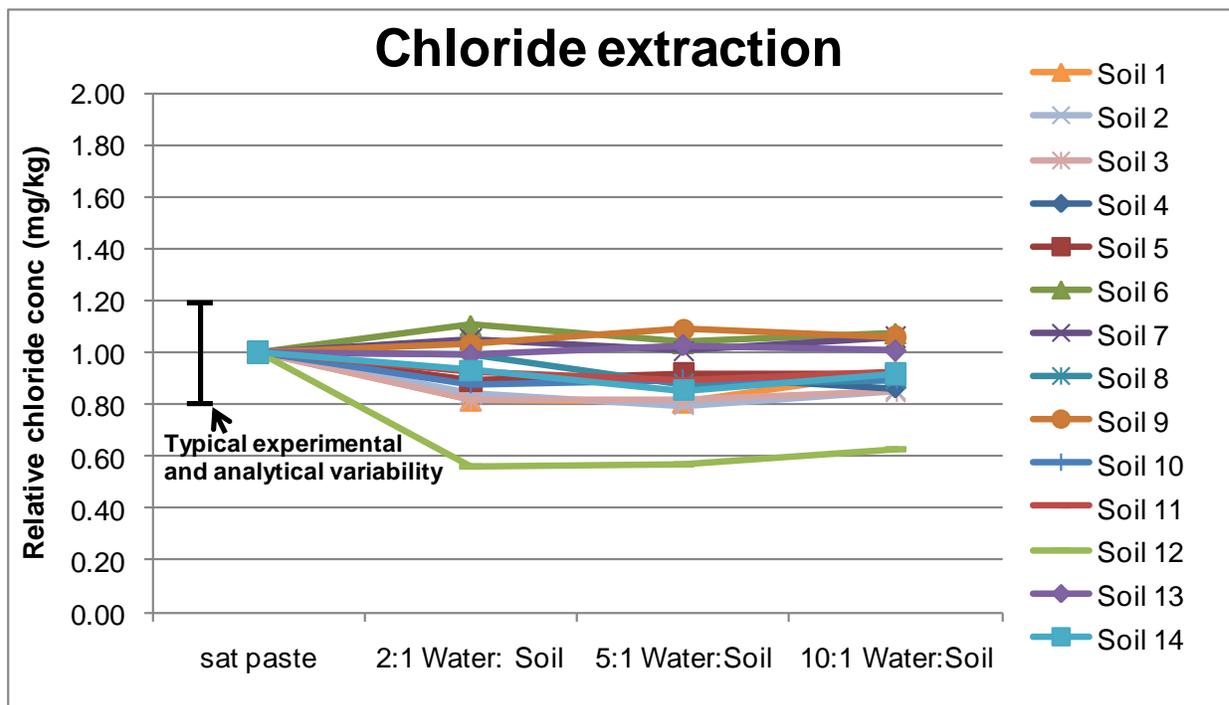
For the sulfate extractions (Figure 6.6), four of the fourteen samples showed extractions more than 20% above baseline, with two of these samples ranging from 60% to 90% higher for the 10:1 extractions compared to baseline.　Though an apparent plus-or-minus 20% variability remains apparent, these sulfate extractions results suggest a pool of either precipitated or adsorbed sulfate in certain soils.

Figure 6.6. Sulfate concentrations for 14 Alberta soils under 4 different extractions
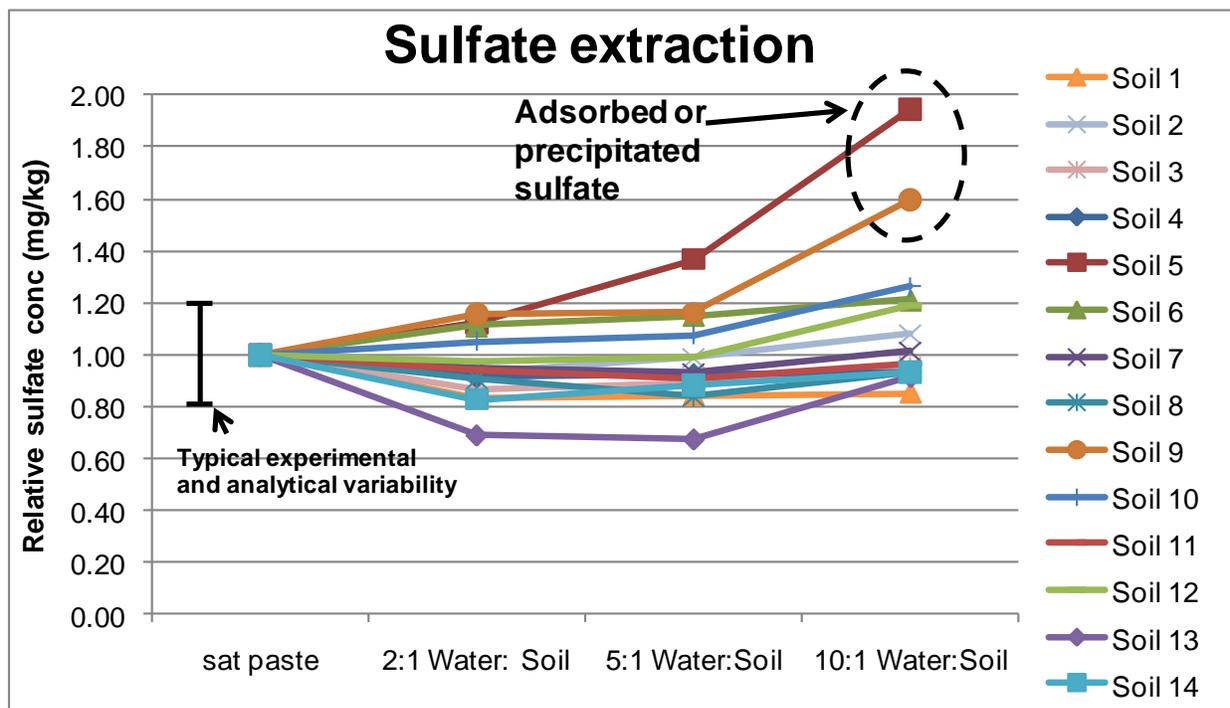
Overall, both the initial and follow-up desorption experiments show a relative absence of chloride sorption and some evidence of either sulfate sorption or precipitation which may release additional sulfate as additional water is used for extraction. This has relevance for the leaching / transport of sulfate through soils, and may imply some measure of sulfate retardation compared to the apparently non-sorptive chloride. Further extraction / desorption tests on a larger set of soils could help provide additional insight into whether adsorption or precipitation is the primary pool of this additional extracted sulfate, or whether this effect is a combination of the two.

7   REMEDIATION OF SAR WITH SULFATE SALTS

Using similar leaching column apparatus as described in Section 4, a variety of SAR-impacted soil cores were leached with either calcium or magnesium sulfate to compare their ability and relative efficiency for remediating SAR impacts. These soil columns were either field-impacted to a high SAR / low EC state or relatively unimpacted soils were preleached with high SAR / low EC solutions in order to results in reduced hydraulic conductivity compared to baseline.

Calcium sulfate (gypsum) is more commonly used for remediation, though the limited solubility has both potential benefits and drawbacks. One potential benefit is the inherent upper limit on the EC contribution from gypsum regardless of the application rate to soils. This limits the potential negative effects on soil electrical conductivity, especially in the root-zone where elevated EC can impair plant growth due to increased osmotic stress. It also allows dry gypsum powder to serve as a gradual 'slow-release' amendment which slowly dissolved and leaches through soil as allowed by solubility limits. On the other hand, if SAR-impacted soils also have a relatively high EC, significant quantities of gypsum may be required to decrease SAR and the limited gypsum solubility may slow the time-frame for remediation. Magnesium sulfate could potentially provide low-SAR, divalent cations more rapidly due to the higher solubility relative to calcium sulfate. Calcium chloride is also a potentially useful remedial salt with high solubility, though the addition of chloride ions to soils must be carefully considered due to potential risks to drinking water and other receptors. Similar issues also apply to calcium nitrate, with nitrate being a highly soluble but potentially toxic anion in both soil and groundwater.

Table 7.1 shows the solubility of these potential remedial salts, though as discussed above several factors in addition to solubility must be considered when evaluating their overall effectiveness.

Table 7.1. Solubility of potential remedial salts for SAR-impacted soils at 20°C

Salt	Typical hydration form	Solubility (g/100 mL)
Calcium sulfate (gypsum)	$CaSO_4 \cdot 2H_2O$	~0.2
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	~71
Calcium chloride	$CaCl_2 \cdot 2H_2O$	~75
Calcium nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	~129

Figure 7.1 shows an example of effective remediation with calcium sulfate at an EC of approximately 2 dS/m (near the solubility limit for gypsum). It is noteworthy that the recovery of hydraulic conductivity appears to be linear when displayed on a log scale and plotted against pore volumes. It should also be noted that remediation may often be slow on a time-scale during the initial stages due to the restricted initial rate of leaching through the impacted soil. It appears that hydraulic conductivity losses due to SAR may occur relatively quickly on a time-scale due to the high initial hydraulic conductivity whereas recovering from these losses via remediation may take significantly longer.

Figure 7.1. Example #1 of effective remediation with calcium sulfate (gypsum)
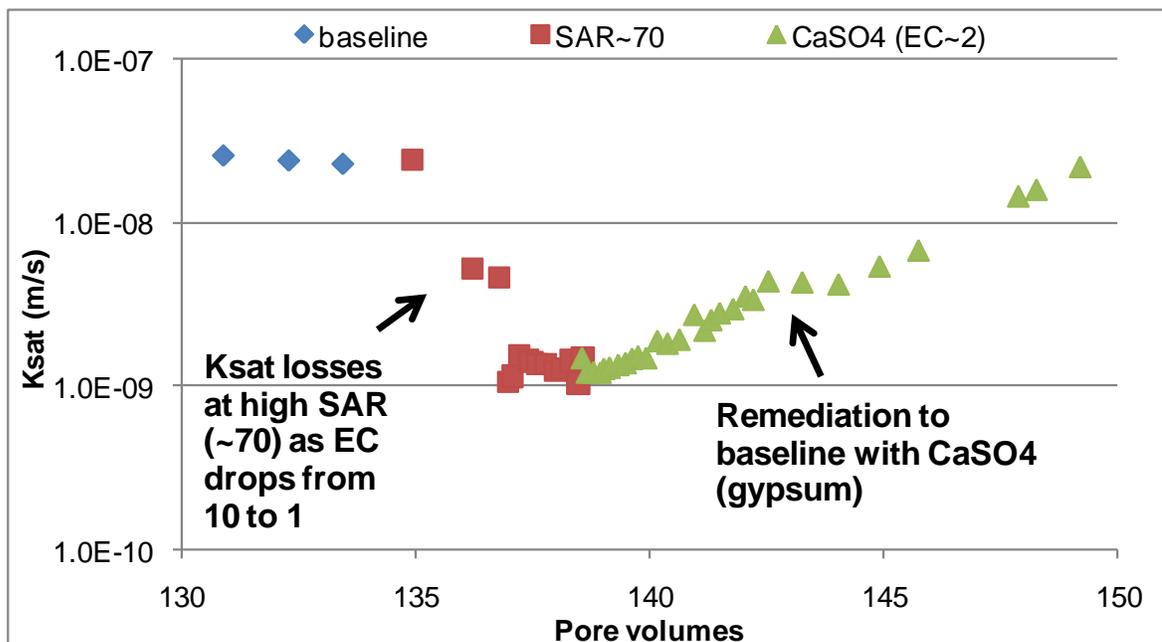
Figure 7.2 shows another typical example of effective remediation with calcium sulfate where the initial SAR-impacted soil is at relatively low EC. After reaching a remediated apparent steady-state with gypsum at approximately 1.6 dS/m, the remedial solution was then switched to magnesium sulfate to evaluate whether any additional changes were observed. Hydraulic conductivity remained essentially unchanged, suggesting that as long as sufficient time is provided calcium sulfate is typically able to reach a similar remediated endpoint as magnesium sulfate despite the potentially higher EC of the latter.

Figure 7.2. Example #2 of effective remediation with calcium sulfate (gypsum)
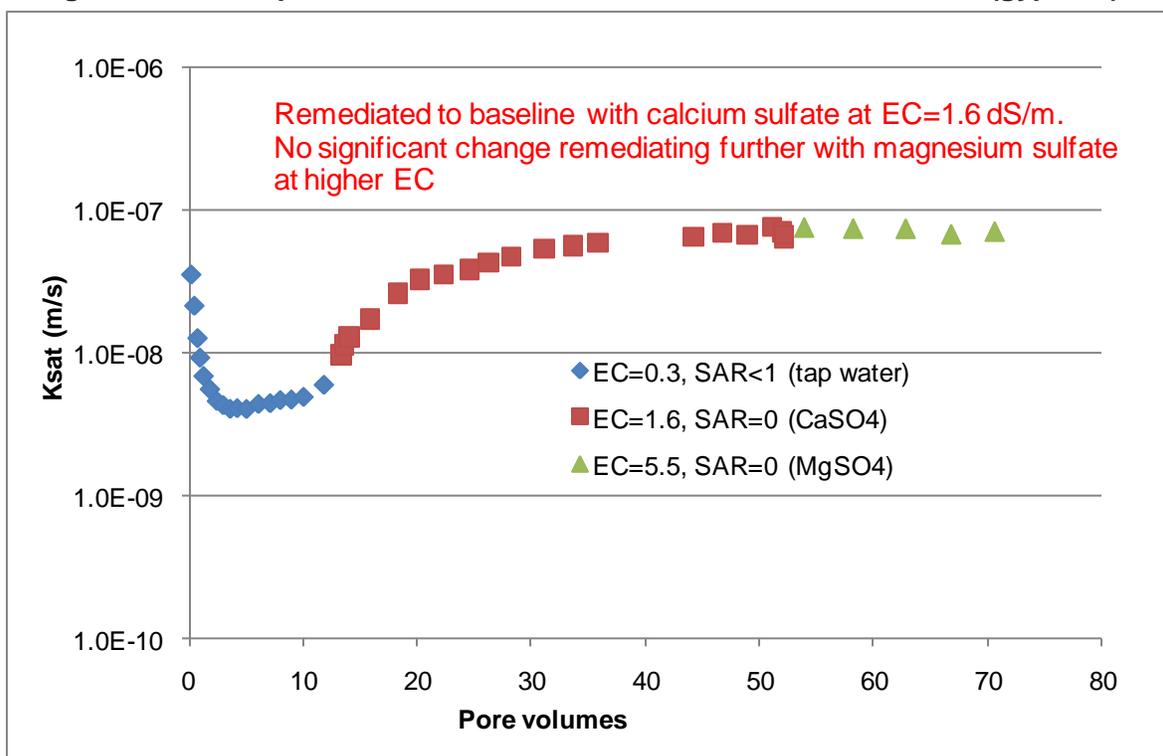
While gypsum was observed to be effective in remediating SAR impacts in many situations such as shown above, there were also situations where the maximum potential EC of gypsum (based on its solubility) limited its effectiveness. Figure 7.3 shows one such example, where soil equilibriated at SAR~70 and EC~5 showed an further reduction in hydraulic conductivity upon leaching with 2 dS/m calcium sulfate. This is likely due to EC reducing faster than SAR, and thus benefits of reducing SAR were temporarily outweighed by the more rapid loss of EC. When the remedial solution was later changed to approximately 8 dS/m magnesium sulfate, the rapid observed increase in hydraulic conductivity was likely due to the simultaneous decrease in SAR and increase in EC. As in the previous example, the initial portion of the remediation stage was observed to be linear when K_{sat} is plotted on a log scale and the time-scale is expressed in terms of pore volumes. It is worth noting that the hydraulic conductivity losses of the calcium sulfate solution may have eventually reversed and began to remediate if the calcium sulfate solution was continued for a sufficient amount of time without switching to magnesium sulfate.

Figure 7.3. Example where MgSO4 remediates more effectively than CaSO4
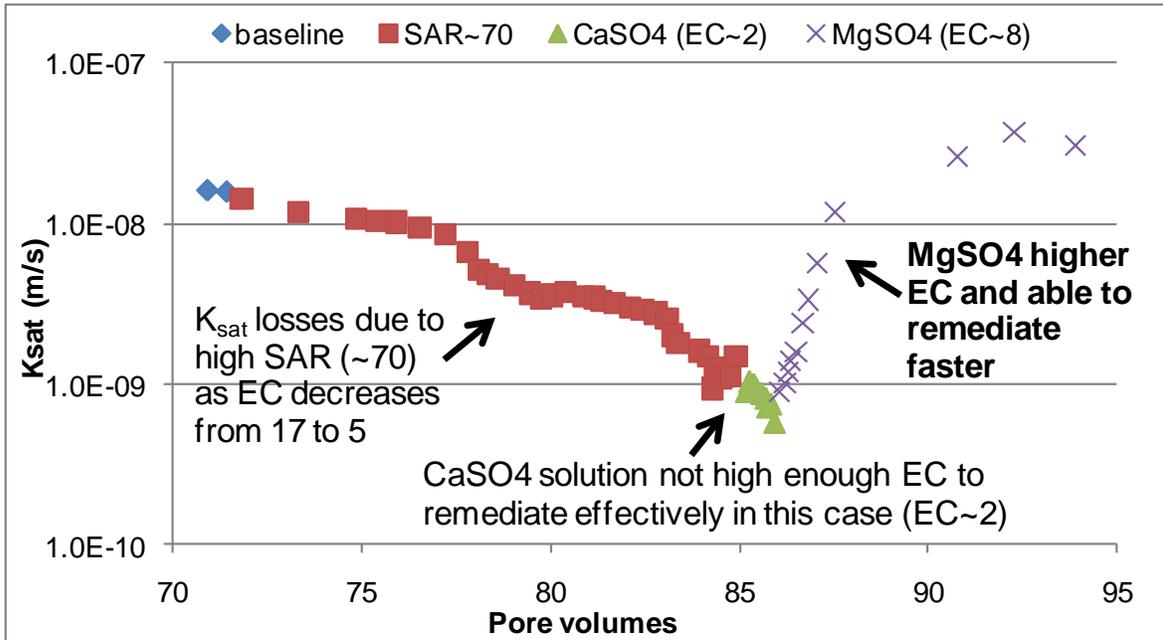
8   SITE-SPECIFIC SULFATE GUIDELINE DEVELOPMENT USING MODIFIED SST

As an example of a practical application of this sulfate-related research, subsoil chloride protocols from the Alberta Environment 'Subsoil Salinity Tool' (SST) may potentially be modified to generate site-specific guidelines for subsoil sulfate for various receptors. For example, for the root-zone soil-dependent biota receptor, this may be accomplished by first making the conservative assumption that sulfate travels at similar rates as chloride and that sulfate has similar toxicity to chloride when both are expressed in terms of electrical conductivity (Equilibrium Environmental, 2010). This is highly relevant for drill sumps where sulfate-containing drilling waste is disposed near the root-zone, and is also relevant for other anthropogenic sulfate impacts such as sulfur block runoff. In such cases, it may be useful to determine what quantity of sulfate in subsoil below the root-zone may be tolerated without predicting unacceptable root-zone EC increases in the future due to sulfate redistribution. 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.

One key assumption to creating such guidelines is the transport rate of sulfate relative to chloride. To illustrate the general technique, a preliminary assumption was first made that sulfate travels at the same speed as chloride. This implies the general absence of significant sorption and/or precipitation effects, though several experiments described in previous sections suggest that certain conditions may involve significant sorption and/or precipitation of sulfate salts (especially calcium sulfate) resulting in retardation of sulfate relative to chloride. This preliminary assumption of sulfate transporting at the same speed as chloride likely results in conservative subsoil guidelines in cases where transport to receptors such as the root-zone or aquatic life receptors is required.

If sorption or precipitation is instead assumed to occur for sulfate, transport to receptors would generally be slower and the estimated future-day risk generally lower. On the other hand, the assumption of rapid sulfate transport (similar to chloride) implies that current-day root-zone exceedances due to sulfate may leach out of the root-zone at a relatively rapid rate similar to chloride. This has relevance for pipelines where subsoils with elevated sulfate have been brought to the surface during construction activities. Additional leaching research and/or sorption experiments would be useful to further investigate this assumption, particularly at higher sulfate levels where sorption / precipitation effects may become more significant. Additional leaching columns experiments are currently in progress and will be used to fine-tune this approach.

9   CONCLUSIONS, WORK IN PROGRESS, AND NEXT STEPS

Conclusions from this phase of this sulfate research project are shown below, followed by a summary of current work-in-progress and next steps.

9.1   CONCLUSIONS

- 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.

- Based on the low-sulfate leaching experiments described above, follow-up leaching experiments at higher (11,000 mg/L) sulfate were performed at slower overall leaching rates. Solubility limits for calcium sulfate were clearly observed, and evidence of sulfate retardation relative to chloride was apparent in three experiments with various gypsum

concentrations and soil compaction rates. This suggests the presence of sorption and/or precipitation reactions for sulfate, both of which would have the effect of slowing sulfate transport relative to an in inert tracer such as chloride.

- Preliminary sulfate adsorption experiments did not show dramatic adsorption effects at 1,000 mg/L sulfate, though the high water:soil ratios typical for adsorption isotherms compared to environmental levels makes precipitation effects less likely. The co-presence of chloride at 1,000 mg/L may also influence sulfate sorption behavior, and evaluating lower chloride concentrations in conjunction with higher sulfate concentrations would be useful in batch adsorption experiments.

- 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 precipitated 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.

9.2   WORK IN PROGRESS AND NEXT STEPS

- Evaluating relative leaching rates of chloride and sulfate under conditions of higher sulfate concentrations, different cation ratios, lower chloride concentrations, and lower flow rates is in progress.   These conditions may be more representative of certain typical scenarios encountered where levels or either natural sulfate salts or anthropogenically-introduced sulfate salts may be relatively high. Preliminary leaching experiments under these conditions show evidence of sulfate retardation compared to chloride, and additional investigation could allow the estimation of retardation factors and potentially distribution coefficients for sulfate under various conditions.

- Additional investigation into the influence of potential sulfate precipitation / dissolution reactions on sulfate transport rates, especially under leaching conditions with high sulfate concentrations potentially in conjunction with elevated calcium concentrations is in progress. Preliminary leaching experiments under these conditions showed evidence of sulfate precipitation and/or sorption reactions, with further investigations in progress.

- 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 root-zone EC exceedances in the future due to upward sulfate redistribution.

- Additional leaching research is currently in-progress to fine-tune this SST approach to guideline development, particularly including higher background EC environments that are either impacted or non-impacted with chloride.

10   **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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