MILLENNIUM
EMS Solutions Ltd.

6111 91 Street
Edmonton, AB T6E 6V6
tel: 780.496.9048
fax: 780.496.9049

Suite 325, 1925 18 Avenue NE
Calgary, AB T2E 7T8
tel: 403.592.6180
fax: 403.283.2647

#106, 10920 84 Avenue
Grande Prairie, AB T8X 6H2
tel: 780.357.5500
fax: 780.357.5501

10208 Centennial Drive
Fort McMurray, AB T9H 1Y5
tel: 780.743.4290
fax: 780.715.1164

toll free: 888.722.2563
www.mems.ca

Eco-Toxicity of Sulphate Relative to Chloride

Prepared for:
Petroleum Technology Alliance Canada (PTAC)

Prepared by:
Millennium EMS Solutions Ltd.
Suite 325, 1925 – 18th Avenue NE
Calgary, Alberta
T2E 7T8

December 2013
File # 12-165

Table of Contents

Page

Table of Contents i
List of Tables ii
List of Appendices ii
Executive Summary iii

1.0 INTRODUCTION 1
1.1 Objective and Scope of Work 1
1.2 Acknowledgements 2
2.0 BACKGROUND 2
2.1 Management of Sulphate Salinity in Soil in Alberta 2
2.2 Quantification of Salinity in Soil 2
2.3 Mechanisms of Phytotoxicity for Chloride and Sulphate 2
2.4 Studies Investigating the Relative Toxicity of Chloride and Sulphate to Plants 2
2.4.1 Crop Species 3
2.4.2 Boreal Species 4
2.4.3 Summary 5
3.0 EXPERIMENTAL DESIGN 6
4.0 RELATIONSHIP BETWEEN SALT CONCENTRATION AND EC 6
5.0 RESULTS - SULPHATE AND CHLORIDE ECOTOXICITY 7
5.1 Results 7
5.2 Calculation of Species Sensitivity Distributions and Guidelines 12
6.0 DISCUSSION 13
7.0 SUMMARY 13
8.0 CLOSURE 15
9.0 REFERENCES 16

List of Tables

Page

Table 1 Summary of IC_{25} Values for Chloride in Fine and Coarse Soil 8
Table 2 Summary of IC_{25} Values for Sulphate in Fine and Coarse Soil 9

Table 3	Summary of IC_{25} Values for Chloride – Expressed as EC - in Fine and Coarse Soil	10
Table 4	Summary of IC_{25} Values for Sulphate – Expressed as EC - in Fine and Coarse Soil	11
Table 5	Guideline Values for the Ecological Direct Contact Pathway for Chloride and Sulphate	12

List of Appendices

Appendix A Figures
Appendix B Millennium EMS Solutions Ltd. Third Party Reliance Agreement

Executive Summary

Introduction

The overall objective of this project was to examine the relative toxicity of chloride- and sulphate-based salinity to plants. A literature review was conducted to assess the information already available, and laboratory toxicity tests were commissioned using relevant plant species, Alberta soils and current Environment Canada Protocols.

Methodology

The effect of chloride and sulphate on plant growth endpoints was assessed in a series of ecotoxicity tests using the current Environment Canada protocol. Key elements of the experimental design included:

- Two toxicants were used, sodium chloride and sodium sulphate.
- Three plant species relevant to Alberta were tested, barley, alfalfa and northern wheatgrass.
- Tests were completed in two Alberta soils: one fine-grained and one coarse-grained soil.
- Triplicate chemical analyses were conducted on each test treatment.
- Guidelines for the ecological direct contact exposure pathway were calculated using the current ESRD/CCME protocol.

Results

The weight of evidence from the literature suggests that sulphate is generally less toxic to plants than chloride.

Ecological direct contact guideline values were calculated from toxicity data collected in this project. In most cases, the guidelines calculated for fine and coarse soils were similar and the datasets were combined. Guideline values calculated for sensitive land uses (natural area, agricultural and agricultural) are as follows:

- Chloride: 840 mg/kg, or an EC of 5.3 dS/m.
- Sulphate: 2,500 mg/kg, or an EC of 8.5 dS/m.

Complete results are available in Table 5 of this document, including guideline values for commercial and industrial land uses. Data from this project clearly indicate that sulphate is less toxic than chloride to the plant species tested. It is also noted that the EC-based guideline values indicated above are significantly higher than the EC-based salinity guidelines in the current Alberta Tier 1 guidelines document (2dS/m and 3 dS/m for topsoil and subsoil, respectively).

1.0 INTRODUCTION

Management of salts in the top 1.5 m of Alberta soils is currently achieved based on soil electrical conductivity (EC). The Alberta guidelines for EC in soil are based on the toxicity of sodium chloride to plants. Deeper soils may be managed either using EC, or based on the concentration of chloride ion, using the subsoil salinity tool (SST). Thus, salinity in soils in Alberta is based on the toxicity of the chloride ion, whether the salinity is related to chloride or sulphate.

Alberta soil EC guidelines (AENV, 2010) are based primarily on various research databases of plant salt tolerance including the United States Department of Agriculture (USDA) salinity databases and Howatt (2000). Plant salt tolerance studies commonly use sodium chloride as the source of salt (Howatt, 2000; Maas, 1996). However, research reported in Howatt (2000) suggests that some plants may be less sensitive to sulphate than to chloride.

Numerically, the most frequent occurrences of salinity releases at oilfield sites in Alberta are related to chloride, since that is typically the anion that predominates in saline produced water. However, there are a significant number of oilfield sites in Alberta that, historically or currently, store elemental sulphur produced from sour gas sweetening operations. When these sulphur storage sites are decommissioned, environmental assessment activities may reveal areas of soil with elevated sulphate. Given the large footprint of some sulphur storage facilities, the potential size of any plume of elevated sulphate can be correspondingly large.

This study seeks to develop a better understanding of the relative toxicity of chloride and sulphate to plants, and thus provide the tools to address the current inconsistency, where sulphate salinity is managed based on the toxicity of chloride.

1.1 Objective and Scope of Work

The overall objective of this project was to determine whether sulphate has a significantly different toxicity to chloride in Alberta soils for a representative selection of Alberta plants.

The scope of work of this project was as follows.

- Conduct a thorough literature review of the relative ecotoxicity of sulphate and chloride to plants.
- Conduct ecotoxicity testing with both chloride and sulphate on three plant species in two soil types using the Environment Canada (2005) protocol.
- Analyze chemical data to determine the relationship between anion concentrations and EC for each soil.

- Develop species sensitivity distributions and ecological direct contact guidelines for sulphate and chloride based on the new data collected in this report, both on the basis of anion concentration and on the basis of EC.
- Generate a detailed report on the toxicity testing including all data.
- Generate an overall interpretive report on the findings.

1.2 Acknowledgements

This work was made possible by funding from Petroleum Technology Alliance Canada (PTAC) under project number #09-9191-50. Thanks to James Agate, the CAPP project sponsor for important contributions to the project. Thanks also to Darlene Lintott of Exova for completing the ecotoxicological work and for valuable insight into experimental design.

2.0 BACKGROUND

2.1 Management of Sulphate Salinity in Soil in Alberta

Currently, sulphate plumes in Alberta are conservatively assessed based on EC guidelines (AENV, 2010) that are in turn based on plant sensitivity to chloride. Research reported in Howatt (2000) suggests that plants may be less sensitive to sulphate than they are to chloride. If this is correct, then a less stringent guideline value may be appropriate for sulphate than that which is used for chloride.

2.2 Quantification of Salinity in Soil

Two methods of quantifying salinity in soil are in common use, and both are used in this project. The first is to use the concentration of the appropriate anion (chloride or sulphate) in a saturated paste extract expressed as mg of anion per kg dry weight of soil. The second method is to express the soil salinity in terms of the electrical conductivity (EC) in units of dS/m.

2.3 Mechanisms of Phytotoxicity for Chloride and Sulphate

Both chloride and sulphate ions can negatively impact the development and growth of plant species, often through different pathways. It has been suggested that the toxicity of chloride may be due to its effects on the properties and function of cell membranes (Kuiper, 1968; Franklin and Zwiazek, 2004; Nguyen et al., 2006) whereas Na_2SO_4 toxicity towards plants could be largely explained by the effect on the water potential resulting in osmotic stress to the plant (Redfield and Zwiazek, 2002).

2.4 Studies Investigating the Relative Toxicity of Chloride and Sulphate to Plants

A literature review was conducted to identify and assess studies that compared the phytotoxicity of sulphate relative to chloride.

2.4.1 Crop Species

In a study completed by Rogers et al. (1998) on the growth of alfalfa in sodium sulphate (Na_2SO_4) and sodium chloride (NaCl) affected soils, it was determined that, despite having chloride concentrations in the external solution approximately half that of sulphate, shoot concentrations of chloride in alfalfa plant tissue was 40% greater than sulphate shoot concentrations. From this, the authors were able to speculate that alfalfa is more tolerant to salinity in situations where sulphate dominates. They arrived at this conclusion by comparing dry matter production of the plant grown in sodium sulphate from their study and extrapolating the data against previous studies which quantified dry matter production of alfalfa in sodium chloride dominated soils. The comparison showed approximately 22% greater dry mass production of the plants in sodium sulphate dominated soils than sodium chloride affected soils operated under identical background conditions. The authors suggest this plant species may better restrict sulphate accumulation in plant tissue than chloride accumulation thus better withstanding the toxic effects associated with the accumulating anions.

The theory that chlorides are more toxic than sulphates at approximately equal osmotic values to alfalfa is bolstered by work completed in 1939 and 1940 and communicated by Magistad (1942). Soltanpour et al. (1999) used two varieties of alfalfa and inferred that plant dry matter reduction would be the same in iso-conductive chloride and sulphate solutions.

In addition to alfalfa, numerous other crop plants have been utilized to test for differences in the relative toxological effects of sulphate and chloride salinity. Early on, Eaton (1942) discussed how 50 milliequivalents of chloride brought about growth depressions of dwarf milo, alfalfa, and cotton that were roughly equal to those indicated for 100 milliequivalents of sulphate. The toxicity of chloride to these particular plants, as measured in milliequivalents, was thus about twice as great as the toxicity of sulphate. On the basis of the similarity in the toxicity of 50 milliequivalents of chloride and 100 milliequivalents of sulphate to milo, alfalfa, and cotton, Eaton suggested that if the concentrations of the chloride and sulphate salts had been measured in terms of electrical conductivity, freezing-point depression, or in terms of moles of salt or of total solids, an equal toxicity of the two ions could have been indicated.

In a study performed by Meiri et al., (1971) the authors were able to show that sodium chloride and sodium sulphate treatment of bean plants affected growth (dry total weight) very similarly under both low and high salinity environments. A couple different effects on plant physiological processes between the two media did emerge, however. First, they demonstrated that the relative water content of leaves decreased with increasing salinity to a greater extent in sulphate-salinated media. Second, the osmotic potential of sap was reduced with increasing salinity to a greater extent in chloride-salinated media. Bean seedlings were also the plant of choice for Stoeve and Kaymanakova (2008) who noted at iso-molar concentrations, sodium sulphate treatments had slightly greater toxic effects on plants than sodium chloride treatments.

Using four different potato cultivars, Bilski et al. (1987) found, on a mole basis, Na_2SO_4 slowed growth more than NaCl and the addition of $CaSO_4$ reduced the deleterious effect of NaCl or Na_2SO_4 solutions.

In addition to typical crop species, non-traditional crops have also been studied. Using four rose rootstocks, Niu and Rodriquez (2008) determined salinity tolerance of rose plants, like many other crops, depends on species, rootstock selection, substrate or soil type, and environmental conditions. They postulate the reason why chloride-dominated salinity leads to a larger negative effect on growth and visual quality in most crops might be due to the lower requirement for Cl- or lower tissue Cl- threshold compared with sulfur or nitrogen. The differences in salt damage or Cl- toxicity are mainly related to the differences in sensitivity to excessive Cl- levels in leaf tissue or different thresholds of leaf Cl- levels among genotypes. Overall, the four rose rootstocks responded differently to sulphate and chloride suggesting species-specific tolerance and resistivity mechanisms.

2.4.2 Boreal Species

In a study completed by Franklin et al. (2002) examining Jack Pine seedlings and their developmental responses in sodium sulphate and sodium chloride affected soils the authors were able to show seedlings were visibly more adversely affected by NaCl treatment than by Na_2SO_4. A significantly greater amount of needle necrosis occurred in the NaCl-treated seedlings than in those treated with Na_2SO_4, but necrosis was not related to levels of chloride in shoot tissue. The authors proposed that the presence of chloride resulted in an increase in the translocation of sodium and other cations to the shoot. Accumulation of these elements, particularly sodium, in the needle tissue may then result in injury.

Similarly, Renault et al. (2001) also noted a positive relationship between increasing salt concentration and sodium accumulation in the plant tissue. Using *Cornus stolonifera* seedlings (Red-Osier dogwood) they demonstrated, after four weeks of treatment, a decrease in plant dry weights and an increase in the amount of Na^+ in plant tissues to be concurrent with increasing salt concentration. Sodium tissue content was higher in plants treated with sodium chloride than sodium sulphate and it was greater in roots than shoots. However, chloride concentration in the sodium chloride treated plants was higher in shoots than in roots. Results also demonstrated that in equimolar sodium concentrations, 50 mM sodium sulphate reduced shoot and root dry weights more than sodium chloride. The authors suggested that the differing effects sodium chloride and sodium sulphate imparted on Red-Osier Dogwood seedlings implied specific anion effects.

Examining three tree species, Croser et al. (2001) showed minimal differences in the germination, emergence, and early growth of *Picea mariana* (Black Spruce), *Picea glauca* (White Spruce), and *Pinus* *banksiana* (Jack Pine) seedlings. Increased salinity, regardless of salt type, negatively impacted the emergence and growth of the three conifer species. They speculated that the results may be due to osmotic factors where seeds cannot take in water due to negative osmotic pressure and direct toxicity during later stages of seedling growth. The authors did notice, however, hypertrophia of roots belonging to trees in response to sodium sulphate.

In a similar study examining the same three species, Nguyen et al. (2006) demonstrated an overall greater phytotoxicity of NaCl compared with Na_2SO_4 as the NaCl treatment produced greater needle necrosis compared with Na_2SO_4.

Redfield and Zwiazek (2002) observed a difference in the reaction of black spruce seedlings to sodium chloride and sodium sulphate. Using branches removed from the seedlings, pressure–volume curves were constructed following the treatment of seedlings with 60 mM NaCl, 120 mM NaCl, or 90 mM Na_2SO_4 in solution culture. Following the conclusion of their study, seedlings treated with NaCl solutions had greater needle electrolyte leakage and visible needle injury compared with equimolar and iso-osmotic solutions of Na_2SO_4, suggesting that chloride played a role in needle injury. At turgor loss point, a more negative osmotic potential was significantly correlated with lower electrolyte leakage in seedlings treated with Na_2SO_4 but not in those treated with NaCl. Overall, both concentrations of NaCl produced more visible needle injury and greater shoot electrolyte leakage than sodium sulphate. The authors suggest that, in contrast with NaCl, Na_2SO_4 injury to black spruce seedlings may be largely due to osmotic stress and that drought tolerance parameters may be more helpful in predicting salt tolerance in plants treated with Na_2SO_4 than in those treated with NaCl.

In a greenhouse study by M.R. Carter (1980) on the response of Siberian larch seedlings exposed to sulphate and chloride salinity, seedlings began to decline under sulphate salinity between 2.0 and 5.3 mmhos/cm while the addition of chloride caused an initial top growth decrease, chlorosis, and reduction in survival between 1.4 and 3.6 mmhos/cm; the latter salinity level being associated with 20 meq/L of Cl- and 1.5% Cl- in the saturation paste extract and needles, respectively. In general, presence of chloride salinity caused a greater increase to occur in the cation content of the needles than sulphate salinity. Accumulation of organic anions in the needles was also related-to cation concentration and needle chlorosis. Siberian larch would be classed as moderately salt-tolerant under sulphate salinity, and less so where chloride is present.

2.4.3 Summary

Overall, the available literature on the relative phytoxicity of chloride and sulphate suggests that sulphate is often, though not always, less toxic than chloride to a range of plant species. It should be noted, however, that there are challenges associated with interpreting the different ways the studies were conducted, with some studies comparing equi-molar solutions of chloride and sulphate, and other studies comparing equi-osmotic or iso-conductive solutions. In addition, some of the older studies are lacking key details, and some studies inferred their conclusions indirectly, rather than basing them on measurements taken in the study. Overall, therefore, the current study has a significant advantage over all the literature data as it allows clear comparisons to be made between these anions both on a concentration basis, and on the basis of EC.

A total of 14 studies are summarized here looking at the relative toxicity of sulphate and chloride in a range of crop, garden, and boreal species. Overall, 9 out of 14 studies found sulphate to be less toxic than chloride, while 2 studies showed sulphate to be more toxic, and the remaining 3 studies showed no clear difference or had equivocal results. Overall, therefore, the weight of evidence suggests that sulphate is expected to be less toxic than chloride to a range of plant species.

3.0 EXPERIMENTAL DESIGN

The ecotoxicological testing work on this project was subcontracted to Exova, and overseen by Darlene Lintott. A full report (Exova, 2013) is available on the PTAC website, including experimental design, methodology, and detailed results. Key elements of the experimental design are summarized here.

- Two toxicants were used, sodium chloride and sodium sulphate.
- Three plant species were tested, barley, alfalfa and northern wheatgrass.
- Tests were completed in two Alberta soils: a fine-grained clay loam soil from Delacour, Alberta, and a coarse-grained sandy loam from Vulcan Alberta.
- Eight to ten test concentrations were used in each test, with EC ranging from control levels to maximum values of approximately 30 to 40 dS/m.
- The Environment Canada (2005) toxicity testing protocol was used throughout.
- Triplicate chemical analyses were conducted on each test treatment including saturated paste EC, chloride and sulphate.

4.0 RELATIONSHIP BETWEEN SALT CONCENTRATION AND EC

Triplicate chemical analyses were conducted on each test treatment. Complete data are available in Exova (2013). The primary purpose of this testing was to quantify the chloride concentration, sulphate concentration and EC to which each group of organisms was exposed. However, an additional benefit of this analysis is that it enabled a good correlation to be made between EC and chloride or sulphate concentration for each of these two Alberta soils.

The correlations for EC vs chloride are shown in Figure 1, while the correlations for EC vs sulphate are shown in Figure 2. All correlations were very strong, with R^2 values in excess of 0.99. The equations of the regression lines are summarized below:

- Chloride in fine soil: EC = (chloride*0.00431)+1.12
- Chloride in coarse soil: EC = (chloride*0.00581)+1.33
- Sulphate in fine soil: EC = (sulphate*0.00202)+1.31
- Sulphate in coarse soil: EC = (sulphate *0.00298)+1.61

In all cases, EC is electrical conductivity in dS/m, and chloride and sulphate concentrations are in mg/kg.

These relationships are frequently useful in the management and risk assessment of salts in soils, since soil salinity modelling is normally conducted based on ion concentrations, while current soil salinity thresholds are based on EC.

5.0 RESULTS - SULPHATE AND CHLORIDE ECOTOXICITY

5.1 Results

Complete ecotoxicity results are available in Exova (2013), including all raw data and analysis. IC_{25} data are summarized in this report, as these are the values that are used to develop soil guidelines in Alberta (CCME, 2006). The IC_{25} is the concentration required to reduce a test parameter (shoot length, root mass, etc) by 25% from the value in a control sample. IC_{25} values for chloride in coarse and fine soil are summarized in Table 1. IC_{25} values for sulphate in coarse and fine soil are summarized in Table 2. Tables 3 and 4 repeat the data in Tables 1 and 2, respectively, but are expressed in terms of soil EC, rather than the concentration of chloride or sulphate.

Table 1 Summary of IC_{25} Values for Chloride in Fine and Coarse Soil

		IC_{25} Value (mg/kg)	
Test Species	**Endpoint**	**Fine Soil**	**Coarse Soil**
Barley	Shoot Length	2,618	2,218
Barley	Root Length	1,892	2,455
Barley	Shoot Biomass	2,249	1,469
Barley	Root Biomass	1,556	1,256
Alfalfa	Shoot Length	724	455
Alfalfa	Root Length	1,774	1,538
Alfalfa	Shoot Biomass	929	570
Alfalfa	Root Biomass	802	1,811
Northern Wheatgrass	Shoot Length	2,254	1,268
Northern Wheatgrass	Root Length	1,021	1,069
Northern Wheatgrass	Shoot Biomass	719	681
Northern Wheatgrass	Root Biomass	899	847
25th Percentile		**875**	**806**
50th Percentile		**1,289**	**1,262**
25th Percentile of Combined Fine and Coarse		**836**	
50th Percentile of Combined Fine and Coarse		**1,262**	

Table 2 Summary of IC_{25} Values for Sulphate in Fine and Coarse Soil

		IC_{25} Value (mg/kg)	
Test Species	**Endpoint**	**Fine Soil**	**Coarse Soil**
Barley	Shoot Length	6,012	3,811
Barley	Root Length	2,223	1,828
Barley	Shoot Biomass	5,470	3,048
Barley	Root Biomass	2,723	2,218
Alfalfa	Shoot Length	5,408	2,630
Alfalfa	Root Length	4,055	2,371
Alfalfa	Shoot Biomass	4,487	2,582
Alfalfa	Root Biomass	3,013	2,193
Northern Wheatgrass	Shoot Length	7,311	4,966
Northern Wheatgrass	Root Length	2,710	3,724
Northern Wheatgrass	Shoot Biomass	5,082	1,936
Northern Wheatgrass	Root Biomass	3,776	3,266
25th Percentile		**2,941**	**2,212**
50th Percentile		**4,271**	**2,606**
25th Percentile of Combined Fine and Coarse		**2,529**	
50th Percentile of Combined Fine and Coarse		**3,157**	

Table 3 Summary of IC_{25} Values for Chloride – Expressed as EC - in Fine and Coarse Soil

		IC_{25} Value (mg/kg)	
Test Species	**Endpoint**	**Fine Soil**	**Coarse Soil**
Barley	Shoot Length	13.15	13.46
Barley	Root Length	10.00	14.45
Barley	Shoot Biomass	11.51	9.86
Barley	Root Biomass	8.26	8.67
Alfalfa	Shoot Length	3.72	3.65
Alfalfa	Root Length	8.67	9.27
Alfalfa	Shoot Biomass	5.12	4.29
Alfalfa	Root Biomass	4.57	10.81
Northern Wheatgrass	Shoot Length	11.80	8.87
Northern Wheatgrass	Root Length	5.96	7.80
Northern Wheatgrass	Shoot Biomass	4.46	5.48
Northern Wheatgrass	Root Biomass	5.37	6.64
25th Percentile		**5.0**	**6.4**
50th Percentile		**7.1**	**8.8**
25th Percentile of Combined Fine and Coarse		**5.3**	
50th Percentile of Combined Fine and Coarse		**8.5**	

Table 4 Summary of IC_{25} Values for Sulphate – Expressed as EC - in Fine and Coarse Soil

		IC_{25} Value (mg/kg)	
Test Species	**Endpoint**	**Fine Soil**	**Coarse Soil**
Barley	Shoot Length	14.19	12.39
Barley	Root Length	6.58	7.01
Barley	Shoot Biomass	13.30	10.30
Barley	Root Biomass	7.18	8.09
Alfalfa	Shoot Length	12.53	9.59
Alfalfa	Root Length	11.35	8.83
Alfalfa	Shoot Biomass	10.84	9.44
Alfalfa	Root Biomass	7.73	8.39
Northern Wheatgrass	Shoot Length	16.18	16.75
Northern Wheatgrass	Root Length	7.19	12.82
Northern Wheatgrass	Shoot Biomass	12.08	8.79
Northern Wheatgrass	Root Biomass	9.51	10.64
25th Percentile		**7.6**	**8.7**
50th Percentile		**11.1**	**9.5**
25th Percentile of Combined Fine and Coarse		**8.3**	
50th Percentile of Combined Fine and Coarse		**9.9**	

5.2 Calculation of Species Sensitivity Distributions and Guidelines

A species sensitivity distribution (SSD) is simply a set of toxicity values, ranked in order, for a range of species for a particular toxicant. In this case, following the CCME (2006) protocol, the measure of toxicity that is ranked is the IC_{25}.

A graphical representation of the species sensitivity distributions for chloride in fine soil, chloride in coarse soil, and the combined fine and coarse dataset for chloride is provided in Figure 3. Figure 4 provides a similar presentation for sulphate. Figure 5 compares the SSDs for chloride and sulphate. Figures 6, 7, and 8 repeat Figures 3, 4, and 5, respectively, but are expressed on the basis of EC, rather than chloride or sulphate concentration.

The CCME (2006) protocol specifies that guidelines for the ecological direct contact pathway for "sensitive land uses" (agricultural and residential, also applies to natural area in Alberta) are calculated as the 25th percentile of an SSD generated from IC_{25} values. The guideline for commercial and industrial land use is the 50th percentile of this same distribution. The 25th and 50th percentiles of the distributions for each toxicant and soil type are included on Tables 1 to 4. Guideline values are summarized in Table 5.

Table 5 Guideline Values for the Ecological Direct Contact Pathway for Chloride and Sulphate

Anion	Fine Soil	Coarse Soil	Combined
Guidelines based on Anion Concentration in mg/kg			
Chloride (NA, Ag, Res)	880	810	840
Chloride (Com, Ind)	1,300	1,300	1,300
Sulphate (NA, Ag, Res)	2,900	2,200	2,500
Sulphate (Com, Ind)	4,300	2,600	3,200
Guidelines based on EC in dS/m			
Chloride (NA, Ag, Res)	5.0	6.4	5.3
Chloride (Com, Ind)	7.1	8.8	8.5
Sulphate (NA, Ag, Res)	7.6	8.7	8.3
Sulphate (Com, Ind)	11.1	9.5	9.9

Notes:
NA, Ag, Res = natural area, agricultural or residential land
Com, Ind = commercial or industrial land
All values rounded to 2 significant figures
"Combined" are values from the combined fine and coarse datasets.

6.0 DISCUSSION

Figure 3 shows the SSD for chloride in fine and coarse soils. These curves lie very close to each other, and therefore it is appropriate to use the combined dataset to develop guideline values that would apply to both soil textures (Table 5).

Figure 4 shows the SSD for sulphate in fine and coarse soils. These curves lie further form each other, and therefore there may be value in calculating separate guidelines for coarse and fine soils, however, it is still a reasonable approach to combine the two datasets and use the greater statistical power to develop guideline values that would apply to both soil textures (Table 5).

Figure 5 compares the combined SSDs for chloride and sulphate. These two curves are significantly separated, and it is clear that sulphate is less toxic than chloride to the plants tested, and that the guideline for sulphate would be correspondingly higher.

A slightly different picture emerges when we consider the SSDs for data expressed on the basis of EC. Figure 6 shows that the SSDs for fine and coarse soil are similar for chloride and Figure 7 shows that the SSDs for fine and coarse soil are similar for sulphate, and thus in both cases it is appropriate to use the combined dataset to develop guideline values that would apply to both soil textures (Table 5).

Figure 8 compares the combined SSDs for chloride and sulphate, expressed on the basis of EC. As with Figure 5, the two curves are significantly separated, and it is clear that sulphate is less toxic than chloride to the plants tested on an EC basis, and that the guideline for sulphate would be correspondingly higher.

It is noted that the guideline values calculated for chloride and sulphate on an EC basis for natural area, agricultural and residential land are 5.3 dS/m and 8.3 dS/m, respectively. This is higher than the current Alberta salinity guidelines for these land uses which are 2 dS/m and 3 dS/m for topsoil and subsoil, respectively.

7.0 SUMMARY

A literature review conducted compiling the results of studies that compared the phytotoxicity of chloride and sulphate found that the weight of evidence pointed to sulphate having a lower overall phytoxicity than chloride.

Analytical data collected during the project were used to develop relationships between chloride or sulphate concentration and soil EC for the two Alberta soils used.

Ecotoxicity testing was conducted to determine the relative effects of chloride and sulphate on plant growth. Three relevant plant species - barley, alfalfa, and northern wheatgrass – were tested using two Alberta soils, one coarse- and one fine-grained with sodium chloride and sodium sulphate. Soil remediation guidelines protective of the ecological direct contact pathway were calculated both on the basis of anion concentration in soil and also on the basis of EC. Guideline values are summarized in Table 5.

In this project, sulphate was shown to be less toxic to plant than chloride, and accordingly the guidelines calculated for sulphate were higher than the corresponding guidelines calculated for chloride. This was true both for guidelines calculated on the basis of anion concentration and also for guidelines calculated on the basis of EC.

Overall, the salinity guidelines calculated in the project were higher than the current guideline values in the Alberta Tier 1 guidelines, reflecting a different dataset, and a different methodology.

8.0 CLOSURE

We trust that the information presented herein meets your requirements. Should you have any questions, please call the undersigned at (403) 592-6180.

Yours truly,

Millennium EMS Solutions Ltd.

Prepared by:

Miles Tindal, M.Sc..
Principal, Risk Assessment

9.0 REFERENCES

AENV (Alberta Environment). 2010. Alberta Tier 1 Soil and Groundwater Remediation Guidelines. December 2010.Brost, E.J. and G.E. DeVaull. 2000. Non-aqueous phase liquid (NAPL) mobility limits in soil. American Petroleum Institute - Soil and Groundwater Research Bulletin No. 9, 10 pp.

Bilski, J.J., Nelson, D.C. and Conlon, R.L. 1987. The response of four potato cultivars to chloride salinity, sulfate salinity and calcium in pot experiments. *American Journal of Potato Research.* 65(2): 85-90.

Carter, M.R. 1980. Effects of sulfate and chloride soil salinity on growth and needle composition of Siberian Larch. *Canadian Journal of Plant Science*. 60: 903-910.

CCME (Canadian Council of Ministers of the Environment), 2006. A protocol for the derivation of environmental and human health soil quality guidelines. PN 1332. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.

Croser, C., Renault, S., Franklin, J., and Zwiazek, J. 2001. The effect of salinity on the emergence and seedlings growth of *Picea mariana, Picea glauca, and Pinus banksiana*. *Environmental Pollution*. 115(1): 9-16.

Eaton, F.M. 1942. Toxicity and accumulation of chloride and sulfate in plants. *Journal of Agricultural Research.* 64(7): 357-399.

Environment Canada, 2005. Biological Test Method: Test for Measuring Emergence and Growth of Terrestrial Plants Exposed to Contaminants in Soil. Method Development and Applications Section, Environmental Science and Technology Centre, Environment Canada, Ottawa, Ontario. EPS 1/RM/45 – February 2005.

Exova, 2013. Ecotoxicity of Sulphate Relative to Chloride. Unpublished report prepared by Darlene Lintott, Exova, Edmonton, Alberta. Dated November 18, 2013.

Franklin, J. A. and Zwiazek, J. J. 2004. Ion uptake in *Pinus banksiana* treated with sodium chloride and sodium sulfate. *Physiologia Plantarum* 120: 482–490.

Franklin, J.A., Zwiazek, J.J., Renault, S., and Croser, C. 2002. Growth and elemental composition of jack pine (*Pinus banksiana)* seedlings treated with sodium chloride and sodium sulfate. *Trees—Structure and Function*. 16(4-5): 325-330.

Howat, D. 2000. Acceptable Salinity, Sodicity and pH Values for Boreal Forest Reclamation. Alberta Environment, Envir. Sci. Div., Edmonton, Alberta. Report

Kuiper, P. J. C. 1968. Lipids in grape roots in relation to chloride transport. *Plant Physiology.* 43: 1367–1371.

Maas, E.V. 1996. Plant response to soil salinity. Conference proceedings from: Productive Use and Rehabilitation of Saline Lands. Albany, West Australia. ISBN: 186308-046-5.

Magistad, O.C., Ayers, A.D., Wadleigh, C.H. and Gauch, H.G. 1942. Effects of salt concentration, kind of salt, and climate on plant growth in sand cultures. *Plant Physiology.* 18: 151-166.

Meiri, J.K. and Poljakoff-Mayber, A. 1971. Response of bean plants to sodium chloride and sodium sulfate salinization. *Annals of Botany*. 35(4): 837-847.

Nguyen, H., Polanco, M.C. and Zwiazek, J.J. 2006. Gas exchange and growth responses of Ectomycorrhizal *Picea mariana, Picea glauca,* and *Pinus banksiana* seedlings to NaCl and Na_2SO_4. *Plant Biology*. 8: 646-652.

Niu, G. and Rodriguez, D.S. 2008. Responses of growth and ion uptake of four rose rootstocks to chloride- or sulfate-dominated salinity. *Journal of the American Society for Horticultural Science*. 133(5): 663-669.

Redfield, E.B. and Zwiazek, J.J. 2002. Drought tolerance characteristics of black spruce (*Picea mariana*) seedlings in relation to sodium sulfate and sodium chloride injury. *Canadian Journal of Botany*. 80:773-778.

Renault, S., Croser, C., Franklin, J. and Zwiazek, J. 2001. Effects of NaCl and Na_2SO_4 on red-osier dogwood (*Cornus stolonifera* Michx) seedlings. *Plant and Soil.* 233: 261-268.

Rogers, M.E., Grieve, C.M., and Shannon, M.C. 1998. The response of Lucerne (*Medicago sativa* L.) to sodium sulfate and chloride salinity. *Plant and Soil*. 202: 271-280.

Soltanpour, P.N., Al-Wardy, M.M., Ippolito, J.A., Rodriguez, J.B., Self, J., Gillaume, M. and Mathews, D. 1999. Chloride versus sulfate salinity effects on alfalfa shoot growth and ionic balance. *Soil Science Society of America Journal.* 63: 111-116.

Stoeve, N. and Kaymanakova, M. 2008. Effect of salt stress on the growth and photosynthesis rate of bean plants (*Phaseolus vulgaris* L.). *Journal of Central European Agriculture.* 9(3): 385-392.