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Application of the Waxman Smits Model for Estimating Groundwater Quality from

In-Situ Measurements of Electrical Conductivity

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Application of the Waxman Smits Model for Estimating Groundwater Quality From In-Situ Measurements of Electrical Conductivity" submitted by John Kasimir Leszkowicz in partial fulfillment of the requirements for the degree of Master of Engineering.

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ABSTRACT

The Waxman Smits model suggests a non-linear relationship between the bulk resistivity of formations containing clay minerals and the resistivity of the fluid in the pores. This model is applied to a site involving fine-grained soil deposits containing approximately 25% clay, and where shallow groundwater has been impacted by industrial activities. Quantitative estimates of pore water electrical conductivity from bulk electrical conductivity measurements in glacial till deposits can be made using a reasonable fit of data routinely collected during environmental site investigations. Data required to apply the Waxman Smits model includes: pore water electrical conductivity, cation exchange capacity, density and porosity of site soils, and interpreted electrical resistivity survey data. The most sensitive model parameters are: porosity, cation exchange capacity, cementation factor, and degree of saturation. Calibration and use of this model on sites with a history of subsurface disturbance or geologic heterogeneity is difficult.

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iv

TABLE OF CONTENTS

Approval pagei	ii
Abstractii	i
Acknowledgementsi	v
Table of Contents	v
List of Tables	/i
List of Figuresv	ii
List of Symbols, Abbreviations and. Nomenclaturevii	ii
1. INTRODUCTION1	1
1.1 Background	1
1.2 Goals and Objectives	5
1.3 Organization	3
2. LITERATURE REVIEW	7
2.1 Petrophysics	7
2.2 Electrical Resistivity Imaging	Э
2.3 Electrical Conductivity of Aqueous Solutions	כ
2.4 Strengths and Weaknesses of Some Published Clay Conductivity Models	3
2.5 Rationale for Selection of the Waxman Smits Model	1
3. APPLICATION OF THE WAXMAN-SMITS MODEL	3
3.1 Site Description	3
3.2 Groundwater EC Measurements	3
3.3 Bulk EC Data Collection and Interpretation 27	7
3.4 Fitting of the GPRP Site Data to the Waxman Smits Model	I
3.5 Discussion on the Fit of the Model 36	3
3.6 Sensitivity Analysis of Waxman Smits Parameters	3
3.7 Significance of Selected Parameters 42	2
3.7.1 Clay Content Based on Cation Exchange Capacity	2
3.7.2 Degree of Saturation	ł
3.8 Sensitivity of Using the Waxman Smits Model to Predict σ_w from σ data	5
3.9 Usefulness of the Waxman Smits Model 56	3
3.9.1 Porosity	,
3.9.2 Cation Exchange Capacity 58	3
3.9.3 Saturation	3
3.9.4 Cementation Factor 59)
4. CONCLUSIONS AND RECOMMENDATION)
5. LIST OF REFERENCES	

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LIST OF TABLES

Table 1: Strengths and Weaknesses of Clay Conduction Models Considered	. 20
Table 2: Results of CEC Laboratory Analyses	. 24
Table 3: Thicknesses of the Subsurface Layers used in the 3-D ERI	. 30
Table 4: Details of August 2001 Collocated Data Points from the GPRP Research Site	. 33
Table 5: Summary of Sensitivity Analysis With Respect to σ	. 41
Table 6: σ_w Prediction Sensitivity Analysis Summary	54

LIST OF FIGURES

Fig. 1: EC Measurement from a Push Conductivity Tool 2)
Fig. 2: Log (EC at 8°C) versus Log (Ionic Charge Concentration) in Research Site Groundwater	
Samples (from Toews, 2001) 4	ļ
Fig. 3: Photograph of Electrode Array9)
Fig. 4: Photograph of Electrical Resistivity Survey Data Acquisition Set Up 10)
Fig. 5: Temperature Correction of Groundwater EC Measurements 12)
Fig. 6: Plan of Research Site Indicating Electrical Resistivity Imaging (ERI) Survey Zones)
Fig. 7: ERI Data Collection at the Gas Plant Remediation Project Site	}
Fig. 8: Cross-Section showing Variation in 3-D ERI Bulk EC Data)
Fig. 9: Search Criteria for 3-D ERI Bulk EC Data Nearest a Piezometer	
Fig. 10: Selected Fit of Waxman Smits Model to EC Data from GPRP Site	ì
Fig. 11: Scaled Sensitivities With Respect to σ)
Fig. 12: Significance of Clay Content as Indicated by CEC 43	;
Fig. 13: Significance of Degree of Saturation, S _w	
Fig. 14: σ_w Prediction Sensitivity Analysis: EC with Respect to "a"	ļ
Fig. 15: σ_w Prediction Sensitivity Analysis: EC with Respect to Cementation Factor, m	i
Fig. 16: σ_w Prediction Sensitivity Analysis: EC with Respect to Porosity, Φ	,
Fig. 17: σ_w Prediction Sensitivity Analysis: EC with Respect to c_1	ì
Fig. 18: σ_w Prediction Sensitivity Analysis: EC with Respect to c_2)
Fig. 19: σ_w Prediction Sensitivity Analysis: EC with Respect to c_3)
Fig. 20: σ_w Prediction Sensitivity Analysis: EC with Respect to ρ_s	
Fig. 21: σ_w Prediction Sensitivity Analysis: EC with Respect to CEC	
Fig. 22: σ_w Prediction Sensitivity Analysis: EC with Respect to S _w	;
Fig. 23: σ_w Prediction Scaled Sensitivities	
Fig. 24: Affect of σ _w Prediction Due to Heterogeneous Porosity	,

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

The following symbols [and units] are used in this thesis:

- a = empirical constant used to determine the formation resistivity factor, [dimensionless];
- B = equivalent conductance of clay exchange cations (sodium) as a function of σ_w at 25° C, [(S/m)/ (meq/ml)];
- c₁ = maximum equivalent ionic conductance of the sodium exchange ions, [dimensionless]
- c₂ = empirical constant, [dimensionless];
- c_3 = determined by the rate of increase of the counter ion mobility from that at zero σ_w up to its constant value at very high values of σ_w , [dimensionless];
- CEC = Cation Exchange Capacity, [meq/100g (equivalent to cmol/kg)];
- EC = Electrical conductivity [S/m];
- ERI = Electrical Resistivity Imaging;
- F = Formation resistivity factor, [dimensionless];
- GPRP = Gas Plant Remediation Project;
- m = cementation exponent, [dimensionless];
- n = saturation exponent, [dimensionless];
- CPT = Cone Penetrometer Test (Push Conductivity Tool is a specialized type of CPT)
- Qv = volume concentration of clay exchange cations, [meq/ml];
- S_w = degree of saturation with water, [dimensionless fraction];
- ϕ = porosity, [dimensionless fraction];
- σ = electrical conductivity of the formation, [S/m];
- σ_w = electrical conductivity of the pore-water, [S/m]; and
- ρ_s = dry density of the soil particles, [g/ml].

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1. INTRODUCTION

1.1 Background

In situ remediation and natural attenuation of contamination have become popular methods for managing contaminated sites. However, before implementation of these kinds of remediation programs, characterization of subsurface contamination is required. After implementation, monitoring the progress of remediation is needed to assess its effectiveness. Most commonly used methods to characterize or assess subsurface contamination involve collecting representative samples of soil and analysis of targeted species in the laboratory. Groundwater samples are also collected for laboratory analyses, most often via the installation of monitoring wells. Significant problems often arise during sample collection and analysis in the laboratory: sampling is destructive in the sense that the ground surface must be disturbed and soil must be excavated in order to remove the samples; the measurements of groundwater quality represent water quality at only a limited number of point sample locations; and the results must be interpolated over a large area. Sampling and analysis of soils groundwater are time consuming and expensive. Often, contamination is associated with high ionic content in groundwater that makes the contaminated zones electrically more conductive than uncontaminated background areas. In addition, as remediation progresses, ionic content and subsequently electrical conductivity (EC) will change.

In an attempt to be more effective in characterization and assessment of contamination, in situ test probes have been developed, such as those used in the cone penetration test (CPT) sometimes called a push tool, to determine the electrical conductivity of soil-fluid systems. CPT is very useful to validate results of Electrical Resistivity Imaging. The main limitations are cost, and horizontal coverage and depth of penetration. Also, a CPT only provides one dimensional electrical conductivity data which makes interpretation difficult when the actual distribution of

contaminants is heterogeneous. Figure 1 is a plot of the electrical conductivity versus elevation or depth of penetration of a CPT probe pushed at a research site in the summer of 2000. The variability of the EC data derived from the CPT is significant over a short vertical distance. This makes it difficult to select a representative value for EC and to consider this hard data. The technique is often used to infer relative changes in EC which may be caused by changes in clay mineralogy (stratigraphy) or due to changes in groundwater conductivity (potential contamination).

Fig. 1: EC Measurement from a Push Conductivity Tool



Push Tool Run ID: PCT0007

2

Other researchers have developed different in situ test probes, such as Ferré et al. (1998) who describe the use of time-domain reflectometry probes. However, these kinds of tools also have severe limitations in heterogeneous formations and provide one-dimensional data.

EC of the soil-fluid system is not only a function of soil and pore fluid, but also of the chemical composition, grain size, and shape of the soil particles (Kaya and Fang, 1997). Furthermore, many ground water and soil contaminants and their degradation by-products have significantly different electrical conductivities from clean water. Therefore, EC measurements alone will lead to some degree of ambiguity in the results, and give only qualitative information about the changes in the chemical composition of the soil-pore fluid. When EC is correlated with water quality, as shown in Figure 2 where groundwater electrical conductivity data is normalized by applying the logarithm to EC readings at 8°C and then plotted against the logarithm of ionic charge concentrations, it can be used as secondary information for interpolation of water quality data using geophysical methods. With the addition of secondary data, fewer primary data samples may be required which will lower the analytical costs and a better estimate of the distribution of water quality will be obtained.

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Recent technological advances in the geophysical field of resistivity surveying can provide cost effective and nondestructive methods for collecting subsurface EC data (Barker and Moore, 1998). Electrical resistivity tomography (ERT), or more recently referred to as electrical resistivity imaging (ERI), techniques have recently become an important engineering and environmental site investigation tool (Bentley and Gharibi, in review). Commercially available resistivity systems are more efficient than those that were available a decade ago (Bentley et al., 2001). Repeating an ERI survey across the same location at different times is known as time-lapse ERI surveying. Changes in the resistivity image may be used to infer changing groundwater quality at the site.

When subsoils contain only sands made up of minerals that are semiconductors or insulators, such as silicates and oxides, conducting electrical currents will arise primarily from the flow of ions within the pore spaces of the formation. Quantitative estimates of groundwater EC by interpretation of bulk EC data (such as from ERI surveys) taken in sand formations are accurately and routinely made using an empirical mathematical relationship developed by a petroleum well log specialist (Archie, 1942). However, EC in formations containing clay minerals is more complicated. Ions in a diffuse double layer around clay particles provide pathways for electrical currents along the clay surface in addition to the electrical current flow by ions in the pore fluid. The EC of the surface layer of the clay particles depends on the EC of the pore water, and therefore the overall bulk conductivity of the saturated rock is a nonlinear function of pore water EC. A wide variety of mathematical models have been used by petroleum reservoir analysts to model conductivity in formations containing clay minerals. One of these is the Waxman Smits (1968) model, which is assessed in this thesis for use in estimating pore water quality from ERI data collected at a contaminated gas plant site in Alberta. The subject research site is described later in this thesis.

1.2 Goals and Objectives

The overall goal of this thesis is to explore a way to make quantitative estimates of water EC from insitu measurements of bulk EC at a contaminated site with fine grained clayey sub soils.

Specific objectives of this research are:

- To review the literature and select one model that describes the relationship between bulk and pore water ECs;
- To make a physically plausible fit of model to the best available in situ EC data;
- To use the selected fit of the model to quantitatively predict groundwater EC from in situ measurements of bulk EC;
- To conduct a sensitivity analysis of the parameters in the model equation, and the sensitivity of model parameters when predicting water EC; and,

• To draw conclusions from the results of the above work and recommendations for potential further study.

1.3 Organization

This thesis is organized in the following manner:

Chapter 1 is the introduction, providing objectives and background information.

Chapter 2 includes a review of the literature in multi-disciplinary topics, all related to the measuring electrical conductivity in the subsurface. It commences with a brief history of petrophysics, then summarizes recent developments in Electrical Resistivity Imaging at the University of Calgary Department of Geology and Geophysics. The third portion of this Chapter looks at the electrical conductivity of aqueous solutions and the need to make corrections for solution temperature. The fourth part examines some of the aspects of different models linking clay conduction with electrolytic conduction. The fifth and final part of this Chapter provides the rationale for choosing the Waxman Smits model.

Chapter 3 describes the details of the application of the Waxman Smits model using insitu data collected at a remediation site. It includes a description of the site, fitting of site data to the model, and a sensitivity analysis of the fitted model.

Chapter 4 provides some conclusions and rercommendations.

Chapter 5 lists all references.

2. LITERATURE REVIEW

2.1 Petrophysics

The term petrophysics has been used to describe the physics of particular rock types (Archie, 1950). Geophysics is used to describe the physics of larger rock systems composing the earth. Archie was one of the first to study the petrophysics of oil and gas reservoir rocks, and he laid the foundation for many of the principles applied to modern-day petroleum well log analysis. Archie's 1942 paper outlined methods to interpret electrical resistivity logs carried out in exploratory drill holes in potential petroleum reservoir media. His investigations focused on direct current (dc) measurements in clean, consolidated and unconsolidated sands. Archie modeled the relationship between bulk resistivity of the porous medium and the resistivity of the water within the pore space of the medium. The electrical conductivity (EC) of a material within a geological formation is the inverse of the electrical resistivity. Most non-clay minerals are insulators. Therefore, there will be a greater resistance to an applied direct current (dc) voltage when the formation is unsaturated. When saturated, currents are primarily due to the flow of ions within the pore fluids. Archie showed that, in brine-saturated, clean (free of clay minerals) sands; the ratio of the conductivity of the pore fluid to the bulk conductivity of the fully saturated rock is equivalent to a term called the formation factor. This ratio can be expressed as:

$$F = R/R_w = \sigma_w / \sigma \tag{1}$$

Where, F is the formation factor, R is the bulk resistivity, R_w is the resistivity of the pore fluid, σ_w is the conductivity of the pore fluid, and σ is the bulk conductivity. For clean sands, Archie developed an expression, well-known to oil reservoir petrophysicists, providing an empirical relationship between the formation factor and porosity. This relationship is often called Archie's first law:

Where, ϕ represents porosity, and the exponent m is called the cementation factor. The cementation factor typically varies between 1.3 and 2.5 for most sedimentary rocks. Mavko et al. (1998), report that carbonate formations have a maximum cementation factor of 5, and a minimum of 1. The minimum occurs when porosity is 100% and the fluid is brine, such as the case of an open fracture in consolidated formations. Archie's second law (1942), expressed in EC terms, relates σ_t , conductivity of a partially saturated rock, to porosity, pore-water conductivity and water saturation S_w:

$$\sigma_{t} = (S_{w}^{n} \phi^{m}) \sigma_{w}$$
(3)

The saturation exponent, n, derived empirically, is approximately 2 for water-wet media (Mavko et al., 1998). When a formation contains clay minerals, however, Equations (2) and (3) are no longer valid. Excess ions in a diffuse double layer around clay particles provide current conduction pathways along the clay surface in addition to the current flow by ions diffusing through the pore fluid. The conductivity of the surface layer depends on the conductivity of the pore fluid, and hence the overall bulk conductivity of the saturated rock is a non-linear function of the pore fluid conductivity. As pointed out by Schlumberger (1989), Mavko et al. (1998), for many researchers who have tried to apply the work by Archie, the interpretation of shaley sandstone resistivity has been a significant problem in well log analysis. Interpretation becomes particularly troublesome whenever clay conductivity becomes a significant portion of the formation's bulk conductivity. This can occur in formations having large clay content, or in formations having low pore-water conductivity. This can also occur in unconsolidated and shallow soil-pore water systems where fine grained subsoils predominate.

(2)

2.2 Electrical Resistivity Imaging

The ERI method used at the University of Calgary Department of Geology and Geophysics site involves a DC resistivity imaging method (Bentley et al., 2001). In resistivity imaging, current is injected into the ground through current electrodes and voltages are measured at voltage electrodes. Figure 3 is a photograph showing the layout of the electrode array along one of the 2-D lines.



Fig. 3: Photograph of Electrode Array

Bentley and Gharibi (in review) report on the results of two 3-D ERI surveys with different designs. Both designs used orthogonal sets of 2-D lines. Current and potential electrode pairs are placed parallel within the lines. The survey is completed as a pseudo 3-D survey with orthogonal 2-D lines used to reduce potential grid orientation effects. Both Wenner and dipole-dipole arrays (Griffiths

and King, 1981) were used. The Wenner array has the advantages of better depth resolution, less susceptibility to acquisition noise and fewer measurement points for the same line coverage than the dipole-dipole array (Ward, 1990). The dipole-dipole array has better horizontal resolution and better depth coverage at the ends of the 2-D lines.

Figure 4 is a photograph of the typical set up of the resistivity survey data acquisition instruments.



Fig. 4: Photograph of Electrical Resistivity Survey Data Acquisition Set Up

2.3 Electrical Conductivity of Aqueous Solutions

The electrical conductivity (EC) of an aqueous solution is a measure of its ability to carry an electrical current by means of ionic motion. The conductivity increases with increasing temperature, because the viscosity of the fluid decreases. Different ions have different charge and mobility, so the magnitude of the change in EC caused by a change in temperature is different for waters with different chemistry.

In addition, the magnitude of the change in EC with change in temperature also varies with the concentration. The dependency of conductivity on temperature is expressed as a percentage change per degree Celsius at a particular temperature, commonly as (percent change)/°C at 25°C. For common ionic salt solutions, this value is about 2%/°C. As a small difference in temperature causes a large change in conductivity, it is necessary to compensate conductivity readings for temperature. The readings are usually normalized to the equivalent conductivity at 25°C. Most portable EC meters used in hydrogeologic practice automatically compensate for temperature differences with some form of built-in sensor circuitry. An adjustable knob or software setting allows the user to adjust the temperature coefficient (or slope) from 0% (without compensation) to 2.5%/°C or more (on some models). Most meters have a default temperature coefficient of 2%/°C, or the user typically sets the meter to use the slope of 2%/°C. With this slope, the meter automatically calculates and displays conductivity readings normalized to 25°C. The meter also typically displays the temperature of the groundwater sample, and if done in the field, this is the in-situ temperature. When comparing electrical conductivity of groundwater to bulk electrical conductivity of the formation, as measured in electrical resistivity survey methods, it is necessary to correct groundwater conductivity to the in-situ temperature at which the bulk conductivity measurements are made.

To minimize temperature correction problems, EC was measured in the field at ambient in situ temperatures so that only the temperature compensation from the meter needs to be corrected to ambient in situ temperature. If the EC measurement cannot be done in the field, but done later in the lab, it should be measured at a temperature that is as close to the in situ temperature as possible to minimize the temperature correction. Figure 5 provides a graphical representation of the method used to correct the groundwater EC to the in-situ temperature.



Fig. 5: Temperature Correction of Groundwater EC Measurements

 M_w = Temperature Coefficient of the Solution

If a measurement of EC is made at the lab temperature (Point C), the compensation factor of the EC meter can be used to correct the EC reading to 25° C, (Point D) but it is the temperature coefficient of the water sample that must be used to determine the true in-situ EC (Point A). If a measurement is made in the field with a portable EC meter, the corrected EC (Point B) is converted using the slope of the meter to give the EC at point A. From Figure 5, it can be seen that corrected EC obtained in the field (Point B) is different than the corrected EC using a sample taken back to the lab (Point D).

An additional problem is that the slope factor of the solution is not known, but is assumed to be 2%/° C. However, the true temperature compensation coefficient depends on the details of the chemistry, the concentration of the solution and the standard temperature to which the EC is being corrected.

2.4 Strengths and Weaknesses of Some Published Clay Conductivity Models

Schlumberger (1989) provides a comprehensive summary and background on nine models or techniques used in open hole petroleum well logging to quantitatively interpret fluid saturation and porosity in rocks containing high proportions of clay minerals, such as those found in shale. Argaud et al. (1989) suggested more than thirty models were available. Sen and Goode (1992), mention that over 50 models of clay conductivity have been published. However, most of the methods described in these papers require the use of sophisticated borehole logging equipment designed for exploration of relatively deep rock formations. Mavko et al. (1998) provide a brief description of some of the models most widely accepted by petrophysicists, some of which do not require borehole logging.

Simandoux (1963) described, in a French journal, electrical measurements performed using alternating current with a frequency of approximately one megahertz applied to samples of a porous medium. He was interested in two electrical parameters – conductivity and dielectric constant. Mavko et al. (1998) provide a very brief English translation of the model Simandoux developed:

$$\sigma = (1/F)\sigma_w + V_{sh}\sigma_{sh}$$
⁽⁵⁾

Where: V_{sh} is a term used to express volume of shale, as determined from well logs; and σ_{sh} is the conductivity of fully brine-saturated shale. Mavko asserts that the Simandoux model is applicable to log interpretation and may be used without

core data, however it does not have a significant physical basis or does not allow a complete representation of conductivity behavior for all ranges of σ_w .

IWaxman and Smits (1968) developed one of the first models which attempted to describe the physics of the diffuse double layer surrounding clay particles. The general form of the Waxman-Smits equation can be written:

$$\sigma = (1/F) (\sigma_w + ((BQ_v)/S_w)) S_w^n$$
(6)

In equation (6),

$$F = a\phi^{-m}, \tag{7}$$

F is the formation factor, but is <u>not</u> as written in equation (2). Here an empirical constant "*a*", usually greater than 1, is used to distinguish the formation factor for shale-sand formations from the formations containing clean (no shale) sands considered in Archie's expression (Mavko et al., 1998). The B term in equation (6) is derived by the expression:

$$B = c_1 (1 - (c_2 \exp(-\sigma_w/c_3)))$$
(8)

The values of the constants c_1 , c_2 and c_3 as empirically determined by Waxman and Smits are: 4.6, 0.6, and 1.3, respectively (Mavko et al., 1998).

In equation (6), the term Q_v is described as the charge per unit pore volume, which is derived from measurements of density of the soil particles, the cation exchange capacity (CEC) determined from laboratory analysis on soil core samples, and estimates of porosity based on soil density/moisture content probes at the site. Specifically: In this equation, CEC is the cation-exchange capacity, ϕ is the porosity, and ρ_s is the density of the soil particles. The value of the density of the soil particles can be calculated using data collected from X-ray diffraction (XRD) analysis of soil samples. XRD results provided the fraction of clay and other minerals present in the subsoil. Average solid density can be estimated using published values of mineral densities for both clay and non-clay fractions. The calculation for ρ_s used in this thesis is written:

 $\rho_s = (clay fraction)^*((dry density of clay soils)+(non-clay fraction))^*(dry density of non-clay soils)$ (10)

The densities of clay soils and non-clay soils were obtained from published values found in Holtz and Kovacs (1981).

Waxman and Smits and other researchers have investigated the parameter B, which describes the average mobility of cations. In Waxman and Smits' equation, B is a source of uncertainty, and several expressions for it have been developed since their 1968 work. For example, Juhász (1981) gives the following expressions for B:

$$B = (-1.28 + 0.225T - 4.059 \times 10^{-4} T^{2}) / (1 + Rw^{1.23} (0.045T - 0.27))$$
(11)

Where T is the temperature in degrees Celsius. Juhász, as well as most of the other researchers, developed this equation for application in deep basins where temperatures change significantly with depth. In the shallow fine grained sediments discussed ion this thesis, temperature in situ does not change significantly with depth. The Waxman-Smits-Juhász (Juhász, 1981) model does not require CEC data because Juhász uses V_{sh}, derived from petroleum well logs, to estimate Qv by normalizing it to the shale response of the well logging tool.

(9)

The dual water model (Clavier et al., 1984) divides the total water content into the bound clay water, whose conductivity depends only on the clay cations, and the bulk water (sometimes called the "free" water) away from the clay, whose conductivity corresponds to the ions in the bulk water. The bound water reduces water conductivity, σ_w . The dual water model formula (Mavko et al., 1998) is:

$$\sigma = \phi^{m} \left[\sigma_{w} \left(1 - \alpha v_{Q} Q_{v} \right) + \beta Q_{v} \right]$$
(12)

Where: v_{Q} is the amount of clay water associated with 1 milliequivalent of clay cations, β is the equivalent conductivity of sodium counterions (counterions are cations which cling to the surface of a clay particle in the dry state), and α is the expansion factor for the diffuse layer (Clavier et al., 1984). In the dual water model, $\alpha = 1$ when salt concentration exceeds 0.35 mol/ml. At lower salinities α is a function of σ_w , and is given by:

$$\alpha = \sqrt{(\gamma_1(n_1)/\gamma(n))} \tag{13}$$

Where: (n) = salt concentration in bulk water at 25° C in mol/mL; γ = NaCl activity coefficient at that concentration; (n₁) = 0.35 mol/mL; and γ_1 = 0.71, the corresponding NaCl activity coefficient. The expression for α is derived from the Gouy layer thickness, x_d, related theoretically to (n) in the bulk water at 25 ° C by:

$$x_{d} = 3.06 \sqrt{1/\gamma(n)}$$
 (14)

Although v_Q and β have temperature and salinity dependence, Mavko et al. (1998) suggest that Clavier et al. (1984) used the following values: $v_Q = 0.28$ mL/meq and $\beta = 2.05$ (S/m)/(meq/cm³). These values are based on analyses of CEC data for clays and conductivity data on core samples. At low salinities, v_Q varies with \sqrt{T} and increases by about 26 percent from 25 to 200°C (Mavko et al. 1998).

Sen and Goode (1988), generalizing from theoretical solutions for electrolyte conduction past charged spheres in the presence of double layers, proposed the following shaley-sand equation:

$$\sigma = 1/F (\sigma_w + (AQ_v/1 + (CQ_v/\sigma_w))) + E Q_v$$
(15)

The constants A and C depend on pore geometry and ion mobility, and the term EQ_v accounts for conductivity by the surface layer cations even when σ_w is zero.

Sen and Goode (1992) extend the conductivity equation for shaley sand previously proposed at room temperature by including temperature dependence. For NaCl brine, and in the salinity range over which their experiments were performed, equation (13) takes the form:

$$\sigma = \Phi^{m}(\sigma_{w} + 1.93m\mu_{t}Q_{v}/1 + (0.7\mu_{T}/\sigma_{w})) + 1.3 \Phi^{m}\mu_{T}Q_{v}$$
(16)

In equation (15), $\mu_T = \mu_{DL}(T)/\mu_{DL}(T=71.6^{\circ}F)$ and represents the ratio of the mobility of the double layer at a given temperature to that at room temperature. The term μ_{DL} is the effective mobility of cations in the double layer.

Another model developed by Vinegar and Waxman (1984), in a variation of the dual water model, assumed that two mechanisms of conduction, namely electrolytic conduction and clay conduction occur in parallel. Thus:

$$\sigma_{\rm rock}^{*} = (\sigma_{\rm s} \Phi^{\rm m}) + \sigma_{\rm clay}^{*}$$
(17)

Where the asterisks denote mathematically complex quantities (both a real and an imaginary component). The clay conduction, they postulate, produces a response that is in phase and a response which is out of phase (quadrature response) with

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the source of current (Park and Dickey, 1989). The quadrature response occurs because clays act as semi-permeable membranes. The mobilities of the cations and anions are different in the very fine pores within clay and thus differential separation of charge occurs when current is applied to a rock. These charges must redistribute themselves when the applied current changes and this redistribution lags behind the change in current. This lag results in a quadrature response, which is not exactly in phase with the source. To measure the phase conductivity, Park and Dickey (1989) used resistivity measured by geoelectrical soundings. Induced Polarization (IP) measurements are used to determine the quadrature conductivity.

In the field of soil science, Rhoades et al. (1989) discuss another kind of model for the relationship between bulk soil electrical conductivity, volumetric content, and electrical conductivity of soil water. Their model, somewhat like the dual water models discussed, also distinguishes between the water and salt present in the soil in the "immobile" (fine pores) and "mobile" (large pores) phases. However the model put forth by Rhoades et al. 1989) assumes that the specific electrical conductivity of soil containing dissolved electrolytes (salts) in the soil solution can be represented by a conductance in three elements:

- i. Conductance through alternating layers of soil particles and interstitial soil solution (a solid-liquid series-coupled element),
- ii. Conductance through or along the surfaces of the soil particles (primarily associated with exchangeable cations) in direct contact with one another (a solid element), and
- iii. Conductance through the interstitial soil solution (a liquid element).

Rhoades et al. (1989) focus on the "solid-liquid series" model and to find practical ways to apply their model to diagnosing soil salinity, in terms of the electrical conductivity of the extract of saturated soil pastes at conditions of low electrical conductivity of pore water.

Table 1 provides a summary of the strengths and weaknesses of the alternative models and compared with the chosen Waxman and Smits model. The limitations of all of the models which are used to interpret resistivity logs in petroleum wells is that they involve much empiricism, and empirical relations should be re-checked for specific locations and formations. The remainder of this thesis discusses a physically plausible fit of the Waxman Smits model and an analysis of the sensitivity of its parameters.

Name of Model	Reference Paper(s)	Strengths	Weaknesses		
Simandoux	Simandoux (1963)	Simple extension of Archie's Law	Requires additional data measured from petroleum well logs and does not apply over all ranges of σ_w .		
Waxman-Smits	Waxman Smits (1968)	All necessary data collected or derived from samples typically collected during typical environmental site characterizations.	Some uncertainty in parameter B, mobility of cations.		
Waxman-Smits- Juhász	Juhász (1981)	Takes temperature into account in determining B	Requires additional data measured from petroleum well logs		
Dual Water	Clavier et al. (1984), Sclumberger (1989) and Mavko et al. (1998)	Takes into account the ion-free water adsorbed (bound) to clay particles, which reduces water conductivity	Requires additional data not readily obtained during typical environmental site characterizations.		
Sen and Goode	Sen and Goode (1988) and (1992)	Takes into account pore geometry and ion mobility along the surface of clay particles even when water EC is zero. Also consider temperature dependence of the mobility of counter- ions.	Relationship developed by generalizing from theoretical solutions for electrolytic conduction past charged spheres in the presence of double layers. Temperature effects are much more important in deep basins.		
Vinegar and Waxman	Park and Dickey (1989)	Interesting postulation that rocks have a mathematically complex quantity of conduction (both real and imaginary components) caused by clay.	Requires, in addition to resistivity surveys, induced polarization soundings, a geophysical method not available to the research group.		
Solid-liquid series- coupled model	Rhoades et al. (1989)	Relates bulk soil electrical conductivity, soil water content and conductivity, and soil salinity.	A method which relies mainly on tests on saturated pastes of very near surface soil samples and not on the deeper in-situ data obtained from geophysical methods, such as resistivity.		

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Table 1: Strengths and Weaknesses of Clay Conduction Models Considered

2.5 Rationale for Selection of the Waxman Smits Model

At the subject decommissioned sour gas processing plant site, a research program was conducted to investigate the utility of electrical resistivity imaging (ERI) for monitoring changing soil and water quality. A model that can be used to estimate groundwater EC from ERI measurements across a wide range of geologic heterogeneity in shallow soil-pore water systems was therefore desired. More recent research papers discuss other variations of the Waxman Smits model to estimate conductivity of pore water corrected for the influence of the electric double layer of clay. The Vinegar and Waxman model as described by Park and Dickey (1989) requires data from induced polarization surveys, which did not take place at the subject research site. Also, it was desired to select a model which uses parameters that could be derived from standard laboratory procedures, rather than those that derive their parameters from other geophysical data in the form of well logs, such as Simandoux (1963). The model presented by Sen and Goode (1992) takes into account clay geometry, or tortuosities that influence clay conductivity. and they also explore more fully the temperature dependence of the mobility of cations. The model closest to the required criteria was the one developed by Waxman and Smits (1968). They used a simple relationship between the bulk EC of water-saturated shaley sand to the water EC and the cation-exchange capacity (CEC) per unit pore volume of the formation. Their equation applies to formations with a wide range of cation-exchange capacities and can be extended to cases where the degree of water saturation may be varied.

In the final selection of the Waxman-Smits model for analysis in this thesis, the author noted that it would be valid for all conditions of soil saturation and clay fractions typically found at a research site described later in this thesis.

The temperature dependence of the mobility of cations is not considered to be a major influence on the Waxman Smits relationship and is ignored in this thesis.

Unlike the significant changes in temperature with depth expected in oil well logs, subsurface temperature at the research site did not significantly change throughout depth of vertical penetration of the ERI or groundwater EC measurements. Nevertheless, potential temperature effects on groundwater EC readings were controlled by correcting water conductivity data from the research site to the in situ temperature at which the ERI surveys were conducted.

3. APPLICATION OF THE WAXMAN-SMITS MODEL

3.1 Site Description

The research site is a decommissioned sour gas (gas containing significant hydrogen sulphide) processing plant located in Alberta. A site plan is presented in Figure 6. The site is referred to as the Gas Plant Remediation Project (GPRP) by the University of Calgary research team. The gas plant was operated from the late 1970's until the early 1990's, and had a single sour gas well. Monoethanolamine (MEA) and glycol were used in the processes of removing hydrogen sulphide, carbon dioxide and water from the sour gas (Mrklas, et al., 2001). These compounds were released over the course of many years during plant operations. MEA degrades to ammonium and acetic acid and glycol degrades to acetic acid (Mrklas, et al., in review). These degradation products increase the electrical conductivity of soil water and cause zones of elevated bulk EC in the subsurface.

Once the gas plant was closed, the treatment infrastructure was removed and the gas well abandoned in accordance with Alberta Energy Utility Board (EUB) requirements. Extensive investigations had been conducted at various locations across the site since closure. Drilling and piezometer installations, horizontal well and hydraulic fracturing research, bioventing and in-situ bioremediation experiments, push conductivity tool (CPT) surveys and 2-D ERI surveys were done between 1997 and a period of The research demonstrated that soil and water quality varied over horizontal distances on the order of one meter and that zones of high EC were as thin as 0.5 m in the vertical (Bentley and Gharibi, in review). Most of the elevated concentrations are within 6 metres below ground level (mbgl).

The surficial geology at the site includes 4 to 6 metres of glacial deposits comprised mainly of sandy silt till or silty clay till overlying weathered siltstone bedrock. Sand lenses and some gravel were found within the till in a few of the

boreholes. X-ray diffraction (XRD) analysis indicates the subsoils contain 27% clay (by weight) including illite (12%), kaolinite (5%), and smectite (10%), (Kruchkowski, 2000).

Results of work using a neutron density tool and volumetric soil moisture conducted by Butterfield (2001), and measurements of soil moisture content measured by Mrklas (2001) indicate an average density of the soil solids of 2.67 g/ml, an average soil porosity of approximately 0.23, and a gravimetric moisture content varying between 12 and 25 %. The effective cation exchange capacity was determined from analysis of soil samples using the BaCl₂ method (Carter, 1993). Four soil samples collected from boreholes drilled outside of the areas impacted by amines and glycols were submitted to a commercial laboratory for CEC analysis. The results are given in Table 2. Average CEC is 28.25 meg/100 g.

Borehole No.	Depth (mbgl)	CEC Result (meg/100 g)
P99-1	4	38
P99-1	6	24
P99-1	9.5	26
P99-4	2	25

Table 2: Results of CEC Laboratory Analyses

Single and nested piezometers (50 mm inside diameter) have been installed at the site. The depth of the groundwater table varies significantly across the site and in accordance with seasonal conditions. Water levels in piezometers vary from near ground surface to 3 metres below ground surface (mbgs). Slug test analyses in the piezometers indicate a coefficient of permeability of the till on the order of 2 X 10⁻⁷ m/s. The significant clay content accounts for this low value of permeability. Sand lenses and fractures have resulted in localized zones of higher permeability. The clay content provides background bulk electrical conductivity in the range of 50 to 70 mS/m.



Fig.6: Plan of Research Site (outer grid dimensions in metres)

Source: Dr. M. Gharibi, Department of Geology and Geophysics, University of Calgary

EC in poor groundwater quality areas varies remarkably over very short distances both horizontally and vertically. Water samples from piezometers that are separated by one or two meters can have significantly different electrical conductivity values. Glycol does not have a strong EC signature, but dissolved amines contribute to the EC of water. Acetic acid and ammonium also contribute to a strong bulk EC signature that can be greater than 200 mS/m. The highest bulk and groundwater ECs, observed at the site, were 500 and 1600 mS/m, respectively.

3.2 Groundwater EC Measurements

Groundwater samples were collected from the site monitoring wells (piezometers) within ERI zones 1 and 2, during the time when the ERI surveys were done in August 2001. The gas plant property has dimensions of approximately 120 m in the NE-SW direction, and 80 m in the NW-SE direction. Refer to Figure 6 for the relative locations of the ERI zones. Zone 1 is an area 27 m by 27 m; Zone 2 is an area 27 m by 41 m. Zone 2 contains most of the contamination plume. All groundwater EC readings were corrected to the observed average in situ temperature of 8° C (personal communication with Dr. Gharibi).

Following is the correction applied to convert EC normalized to 25° C by a field EC meter, to the in-situ temperature (Mrklas, 2001):

 $y = x - (x^* 0.021^* (25 - T))$ (18)

Where: y = EC corrected to in-situ temperature; x = EC at 25° C as given by the meter; and, T = the average in - situ temperature (8°C).

The constant 0.021 represents the temperature compensation coefficient of the EC meter (2.1%).

3.3 Bulk EC Data Collection and Interpretation

Three resistivity survey zones were done in August 2001, using pseudo 3-D resistivity survey techniques (Bentley and Gharibi, in review). Zone 1 involved an area where eight 2-D lines were surveyed orthogonally opposite another eight 2-D lines, with each line 27 metres in length. Zones 2 and 3 were both surveyed using orthogonal sets of 8 by 21 lines, with the lengths of the lines 27 m and 41 m, respectively. Refer to Figure 6 for the layouts of the orthogonal sets of 2-D survey profiles used in the August 2001 3-D ERI survey and to Figure 7 for the typical set up for ERI data collection.



Fig. 7: ERI Data Collection at the Gas Plant Remediation Project Site

Every ERI survey had current and potential electrodes placed in different combinations of dipole-dipole or Wenner arrays.

The ERI data inversion algorithm uses the current and voltage data to produce images of the subsurface resistivity (conductivity) distribution. Each zone was inverted independently. 3-D inversions for each zone was done using all of the data within the zone to create a 3-D image of the EC for the subsurface below the zone The inversion method was based on the work presented by Loke and Barker (1996). Figure 8 provides three cross sections showing the electrical conductivity of the subsurface in Zone 2, produced after 3-D data inversion.

Fig.8: Cross-Section showing Variation in 3-D ERI Bulk EC Data

Electrical Resistivity Imaging Survey - Zone 2 Gas Plant Remediation Research Site

X and Y unit electrode spacing 1 m. Iteration 14



Bulk Electrical Conductivity - Gray Scale Units: mS/m



Table 3 indicates the depths of the layers which have been modeled in the inversion algorithm. The depths of the various layers increase with depth because the ERI method is a diffusive process in which resolution decreases with depth. The 0.35 m first layer thickness is a default value in the inversion algorithm and was suitable for the GPRP ERI survey data (personal communication, M. Gharibi). The depth to the deepest model layer was set to be slightly more than the maximum depth of the investigation, as established during design of the ERI survey. These layers control the vertical dimension of the "block", which is 1 m wide laterally, and as thick as the layer in which it is situated.

Layer No.	Depth (mbgs)
1	0-0.35
2	0.35-0.75
3	0.75-1.22
4	1.22-1.75
· 5	1.75-2.36
6	2.36-3.06
7.	3.06-3.87
8	3.87-4.8
9	4.8-5.88
10	5.88-7.11
11	7.11-8.52

Table 3: Thicknesses of the Subsurface Layers used in the 3-D ERI

3.4 Fitting of the GPRP Site Data to the Waxman Smits Model

Prior to the 3-D electrical resistivity imaging work completed in 2001, there were a number of 2-D ERI surveys done at the GPRP site in 2000. Prior to that, a number of runs of the Cone Penetrometer Tool (CPT) were carried out at the site in the late 1990's. Unfortunately, the σ_w data quality from the time of the CPT investigations and the σ data quality from the 2-D resistivity were not high. The investigators performing the water EC measurements did not report whether their values were corrected for temperature. The 2-D resistivity imaging profiles were believed to produce misleading images due to out of plane resistivity anomalies and violation of the 2-D assumption (Bentley and Gharibi, in review). Therefore, using those data for the model fitting would have introduced further ambiguity of the results. Sufficient confidence in the data collected during the 3-D ERI survey of August 2001 existed to proceed with fitting the Waxman-Smits model to the site data.

Figure 9 shows the criteria used in the search algorithm to find bulk EC measurement points with collocated (matching) groundwater EC measurements from the piezometers. A collocated data pair is where the nearest groundwater EC is compared to the inversion bulk EC of an ERI model or block of soil whose centroid is closest to the cylindrical shaped space surrounding the piezometer (see Figure 9). The cylindrical search area had a 0.9 m radius from the centre-line of the piezometer. In an attempt to match as closely as possible the bulk EC in the collocated block with pore water EC representing the saturated soil conditions surrounding the piezometer screen, the ERI – derived EC data was from the nearest block centroid found within the cylindrical space surrounding the screen. The bulk EC for the block nearest the piezometer is used to make up a pair of collocated data points.

The piezometer provides a sample of water which does not necessarily represent the EC of water in the pore spaces of the matched block of soil. Heterogeneities, such as lenses of coarser grained subsoils or induced fractures, may provide a pathway of groundwater flow into the piezometer, causing the sampling of water which may have come from distances greater than the 0.9 m radius modeled in Figure 9.





Table 4 provides a listing of the piezometers, the EC measured in the groundwater samples extracted from them, the coordinates of the centres of the piezometers screens compared with the collocated ERI derived bulk EC data, the coordinates of the ERI blocks. It also lists the horizontal and vertical offsets calculated using the shortest distance between the centroid of the piezometer screen and the centroid of the block from the ERI. The negative sign in some of the vertical offsets indicate that the centroid of the ERI block is higher in elevation than the centroid of the piezometer. Lengths of the piezometer screens are also shown in Table 4.

Piezometer	Coordin C	ates of Pie entroid (n	ezometer n)	Ground- water EC	Screen	ERI Zone	Coordinates of ERI Block Centroid (m)		Bulk EC	Horizontal	Vertical	
	x	У	z	corrected	Lenger		x	У	z	(mS/m)	Onset	Unser
				to 8° C (mS/m)	(m)							
P99-2A	986.87	961.75	886.06	78.156	0.3	zone1	986.655	961.416	885.784	83.542	0.397	0.276
P99-2B	986.87	961.75	884.04	170.387	0.3	zone1	986.655	961.416	884.369	84.296	0.397	-0.329
P97-1A	1024.92	925.224	885.775	56.414	0.75	zone2	1024.508	925.301	885.876	75.047	0.419	-0.101
P97-1B	1024.92	925.224	884.075	70.786	0.75	zone2	1024.508	925.301	884.461	108.307	0.419	-0.386
P97-2A	1023.32	923.944	885.795	206.271	0.75	zone2	1023.072	923.909	885.786	68.956	0.25	0.009
P97-2B	1023.46	923.815	884.095	36.982	0.75	zone2	1023.072	923.909	884.371	118.161	0.399	-0.276
P97-3A	1021.93	922.709	885.751	114.312	0.75	zone2	1021.637	922.516	885.731	67.545	0.351	0.02
P97-3B	1021.82	922.547	884.051	59.995	0.75	zone2	1021.637	922.516	884.316	94.787	0.186	-0.265
P97-4A	1017.87	932.62	885.663	564.016	0.75	zone2	1017.545	932.479	885.458	91.216	0.354	0.205
P97-4B	1017.9	932.544	884.413	182.282	0.75	zone2	1017.545	932.479	884.701	108.554	0.361	-0.288
P97-5A	1015.73	931.819	885.393	156.47	0.75	zone2	1015.413	931.804	885.348	161.316	0.317	0.045
P97-5B	1015.68	931.721	883.893	143.699	0.75	zone2	1015.413	931.804	883.721	95.85	0.28	0.172
P97-6B	1014.12	933.019	883.858	198.138	0.75	zone2	1014.021	933.24	883.776	119.589	0.242	0.082
P97-7A	1012.56	932.069	886.055	793.021	0.75	zone2	1012.585	931.847	885.954	164.096	0.223	0.101
P97-7B	1012.65	932.086	884.355	196.04	0.75	zone2	1012.585	931.847	884.539	186.846	0.248	-0.184
P97-8B	1013.04	937.507	884.723	394.322 .	0.75	zone2	1012.671	937.503	884.886	139.47	0.369	-0.163
P97-9A	1010.77	935.633	885.732	348.311	0.75	zone2	1010.518	935.415	885.426	124.409	0.333	. 0.306
P97-11A	1006.82	940.223	886.277	120.656	0.75	zone2	1007.058	940.417	886.196	169.635	0.307	0.081
P97-11B	1006.84	940.346	884.627	643.501	0.75	zone2	1007.058	940.417	884.781	126.887	0.229	-0.154
P97-12A	1005.63	939.222	886.191	226.86	0.75	zone2	1005.622	939.025	886.059	186.047	0.197	0.132
P97-13A	1010.41	937.597	886.27	158.178	0.75	zone2	1009.843	937.546	886.154	152.416	0.569	0.116
P97-13B	1010.37	937.549	884.62	240.616	0.75	zone2	1009.843	937.546	884.739	101.864	0.527	-0.119
P98-3	1021.64	939.391	886.146	677.048	2.4	zone2	1021.895	939.485	886.111	87.344	0.272	0.035
P98-4	1021.68	926.07	886	115.647	N/A	zone2	1021.701	926.758	885.889	57.494	0.688	0.111

Table 4: Details of August 2001 Collocated Data Points from the GPRP Research Site

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By manually varying the parameters in the Waxman Smits model, equation (6) in this thesis, a fit of the collocated data points from the research site was achieved. In plotting the collocated data points, and based on several years of observations, it was noted that the highest observed values of bulk and groundwater EC, 500 and 1600 mS/m, respectively, were not captured in the collocated data (Bentley, 2001). For the purposes of this thesis, the application of the Waxman-Smits model to the Gas Plant Remediation Project (GPRP) research site data was completed when a physically plausible fit of the model included the historically observed maximum EC derived from both ERI and groundwater data.

For the resulting fit of the model shown in Figure 10, values of the constant Waxman Smits parameters are:

- S_w is 1 (soil-pore water system is in a fully saturated condition);
- CEC is 28.25 meq/100 g (average from laboratory measurements);
- ρ_s is 2.67 g/ml (calculated using data from X-ray diffraction analyses);
- average porosity, ϕ is 0.23 (determined from neutron-density probes);
- Q_v, calculated using equation (9), is 0.58 meq/ml;
- a is 1 (adjusted to fit the model to the data);
- the cementation factor m, is 1.255 (adjusted to fit);
- the values of the constants c₁, c₂, were also adjusted to 3.5 and 0.8, respectively;
- the value of c_3 was 1.3, the value reported by Mavko et al. (1998); and,
- B is dependent on the values of σ_w, c₁, c₂, c₃. The plot of the Waxman Smits model was made by setting c₁, c₂, c₃ constant and varying σ_w from zero to the maximum of 1600 mS/m.

The four data points with groundwater EC values between 550 and 800 mS/m are proximate to the former horizontal well or areas disturbed by excavation and are ignored. The effects of geological heterogeneities and experiments done at the

GPRP site i.e., hydraulic fracturing areas, horizontal well, excavated and backfilled zones are not well understood and these points were ignored. Analysis of these effects is beyond the scope of this thesis.

By using the fitted Waxman Smits curve in Figure 10, the bulk EC as determined from the ERI survey at the site provides a reasonable approximation of the pore water EC. If a straight line approximation of the data is used, also shown on Figure 10, the predicted pore water EC would be over estimated.

Fig. 10: Selected Fit of Waxman Smits Model to EC Data from GPRP Site



3.5 Discussion on the Fit of the Model

As observed in Figure 10, when the collocated data pairs are cross-plotted with bulk EC versus groundwater EC, a large amount of scatter in the data is observed. This scatter in the data is caused by several factors including scale of measurement differences. Considering how natural subsurface heterogeneity and induced fractures can cause groundwater flow to be concentrated in limited zones within the subsurface surrounding the piezometer screen the quality of water sampled in a piezometer may not be representative of the same pore water lying within the collocated ERI block. Bulk EC can change dramatically over vertical and horizontal length scales on the order of tens of centimetres to metres. Such small length scales are below, or at the limit of the ERI resolution, which smoothes the bulk conductivity over the entire volume of the block of soil. On the other hand, samples of groundwater from piezometers used to measure pore water EC will mainly be produced from the highest permeability regions, which may or may not be hydraulically connected to the same pore spaces considered by the ERI block. Consequently, the scale and geometry of the sample volumes differ markedly between groundwater and ERI data.

Other possibilities for the inconsistencies with the match of collocated insitu data to the model include:

- imperfect compensation for temperature variations during in situ measurements of groundwater EC;
- varying lengths of the slotted intervals of piezometers at the site;
- Waxman and Smits having derived the B term in their equation considering only sodium in shale. The work at the GPRP site involved analysis for all cations;
- It is also difficult to compare the Waxman Smits model, developed primarily for the application of fluid conductivity in deep shaly sands where brine filled

pore spaces occur, to the shallow subsurface conditions of the GPRP site where pore spaces are at worst impacted with water of relatively low ionic concentrations. By definition brine contains more than 10,000 mg/L of dissolved salts. At the GPRP, the background groundwater is fresh and relatively near the ground surface;

- Groundwater in a piezometer is not necessarily representative of the conductivity of the groundwater in pore spaces of unsaturated soils (i.e., when S_w < 1), a condition expected in subsoils surrounding a piezometer;
- Some piezometers are located near excavated and backfilled areas and near the horizontal well and hydraulically fractured subsoils; and,
- Variability in the subsurface geology combined with the assumption that the Waxman-Smits parameters are constant.

3.6 Sensitivity Analysis of Waxman Smits Parameters

It is assumed from this point forward that the fit of the site data in Figure 10 is reasonable and analysis of the individual Waxman Smits parameters can proceed. This section focuses on the sensitivity of the parameters in the Waxman Smits equation. A summary of the findings is presented in a manner similar to one suggested by Hill (1998), using scaled sensitivities for each independent parameter in the model. For this analysis, the scaled sensitivity is the percent change in the predicted value ofo, given a 5 percent change in the value of the independent parameter. The same 5 percent is used for all parameters as a way to compare the degree of sensitivity between parameters. Five percent is an arbitrary choice, however it is a reasonable amount for most parameters.

As shown in Figure 11, the sensitivity of some parameters changes depending on whether low or high values of groundwater EC are involved. When groundwater EC is not detectable (equivalent to 0 mS/m), the most sensitive parameters are c_2 , m, ϕ and a, with an extremely high sensitivity of the value of σ affected 20 percent by a 5 percent change in c_2 . However, when groundwater EC is at 1600 mS/m, the most sensitive parameters are m, S_w, ϕ and a, with the highest affect of 9.6 percent increase in the predicted value of σ caused by a 5 percent reduction in the cementation exponent, m.

Details of the sensitivity of Waxman Smits parameters with respect to the predicted σ_w for a given value of σ are provided later.





Table 5 summarizes the sensitivity analysis of the independent Waxman Smits parameters for the fitting of the model to the GPRP data set and using σ_w to calculate σ . The parameters in Table 5 are grouped in the order they appear in equation (6). Note that a sensitivity analysis was done for the fitting of the W-S model to the collocated data points from the ERI survey alone, as well the fitting where the maximum historically observed ECs on the GPRP site was used as a collocated point. Table 5 also summarizes the contrast in sensitivity when σ is near zero or at the maximum value for the both fittings.

The "base case" refers to value of the parameter fitted to the model prior to performing the sensitivity analysis. At the bottom of Table 5, some of the parameter values were manipulated to values that are believed by the author to be the practical limits.

Parameter	Units	Parameter Value				E	ffect on σ	(% Char	nge)	
								rease	Inci	rease
		Base Case	Decrease	% change	Increase	% change	σ _w = 0 mS/m	σ _w = 1600 mS/m	σ _w = 0 mS/m	σ _w = 1600 mS/m
F	none									
а	none	1	0.95	-5.0	1.05	5.0	5.3	5.3	-4.8	-4.8
m	none	1.255	1.19225	-5.0	1.31775	5.0	9.6	9.6	-8.8	-8.8
φ	none	0.23	0.2185	-5.0	0.2415	5.0	-7.6	-6.9	7.9	7.1
В	(S/m)/(meq/ml)	t.								
C1	none	3.5	3.325	-5.0	3.675	5.0	-5.0	-2.5	5.0	2.5
C ₂	none	0.8	0.76	-5.0	0.84	5.0	20.0	0.8	-20.0	-0.8
C ₃	none	1.3	1.235	-5.0	1.365	5.0	0.0	0.9	0.0	-0.9
Qv	meq/ml									
CEC	meq/100g	0.2825	0.2684	-5.0	0.2966	5.0	-5.0	-2.5	5.0	2.5
ρ _s	g/ml	2.67	2.537	-5.0	2.804	5.0	-5.0	-2.4	5.0	2.4
Sw	none	1	0.95	-5.0			-5.0	-7.4		
Practical										
Ranges:										
φ	none	0.23	0.18	-21.7	0.36	56.5	-23.6	-25.1	45.8	60.9
Sw	none	1	0.5	-50.0			-50.0	-63.6		
CEC	meq/ml	0.2825	0	-100.0	1.5	431.0				
а	none	1	0.62	61.3	1.6	158.1	61.3	61.3	-37.5	-37.5
m	none	1.255	1.255	0.0	2.5	99.2	0.0	0.0	-84.0	-84.0

Table 5: Summary of Sensitivity Analysis With Respect to σ

3.7 Significance of Selected Waxman Smits Parameters

This section illustrates the significance of the two readily discernible physical parameters, clay content and degree of saturation. They are often discerned qualitatively in the field by geologists or other scientists when conducting site investigations. Here, these parameters are discussed with respect to the GPRP site.

3.7.1 Clay Content Based on Cation Exchange Capacity

The significance of clay content, as determined by the CEC, in any bulk conductivity measurement must be taken into account if precise predictions of pore water conductivity are desired. As seen in Figure 12, when there is no clay in the subsoil, the soil has no Cation Exchange Capacity, and the relationship between bulk and groundwater EC is linear, as predicted by Archie's Law. It is seen that even a relatively low CEC, like the average of 28 meq/100 g found at the GPRP site causes a significant change in the relationship between bulk and groundwater EC. Clays that have a high CEC are expected to increase the value of the bulk conductivity. The values of CEC used in Figure 12 for the hypothetical situations other than the GPRP site are from Grim (1968).



Fig. 12: Significance of Clay Content as Indicated by CEC

When bulk EC is measured for the GPRP soil at 600 mS/m, the pore water EC is predicted to be approximately 2000 mS/m. But if the GPRP soils were free of clay (see the plot of σ versus σ_w for CEC = 0 in Figure 12), a bulk conductivity of 300 mS/m should predict the same conductivity of the pore water. When clay is present, the bulk conductivity is attributable to the electric double layer effects of the clay, and the remainder to the inter-connected pore water conductivity.

Unsaturated soil conditions also can have a significant impact on the ability to use bulk conductivity measurements to predict groundwater quality as illustrated by Figure 13. In the subsurface at the GPRP site however, the fine grained soils are typically at or near saturation and the water samples and ERI data blocks were always taken from the saturated zone.



Fig. 13: Significance of Degree of Saturation, Sw

3.8 Sensitivity of Using the Waxman Smits Model to Predict σ_w from σ data.

The sensitivity of Waxman Smits parameters with respect to its use to quantitatively predict σ_w for a given value of σ are discussed in the following sections.

When the parameter "*a*" is increased the effect on the value of the independent variable σ is negative. However, when *a* is increased the predicted value of σ_w is increased by the same proportion. This is illustrated in Figure 14, where a 5 per cent increase in the parameter *a* will cause the predicted value of σ_w to also increase approximately 5 per cent.





When the cementation factor is increased the predicted value of σ_w is increased by a larger proportion. In Figure 15, we see that a 5 per cent increase in *m* can mean that one would predict an approximately 20 per cent larger value for σ_w significantly in areas where σ is 100 mS/m. Where σ is large the prediction of σ_w is higher for a given value of σ . For example, at $\sigma = 450$ mS/m, a 5 per cent increase in *m* results in a 14.3 per cent overestimation of σ_w .

Fig. 15: ow Prediction Sensitivity Analysis: EC with Respect to Cementation Factor, m



When porosity is increased the effect on estimating σ_w using measurements of σ is negative. Therefore, when Φ is increased by five per cent, the estimated value of σ_w is reduced. In Figure 16, we see that a five per cent increase in Φ will cause more significant change in the magnitude of the difference for the predicted value of σ_w at low measurements of σ than at high. For example, at $\sigma = 100 \text{ mS/m}$, a 5% increase in Φ results in a 22% lower predicted value of σ_w ; at $\sigma = 450 \text{ mS/m}$, the prediction of σ_w is 11% lower.

Fig. 16: σ_w Prediction Sensitivity Analysis: EC with Respect to Porosity, Φ



-----φinaceedto0.2415

47

When the constant c_1 is increased the effect on estimating σ_w using measurements of σ is negative. Therefore, when c_1 is increased by five per cent, the predicted value of σ_w is reduced. In Figure 17, we see that a 5% increase in c_1 can mean that the reduction of σ_w is also approximately 5% when σ is at 100 mS/m. Where σ_w is large, the magnitude of the prediction of σ_w is lower for a given value of σ . For example, at $\sigma = 450$ mS/m, a 5% increase in c_1 only results in a 3.5% reduction of σ_w .



Fig. 17: σ_w Prediction Sensitivity Analysis: EC with Respect to c₁

48

When the constant c_2 is increased the effect on estimating σ_w using measurements of σ is positive. Therefore, when c_2 is increased by five per cent, the predicted value of σ_w is also increased. In Figure 18, we see that a 5% increase in c_2 can mean that we would not change the predicted σ_w significantly in areas where σ is high (450 mS/m). However, at σ = 75 mS/m, a 5% increase in c_2 results in a 20 % increase of σ_w .



Fig. 18: ow Prediction Sensitivity Analysis: EC with Respect to c2

ERI vs GW EC data (maximum) — Waxman Smits Model Max case (c2 = 0.8) - - c2 decreased to 0.76 ----- c2 increased to 0.84 ;

In Figure 19, we see that applying a 5% increase in the constant $c_{\rm 3}$ has little effect on predicting the value of σ_w in areas where σ is either small or large. Errors in selecting a value of c_3 are not expected to cause disproportionate changes in estimates of σ_w for all values of σ observed at this site.



Fig. 19: ow Prediction Sensitivity Analysis: EC with Respect to c3

c3 decreased to 1.235 -c3 increased to 1.365 In Figure 20, we see that predictions of σ_w are not as sensitive to the soil density parameter, ρ_s as some of the other parameters. However, an inverse relationship exists so that increasing ρ_s results in decreasing the value of σ_w . For example, at σ = 450 mS/m, a 5% increase in ρ_s results in a 3.4 % reduction of σ_w ; at σ = 100 mS/m, a 5% increase in ρ_s results in a 9 % reduction of σ_w .





51

When Cation Exchange Capacity is increased the effect on estimating σ_w using measurements of σ is negative. Therefore, when CEC is increased by five per cent, the predicted value of σ_w is reduced. In Figure 21, we can see that a 5% increase in Cation Exchange Capacity will cause σ_w to be reduced about 10 % in areas where σ_w is at 100 mS/m. Where σ_w is high the prediction of σ_w is less significant for a given value of σ . For example: At $\sigma = 450$ mS/m, a 5% increase in CEC results in approximately 3 % reduction of the predicted value of σ_w .

Fig. 21: ow Prediction Sensitivity Analysis: EC with Respect to CEC



Degree of Saturation cannot be increased beyond 100%. Therefore, the assessment of sensitivity is done for the case where Degree of Saturation is decreased. The effect of reducing saturation on predicting σ_w using measurements of σ is positive. In Figure 22, when S_w is decreased by five per cent, the predicted value of σ_w is increased about 20 % in areas where σ_w is at 100 mS/m. Where σ_w is high the prediction of σ_w is less significant for a given value of σ . For example: At $\sigma = 450$ mS/m, a 5% decrease in S_w results in approximately 11 % increase in the prediction of σ_w .



Fig. 22: ow Prediction Sensitivity Analysis: EC with Respect to Sw

53

The results of the prediction sensitivity analysis, (i.e., σ_w predicted from σ readings) are summarized in Table 6. The Waxman Smits parameters are in the order they appear in equation (6). The parameters most sensitive to this method of predicting σ_w from σ are ϕ , m, c₂, and S_w. The magnitude of the sensitivity of some parameters changes depending on whether low or high values of bulk EC are considered. When bulk EC is low (at or near 100 mS/m), sensitivity is proportionately greater in several parameters.

For this analysis, the prediction scaled sensitivities (after Hill, 1998), or the percent change in the predicted value of σ_w given a 5 percent change in the value of Waxman Smits parameter, are illustrated in Figure 23.

	% Change	Effect on Prediction of σ_w (% Change					
Parameter	Parameter	σ = 100 mS/m	σ = 450 mS/m				
а	+ 5 %	5.0	5.0				
m	+ 5 %	20.0	14.3				
φ	+5%	-22.0	-11.0				
C ₁	+ 5 %	-5.0	-3.5				
C ₂	+ 5 %	-20.0	- negligible				
C ₃	+5%	+ negligible	+ negligible				
CEC	+5%	-3.4	-9.0				
ρ _s	+ 5 %	-10.0	-3.0				
Sw	- 5 %	20.0	11.0				

Table 6: σ	w Prediction	Sensitivity	Analysis	Summary



Fig. 23: ow Prediction Scaled Sensitivities

3.9 Usefulness of the Waxman Smits Model

In making the attempt to fit data from a site like the GPRP site to a model like the Waxman Smits (1968), a question may arise in the mind of a practitioner: Why go through the effort and expense to apply the Waxman Smits model, when a linear regression fit through the collocated data points can be used to predict groundwater EC within the same order of magnitude? Depending on their investigative goals and objectives, each practitioner must answer this question for themselves. The implications of using a straight line fit for the data from the GPRP site are explored in this section.

The first aspect is one of overall accuracy of predictions based all parameters combined. What is the difference in predicted values of groundwater EC for the Waxman Smits versus straight line model? Referring again to Figure 10, the maximum difference between a predicted value of groundwater EC for a straight line model fit of the GPRP data versus a fit using the Waxman Smits model is, when bulk EC is determined to be 285 mS/m. Using the Waxman Smits fitted curve, the predicted groundwater EC is 715 mS/m, but if the straight line approximation is used, the prediction would be 875 mS/m. The magnitude of the difference is zero at the end points, where the model fit lines intersect.

Another aspect of concern when deciding whether to draw a straight line model or applying the Waxman Smits model arise from the knowledge that subsurface conditions are heterogeneous. From the results of the previous section, the most sensitive Waxman Smits parameters are porosity, cation exchange capacity, degree of saturation and cementation factor. The first three parameters are field derived parameters and will be analyzed herein for the range of values observed in site investigation data from the GPRP site, but analysis of cementation factor is based only upon information obtained from the literature. In the sensitivity analysis, the value of porosity at the GPRP site inferred from the neutron probes (Butterfield, 2001) was 23 %. The extreme values of porosity were 18 % and 36 %. The Waxman Smits curve for the average and extreme values of porosity are plotted on Figure 24, together with all of the collocated data points and the straight line fit of the data points. If bulk conductivity is 450 mS/m and the true value of porosity is 23 %, the predicted value of groundwater EC using the Waxman Smits fit and straight line fits are 1375 mS/m and 1415 mS/m, respectively. However, if all other parameters remain constant and porosity increases to 36 % the predicted value of groundwater EC would be 710 mS/m. Assuming 710 is the actual value at a particular location at the site, both data fits would over predict the groundwater EC at that location. When porosity is higher than 23 % at any particular location, the prediction from the Waxman Smits fit is closer.



Fig. 24: Affect of σ_w Prediction Due to Heterogeneous Porosity

3.9.2 Cation Exchange Capacity

The significance of cation exchange capacity (CEC) has been discussed in Section 3.7.1. Figure 12 illustrates that a higher value in CEC causes an increase in curvature of the Waxman Smits model. With respect to variability of CEC using the straight line fit at the GPRP, use of the Waxman Smits fit over a straight line fit is more important when CEC values are high.

Similar to the example for porosity, when CEC is higher than 28.25 meq/100 g (the value used to fit the Waxman Smits model) at any particular location, the prediction from the Waxman Smits fit is closer to the actual value. However, when CEC is lower than 28.25 meq/100 g the straight line fit is closer.

3.9.3 Saturation

The implications of using a Waxman Smits fit versus a straight line fit when considering only the degree of saturation is not as important at the GPRP as porosity and CEC. This is because most of the site is composed of fine grained soils that are or are very nearly saturated. Referring again to Figure 13, it is seen that the Waxman Smits fit for the fully saturated case is the same as in figure 10. If saturation at a particular location at the site is less than 1, the prediction of groundwater EC using a straight line fit would be closer to the actual groundwater EC.

3.9.4 Cementation Factor

As shown in Figure 23, cementation factor (m) directly affects the predicted value of groundwater EC. This is opposite to porosity and CEC, which have an inverse affect on the groundwater EC prediction. Therefore, if a straight line fit was applied rather than the Waxman Smits model at the GPRP, differences in the magnitude of predicted groundwater EC would result. Referring back to Figure 15, when m is higher at some location than the average used to do the data fit, the prediction of groundwater EC using the <u>straight line fit is closer</u> to the actual value. When m is lower at a location, the prediction using the Waxman Smits fit is closer.

4. CONCLUSIONS AND RECOMMENDATION

The Waxman Smits model cannot be easily calibrated to the data collected at the GPRP site. Historical investigations have resulted in significant disturbances to the subsurface and heterogeneous geology causes scatter in the data plot. Even without a strict calibration, a physically plausible fit of the model to the data collected at the GPRP site is possible for analysis of the model parameters. The Waxman Smits model parameters most sensitive to making quantitative predictions of σ_w from σ data are: porosity, cation exchange capacity (CEC), saturation and cementation factor.

If a site is free of clay minerals, the use of the Waxman Smits model is not required and Archie's Law can be applied. A linear regression best fit through collocated data points will provide estimates of electrical conductivity of groundwater in the same order of magnitude. Therefore, the use of the Waxman Smits to predict σ_w in sites containing clay may is most practically applied where the degree of heterogeneity is low. At the GPRP site the degree of variability of porosity and CEC are high. Prediction differences of groundwater EC from ERI data using a straight line fit are within the same order of magnitude as errors due to neglecting heterogeneity of porosity and CEC.

If a practitioner chooses to use the Waxman Smits model, rather than a linear regression model to develop a site specific relationship between groundwater EC and bulk EC, it is very important to fully characterize the porosity and cation exchange capacity of soils at that site. Water within a 50 mm piezometer is not necessarily representative of the same ground for which σ readings are attained by 3D ERI. The effect of this uncertainty should be determined for each new site where these methods are employed. It may be possible to minimize this uncertainty by using a water sampling method where more control over where sampling of pore water is achieved in situ.

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