Equilibrium Environmental Inc.

SUBSOIL SAR AND SULFATE

MANUAL SECTIONS

FOR SUBSOIL SALINITY TOOL (SST)

DRAFT REPORT

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1 INTRODUCTION

The overall objective of this project is to implement risk-based SAR (sodium adsorption ratio) and sulfate guideline algorithms into the Alberta Environment and Sustainable Resource Development (ESRD) Subsoil Salinity Tool (SST). A brief description of the importance and need for subsoil SAR and sulfate guidelines is provided in the two sections below, followed by a general description of the Subsoil Salinity Tool. Since salt guidelines tend to be complex and involve contaminant transport modelling, the implementation of algorithms into a software tool is necessary to expand the reach and application of this research project to other stakeholders and beneficiaries.

By implementing SAR and sulfate guidelines into a standardized tool, the knowledge gained during this research project can be disseminated in a very practical manner to environmental consultants, government agencies, and oil and gas companies. This will allow risk-based remediation guidelines to be developed more rapidly, and accelerate and facilitate the SAR and sulfate assessment and remediation process.

1.1 SUBSOIL SAR

Historically, salt impacts to soil and groundwater have occurred in the upstream oil and gas industry due to produced water infrastructure failures such as pipeline breaks and tank leakage, as well as operational practices. When sodium chloride in produced water is accidentally released to soil, there are salinity and sodicity (elevated Sodium Adsorption Ratio, or “SAR”) related impacts. The negative effects of elevated SAR/sodium on shallow, root-zone soils are well known and include the dispersion of clay particles, clay swelling, and the potential for poor moisture infiltration or surface ‘hard-pan’. In comparison, the potential risks of elevated SAR in subsoil are less understood, but include mechanisms such as reduction in hydraulic conductivity which may potentially lead to water logging of the rooting zone. Understanding potential effects of subsoil SAR/sodicity in the use of common remediation techniques that rely on the leaching of salts through the soil column is also of importance.

Within the upstream oil and gas industry there are numerous well sites and facilities with subsoil salinity/sodicity impacts, which require impact evaluation, remediation, and reclamation. For salt impacted sites in the upstream oil and gas industry, the depth of salinity and sodicity impacts is generally dependant on the produced water release mechanism. Although leaking tanks and surface spills of limited volumes mainly impact rooting zone soils, higher-volume releases from pipeline breaks or flare pits typically result in impacts below the rooting zone as well.

Currently SAR guidelines exist only for impacts in the root zone. There is an urgent need for the development of risk-based subsurface (below the root zone) SAR guidelines for the remediation of salt impacted sites. Uncertainty with application of root zone SAR guidelines for deeper soils is a roadblock for site remediation and reclamation. As a result, remediation may be delayed due to such uncertainty, or remediation of subsoil using generic rooting zone SAR guidelines may result in an over or under protection. For instance, unnecessary volumes of soil may be removed, leading to an inefficient use of energy and resources.

1.2 SUBSOIL SULFATE

Sulfur is a relatively abundant element that occurs in a variety of forms in the environment. One form is sulfate- a fully oxidized inorganic anion derived from sulphur. Soluble sulfate salts (such as sodium sulfate) can contribute toward elevated soil salinity which can reduce vegetative growth and impair groundwater quality. Calcium sulfate (gypsum) is more limited in solubility and its effects on salinity, and is often used by farmers and reclamation practitioners to offset elevated sodium concentrations in sodic soils. Both these salts can originate from natural or anthropogenic sources, and both occur naturally in Western Sedimentary Basin 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 soils followed by replacement with backfill soil where backfill sulfate is substantially lower than background. Commonly, calcium sulfate is used as a calcium-amendment to soil to balance elevated sodium levels at produced water releases though sulfate concentrations are also increased as a result. Drilling muds can contain elevated levels of soluble sulphate salts and historical disposals at drill sumps have resulted in sites experiencing deteriorated soil quality and reductions in vegetation growth. Pipeline installation or other construction practices may also result in elevated sulfate from deeper soils being brought nearer to the root-zone or into shallow subsoil. 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 are currently no soil guidelines for sulfate, with root-zone sulfate concentrations currently managed indirectly via EC guidelines which consider the total effect of all anions including sulfate as well as chloride. Below the root-zone, direct contact with plant roots is of reduced importance and ion-specific, risk-based guidelines for subsoil sulfate based on toxicity and fate and transport modeling would be of great value. Such risk-based subsoil sulfate guidelines will help ensure that any remedial actions are both sufficiently protective but also do not result in the landfilling of needless volumes of soil which may pose minimal risk in-situ.

1.3 SUBSOIL SALINITY TOOL (SST)

The Subsoil Salinity Tool is a software tool which allows generation of Tier 2 salinity guidelines for subsoil using various site-specific data. Tier 1 guidelines are generally applied to root-zone soils (0-1.5m) with the subsoil guidelines intended to prevent future Tier 1 root-zone or groundwater exceedances. The current SST implementation is for chloride with recent PTAC/PERD-funded research also aimed toward implementing subsoil SAR guidelines and subsoil sulfate guidelines.

Standard SST pathways for chloride protect the root-zone (upward migration), livestock watering (from dugout), human drinking water (from DUA), aquatic life (lateral transport), and irrigation water (from dugout). Consultations with ESRD and the PTAC Salinity Working Group have identified three key risk pathways for subsoil SAR including soil structure, the root zone (upward migration), and irrigation water (from dugout). Four key risk pathways have been identified for subsoil sulfate including the root-zone (upward migration), livestock watering (from dugout), irrigation water (from dugout), and human drinking water (from DUA). There is currently no CCME or Alberta surface water guideline for aquatic life for sulfate, but this fifth pathway (aquatic life) could potentially be implemented in the future if such surface water guidelines are implemented.

SAR and sulfate necessitate unique and distinct models from chloride because of a variety of differences in transport characteristics, naturally occurring levels in Alberta soils and groundwater, relative toxicity, etc. Chloride and sulfate contribute to soil salinity, as expressed most commonly by electrical conductivity (EC). Salinity is generally a direct expression of the magnitude of ions in a soil or water. Conversely, SAR contributes to soil sodicity which is an expression of the composition of particular cations (sodium, calcium, and magnesium) and the balance that exists between these ions in a given soil.

This document summarizes key aspects of subsoil SAR and sulfate research which will be relevant to users of the current versions of the Subsoil Salinity Tool modules for SAR and sulfate. This includes primarily high-level conceptual models of the relevant receptors as well as selected aspects of transport models and exposure and risk calculations. The input parameters used in the current versions of the software tool are also discussed and how they influence the calculated guidelines for the various pathways. This is facilitated by various screenshots of the current versions of the subsoil SAR and sulfate modules showing both input parameters and produced guidelines (output).

2 SUBSOIL SAR HELP-FILE INFORMATION

The following section provides a brief overview of general SAR information (Section 3.1), describes the pathways of concern for generating subsoil SAR guidelines (Section 3.2), summarizes each of the input parameters utilized in the SST-SAR module (Section 3.3), and describes the guidelines derived and output parameters generated using the model for each of the pathways of concern (Section 3.4).

2.1 GENERAL SUBSOIL SAR OVERVIEW

2.1.1 General SAR Information

Elevated sodium in soil, as measured by elevated Sodium Adsorption Ration or “SAR”, may be due to natural salts or introduced anthropogenically through various oil and gas operations such as those involving produced water or drilling waste. The negative effects of elevated sodium on surficial soil quality are well known and include the dispersion of clay particles, clay swelling, and a resultant reduction in hydraulic conductivity which may lead to poor infiltration or surface ‘hard-pan’.

SAR is defined in the equation below (Alberta Environment, 2001 and Curtin at al, 1995a), with all concentrations shown on a charge basis (milliequivalents per litre). In general terms SAR thus represents the ratio of sodium to calcium plus magnesium ions, with it generally assumed that magnesium and calcium are similar in their exchange behaviour with soils (Curtin et al, 1994b). It is important to note that the presence of the square-root in the denominator introduces a non-linearity into the equation such that diluting a solution by 2-fold will decrease EC by approximately 2-fold but will reduce SAR by approximately 1.4-fold (square root of 2).

$$SAR = \frac{[Na]}{\frac{\sqrt{[Ca] + [Mg]}}{2}}$$

It is widely reported that water transport can be affected by relative cation concentrations as measured by SAR (Dikinya, 2007, Levy, 2005). Elevated SAR can greatly reduce hydraulic conductivity (K_{sat}), with the magnitude of these K_{sat} losses varying widely depending on a variety of factors (Levy, 2005). K_{sat} losses are typically caused by the swelling and dispersion of clay particles, with the smectite clays common in prairie soils (Curtin, 1994b) generally susceptible to such changes along with other such “2:1” clay minerals (Shainberg, 2001).

Root-zone SAR may result in hard-pan or poor infiltration of rainwater, especially with shear from rain-drops or tillage. Root-zone SAR has been the primary focus of much of the available literature, especially in the context of the application of sodic irrigation waters such as in Curtin et al (1995a and 1994c) and Springer (1999). The sodic waters applied by irrigation may be due to sodium chloride-based impacts or may also be due to natural sulphate salts (Springer, 1999). The periodic exposure of root-zone SAR-impacted soils to low electrical conductivity (EC) rainwater has also been shown to exacerbate these problems in some cases (Minhas, 1986), with the interactions between SAR, EC, and K_{sat} discussed in more detail in a later section. Lesser quantities of research are available regarding SAR in subsoil (defined here as below the root-zone), though subsoil SAR may potentially result in water-logging of soils or creation of a perched water table. If these effects extend sufficiently far upward, the water-logging of root-zone soils could potentially impair plant growth.

2.1.2 SAR/EC/K_{sat} Relationships From Literature

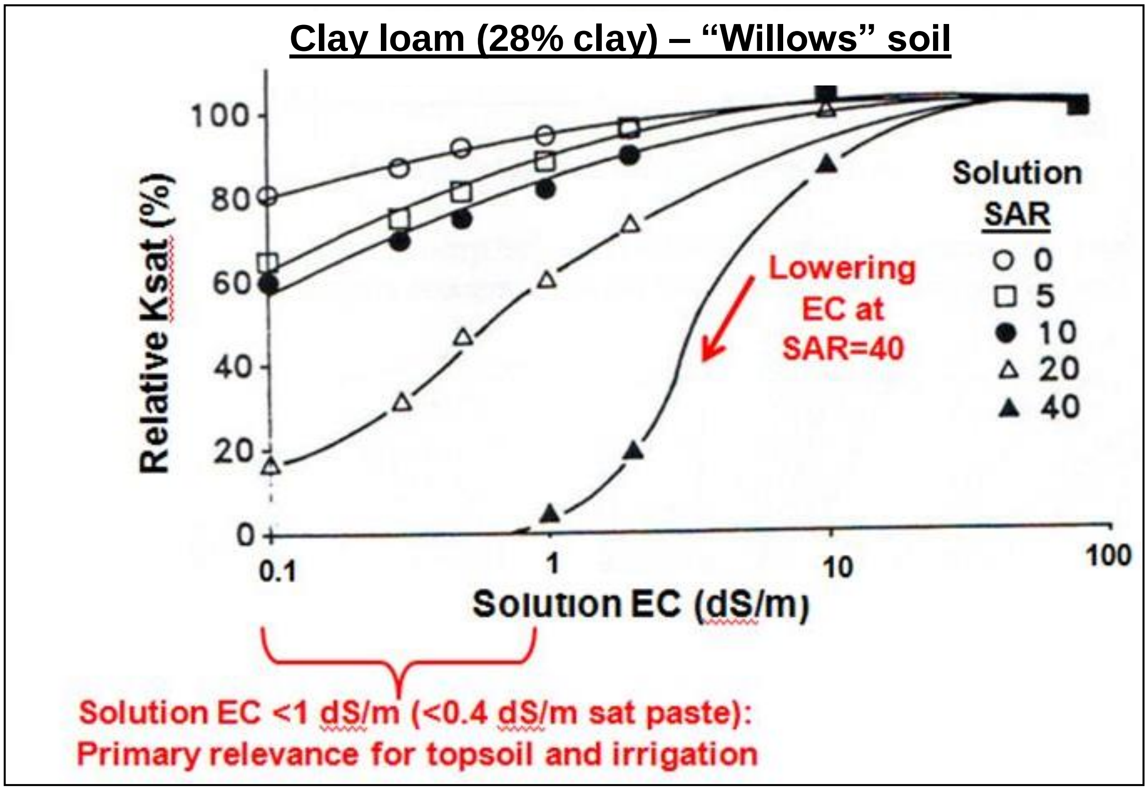
Though elevated SAR is known to have the potential to cause deleterious soil dispersion, it has also been known for more than 50 years that elevated electrolyte concentration (EC) can help protect from these SAR effects (Quirk, 1955). The concept of EC 'thresholds' for SAR effects was introduced in this Quirk 1955 paper, with additional data and refinements related to this concept generated by numerous other researchers in the subsequent decades (Quirk, 2001). For example, it was noted that this protective effect may diminish as salt (electrolytes) are leached from soils by low-EC rainwater (Minhas, 1986). This effect may be more immediately relevant to root-zone soils than subsoils due to the closer proximity of root-zone soils to the source of low-EC rainwater. Regardless, the study of EC/SAR relationships and how they affect K_{sat} has been a common theme for SAR research over many decades.

Useful research was performed by Curtin and Steppuhn examining SAR/EC/K_{sat} relationships through the Agriculture and Agri-Food Canada research branch in Swift Current, Saskatchewan (Curtin et al 1994a, 1994b, 1994c, 1995a, 1995b, Steppuhn 1993). The focus of this research was primarily topsoil, with losses in hydraulic conductivity in topsoil due to SAR potentially further exacerbated in the field by shearing due to tillage and low EC raindrops. This research also has relevance to subsoil, though these exacerbating factors such as tillage and shear by raindrops would not be present in subsoil. This research was also targeted toward the development of irrigation thresholds (Steppuhn, 1993), and thus evaluated several solutions with EC less than 1 dS/m (Cutin, 1994c). This is likely equivalent to less than 0.4 dS/m on a saturated paste basis, and thus some of these low-EC results may be less relevant for subsoil SAR.

The experimental methodology involved repacking topsoil to a fixed bulk density, followed by pre-wetting the soil columns with tap water with EC of approximately 0.6 dS/m and SAR of approximately 1. Solutions of fixed SAR values (up to a maximum of 40) were then leached through the columns while reducing the total electrolyte concentration from approximately 80 dS/m to 0.1 dS/m. Electrolyte concentrations were expressed in meq/L in Curtin (1994c), but are shown in the figures below after converting to electrical conductivity using a typical conversion of 10:1 between meq/L and dS/m. After each change in solution EC, the columns were leached until hydraulic conductivity equilibriated, and results expressed as a percentage relative to the initial baseline.

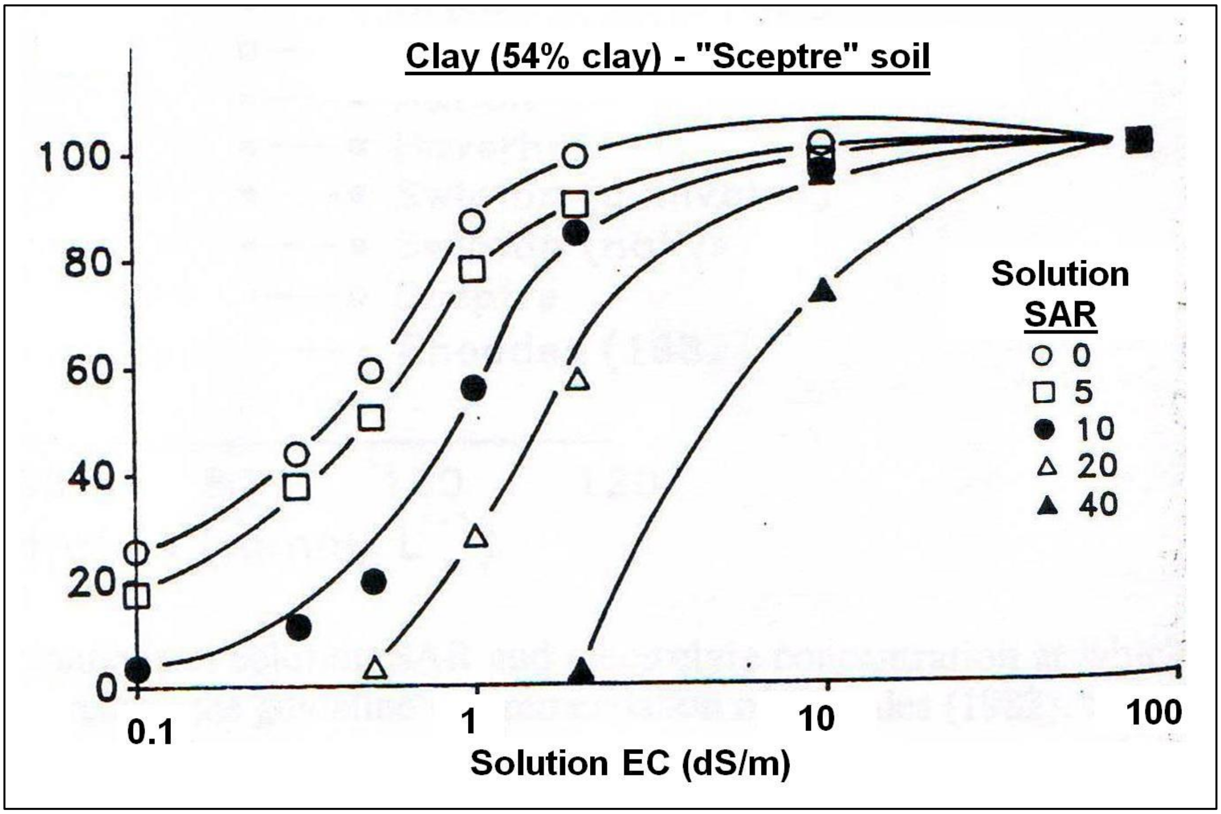
Results were found to be dependent on soil texture, with Figure 2.1 showing an example of EC/SAR interactions for a loam / clay loam soil with 27.5% clay (Curtin, 1994c). At the highest SAR value of 40, K_{sat} was reduced by more than 10-fold below the baseline as EC was reduced from 80 dS/m to approximately 1 dS/m. Lesser effects were seen at lower SAR values, with a notable portion of the effects occurring at solution EC below 1 dS/m. As noted previously, this range of EC below 1 dS/m has primary relevance for topsoil and irrigation, and has lesser relevance for subsoils where background salinity is often above these levels.

Figure 2.1. SAR/EC effects from literature on clay loam soil (28% clay) (Curtin, 1994c)



The behaviour of soil with a higher clay content (53.5% clay) is shown in Figure 2.2 (adapted from Curtin, 1994c). A steeper reduction in hydraulic conductivity as EC decreases is noted compared to Figure 4.1, suggesting that soils with higher clay content may be more sensitive to SAR-induced K_{sat} losses. It is also noteworthy that an approximate 4-fold decrease in K_{sat} was observed at SAR=0 at extremely low EC (0.1 dS/m), though the corresponding K_{sat} reduction was less than 20% at an EC of 1.

Figure 2.2. SAR/EC effects from literature on clay soil (54% clay) (Curtin, 1994c)



In contrast, the behavior of a sandy loam soil with lower clay content (13% clay, "Hatton" soil) is shown in Figure 2.3 (also adapted from Curtin, 1994c). This coarse soil generally exhibited less response to SAR than the soils with higher clay content examined above. For example, a solution SAR of 40 resulted in less than a 2-fold K_{sat} reduction for solution EC above 1 dS/m. A loam soil with 17% clay is shown in Figure 2.4 (cultivated "Swinton" soil), showing a fairly similar response to the above-noted sandy loam.

Figure 2.3. SAR/EC effects from literature on coarse soil (13% clay) (Curtin, 1994c)

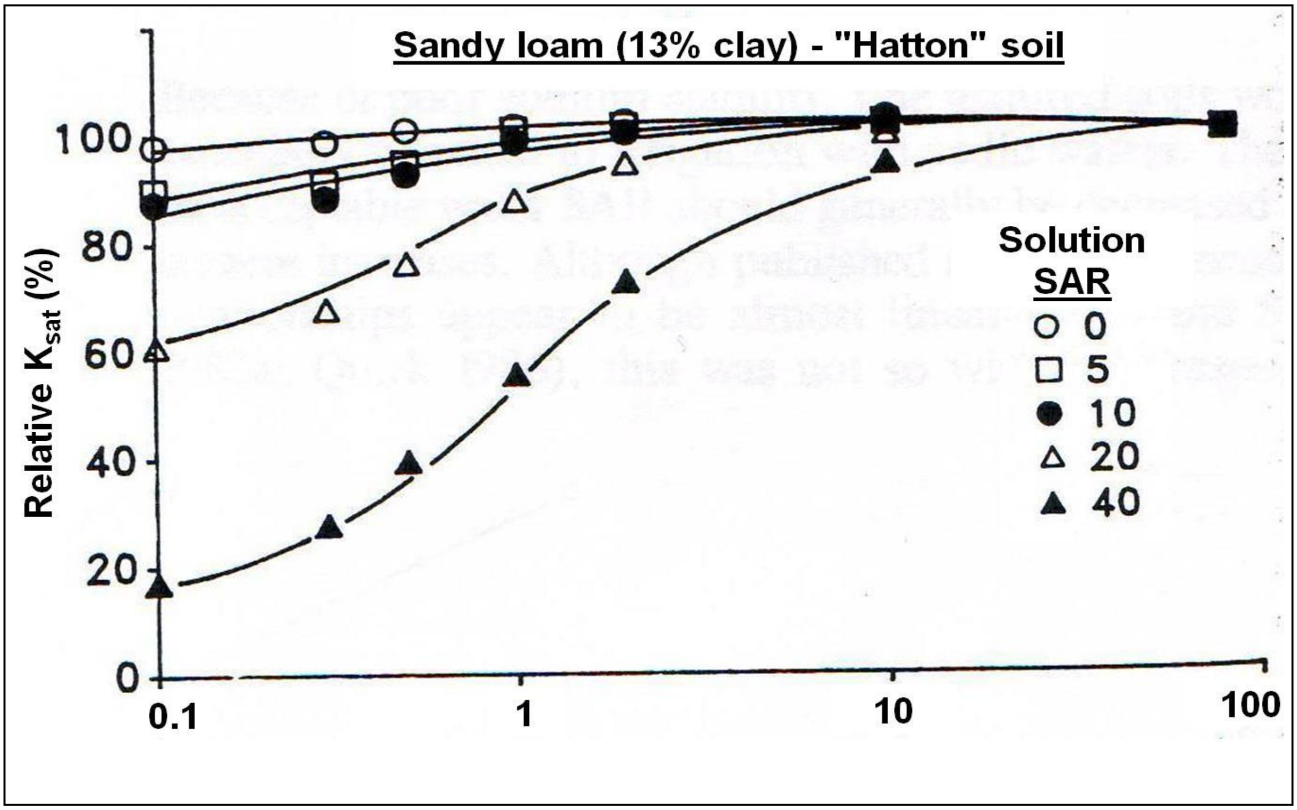
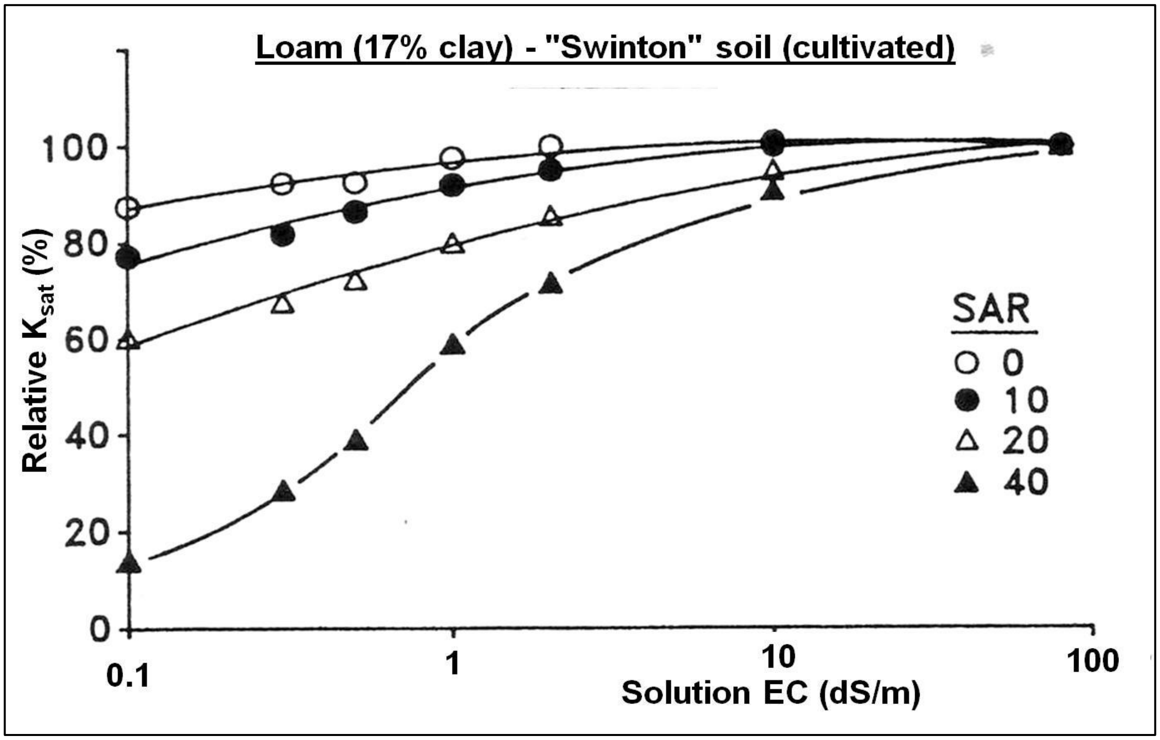
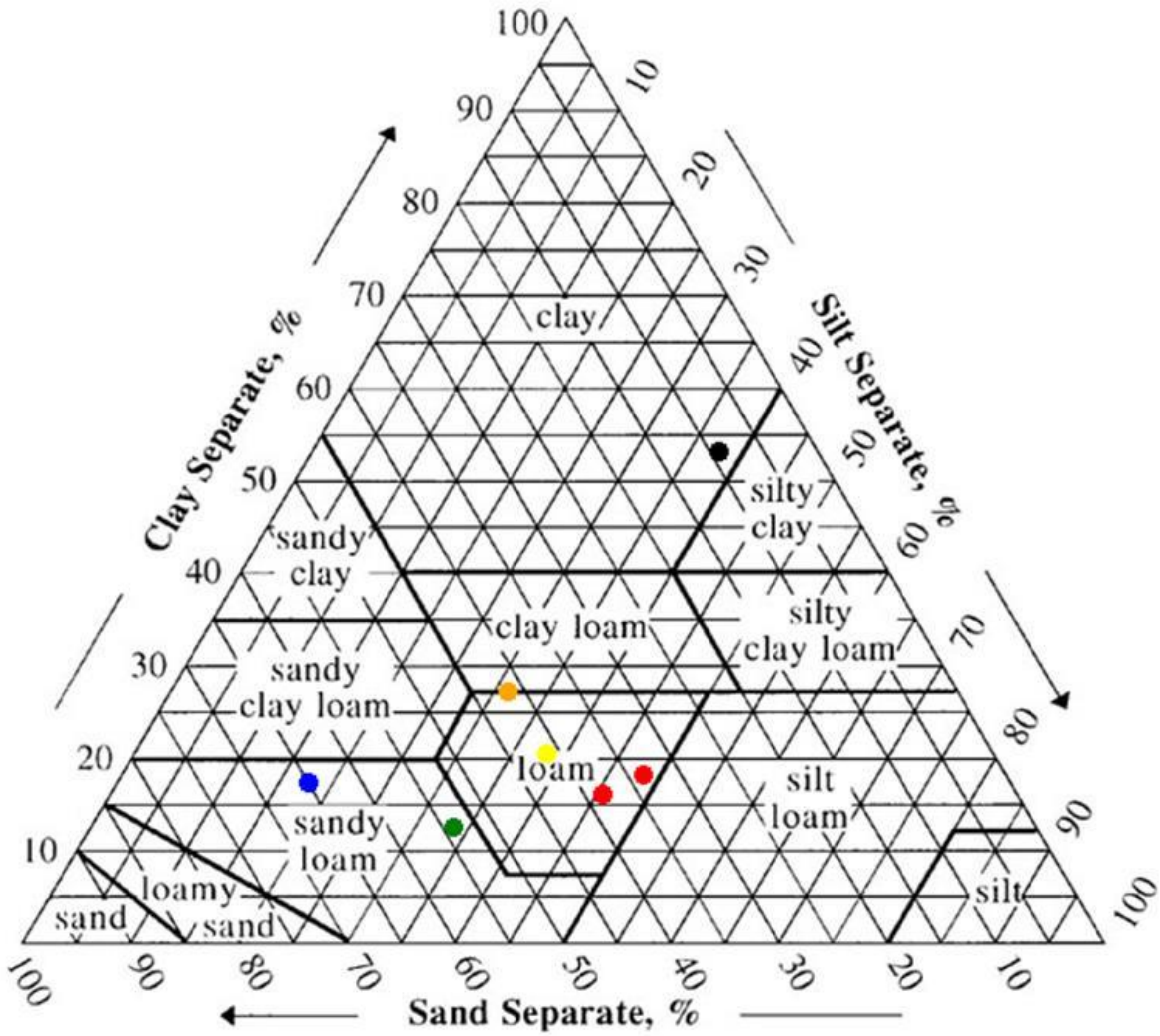


Figure 2.4. SAR/EC effects from literature on loam soil (17% clay) (Curtin, 1994c)



These examples provide empirical evidence that clay content (and hence soil texture) play a role in determining the sensitivity of any individual soil to SAR / EC combinations. Figure 2.5 summarizes the various textures tested in Curtin 1994c, including two sandy loams (13-18% clay), three loams (17-21% clay), one clay loam (28% clay), and one clay (54% clay). This wide range of coarseness and clay content is considered to be representative of substantial portions of prairie soils throughout Alberta and Saskatchewan.

Figure 2.5. Summary of soil types tested in Curtin, 1994c



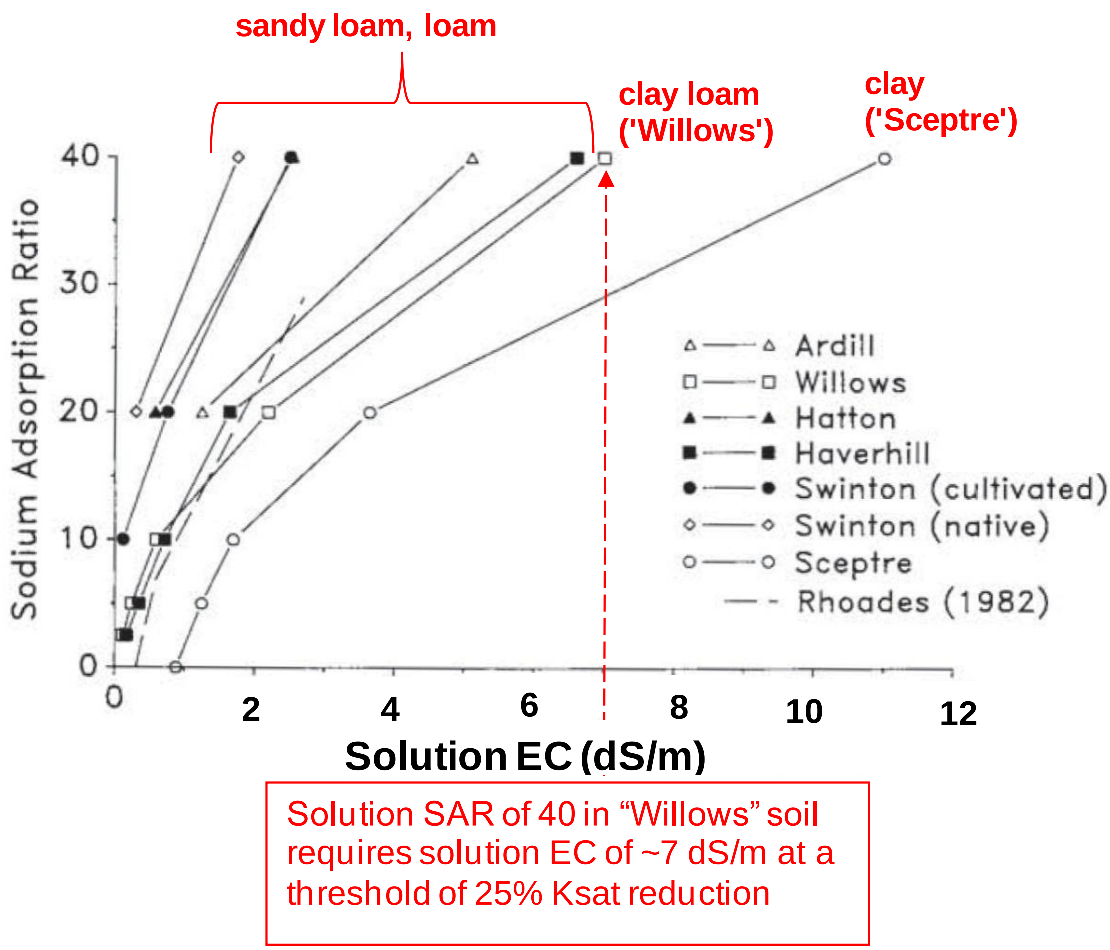
Soil	% Clay	Texture
Hatton	13%	Sandy loam
Ardill	18%	Sandy loam
Swinton (cult)	17%	Loam
Swinton (native)	19%	Loam
Haverhill	21%	Loam
Willows	28%	Clay loam
Sceptre	54%	Clay

2.1.3 K_{sat} Thresholds From Literature

To determine appropriate EC/SAR combinations for irrigation water (a primary purpose from Curtin 1994c, Steppuhn 1993, and numerous other studies from literature), it is necessary to define a ‘threshold’ for K_{sat} losses beyond which SAR-induced effects may be considered excessive. For irrigation water quality, this threshold has often been defined as a 25% K_{sat} reduction as evaluated by these repacked leaching column experiments. It is important to note that this 25% threshold does not necessarily imply that a 25% reduction in hydraulic conductivity in itself will cause unacceptable degradation of root-zone (surface) soils. This threshold is intended to represent the onset of potential soil instability due to SAR effects, which when compounded by other factors present in surface soils could lead to poor infiltration, surface crusting, or hardpan. Such exacerbating factors present in surface soils include wet/dry cycles, dilution by low-EC snowmelt or rainwater, impact and shearing by rain droplets, or shearing by tillage.

Figure 2.6 shows typical threshold curves for various soils demonstrating the range of SAR and EC values for which a 25% reduction in hydraulic conductivity would be predicted (Curtin, 1994c). For Willows soil (loam/clay loam with 27.5% clay), a solution SAR of 40 thus requires a solution EC of approximately 7 dS/m (70 mmol cations/L) to remain stable according to this defined 25% threshold.

Figure 2.6. SAR and EC threshold curve for 25% hydraulic conductivity reduction (Curtin, 1994c)



Notes: -above figure based on solution EC and SAR

-divided electrolyte concentration (mmol/L) by approximately 10 to get solution EC (dS/m)

"Threshold concentration relationships, based on the combination of solution SAR and electrolyte concentration at which a 25% reduction in hydraulic conductivity was observed. The broken line represents the guideline recommendation of Rhoades (1982)" (Curtin, 1994c).

For deeper subsoils below the root-zone, very little has been written in literature regarding suitable SAR thresholds. Compared to root-zone soils, subsoils are not exposed to the exacerbating factors of raindrop impact, direct dilution by low-EC rainwater or snowmelt, or shearing by tillage. Consequently, a threshold which allows a higher hydraulic conductivity reduction appears appropriate for subsoils. Context may be obtained by evaluating natural variability in hydraulic conductivity due to factors other than SAR. For example, it is not uncommon to observe Shelby tube results (a measure vertical hydraulic conductivity) varying by two to three orders of magnitude within the same site despite having low SAR and similar lithology from location to location. Table 2.1 shows examples of such variability, taken from different depth intervals from one predominantly 'clay loam' site and one 'loam' site. In each case, hydraulic conductivity is observed to vary by more than 100-fold within a 3 m depth interval within the same borehole without apparent deleterious effects on water transport.

Table 2.1. Typical variability in hydraulic conductivity in soils within example sites

Borehole	Depth (m bgs)	clay (%)	Texture	K_{sat} (m/s)
Site A, Borehole #20	2.0 – 2.5	28	Clay loam	$4x10^{-9}$
	3.1 – 3.4	38	Clay loam	$2x10^{-10}$
	4.0 – 4.5	41	Clay loam	$1x10^{-9}$
	5.2 – 5.7	43	Clay loam	$8x10^{-11}$
Site B, Borehole #33	2.0 – 2.4	24	Loam	$1x10^{-7}$
	3.0 – 3.3	25	Loam	$1x10^{-8}$
	4.8 – 5.3	22	Loam	$2x10^{-9}$

This substantial natural range in subsoil K_{sat} often observed within sites suggests that factors such as soil texture, clay content, clay composition, depth, the presence of fractures and channels, layering and bulk density effects, and compaction can play a substantial role in determining K_{sat} in the absence of SAR effects. Thus, the influence of SAR on K_{sat} should be considered one factor of many in overall water transport. For this reason plus the reduced sensitivity of subsoils to SAR effects compared to surface soils, preliminary thresholds of up to a 10-fold K_{sat} reduction (final K_{sat} of 10% of the original) were chosen for further evaluation.

As an example of comparing various thresholds, Figure 2.7 shows four thresholds for "Willows" soil based on 25, 50 and 90% hydraulic conductivity (K_{sat}) reductions. A 50% K_{sat} reduction is equivalent to a 2-fold reduction in K_{sat} (100% / 50% = 2 fold) or a 50% % relative reduction of K_{sat} (50% K_{rel}). Likewise, a 90% K_{sat} reduction is equivalent to a 10-fold reduction (100 % / 10% = 10-fold), or a 10% K_{rel}. These were derived from the solution SAR/EC vs K_{sat} relationships from Curtin (1994c), and show that relatively low solutions EC values (1-7 dS/m) are required to meet these K_{sat} thresholds at a solution SAR of 40. This Willows soil (clay loam with a clay content of 28%, near the borderline of loam) is considered representative of a subset of Alberta soils and is likely to be conservative compared to coarser soils with lower clay content.

Figure 2.7. Comparison of literature thresholds for loam/clay loam soil (Curtin, 1994c)

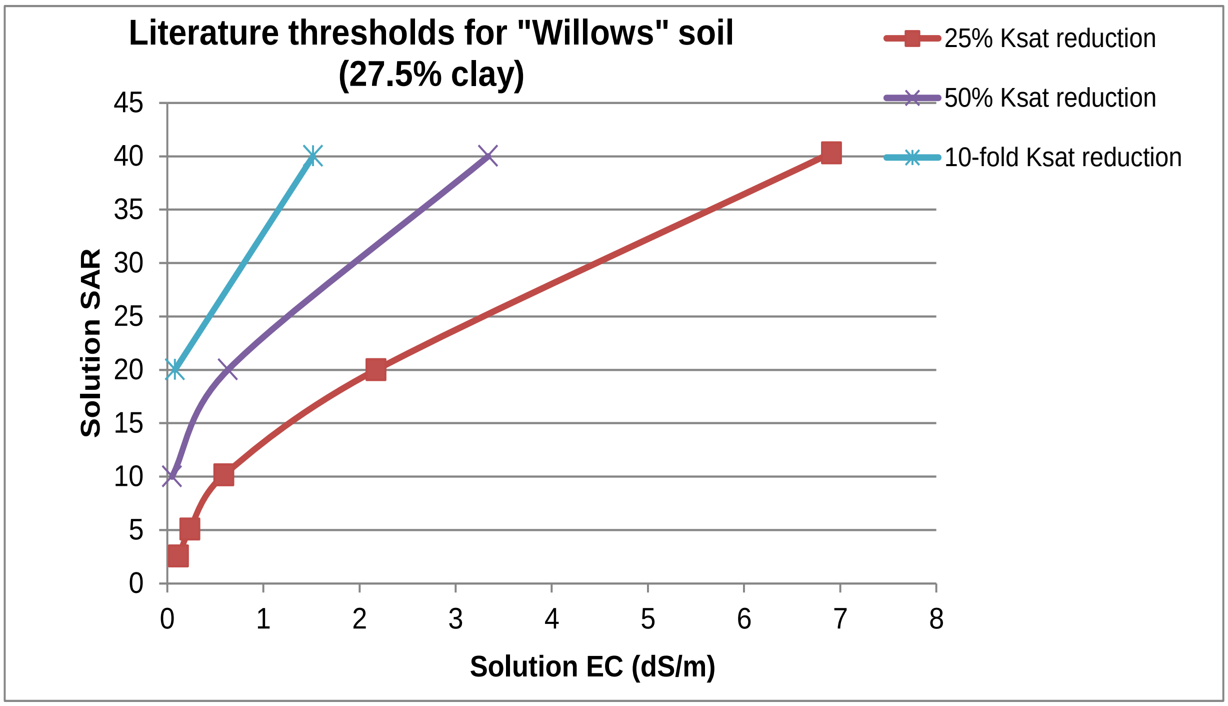


Figure 2.8 shows analogous thresholds for ‘Sceptre’ soil of 54% clay content. This figure shows that Sceptre soil is more sensitive to SAR impacts than Willows soil, likely due to the higher clay content. Higher solution EC solution values of approximately 2-11 dS/m are required to meet these three K_{sat} thresholds at a solution SAR of 40.

Figure 2.8. Comparison of literature thresholds for clay soil (Curtin, 1994c)

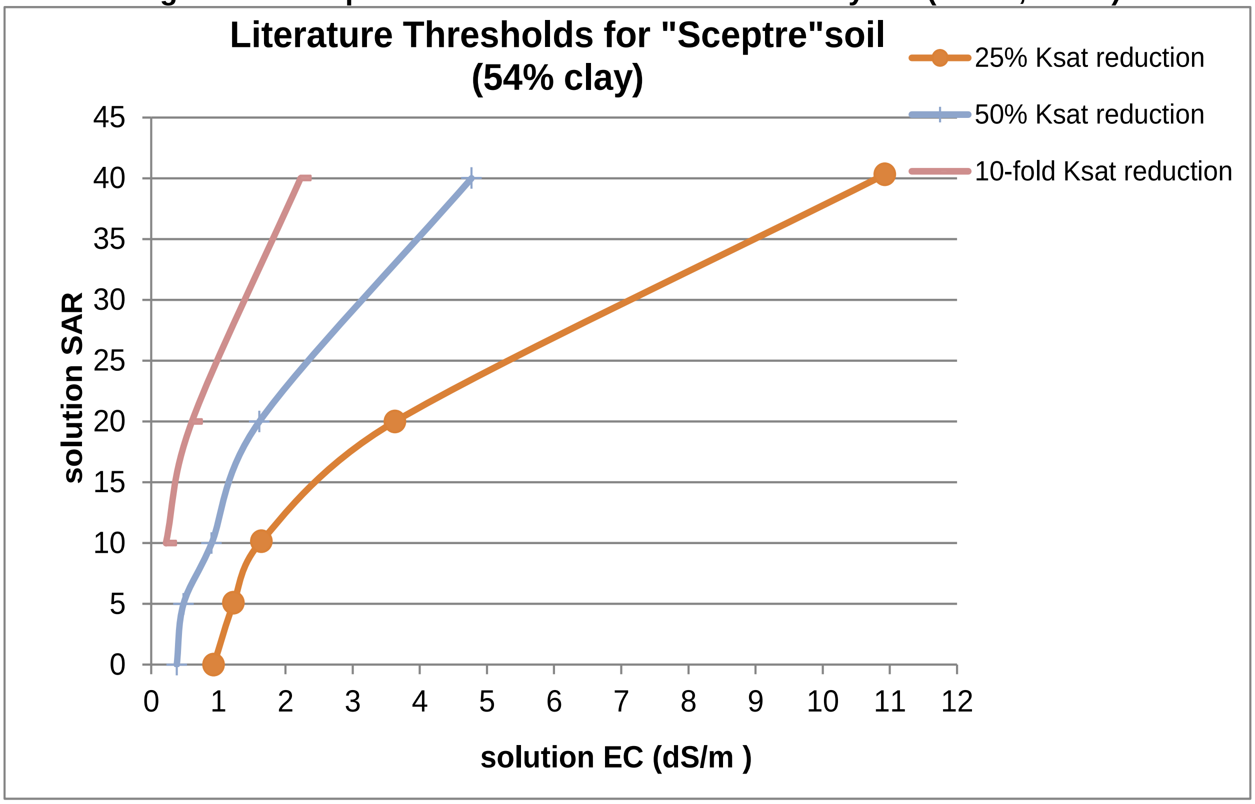
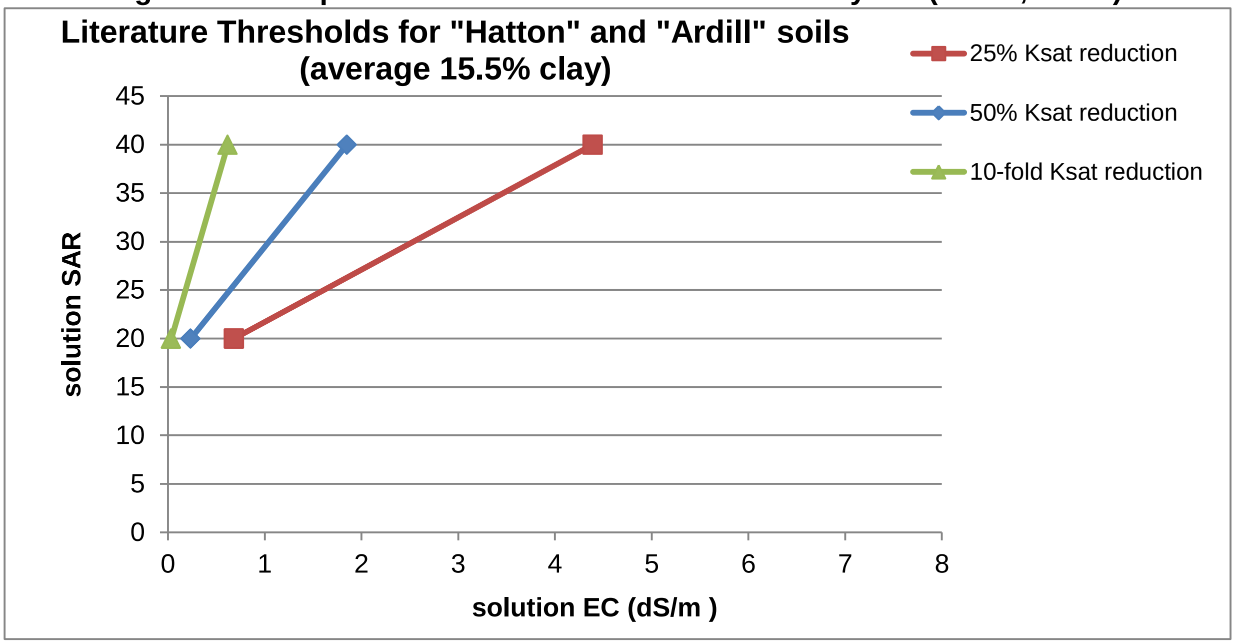


Figure 2.9 shows an analogous threshold for 'Hatton/Ardill' soils, which is the average of two sandy loam soils presented together as one threshold. The average clay content of these two soils is 15.5%. This figure shows that Hatton/Ardill soil is less sensitive to SAR impacts than Willows or Sceptre soil, likely due to the lower clay content. Lower solution EC solution values of approximately 0.5-4 dS/m are required to meet these three K_{sat} thresholds at a solution SAR of 40.

Figure 2.9. Comparison of literature thresholds for sandy soil (Curtin, 1994c)



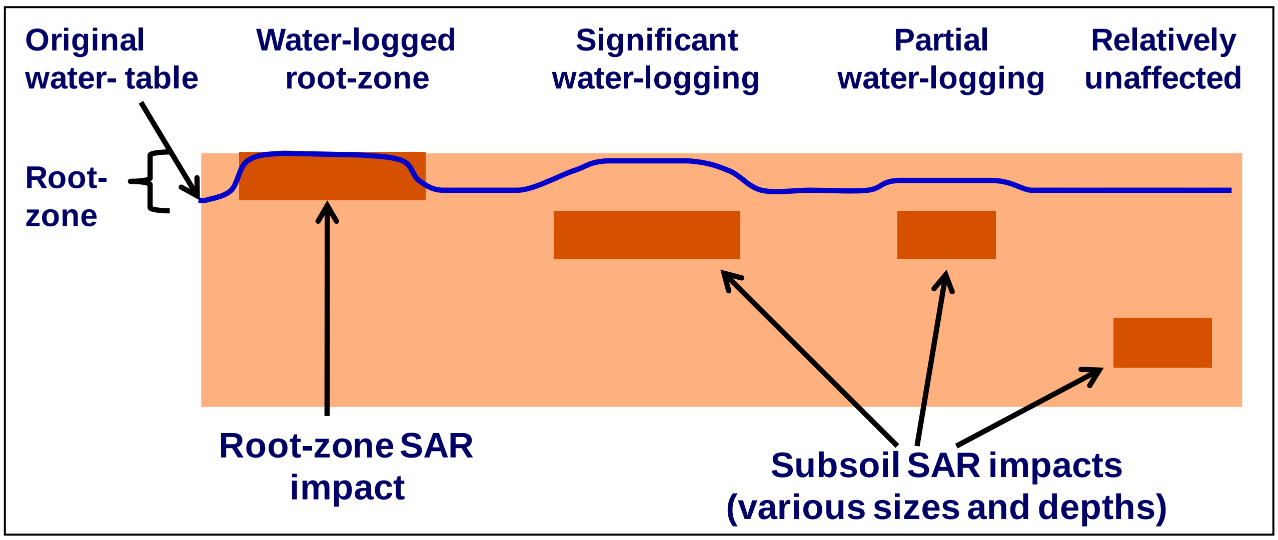
Thus, 'Hatton/Ardill' threshold curves may represent soils with low clay content (< ~ 18%), 'Willows' soil may represent soils with intermediate clay content (~18-50%), and 'Sceptre' those with clay content (> ~50%). The selection of appropriate threshold curves for soil structure may thus be based on soil texture as well as other factors influencing the potential for a water logged root-zone described in the transport modeling section below.

2.1.4 Water-Table Modeling

One aspect of developing subsoil SAR guidelines involves combining the results from EC/SAR/hydraulic conductivity experiments (site-specific and/or from literature) with water-table modeling to evaluate the potential for adverse effects on moisture transport due to SAR. As mentioned previously, the primary potential adverse effect of SAR in subsoil is creating a shallower and/or perched water table through reduction in moisture transport through soil. If this creates a water-logged root-zone, adverse effects on plant growth may be possible.

Figure 2.10 shows a possible conceptual model for the effects of SAR on water table, which would likely be a function of K_{sat} reduction, infiltration rate, impact size, impact depth, original water table depth, soil texture, and other factors. For example, deeper and narrower impacts likely have less effect on water table whereas shallower and wider impacts may be more likely to have potentially adverse effects. These effects may be modelled on either a 1-dimensional (vertical) or 3-dimensional basis for comparison, with the 1-dimensional scenarios less complex due to the absence of lateral transport and assumed infinite lateral source dimensions. The 3-dimensional model scenario is evaluated in the section below.

Figure 2.10. Visualizing SAR effects

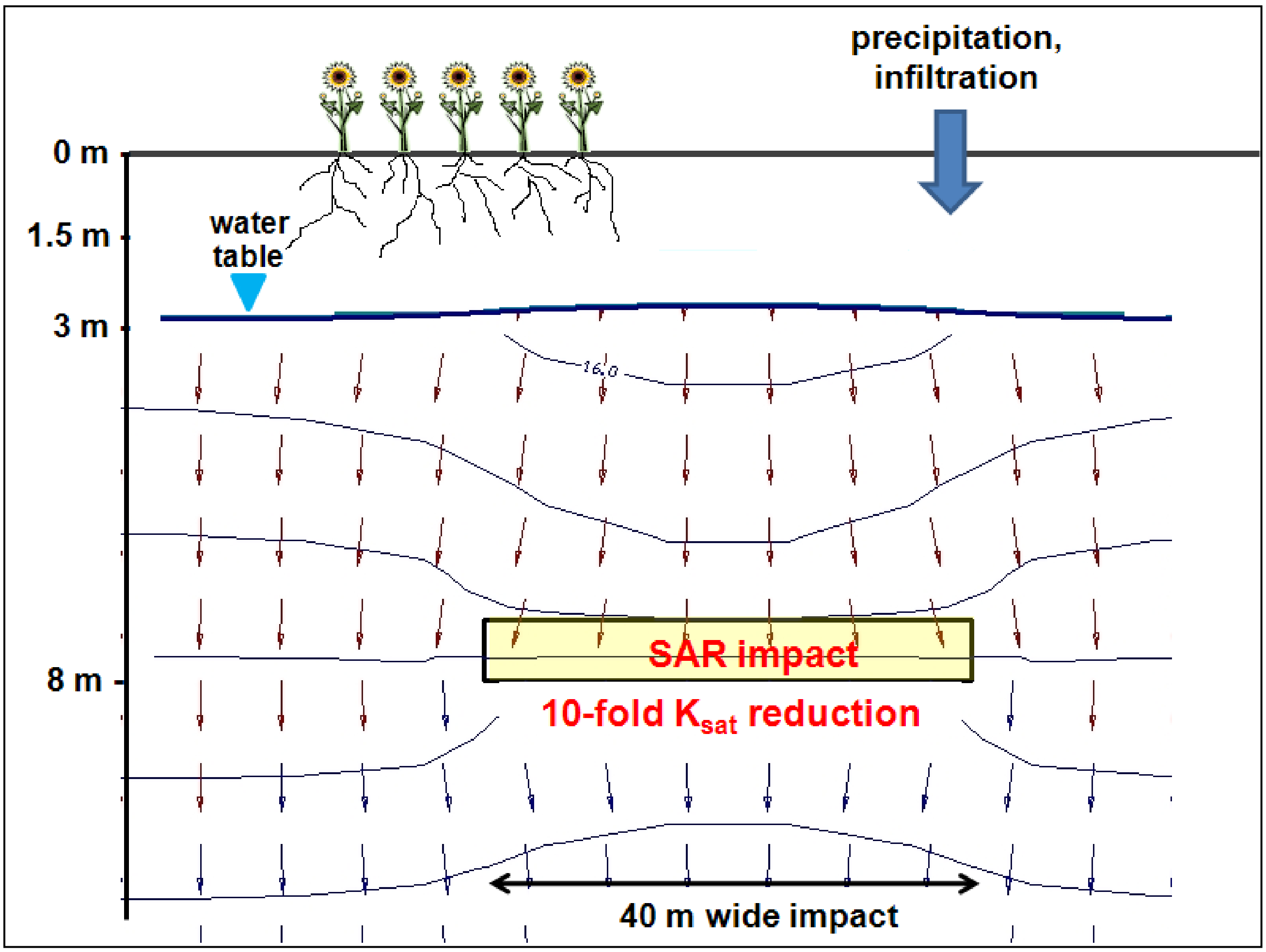


A reasonably detailed and realistic way to examine the interaction between these parameters is through three-dimensional transport modeling using a program such as $Modflow_{TM}$. Such a model allows selecting numerous transport and lithology parameters to create a baseline scenario followed by altering various parameters to evaluate their effects.

For context, a generic baseline model was created consisting of a 3 m water table, 30 mm/year infiltration rate, $1x10^{-8}$ m/s vertical hydraulic conductivity, and a $1x10^{-7}$ m/s horizontal hydraulic conductivity. The baseline scenario has essentially vertical water flow with a flat water table and no lateral flow. This model is not intended to represent any specific site, but rather to show general trends and patterns applicable to a wide range of sites.

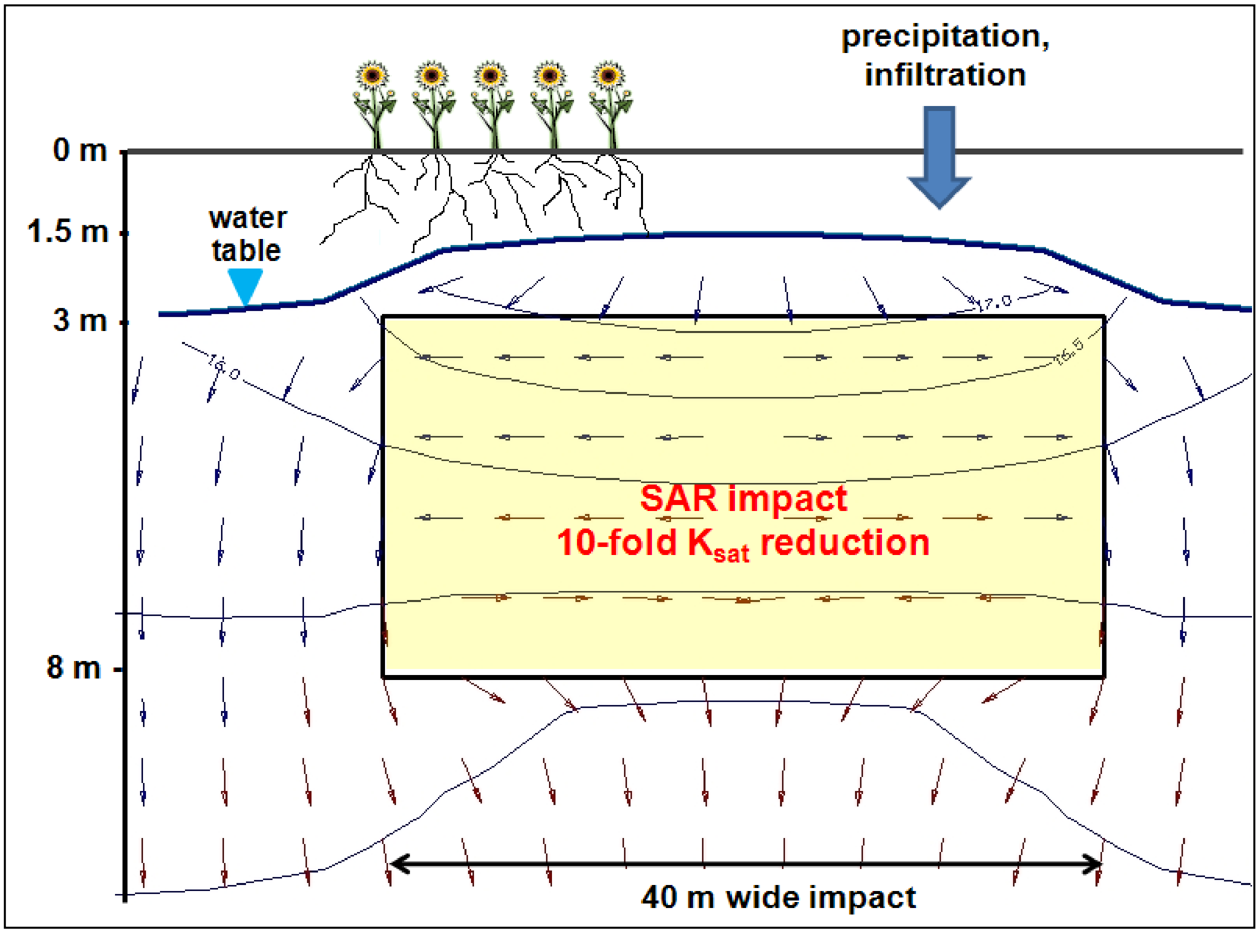
Starting from this baseline scenario, a first model scenario ("Scenario #1") was created to evaluate the potential effects of a 10-fold (1-order-of-magnitude) K_{sat} reduction in a 40 m wide, 1 m thick impact located at from 7 to 8 m deep. Figure 2.11 shows the results of this model scenario graphically, showing a slight disturbance in water flow in the vicinity of the SAR impact as water moves through the impact at a somewhat slower rate and also flows around the edges laterally. The water table is observed to become somewhat shallower above the impact, but the maximum change in water table depth is less than 0.5 m and does not extend into the assumed 1.5 m root-zone which typically contains the majority of root-mass. This scenario is not considered to represent an adverse effect, especially in the context of seasonal water-table fluctuations which can span 1 m or more in many situations.

Figure 2.11. Conceptual model scenario #1: 10-fold K_{sat} reduction at 8 m depth



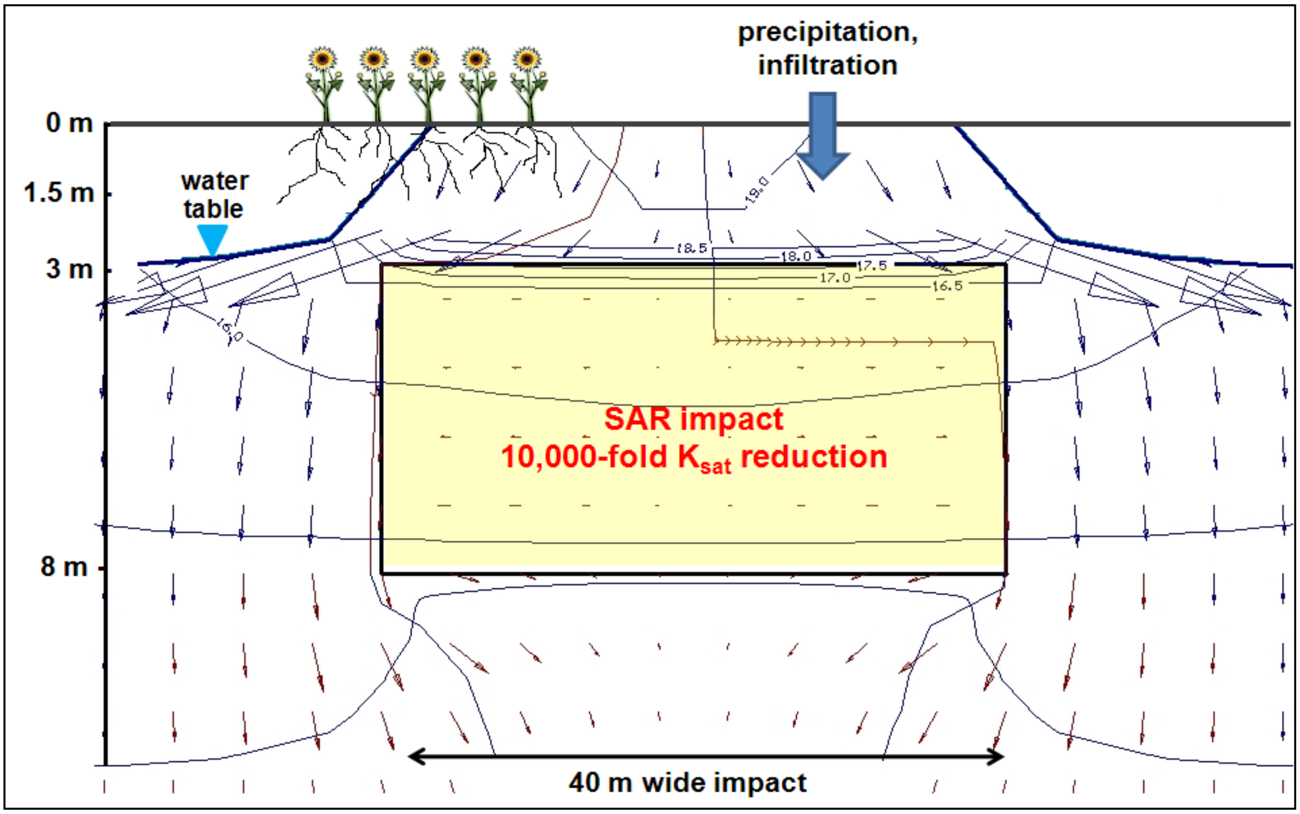
Model scenario #2 involved creating a thicker (5 m thick) SAR impact with the same 10-fold K_{sat} reduction but occurring over the 3 – 8 m depth interval (Figure 2.12). A more visible disturbance in water flow is observed in the vicinity of the SAR impact, with more water traveling around the impact due to the increased restriction to flow through the impact. The modeled water table became shallower by 1 – 1.5 m, approaching the root-zone located at 1.5 m. This scenario still does not represent an apparent adverse effect in terms of creating a water-logged root-zone, but is clearly nearer to such a threshold than scenario #1 was.

Figure 2.12. Conceptual model scenario #2: 10-fold K_{sat} reduction at 3 m depth



To examine a potentially severe SAR impact, scenario #3 simulated a 10,000-fold (4-order-of-magnitude) K_{sat} reduction over the 3 – 8 m depth interval. Figure 2.13 shows results from this scenario, showing a notable reduction in water table depth and water-logging of the root-zone. Compared to scenario #2, water had reduced ability to penetrate through the thick SAR impact and thus required a complete reliance on lateral transport. While this lateral transport was able to minimize effects on water table near the edge of the 40 m wide impact, the effects were more notable toward the center of the impact. This provides an initial indication of the influence of impact size on potential water table effects, and can only be studied in the context of a 3-dimensional rather than 1-dimensional model.

Figure 2.13. Conceptual model scenario #3: 10,000-fold K_{sat} reduction at 3 m depth



Overall, subsoil K_{sat} reductions of 10- to 100-fold appear to be tolerated in many 3-dimensional model scenarios without causing substantial water-logging of root-zone soils. This is especially true of deeper, smaller impacts or in cases with deeper water tables. Overall, when combined with more conservative 1-dimensional models, it appears that 10-fold K_{sat} reductions in subsoil below the root-zone are unlikely to cause substantial water-logging or water-table perching in the majority of scenarios. Thus, a 10-fold K_{sat} reduction threshold appears appropriate for evaluating SAR/EC combinations at contaminated sites.

2.2 Pathways of Concern for Assessing Sodium/SAR Risk

2.2.1 **Primary Pathways**

The standard chloride version of the SST considers the following five pathways for generating subsoil chloride guidelines. Depending on land use, one guideline is generated for each of the above pathways and the lowest guideline is taken is the overall constraining guideline for the Site.

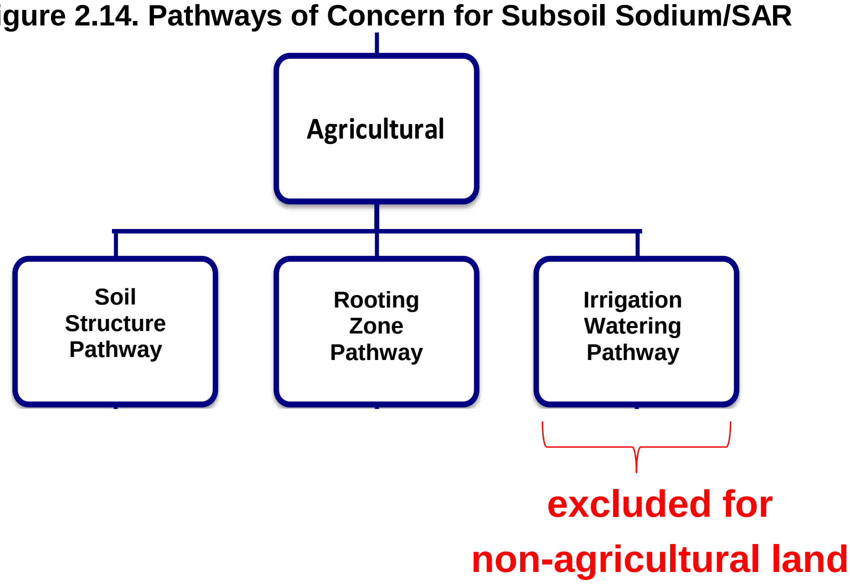
- Protection of the root-zone (from upward chloride migration)
- Protection of livestock water (from a potential dugout)
- Protection of irrigation water (from a potential dugout)
- Protection of a domestic use aquifer (DUA) (from downward leaching)
- Protection of aquatic life (from lateral transport)

For subsoil sodium or SAR, a similar but modified set of pathways is relevant for evaluating risk and generating guidelines. Specifically, it was determined that the primary pathways for subsoil sodium/SAR are:

- Protection of soil structure (from excessive SAR-induced hydraulic conductivity loss)
- Protection of the root-zone (from upward sodium migration)
- Protection of irrigation water (from sodium migration into a potential dugout)

These primary pathways for subsoil sodium/SAR are shown conceptually in Figure 2.14, including the provision that irrigation water be considered solely for agricultural land use. As in the SST chloride module, guidelines for pathways such as upward migration into the root-zone and irrigation water from a dugout are generated by comparing modeled future concentrations of SAR or sodium to relevant Tier 1 guidelines such as root-zone soil SAR guidelines or irrigation water guidelines. Further details of the guideline derivation algorithms are provided in later sections.

Figure 2.14. Pathways of Concern for Subsoil Sodium/SAR



2.2.2 Excluded Pathways

Three other pathways considered in chloride SST modeling are less relevant for sodium/SAR. These include livestock watering, the DUA, and the aquatic life pathways. Each of these pathways are discussed briefly below including the reasons for excluding these pathways for subsoil sodium/SAR.

Livestock water from a dugout pathway

SAR and/or elevated sodium do not appear to pose any additional risk to livestock beyond the assumptions in the standard TDS guidelines for livestock watering used in the chloride module of the SST. Thus, the existing SST protocol for chloride (which also assumes an appropriate balancing amount of sodium is also present) is also sufficiently protective of sodium in livestock water.

DUA pathway

Similar to the livestock water pathway, the existing SST protocol for chloride is sufficiently protective for sodium/SAR for the DUA pathway. The chloride guideline for drinking water (250 mg/L) is sufficiently protective since the drinking water guideline for sodium (200 mg/L) is higher (less constraining) than the stoichiometric amount of sodium which would be associated with 250 mg/L chloride assuming a sodium chloride source of impacts.

Aquatic life pathway

There is currently no freshwater aquatic life guideline for sodium, and thus it is judged that the chloride aquatic life guideline used in the SST (originally 230 mg/L, recently updated to 120 mg/L to be consistent with a CCME update) is sufficiently protective of sodium/SAR. This is due partially to the variable soil sodium concentrations observed in background locations, as well as the reduced transport speed of sodium compared to chloride due to cation exchange reactions.

2.3 INPUT PARAMETERS

A number of site-specific input parameters are required to generate subsoil sodium/SAR guidelines, some of which are based on site data while others may be default values in some cases. In general, the current version of the subsoil SAR module of the SST requires input parameters in the following general categories:

- soil and groundwater information
- root-zone/backfill information
- background subsoil information
- impact information

Figure 2.15 presents a screenshot of the input page for the SAR calculator, including the four general categories of input parameters. Specific input parameters are listed below, with a more detailed description of each provided in the following section.

Soil and groundwater information
- Subsoil Texture
- Root-zone Drainage Rate
- DUA Drainage Rate
- Water Table
- Subsoil Dry Bulk Density

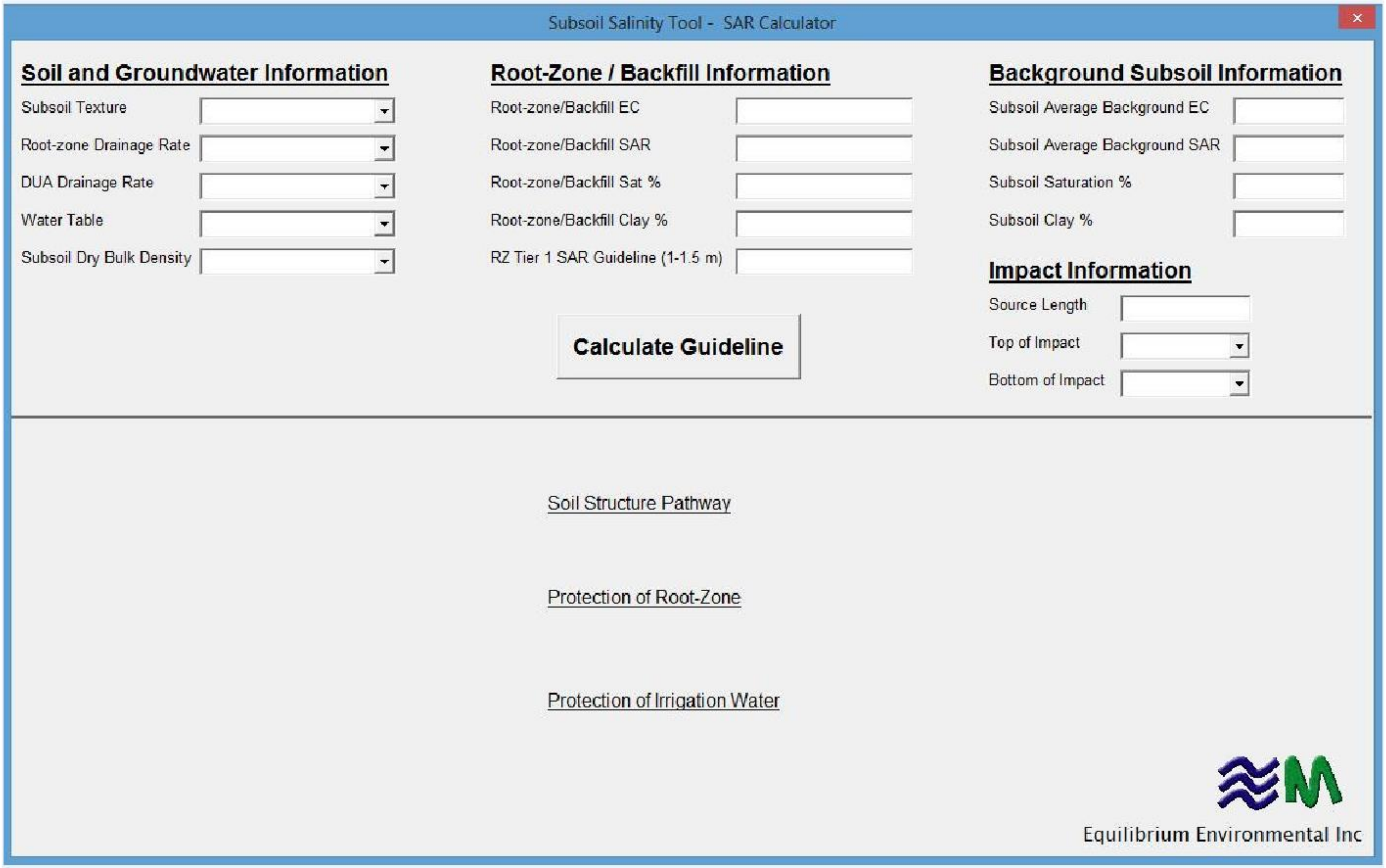
Root-zone / backfill information
- Root-zone/Backfill EC
- Root-zone/Backfill SAR
- Root-zone/Backfill Saturation Percentage
- Root-zone/Backfill Clay Percentage
- Root-zone Tier 1 SAR Guideline (1-1.5m)

Background subsoil information
- Subsoil Average Background EC
- Subsoil Average Background SAR
- Subsoil Saturation Percentage
- Subsoil Clay Percentage

Impact information
- Source Length
- Top of Impact
- Bottom of Impact

Note that some of these input parameters (such as root-zone and DUA drainage rates) will already have been determined by the chloride module of the SST and will be directly populated from these pre-existing values. Other input parameters are specific to subsoil sodium/SAR and will need to be entered in all cases.

Figure 2.15. Screenshot of the Input Parameters for the SAR Calculator



2.3.1 **Subsoil Texture**

Subsoil texture is a standard input parameter from the SST-chloride module and describes whether subsoil at the site is generally fine-grained or coarse-grained based on clay content. As per standard SST protocol, clay content less than 18% is considered 'coarse' and clay content above 18% is considered 'fine. Subsoil texture (along with climate potentially vertical gradient) influences drainage rates as described below. It also influences mixing calculations for the dugout irrigation pathway.

2.3.2 **Root-zone Drainage Rate**

The root zone drainage rate describes the speed with which water is draining downward out of the root zone or upward back up into the root zone. This depends primarily on moisture conditions, climate, soil texture, and vertical gradients, and will be pre-determined by the SST-chloride module.

2.3.3 **DUA Drainage Rate**

The DUA drainage rate is determined in the similar manner as the root-zone drainage rate, and describes the drainage rate assumed when modeling downward sodium transport. Though the DUA is not a primary receptor of concern for subsoil sodium/SAR, the rate of potential downward movement is of relevance for other pathways such as the irrigation water pathway from a dugout. This parameter will generally be higher than the root-zone drainage rate (for conservatism), and will be automatically predetermined by the chloride module.

2.3.4 **Water Table**

The water table depth influences many risk and transport calculations including soil structure, irrigation from a dugout, and upward migration. Water table can be either estimated from field observations and borehole logs (in a 'Tier 2A' scenario for chloride) or directly from monitoring well data (from a 'Tier 2B' scenario). This input parameter will normally be automatically determined from the chloride module.

2.3.5 **Subsoil Dry Bulk Density**

Based on whether subsoil texture is selected as 'fine' or 'coarse', a different subsoil dry bulk density will be selected based on standard SST-chloride protocol. This influences various conversion factors between pore water concentrations and saturated paste concentrations.

2.3.6 **Root-zone/Backfill EC**

The salinity/sodicity of the root-zone is of prime importance in estimating the potential risk of upward migration of sodium/SAR from subsoil into the root-zone. Since it is necessary for the root-zone to meet appropriate Tier 1 guideline for both EC and SAR, in some cases the EC of backfill material will be used here instead if the root-zone was sufficiently impacted that it will need to be excavated and backfilled in order to meet Tier 1 criteria.

2.3.7 **Root-zone/Backfill SAR**

Along with the EC of the root-zone or backfill material, the SAR of the root-zone/backfill is also required to meet appropriate Tier 1 guidelines based on background SAR values. In general, a root-zone or backfill SAR which is substantially lower than the corresponding Tier 1 SAR guideline will leave a higher 'buffer' for sodium concentrations to potentially leach upward into the root-zone from subsoil in the future.

2.3.8 **Root-zone/Backfill Saturation Percentage**

Saturation percentage is used along with EC and SAR to estimate the cation concentrations (sodium, calcium, and magnesium) of the root-zone/backfill material. This provides a baseline root-zone concentration upon which future migration of sodium into the root-zone may be modeled and compared to Tier 1 guidelines.

2.3.9 **Root-zone/Backfill Clay Percentage**

This input parameter influences primarily the irrigation water pathway since soils with higher clay concentrations are generally more sensitive to SAR-induced hydraulic conductivity losses than soils with lower clay content. Thus, sites more clayey surface soils may be more sensitive to sodium/SAR impacted irrigation water and may result in more restrictive irrigation watering guidelines.

2.3.10 **Root-zone Tier 1 SAR Guideline (1-1.5m)**

Based on background SAR statistics for the 1-1.5 m depth interval, a Tier 1 root-zone SAR guideline can be determined to provide a limit on potential future sodium migration into the root-zone. This Tier 1 SAR guideline for the root-zone will generally be either 4 ('Good'), 8 ('Fair'), 12 ('Poor'), or >12 ('Unsuitable').

2.3.11 **Subsoil Average Background EC**

The average background EC in subsoil is used as an input parameter and influences several transport calculations for all three soil pathways. It is used in conjunction with average background subsoil SAR and average background subsoil saturation percentage (described below) to estimate baseline background cation concentrations in subsoil. In general, the relevant depth interval for such background soil statistics is the top 4.5 m of soil, with subsoil SAR generally considered to pose minimal risk at depths of 6 m and below.

Average background EC is also of relevance to the soil structure pathway since it provides some indication of potential future EC levels in the impact area after chloride concentrations have attenuated toward background levels. This reduction in EC toward background may occur faster than the reduction in SAR, and is important in determining the appropriate soil structure guideline to protect against both current-day and future hydraulic conductivity losses.

2.3.12 **Subsoil Average Background SAR**

Along with subsoil average background EC, this input parameter is used to estimate baseline background cation concentrations. In general, elevated SAR values in combination with elevated EC results in estimates of elevated sodium. In contrast, elevated SAR values may not necessarily indicate elevated sodium concentrations if EC is relatively low. Statistics for background subsoil SAR are based on the same depth interval as for subsoil chloride.

2.3.13 **Subsoil Saturation Percentage**

Average subsoil saturation percentage is used along with average subsoil EC and SAR to estimate background cation concentrations and allow conversion between a mg/L basis and mg/kg basis. It also has relevance for other fate and transport calculations whereby pore-water SAR/sodium values are converted to saturated paste concentrations based on bulk density and saturation percentage.

2.3.14 **Subsoil Clay Percentage**

This input parameter describes the average clay content of the subsoil depth interval containing the majority of SAR impacts at the Site. Subsoils with higher clay concentrations generally indicate increased sensitivity to SAR-induced hydraulic conductivity losses, and thus potentially more restrictive guidelines for the soil structure pathway.

2.3.15 **Source Length**

The source length input parameter involves determining the overall length of sodium/SAR-impacted soil relative to background conditions. This primarily influences soil structure risk, since the risk of a water-logged water table is higher for greater impact length and lower for a smaller impact length. The upward migration and dugout irrigation pathways are not influenced by source length (consistent with the SST-chloride module).

2.3.16 **Top of Impact**

The top of impact input parameter influences all three risk pathways, and is determined by comparison to background data. In many cases, the top of impact will be 1.5 m since it is assumed that, at a minimum, the root-zone (top 1.5 m of soil) will be remediated to meet both Tier 1 EC and SAR guidelines. In cases where excavations extend into subsoil, the excavation depth can be used as the top of impact depth.

2.3.17 **Bottom of Impact**

The bottom of impact input parameter is less critical than the top of impact parameter, and is also determined by comparison to background sodium/SAR concentrations. It influences all three risk pathways, with the strongest influence on the upward migration pathway (thicker impacts have greater potential risk of upward migration than thin impacts). In some cases it may be difficult to determine the bottom of sodium/SAR impacts, in which case a maximum bottom of impact of 6 m may be used. Or, alternatively, the bottom of impact for chloride may also be used which will generally be deeper (more conservative) than sodium/SAR due to the reduced transport speed of sodium relative to chloride. Regardless, SAR impacts deeper than 6 m are considered to pose minimal environmental risk due to their distance from the root-zone and potential future dugout depths. In addition, natural lithology changes are frequently encountered at deeper depths which may strongly influence hydraulic conductivity and render SAR-induced effects less important.

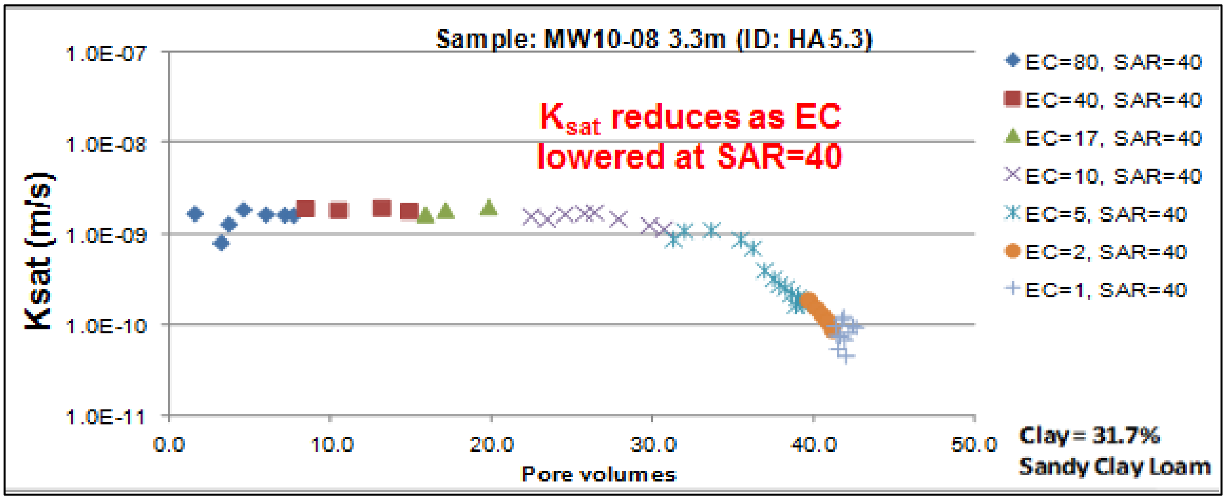
2.4 GUIDELINE OUTPUTS AND CALCULATION ALGORITHMS

After entering all the above input parameters into the SAR/sodium module of the SST (version 3.0 which includes SAR/sodium guidelines), the 'Calculate Guideline' button is clicked and subsoil SAR and sodium guidelines will be generated for the three primary risk pathways where applicable. A brief description of the some of the modeling and calculation assumptions and techniques for each of the three pathways is shown below. The soil structure pathway is shown first, and some of the techniques used for generating a SAR guideline to protect soil structure. The upward migration and dugout irrigation pathways are then described, with guidelines shown on a sodium basis since the primary concern is sodium transport.

2.4.1 **Soil Structure Pathway**

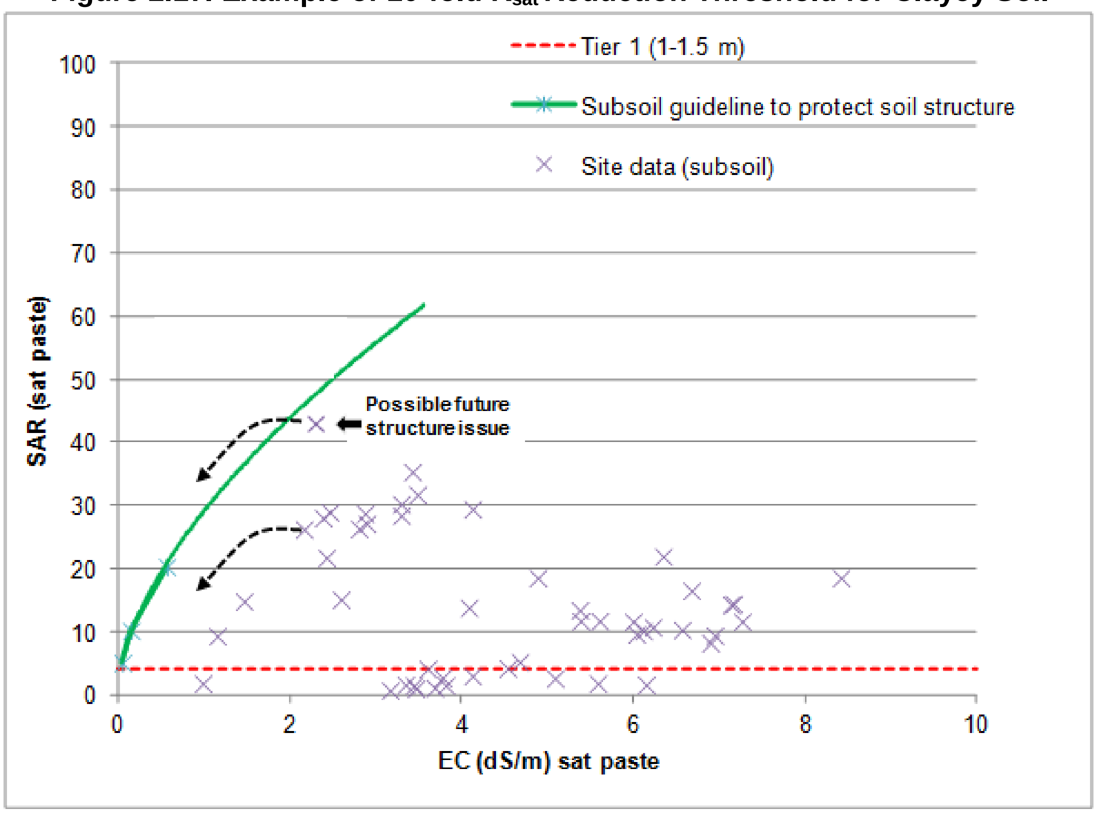
As discussed in the introductory SAR section, elevated SAR can cause dispersion of clay particles, disruption of soil structure, and loss of hydraulic conductivity (K_{sat}). Literature threshold curves previously-described (e.g., Curtin and Steppuhn) have shown EC to have a protective effect on soil structure based on research using repacked soil cores. This literature research has been expanded with additional leaching column experiments on undisturbed Alberta subsoil soil cores to provide maximum relevance to in-situ subsoil conditions. These Alberta experiments have been performed for a variety of soil textures and EC/SAR combinations, and allow an estimation of potential K_{sat} losses as function of texture and EC/SAR. An example of such an experiment is shown in Figure 2.16, showing minimal K_{sat} losses at SAR=40 as solution EC is dropped from 80 to 10 dS/m followed by some K_{sat} losses as EC is reduced to 5 dS/m and then 2 dS/m. For this core, a 10-fold K_{sat} reduction (a typical threshold for potentially acceptable subsoil K_{sat} losses, as previously discussed) was observed at an EC value of 2-5 dS/m for this SAR=40 series.

Figure 2.16. Example of Alberta Leaching Column Experiment Results (Undisturbed Subsoil Core)



When generating a subsoil SAR guideline to protect soil structure, a K_{sat} threshold is chosen by the SST based on soil texture and other factors such as water table depth, drainage rate, impact depth, and dimensions. A typical threshold may be 10-fold, a typical level which may be distinguishable from natural variability and may cause a water-logged root-zone in some cases. A 10-fold K_{sat} reduction threshold for clayey soil is shown in Figure 2.17 based on literature and Alberta leaching column experiments. Site subsoil SAR data should be below/right of threshold for less than 10-fold K_{sat} loss.

Figure 2.17. Example of 10-fold K_{sat} Reduction Threshold for Clayey Soil



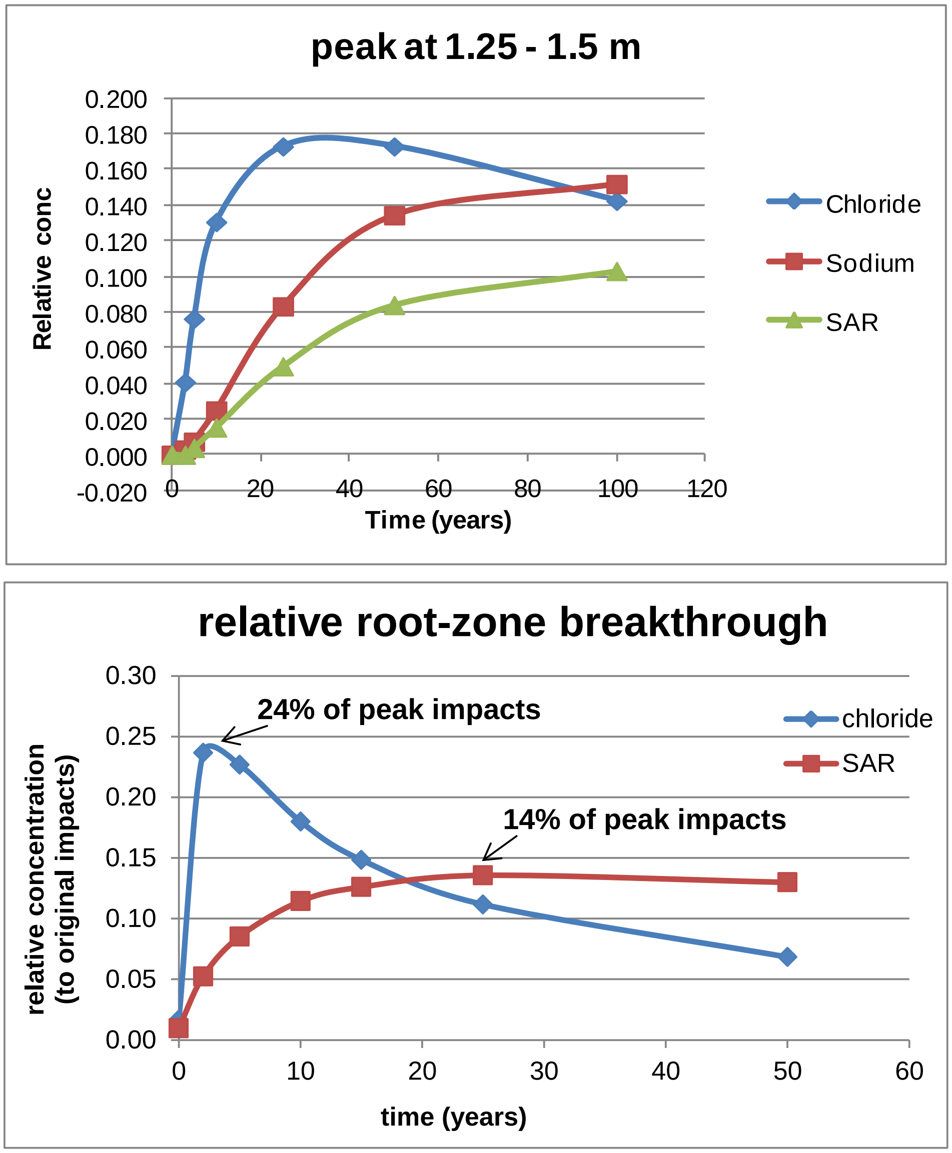
Though present-day soil structure risk may be acceptable, the future EC reduction toward background must be considered since it will often occur faster than SAR reduction toward background. This suggests that some soils which may currently have an EC which is sufficiently protective of soil structure (to the right of this threshold) may in the future have unacceptable reductions if the protective EC is reduced faster than the elevated SAR. This possibility is addressed in the SST by conservatively assuming that EC concentrations in the impact area revert toward background conditions while SAR remains relatively constant. This has the effect of reducing the SAR/EC threshold to a single SAR value based on the background EC of subsoil. This guideline will this be protective of both current-day soil structure risk as well as potential future risk.

2.4.2 **Upward Migration into the Root Zone Pathway**

Elevated SAR/sodium in subsoil may migrate upward into root-zone and cause potential future root-zone Tier 1 SAR exceedances. This is also an important pathway for chloride in the SST. The amount of upward transport is affected by SST input parameters such as climate, soil texture, drainage rate, top of impacts, and bottom of impacts. The acceptable amount of upward transport for a given site is dependent on root-zone salinity and concentrations relative to Tier 1 guidelines, i.e. 'buffers'. The SST protocol currently estimates this upward transport for chloride and it has been modified for SAR/sodium transport.

SAR/sodium tends to transport more slowly than chloride due to the buffering effect of cation exchange reactions. This has been predicted by theory and observed in Alberta leaching column experiments. Leaching of SAR/sodium into the root-zone was modeled to be slower and have a lesser relative peak than chloride. This has been modeled with 'LEACHC' program and is a complex function of water transport, background salinity, cation exchange, and impact characteristics. Figure 2.18 shows two examples of LEACHC modeled data which indicates that relative (normalized) chloride concentrations peak at a greater magnitude than SAR or sodium and over a shorter time-span. In the second example in Figure 2.18, the SAR peak is approximately 55-60% of the magnitude of the chloride peak. This is a fairly typical response, but as noted previously this is a complex function of numerous soil parameters and thus some appropriate simplifying model assumptions have been incorporated into the guideline derivation process.

Figure 2.18. Examples of LEACHC Modeled Data Comparing Chloride, SAR and Sodium



In general, the guideline derivation process for the upward migration pathway involves first estimating the cation composition of the root-zone and/or backfill based on the EC, SAR, and saturation percentage parameters entered into the tool. It is then assumed that calcium/magnesium concentrations will generally stay relatively consistent in the backfill while sodium concentrations, if elevated in subsoil, may potentially migrate upward into the root-zone until a maximum concentration is reached. This transport modeling is based primarily on the SST chloride transport modeling techniques and breakthrough curves, but modified to reflect the slower transport time of sodium relative to chloride as well as the reduction in peak concentrations of sodium/SAR relative to chloride. The maximum allowable sodium concentration in subsoil is then calculated, and expressed as a sodium guideline (on a mg/kg basis) using saturation percentage.

2.4.3 **Dugout Pathway**

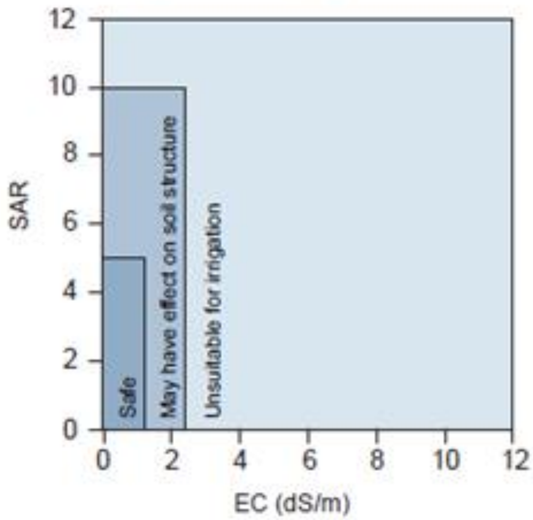
As per the SST protocol for chloride, water may be sourced from a dugout and potentially used for irrigation and livestock watering (in the case of agricultural land use). Though dugouts are intended to collect surface water from broad areas, there is some potential for impacted groundwater (if sufficiently shallow) to mix with this surface water and create potential risk. The relative contributions from surface water and groundwater in the potential future dugout depend on several factors such as soil texture and water table depth. Using standard SST protocol for chloride, the mixing of surface water with groundwater is modeled as a 2:1 mixing (3-fold factor) for coarse soils and as 9:1 mixing (10-fold factor) for fine soils.

Though surface water chloride concentrations are often negligible, relatively low cation concentrations in surface water may have non-negligible effects on SAR calculations since ratios are involved, especially at the mixing ratios used in fine soils. Typical background surface water composition was assumed to be an EC of approximately 0.3 dS/m and SAR of approximately 0.3 based on Alberta Environment (2001), predicting a small (but non-zero) calcium concentration of approximately 30-40 mg/L in surface runoff. The mixing of impacted groundwater with this surface runoff is modeled in the SAR-SST, including the effects of downward sodium transport toward the water table in the case where SAR impacts are above the water table. Note that these SAR migration and mixing calculations are performed on an ion-specific basis by the software tool (eg, calcium, magnesium, and sodium) to maximize the ability to estimate SAR values in irrigation water. These SAR values in irrigation water are then compared to irrigation SAR guidelines described below in order to generate a subsoil sodium guideline.

The water quality guideline for SAR in irrigation water with which the modeled dugout irrigation water composition is compared to is based on guidelines cited in Alberta Agriculture and Rural Development (2010). These are based in-part on the previously-cited Saskatchewan research (Curtin 1994b and Steppuhn 1993), and updated with related research from Alberta (Buckland, 2002). As shown in Figure 2.19, these guidelines are based on SAR and EC combinations rather than solely on SAR due to the protective effects of EC on SAR-induced structural damage. For example, for low EC values (<1 dS/m) a SAR in water of up to 5 is considered 'safe' whereas SAR values of up to 10 may be acceptable with EC values up to approximately 2.5 dS/m. The SST-SAR module determines the appropriate SAR guideline for irrigation water in the dugout based on the estimated EC, and then calculates the appropriate soil sodium concentration estimated not to exceed this guideline.

Figure 2.18. 2010 Irrigation Water Quality Guidelines Combining EC and SAR

Irrigation water quality guidelines for Alberta examine the EC and SAR concurrently according to a threshold concept.



Electrical Conductivity (EC): indicates the level of dissolved salts by measuring the ability of solution to carry an electric current by ions. A high electrical conductivity indicates high salt content, which will stress plants and cause productivity losses.

Sodium Adsorption Ratio (SAR): A measure of the suitability of water as determined by the concentrations of sodium, calcium, and magnesium ions.

2.4.4 **Subsoil Sodium/SAR Guideline Examples**

Once the 'Calculate Guideline' button is pressed the algorithms described above are performed and guidelines are generated for the three pathways. Note that the 'Soil Structure Pathway' guideline is expressed on a SAR basis, while the 'Protection of Root Zone' and 'Irrigation Water' guidelines are shown on a sodium basis.

One example of such guidelines are shown in Figure 2.19, based on a site with coarse soil, relatively low background salinity/sodicity, and relatively thick SAR impacts from 1.5 to 6 m. In this case, the guideline to protect soil structure was determined to be 31 on a SAR basis. The other two pathways showed sodium guidelines of 135 mg/kg (protection of root-zone) and 154 mg/kg (protection of irrigation water), both reflective of this site being relatively sensitive for the pathways considered.

A second example is shown in Figure 2.20, showing a less sensitive site with higher background EC (implying higher background calcium/magnesium concentrations at the same SAR), thinner impacts (3-5 m), and a faster root-zone drainage rate (6 mm/year down rather than 1 mm/year down). In this case, all three guidelines are higher than in the first example due to the modeled reduced risk of upward migration and to soil structure and irrigation water. In this case, a soil structure SAR guideline of 73 is obtained, a sodium guideline of 6892 mg/kg is obtained to protect the root-zone, and a sodium guideline of 845 mg/kg is obtained to protect soil structure. The notable difference in guidelines between the first and second examples demonstrate how various input parameter interact to influence SAR guidelines, with numerous other input parameters (such as soil texture) also having substantial influence as well.

Figure 2.19. Example SAR/Sodium Guidelines for a Relatively Sensitive Site with Thick Impacts

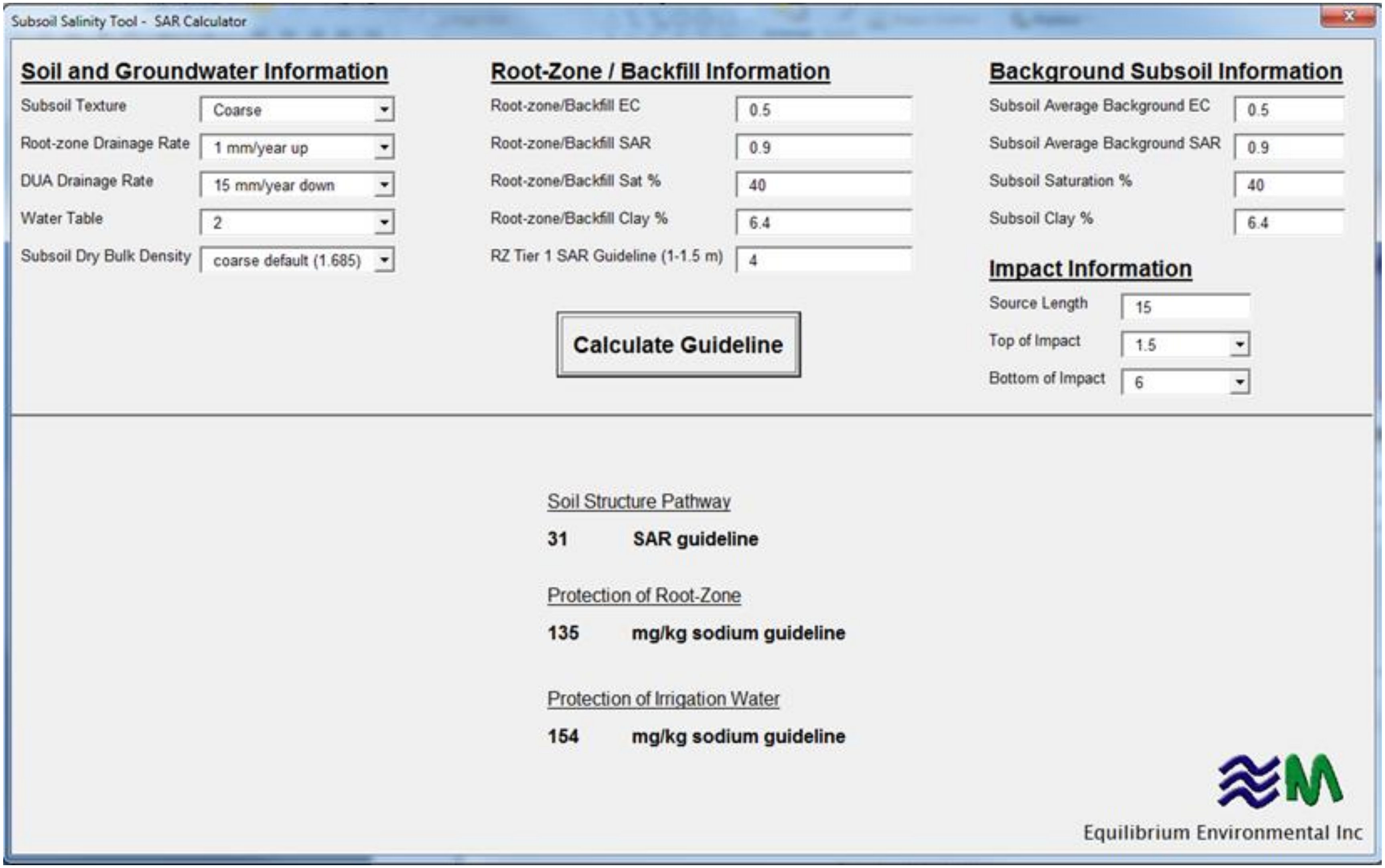
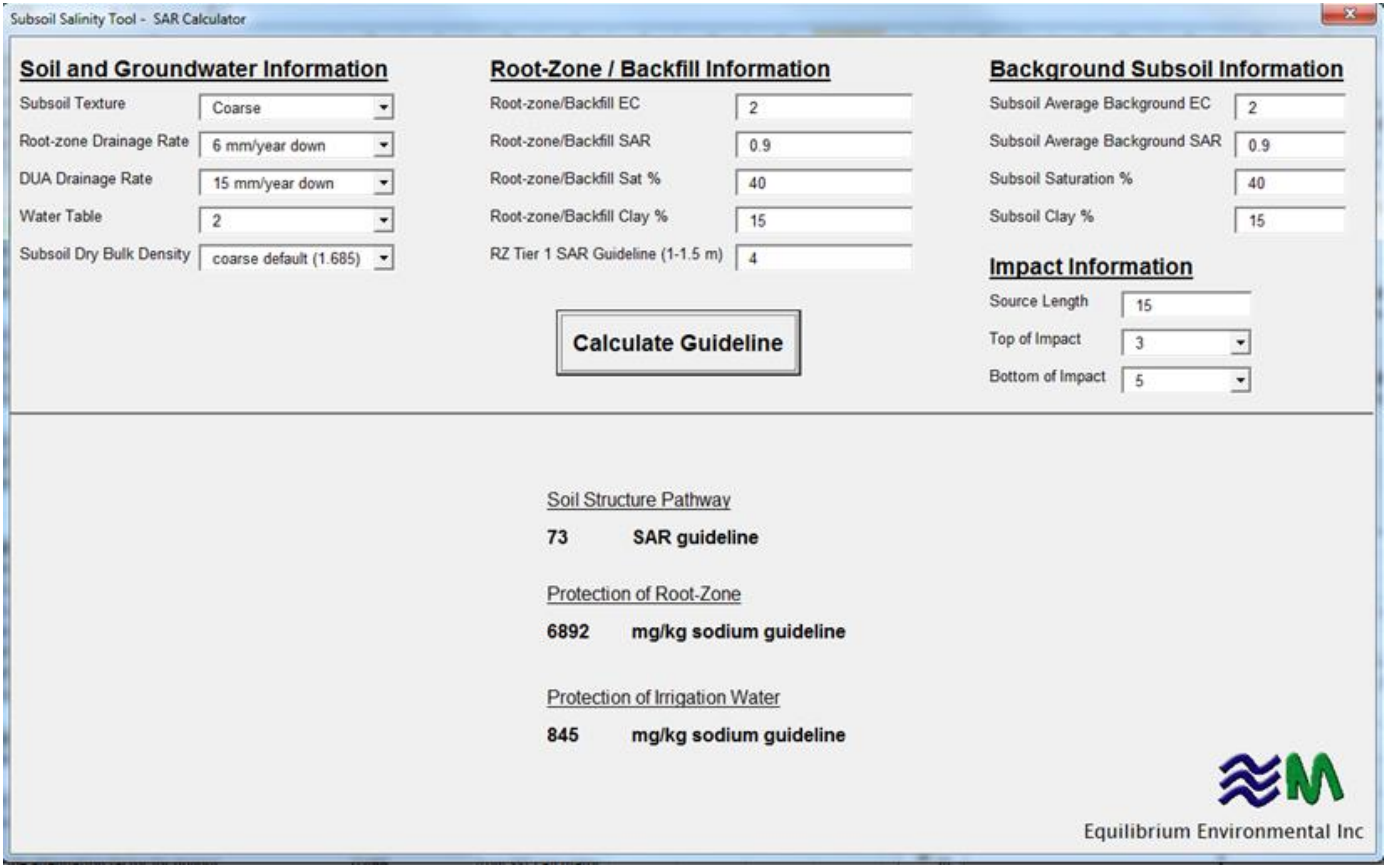


Figure 2.20. Example Sodium/SAR Guidelines for a Less Sensitive Site with Thinner Impacts



3 SUBSOIL SULFATE HELP-FILE INFORMATION

The following section provides a brief overview of general sulfate information (Section 3.1), describes the pathways of concern for generating subsoil sulfate guidelines (Section 3.2), summarizes each of the input parameters utilized in the SST-sulfate module (Section 3.3), and describes the guidelines derived and output parameters generated using the model for each of the pathways of concern (Section 3.4).

3.1 GENERAL SUBSOIL SULFATE OVERVIEW

3.1.1 General sulfate information

Sulfur is a relatively abundant element that occurs in a variety of forms in the environment. One form is sulfate- a fully oxidized inorganic anion derived from sulphur. Soluble sulfate salts (such as sodium sulfate) can contribute toward elevated soil salinity which can reduce vegetative growth and impair groundwater quality. Calcium sulfate (gypsum) is more limited in solubility and its effects on salinity, and is often used by farmers and reclamation practitioners to offset elevated sodium concentrations in sodic soils. Both these salts can originate from natural or anthropogenic sources, and both occur naturally in Western Sedimentary Basin 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 soils followed by replacement with backfill soil where backfill sulfate is substantially lower than background. Commonly, calcium sulfate is used as a calcium-amendment to soil to balance elevated sodium levels at produced water releases though sulfate concentrations are also increased as a result. Drilling muds can contain elevated levels of soluble sulphate salts and historical disposals at drill sumps have resulted in sites experiencing deteriorated soil quality and reductions in vegetation growth. Pipeline installation or other construction practices may also result in elevated sulfate from deeper soils being brought nearer to the root-zone or into shallow subsoil.

There are currently no Tier 1 soil guidelines for sulfate, with root-zone sulfate concentrations currently managed indirectly via EC guidelines which consider the total effect of all anions including sulfate as well as chloride. Below the root-zone, direct contact with plant roots is of reduced importance and ion-specific, risk-based guidelines for subsoil sulfate based on toxicity and fate and transport modeling can be generated using this sulfate module of the SST. Such risk-based subsoil sulfate guidelines will help ensure that any remedial actions are both sufficiently protective but also do not result in the landfilling of needless volumes of soil which may pose minimal risk in-situ.

3.1.2 Sulfate versus chloride toxicity differences

An examination of literature and various soil and groundwater guidelines provides some insight into situations where sulfate and chloride may have different toxicity to various receptors. Some of these comparisons are described below:

Toxicity to plants
Various studies have compared the toxicity of the sulfate anion to the chloride anion to plants, some more directly than others. Interpreting comparisons is complicated by the different measures/units to describe sulfate and chloride, with some studies comparing them on a per mass basis, others on a per mol basis, and others on a per charge (milliequivalent) basis. The United States Salinity Laboratory (1954) states that chloride is generally more inhibitory to plant growth than sulfate when compared on a weight basis, but that this difference tends to disappear when expressed on an osmotic basis such as milliequivalents per liter. There may also be some specific ion effects which differ between chloride and sulfate, but the direction of these trends appears to vary based on conditions and plant species tested. Overall, this has resulted in the general use of electrical-conductivity-based (EC-based) guidelines for root-zone soil and irrigation water to protect plants from the effects of sulfate and other salts such as chloride.

Toxicity to humans
Insight into the human toxicity of sulfate relative to chloride can be obtained by examining the human drinking water guidelines. The CCME human drinking water guideline for chloride is 250 mg/L and is based on taste (an aesthetic objective) rather than toxicity. In contrast, the CCME human drinking water guideline for sulfate is 500 mg/L, and is based on a combination of taste as well as the potential to cause diarrhea (diarrhea in children was noted at magnesium sulfate concentrations of 600 mg/L, CCME/CCREM (1987)).

Toxicity to livestock
Livestock watering guidelines tend to be based on EC or TDS, with a guideline of 3,000 mg/L TDS shown in CCME/CCREM (1987) and used for ‘good’ quality water in the SST-chloride module. There is no distinct chloride guideline for livestock water, suggesting chloride effects are primarily related to the osmotic effects described by these EC/TDS guidelines. In contrast, livestock water also has a sulfate guideline of 1,000 mg/L which is more restrictive than the general TDS guideline. At these concentrations diarrhea has been reported in young animals (CCME/CCREM 1987), suggesting sulfate may be more toxic to livestock than chloride on a comparable weight basis.

Toxicity to aquatic life
The understanding of the toxicity of chloride and sulfate to aquatic life is evolving, due in part to confounding factors such as water hardness and the presence of other cations. The CCME aquatic life guideline for chloride has recently changed from 230 to 120 mg/L, whereas there is currently no CCME or Alberta aquatic life guideline for sulfate. Of note is that water hardness appears to be a modifier for sulfate toxicity as per recent research from British Columbia (Elphick et al 2011), which may factor into future guideline development.

3.1.3 **Sulfate versus chloride transport differences**

Though sulfate salts are generally soluble, there are some differences in solubility and other transport properties which affects sulfate modeling compared to chloride. A brief overview of these differences from literature and Alberta research is shown below.

Solubility

Common chloride salts are essentially fully soluble, with sulfate salts of sodium and magnesium also highly soluble. In contrast, gypsum (hydrated calcium sulfate) has limited solubility of approximately 2000 mg/L, or equivalent to approximately 1,400 mg/L sulfate. This limited gypsum solubility has relevance to fate and transport modeling, especially given the concentrations of calcium typically present in background in sorbed and/or dissolved states.

Contribution to salinity

Sulfate has a different molecular weight and charge compared to chloride, with a molecular weight of 96 g/mol (compared to 35 g/mol for chloride) and a charge of -2 (compared to -1 for chloride). This makes sulfate approximately 30% less charged on a per mass basis than chloride (48 mg/meq for sulfate vs 35 mg/meq for chloride), and thus an equivalent mass of sulfate will contribute less to EC than chloride. When expressed on a per-charge basis (meq/kg or meq/L), soil salinity regressions also show sulfate to contribute somewhat less than chloride to electrical conductivity in some cases.

Biological / chemical stability

Chloride does not typically undergo chemical or biological transformations in soil, and is generally considered an ‘inert’ tracer. In contrast, sulfate may in some cases be generated or depleted by chemical or biological processes such as elemental sulfur oxidation or biological sulfate reduction.

Sorption

Chloride is considered to exhibit negligible sorption and thus shows an effective K_d (partitioning coefficient) of approximately zero. Sulfate is known to undergo some sorption reactions in soil based on literature (Aylmore, 1967 and Sokolova, 2008), though the magnitude and significance of these sorption reactions varies based on concentration and conditions.

Precipitation

Due to the high solubility, chloride does not typically undergo precipitation reactions. In contrast, sulfate has been shown theoretically and experimentally to undergo precipitation reactions under various conditions. One situation this may occur is when transporting elevated sulfate concentrations through calcium-rich soils where the precipitation of gypsum following sodium/calcium exchange reactions can be important.

Retardation

Leaching experiments on Alberta soil cores showed examples of reduced (retarded) sulfate transport relative to chloride. This is likely due to combination of sorption and precipitation reactions, with precipitation likely the primary effect based on literature and transport modeling.

Overall, these differences between sulfate and chloride tend to result in a reduced sulfate transport rate relative to chloride which is approximated in the sulfate module of the SST. Effects such as sulfate biological/chemical transformations are not considered in the tool and considered less predictable and/or important under most relevant conditions.

3.2 Pathways of Concern for Assessing Sulfate Risk

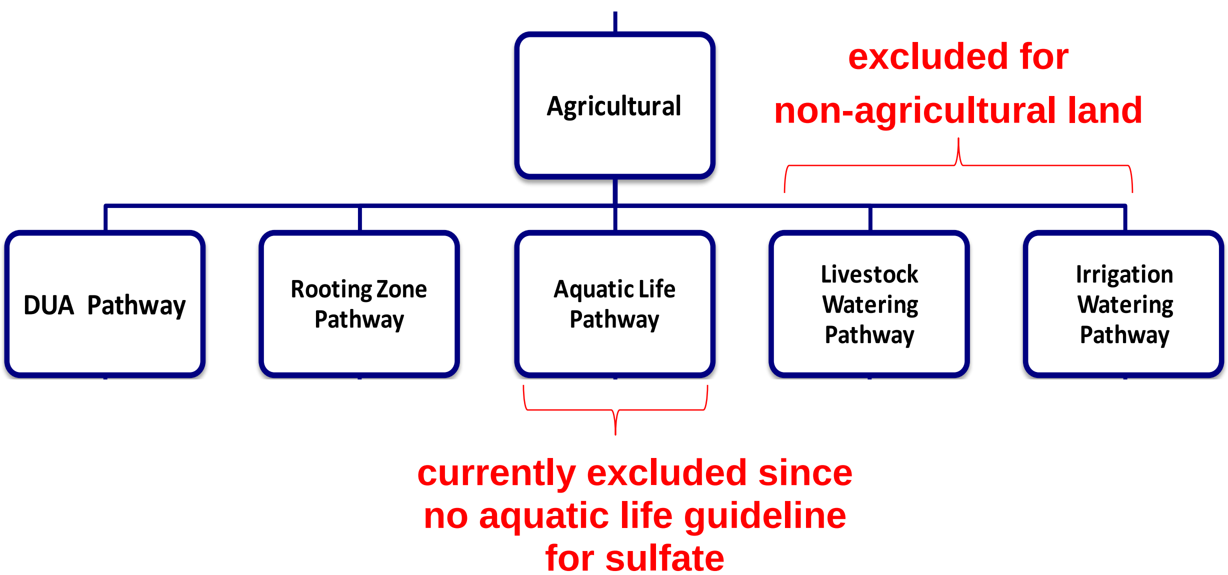
3.2.1 Primary pathways

The standard chloride version of the SST considers the following five pathways for generating subsoil chloride guidelines. Depending on land use, one guideline is generated for each of the above pathways and the lowest guideline is taken is the overall constraining guideline for the Site.

- Protection of the root-zone (from upward chloride migration)
- Protection of livestock water (from a potential dugout)
- Protection of irrigation water (from a potential dugout)
- Protection of a domestic use aquifer (DUA) (from downward leaching)
- Protection of aquatic life (from lateral transport)

For subsoil sulfate, a similar set of pathways is relevant for evaluating risk and generating guidelines. These primary pathways for subsoil sulfate are shown conceptually in Figure 3.1, consisting of the same five pathways as for chloride except the aquatic life pathway which is currently shown as excluded due to the current lack of an aquatic life water quality guideline for sulfate. Note that this pathway may be incorporated in the future if an aquatic life water quality guideline for sulfate is introduced. The figure also shows the provision that irrigation water and livestock water be considered solely for agricultural land use, with the exception that livestock water may be considered on specific grazing leases in natural areas.

Figure 3.1. Conceptual Diagram of the Receptors Considered for Sulfate Risk



As in the SST chloride module, guidelines for pathways such as upward migration into the root-zone and irrigation or livestock water from a dugout are generated by comparing modeled future sulfate concentrations to relevant Tier 1 guidelines such as root-zone soil EC guidelines or irrigation water or livestock water guidelines. Similarly, the DUA pathway has modeled future sulfate concentrations in the DUA compared again the human drinking water guideline. The aquatic life pathway involves transport modeling toward aquatic life receptors and comparison to aquatic life guidelines, but is currently excluded for sulfate as described below.

3.2.2 **Excluded pathways**

Currently there is no Alberta ESRD or CCME aquatic life guideline for sulfate. As such, the aquatic life pathway is not considered in current SST implementation for deriving sulfate guidelines. Potential future development of such a guideline would require evaluating the implications of background sulfate concentrations potentially exceeding such a surface water guideline on a pore-water basis at point-of-discharge to aquatic life receptors. An ‘incremental risk’ approach whereby increases in sulfate concentrations above background levels would likely be useful for this pathway if introduced in the future.

3.3 INPUT PARAMETERS

A number of site-specific input parameters are required to generate subsoil sulfate guidelines, some of which are based on site data while others may be default values. In general, the current version of the subsoil sulfate module requires input parameters in these five categories:

- site information
- soil and groundwater information
- background subsoil information
- root-zone/backfill information
- impact information

Figure 3.2 presents a screenshot of the input page for the sulfate module, including the five general categories of input parameters. Specific input parameters are listed below, with a more detailed description of each provided in the following section.

Site Information

- Tier selection
- Land use

Soil and groundwater information

- Texture
- Root-zone Drainage Rate
- DUA Drainage Rate
- Water Table

Background subsoil information

- Background TDS in shallow groundwater
- Background subsoil sulfate
- DUA depth or maximum depth of drilling

Root-zone / backfill information

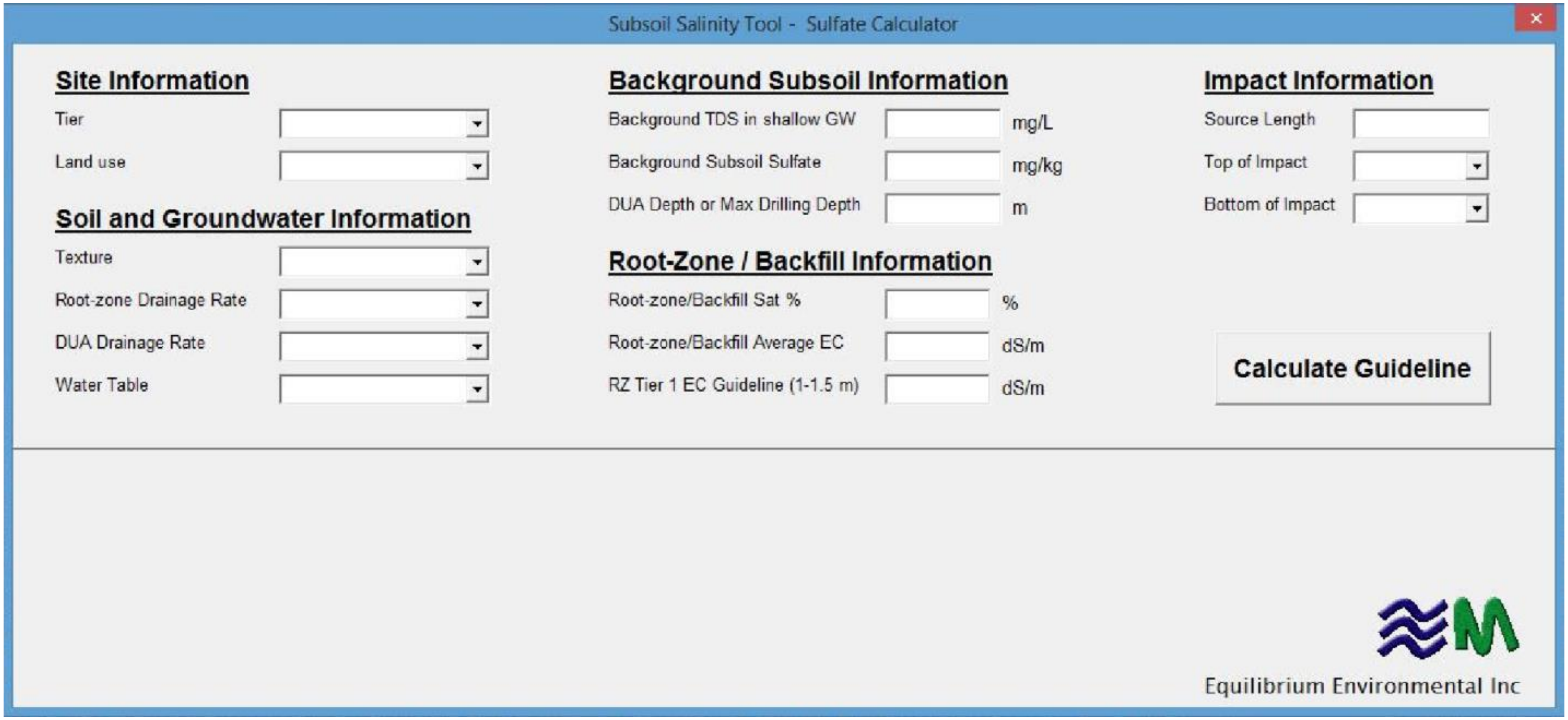
- Root-zone/Backfill Saturation Percentage
- Root-zone/Backfill EC
- Root-zone Tier 1 EC Guideline (1-1.5m)

Impact information

- Source Length
- Top of Impact
- Bottom of Impact

Note that some of these input parameters (such as Tier selection, root-zone and DUA drainage rates) are also present in the chloride module of the SST and can be directly populated from these pre-determined values. Other input parameters are specific to subsoil sulfate and will need to be entered in all cases.

Figure 3.2. Screenshot of the Input Parameters for the Sulfate Calculator



3.3.1 Tier Selection

The Tier selection options are Tier 2A and Tier 2B as per the chloride module of the SST software. Tier 2A is used when monitoring wells are not present and groundwater information is estimated from a combination of site observations, soil data, and default values. Tier 2B uses site-specific groundwater information from monitoring wells and allows over-riding default parameters under various circumstances.

3.3.2 Land Use

Land use primarily affects which pathways are active, such as the exclusion of livestock and irrigation water pathways for non-agricultural land. One exception is the consideration of livestock water on grazing leases in natural areas. Root-zone EC guidelines may also influenced by land use if in commercial or industrial areas.

3.3.3 Texture

Subsoil texture is a standard input parameter from the SST-chloride module and describes whether subsoil at the site is generally fine-grained or coarse-grained based on clay content. As per standard SST protocol, clay content less than 18% is considered ‘coarse’ and clay content above 18% is considered ‘fine. Subsoil texture (along with climate and potentially vertical gradient) influences drainage rates as described below. It also influences mixing calculations for the dugout irrigation and livestock watering pathways.

3.3.4 Root-zone Drainage Rate

The root zone drainage rate describes the speed with which water is draining downward out of the root zone or upward back up into the root zone. This depends primarily on climate, soil texture, and vertical gradients, and will be pre-determined by the SST-chloride module.

3.3.5 DUA Drainage Rate

The DUA drainage rate is determined in the similar manner as the root-zone drainage rate, and describes the drainage rate assumed when modeling downward sulfate transport. This is of primary importance for sulfate transport toward a DUA, though the rate of potential downward movement is also of relevance for other pathways such as the dugout pathways. This parameter will generally be higher than the root-zone drainage rate (for conservatism), and will be automatically pre-determined by the chloride module.

3.3.6 Water Table

The water table depth influences severael risk and transport calculations including the dugout pathways and upward migration. Water table can be either estimated from field observations and borehole logs (in a ‘Tier 2A’ scenario) or directly from monitoring well data (from a ‘Tier 2B’ scenario). This input parameter will normally be automatically determined from the chloride module.

3.3.7 Background TDS in Shallow Groundwater

This parameter is determined in the same manner as in the SST-chloride module, either from soil information (if Tier 2A) or from groundwater information (if Tier 2B). It is used for the two dugout pathways, and influences the background chemistry used to determine ‘buffers’ for both irrigation and livestock watering.

3.3.8 Background Subsoil Sulfate

Background sulfate concentrations can vary from site to site and region to region, and is a factor which is considered in several guideline calculations. This input parameter describes sulfate concentrations in background subsoil over a depth range similar to the impacts. Since some of the sulfate guidelines are calculated using an ‘incremental risk’ approach above background concentrations, it is necessary to characterize background sulfate sufficiently to avoid generating guidelines which are below background concentrations.

3.3.9 DUA Depth or Maximum Drilling Depth

This parameter is the same as for the SST-chloride module, and describes the depth at which a potential DUA has been observed at the site based on either soil logs or monitoring well data. In many cases, a potential DUA will not have been observed to the maximum depth of drilling, in which case the maximum depth of drilling is used for this input parameter. This essentially assumes a DUA may be immediately below the deepest depth drilled.

3.3.10 Root-zone/Backfill Average EC

The salinity of the root-zone is of prime importance in estimating the potential risk of upward migration of sulfate from subsoil into the root-zone. Since it is necessary for the root-zone to meet appropriate Tier 1 guideline for both EC and SAR, in some cases the EC of backfill material will be used here instead if the root-zone was sufficiently impacted that it will need to be excavated and backfilled in order to meet Tier 1 criteria.

3.3.11 Root-zone/Backfill Saturation Percentage

Tier 1 EC guidelines for the root-zone are all determined from saturated paste extracts, and thus saturation percentage is a required input parameter. Saturation percentage is used to convert between pore water concentrations and saturated paste EC values during various guideline calculations.

3.3.12 Root-zone Tier 1 EC Guideline (1-1.5m)

Based on background EC statistics for the 1-1.5 m depth interval, a Tier 1 root-zone EC guideline can be determined to provide a limit on potential future sulfate migration into the root-zone. This Tier 1 EC guideline for the root-zone will generally be either 3 (‘Good’), 5 (‘Fair’), 10 (‘Poor’), or >10 (‘Unsuitable’).

3.3.13 **Source Length**

The source length input parameter involves determining the overall length of sulfate-impacted subsoil relative to background conditions. This primarily influences DUA risk since larger impacts result in reduced estimated dilution upon entering the DUA after vertical leaching. The upward migration and dugout pathways are not influenced by source length (consistent with the SST-chloride module).

3.3.14 **Top of Impact**

The top of impact input parameter influences all four risk pathways, and is determined by comparison to background data. In many cases, the top of impact will be 1.5 m since it is assumed that, at a minimum, the root-zone (top 1.5 m of soil) will meet Tier 1 EC and SAR guidelines (potentially as a result of root-zone excavation). In cases where excavations extend into subsoil, the excavation depth can be used as the top of impact depth for evaluating residual subsoil sulfate concentrations.

3.3.15 **Bottom of Impact**

The bottom of impact input parameter is also determined by comparison to background sulfate concentrations. It influences all four risk pathways, with thicker impacts having greater risks to the various receptors and thus lower guidelines. In some cases it may be difficult to determine the bottom of sulfate impacts due to limited background information at depth, in which case alternate methods or conservative assumptions (such as assuming similar impact depths as chloride, if present) may be used.

3.4 GUIDELINE OUTPUTS AND CALCULATION ALGORITHMS

After entering all the above input parameters into the sulfate module of the SST, the ‘Calculate Guideline’ button is clicked and subsoil sulfate guidelines will be generated for the four primary risk pathways where applicable. A brief description of the some of the modeling and calculation assumptions and techniques for each of the four pathways is shown below.

3.4.1 Upward Migration into the Root Zone Pathway

This pathway protects root zone soils from future upward migration of sulfate from the subsoil into the root zone. The guideline generated for this pathway involves calculation of an EC buffer determined from the Tier 1 root-zone EC guideline compared to the root-zone/backfill average EC. Sulfate transport is then modeled to ensure that future-day root-zone Tier 1 exceedances of EC are unlikely to occur. Upward-migration sulfate guidelines are typically higher than upward migration chloride guidelines due to the relatively lower contribution of chloride to EC on a mg/kg basis (e.g., 1000 mg/kg chloride is approximately equivalent to 1,350 mg/kg sulfate on a charge basis), as well as the need to incorporate background sulfate concentrations into the calculated guidelines. Peak sulfate concentrations are also modeled to be reduced and slowed by sorption/precipitation reactions, also resulting in increased sulfate guidelines compared to chloride.

3.4.2 Domestic Use Aquifer Pathway

The DUA pathway protects groundwater which may potentially be used as a drinking water source at some point in the future. The DUA guideline is calculated in a manner similar to existing chloride protocol, but with a drinking water guideline of 500 mg/L for sulfate rather than 250 mg/L for chloride. The lower transport rate of sulfate relative to chloride reduces relative breakthrough concentrations over equivalent time horizons, resulting in relatively higher guidelines for sulfate. An ‘incremental risk’ approach has also been implemented whereby generated subsoil sulfate guidelines are added to background subsoil sulfate concentrations such that the additional sulfate concentrations (above background) do not result in DUA sulfate concentrations increasing by more than 500 mg/L.

3.4.3 Livestock Watering Pathway

This pathway protects waters which have the potential to be ingested by livestock. The current chloride-SST livestock watering guidelines are on mg/L TDS basis, with categories from ‘Good’ (<3000 mg/L) to ‘Marginal’ (3000-7000 mg/L) to ‘Unusable’ (>7,000 mg/L). Alberta ESRD and CCME also have a livestock watering guideline of 1,000 mg/L sulfate which is more restrictive and has been implemented into the subsoil sulfate calculations. Since background groundwater concentrations in subsoil will often exceed 1,000 mg/L sulfate, an incremental risk approach is currently implemented to be consistent with the DUA pathway. The standard adjustment factors used in the SST-chloride module for mixing with surface water are also used here, comprised of a 3-fold factor for coarse soils and a 10-fold factor for fine soils.

3.4.4 **Irrigation Watering Pathway**

This pathway protects dugout waters which have the potential to be used to irrigate crops, and are based on the same irrigation salinity guidelines as in the SST-chloride module. Irrigation water guidelines are normally based on EC and/or TDS as predictors of plant risk. The standard chloride-SST protocol (eg, mixing with surface water into dugout) is utilized for sulfate with the guidelines adjusted for the reduced contribution of sulfate to EC on a mg/L basis.

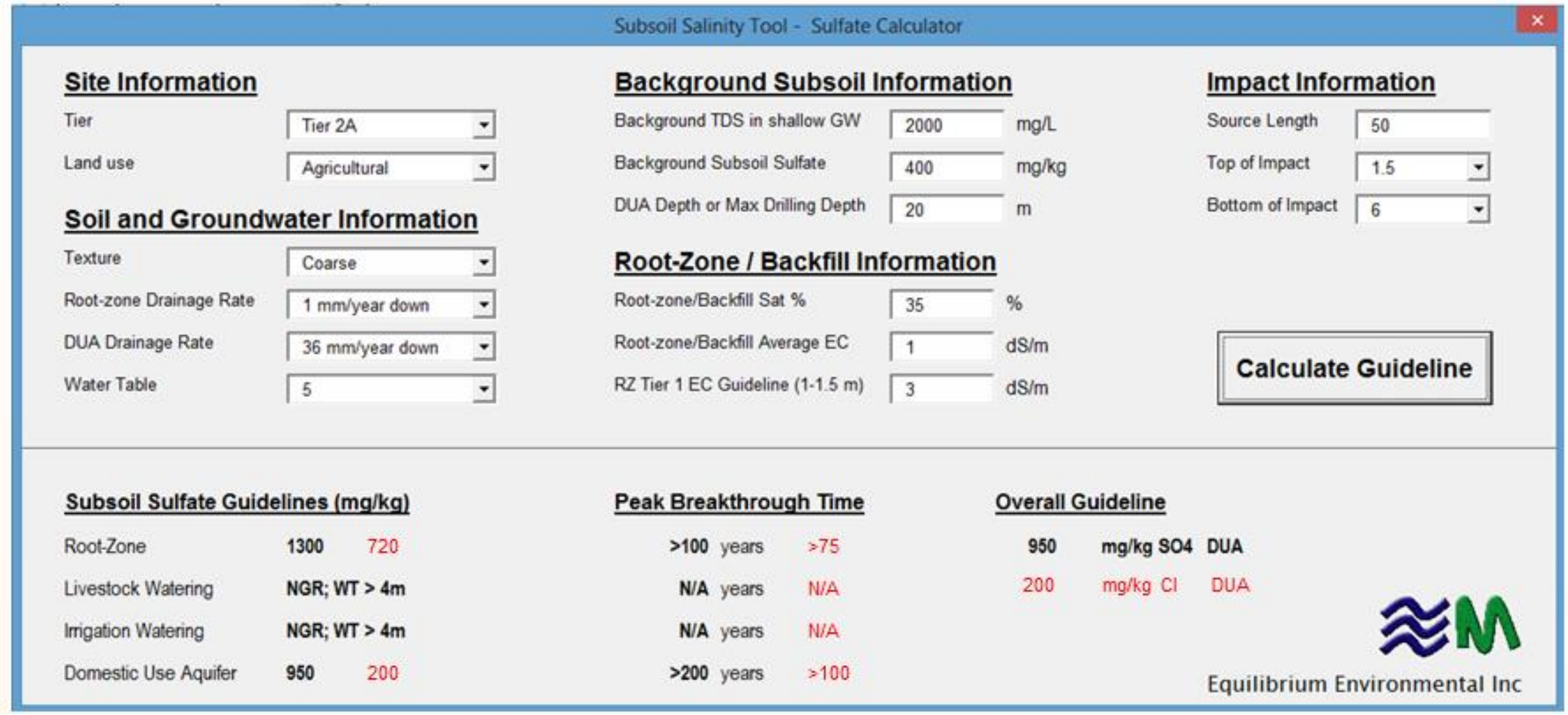
3.4.5 **Subsoil Sulfate Guideline Examples**

Once the ‘Calculate Guideline’ button is pressed the algorithms described above are performed and subsoil sulfate guidelines are generated for the current four pathways.

One example of such guidelines is shown in Figure 3.3, based on a hypothetical site with coarse soil, relatively low background soil salinity in the root-zone (‘Good’ category for EC), background subsoil sulfate of 400 mg/kg, and relatively thicker sulfate impacts from 1.5 to 6 m. In this case, the guideline to protect the DUA was most constraining at 950 mg/kg sulfate, with the next lowest guideline (root-zone) at 1300 mg/kg sulfate. Note that the livestock and irrigation water guidelines are excluded in this case because the water table is deeper than 4 m as per standard SST-chloride protocol. Peak breakthrough times are also shown for each of the relevant pathways. For this example, the comparable chloride guidelines and breakthrough times are shown in red text for comparison purposes, but will not be shown in the tool itself. In each case, the sulfate guidelines are shown to be higher than the comparable chloride guidelines for the various reasons described earlier. In particular, sulfate guidelines will always be higher than the background sulfate concentration due to the incremental risk calculations performed.

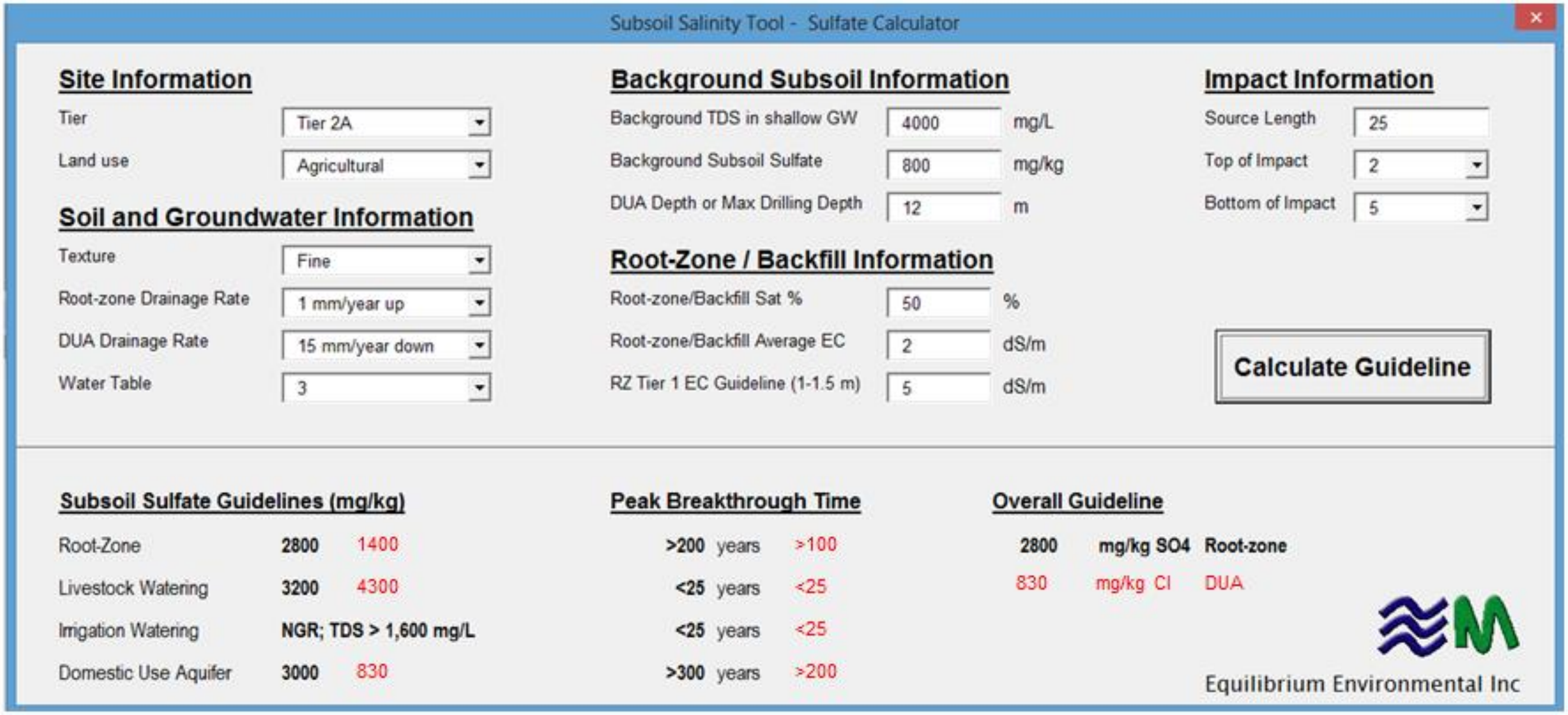
A second example is shown in Figure 3.4, showing a fine-textured site with higher background EC/salinity. The combination of lower DUA drainage rate and higher higher root-zone EC buffer results in higher subsoil sulfate guidelines for both the DUA and root-zone pathways (3000 mg/kg and 2800 mg/kg, respectively). The water table was also changed to 3 m in this case, thus activating the livestock watering pathway with a guideline of 3200 mg/kg. The irrigation water pathway was also activated by this water table change, but was re-excluded due to elevated background TDS above acceptable irrigation cutoff levels as per standard SST-chloride protocol. The notable difference in guidelines between the first and second examples demonstrates how various input parameter interact to influence sulfate guidelines, with numerous other input parameters also having substantial influence as well.

Figure 3.3. Example Sulfate Guidelines for a Coarse Site with Thicker Impacts



Note: chloride guidelines and breakthrough times shown in red text for comparison purposes only (not shown in actual tool output)

Figure 3.3. Example Sulfate Guidelines for a Fine Site with Thinner Impacts



Note: chloride guidelines and breakthrough times shown in red text for comparison purposes only (not shown in actual tool output)

4 CLOSURE

This document was prepared by Equilibrium Environmental Inc. under contract to the Petroleum Technology Alliance of Canada (PTAC) solely for the purpose of providing information relevant to the development of subsoil salinity guidelines. 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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