POTENTIAL EFFECTS OF GEOLOGIC STORAGE OF CO2 ON SURFACE WATER AND SHALLOW GROUNDWATER

ShuangShuang Xie
Clemson University, shuangs@g.clemson.edu
POTENTIAL EFFECTS OF GEOLOGIC STORAGE OF CO$_2$
ON SURFACE WATER AND SHALLOW GROUNDWATER

A Thesis
Presented to
The Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Sciences

By
Shuangshuang Xie
August 2014

Accepted by:
Dr. Lawrence C. Murdoch, Committee Chair
Dr. Ronald W. Falta
Dr. Timothy A. DeVol
ABSTRACT

Storage of supercritical phase CO\textsubscript{2} in deep saline aquifers is being considered to reduce greenhouse gases in the atmosphere, and this process is expected to increase the pressure in these deep aquifers. One potential consequence of pressurization is an increase in the upward flux of saline water. Saline groundwater occurs naturally at shallow depths in many sedimentary basins, so an upward flux of solutes could degrade the quality of aquifers, and threaten aquatic ecosystems where groundwater discharge is important. The objective of this research is to evaluate the impacts associated with increasing the upward flux of saline water as a result of CO\textsubscript{2} storage, or other effects. The approach was to develop and evaluate simulations of salt concentration in a fresh water aquifer overlying saline groundwater that is subjected to changes in flux. The first task was to verify the solution of benchmark problems of density-dependent flow using the computational codes COMSOL Multiphysics. The COMSOL code was then used to analyze idealized 2D and 3D geometries representing the essential details of a shallow, fresh water aquifer underlain by a saline ground water in a sedimentary basin. The analysis was conducted in two stages, one that simulated the development of a fresh water aquifer by flushing out salt water, and another that simulated the effect of a pulse-like increase in the upward flux from the basin. The effects of saline encroachment were evaluated using a sensitivity analysis of key parameters, and the results were formulated in both dimensioned and dimensionless form.
The results indicate that the depth of the fresh/salt interface is a function of the recharge rate, duration of fresh water flushing/basin flux rate, density of the saline water, as well as the formation anisotropy. The fresh/salt interface was found to be more uniform and shallower as the density of the salt water increased. Increased upward flux of saline water raised the fresh/salt interface, and it increased the salinity of water discharging to streams. The magnitudes of these effects are evaluated using the proposed impact assessment criteria 1) maximum concentration in stream 2) mass loading rate to the stream 3) fractional change in freshwater layer thickness. The magnitude of the impact generally increased with increased depth to fresh/salt transition zone and increased basin flux rate. Using criterion 1) and 2) the effect appeared to be low with initial transition depth of 200 meters and basin flux of less than the recharge rate (Re). Severe impact occurred with basin flux was equal to 10xRe. According to Criterion 3) impacts are categorized generally by basin flux rate. Low impact occurred with basin flux was equal to 0.1xRe, significant impact when the flux was equal to the recharge, and severe impact occurred with basin flux was 10xRe. The impact of increases in chloride concentration in the fresh water system lasted longer than 3 times injection period.

The significant contributions of this study include 1) identification of important controls on development of freshwater aquifers underlain saline water aquifer; 2) evaluation of the expected impacts posed by increased flux from saline aquifers caused by CO$_2$ storage.
DEDICATION

To grandpa, who lead me into nature

To my dearest mom and dad
ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Larry Murdoch, for his patience through my research, thesis writing and coursework at Clemson. Special thanks also go to my committee members Dr. Ronald Falta and Dr. Timothy DeVol, for offering me suggestions on thesis and generous help on career development.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td><strong>CHAPTER I. INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>Objective</td>
<td>8</td>
</tr>
<tr>
<td>Approach</td>
<td>8</td>
</tr>
<tr>
<td>Background: Numerical Models</td>
<td>8</td>
</tr>
<tr>
<td>Background: Benchmark Problems</td>
<td>10</td>
</tr>
<tr>
<td>Importance of this study</td>
<td>12</td>
</tr>
<tr>
<td>Thesis Outline</td>
<td>13</td>
</tr>
<tr>
<td><strong>CHAPTER II. RESEARCH METHODOLOGY</strong></td>
<td>14</td>
</tr>
<tr>
<td>Study Workflow</td>
<td>14</td>
</tr>
<tr>
<td>Governing Equations</td>
<td>16</td>
</tr>
<tr>
<td>Numerical Method</td>
<td>28</td>
</tr>
<tr>
<td><strong>CHAPTER III. ANALYSIS OF BENCHMARK PROBLEMS</strong></td>
<td>31</td>
</tr>
<tr>
<td>Henry Problem</td>
<td>31</td>
</tr>
<tr>
<td>Elder Problem</td>
<td>36</td>
</tr>
<tr>
<td>HYDROCOIN Case 5 Problem</td>
<td>42</td>
</tr>
<tr>
<td><strong>CHAPTER IV. ANALYSIS OF SALT TRANSPORT CAUSED BY PRESSURE</strong></td>
<td>47</td>
</tr>
<tr>
<td>Conceptual Model</td>
<td>47</td>
</tr>
<tr>
<td>Numerical Model</td>
<td>50</td>
</tr>
<tr>
<td>Initial conditions and boundary sequence</td>
<td>52</td>
</tr>
<tr>
<td>Characterization of Stage 1 Freshwater Flushing</td>
<td>66</td>
</tr>
<tr>
<td>Characterization of Stage 2 Basin Flux</td>
<td>91</td>
</tr>
</tbody>
</table>
Table of Contents (Continued)                                           Page

3D Numerical Analysis ........................................................................ 102

CHAPTER V.  IDENTIFICATION OF IMPACTS ........................................ 116

  Impacts to Surface Water Based on Concentration .......................... 116
  Impacts to Surface Water Based on Mass Loading Rate ................ 119
  Impacts to Ground Water .......................................................... 122

CHAPTER VI.  CONCLUSIONS ............................................................. 125

  Freshwater Flushing ................................................................. 126
  Basin Pulse .............................................................................. 128
  Impact Assessment ..................................................................... 131
  Implications to CO₂ Storage ..................................................... 134

REFERENCES ................................................................................ 136
LIST OF TABLES

Table 1 Model conditions ........................................................................................................... 54
Table 2 Model parameters ........................................................................................................... 54
Table 3 Maximum concentration, and mass loading rate discharging to stream and the
fractional change of the thickness of the freshwater layer predicted from 2D analyses at
the end of a 50-year-long pulse for various basic fluxes and transition depths. Impact
levels from Chapter 5, green=Low impact; Yellow = significant impact; red= severe
impact........................................................................................................................................ 133
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Generalized ground-water flow patterns in a multilayer, regional aquifer system. Groundwater discharges into surface discharge areas; blue arrows show groundwater flow directions (Barlow 2003).</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Depth to saline ground water, generalized by National Research Council (2008) from Feth (1965).</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>Overview of research methodology.</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Mass flux through a control volume in the x direction.</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>Viscosity of NaCl solutions as a functions of concentration and temperature using Eqn. 24 (Ozbek 2010)</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>Conceptual model of Henry problem (side view of vertical plane).</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>COMSOL mesh construction for Henry problem.</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>COMSOL simulation of Henry's problem with 25%, 50% and 70% saltwater concentration contours.</td>
<td>34</td>
</tr>
<tr>
<td>9</td>
<td>Conceptual model of Elder problem (side view of vertical plane).</td>
<td>37</td>
</tr>
<tr>
<td>10</td>
<td>COMSOL mesh construction for Elder problem (two symmetric half planes each representing either side of the plume).</td>
<td>39</td>
</tr>
<tr>
<td>11</td>
<td>COMSOL simulation of Elder problem in time series (Left: COMSOL simulation (color legend is normalized concentration); Right: previous published benchmark problems using SEAWAT, SUTRA and Elder experiments)</td>
<td>40</td>
</tr>
<tr>
<td>12</td>
<td>20% and 60% source concentration contours measured by Elder and simulated by COMSOL and in other published studies.</td>
<td>41</td>
</tr>
</tbody>
</table>
Figure 13 Conceptual model of HYDROCOIN Case 5 problem. ........................................ 43
Figure 14 COMSOL mesh for Hydrocoin problem .......................................................... 43
Figure 15 Concentration contours simulated by COMSOL (dash-dot), MOCDENSE (red dash) and SEAWAT (Langevin 2001); Concentration contours were in magnitude of 0.05, 0.1, 0.2 and 0.3 from top to bottom. ..................................................................................... 45
Figure 16 Conceptual model showing a shallowly dipping aquifer receiving recharge with streams crossing perpendicular to strike. Freshwater occurs at shallow depths and is underlain by saline water. Brown layer is an aquitard which is assumed to perfectly seal the groundwater flow within lower formation. Injection of CO₂ deep within the basin increases the pressure and causes upward flow, displacing the fresh/salt interface upward and increasing the risk of contaminating shallow aquifers with salt. Dashed line shows a location of the 2D model ............................................................................................... 49
Figure 17 Geometry and boundary conditions for the 2D problem. Numbers are dimensions in meters .................................................................................................................. 51
Figure 18 Baseline finite element mesh used for the analysis .............................................. 56
Figure 19 Mesh in vicinity of stream, blue line, minimum element width is 0.7 m .......... 57
Figure 20 Mesh generated using $\chi=0.3$ and $\chi=2.0$ ......................................................... 59
Figure 21 Concentration distribution after Freshwater Flushing Stage of 300 yrs (Top to bottom: $\chi=0.3$, 0.5, 1, 1.5, 2.0) ......................................................................................... 61
Figure 22 Concentration profile beneath the upland with different mesh density .......... 63
Figure 23 Concentration profile across the stream with different mesh density .......... 64
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>Representative cross section concentration distribution (color, in mol/m$^3$) created when freshwater flushes salt water. White line is 8.55 mol/m$^3$ (500 ppm), indicating fresh/salt interface; blue lines are streamlines indicating flow paths; yellow arrow shows how $D_L$ is defined.</td>
</tr>
<tr>
<td>25</td>
<td>Cross sections of the development of a fresh water aquifer by flushing salt water at five simulation time spot. (Upper Row: background scenario with constant density; Lower Row: test scenario with dependent density)</td>
</tr>
<tr>
<td>26</td>
<td>Hydraulic head (m) and salt flux (mol/m$^2$ s) distribution (no-flow bottom boundary)</td>
</tr>
<tr>
<td>27</td>
<td>Hydraulic head (m) and salt flux (mol/m$^2$ s) distribution (constant head bottom boundary)</td>
</tr>
<tr>
<td>28</td>
<td>Fresh/brackish interface with no-flow boundary (white) and constant head boundary (cyan) after 8x10$^{11}$s flushing.</td>
</tr>
<tr>
<td>29</td>
<td>Normal convective flux (mol/(m$^2$ s)) through bottom boundary during freshwater flushing stage (positive: outward domain; negative: inward domain).</td>
</tr>
<tr>
<td>30</td>
<td>Freshwater/brackish interface with viscosity of 1.01mPa s (red), 1.04mPa s (green) and 1.09mPa s (yellow).</td>
</tr>
<tr>
<td>31</td>
<td>Freshwater/brackish interface with viscosity of 1.01mPa s (red), 1.04mPa s (green) and 1.09mPa s (yellow). Close up view beneath the upland in Figure 30.</td>
</tr>
<tr>
<td>32</td>
<td>Dimensioned and dimensionless configuration with varying anisotropy.</td>
</tr>
</tbody>
</table>
Figure 33 $D_L$ as a function of time for different values of $R$ and $D$ using dimensioned (a.) and dimensionless (b.) axes. $R/D$ is held constant at $R/D=0.05$ m$^{-1}$ ........................................ 83

Figure 34 Dimensioned salt-fresh interface depth below upland with/without density-dependent coupling (fixed $k/R$ ratio). .......................................................... 86

Figure 35 Dimensionless characteristic salt-fresh interface depth below upland with/without density-dependent coupling (fixed $k/R$ ratio). .......................................................... 86

Figure 36 $k/R$ ratio change with fixed $R$ of $10^{-8}$ m/s, permeability $= 10^{-14}$ m$^2$ (Blue), $10^{-14}$ m$^2$ (Red), $10^{-14}$ m$^2$ (Green) under constant concentration condition. ............................... 88

Figure 37 $k/R$ ratio change with fixed $k$. (Upper: dimensioned scaling; Lower: dimensionless scaling) .................................................................................................................... 90

Figure 38 Upper: Salt concentration across stream for pulses lasting 5 years (red), 20 years (green), and 50 (blue) years. Columns are for different magnitudes of $q_b$. Lower: Cross sections of concentration (color) and the fresh/salt interface (lines) before and after pulse of basin flux). Column 1: initial $D_L = 200$ m; Column 2: initial $D_L = 300$ m; Column 3: initial $D_L = 400$ m. ........................................................................................................... 93

Figure 39 Vertical profile of salt concentration measured up to 500 m beneath upland/stream before and after 50 year basin pulse ........................................................................................................... 95

Figure 40 Average concentration of water discharging to streams during and following a 50-yr-long pulse of increased flux from the basin (basin flux=0.1Re (upper), 1.0Re (middle) and 10Re (lower); Initial concentration $=1000$[mol/m$^3$]). Pulse ends at t=50 yrs (1.58e9[s]) ........................................................................................................... 97
Figure 41 Average concentration (mol/m$^3$) of water discharging to streams during and following a 50-yr-long pulse of increased flux from the basin (basin flux=0.1, 1 and 10 recharge flux; c=600[mol/m$^3$]). Peak concentration occurs at t=50 yrs ($1.58\times10^9$[s]).

Figure 42 Hydraulic head and flow vectors early in the flushing stage (t = 0.5Gs, 15.9yrs). Dark red is +4m. Dark blue is 0m.

Figure 43 Change in pressure head as a function of time at 50m depth in unconfined part of the aquifer (x=250m, y=1000m).

Figure 44 Development of a dipping freshwater aquifer by flushing of connate salt water, $C_i=600$mol/m$^3$ (35kg/m$^3$). Case 1, c.h. boundary on downdip side. Color on vertical sections is concentration, blue = 0.1$C_i$, dark red > 0.5$C_i$. Particle traces are colored with $\log(t_{max})$, where $t_{max}$ is the maximum time in that frame. Green balls are the current position of a particle. Stream is the double yellow line. Confining unit is grey.

Figure 45 Volumetric flux of water out of lower boundary as a function of time normalized to the recharge flux.

Figure 46 Conditions after 2000Gs of flushing connate salt water with fresh water in recharge area. a.) Particle traces with relative velocity in as color (red=fast, blue=slow). Green isosurface bounds freshwater zone ($C<1000$mg/l). b. Concentrations at surface.

Figure 47a. Maximum (green) and average (blue) concentration of salt in ground water discharging to stream during fresh water flushing. b. Mass rate of salt discharging to stream during fresh water flushing.
Figure 48 Pressure head at the lower boundary (green) and at 50 m depth in the unconfined aquifer at (250m, 1000m) the same location as in Figure 43 (blue)............ 111

Figure 49 Maximum and average concentration of groundwater discharging to stream as a function of time. Pulse of increased pressure from basin from 2000 to 2003 Gs....... 113

Figure 50 Mass rate as a function of time during and following a pulse from the basin.114

Figure 51 Concentrations on boundaries at different times using same color scheme and perspective view as Figure 56. The top surface of the outcrop and above the fresh water isosurface (green) was transparent to show the position of the isosurface. The blue surface was fresh water at the bottom of the aquifer. Elevated pressure occurred as a pulse $2000G_t < t < 2003G_s$. Bottom row was enlargement of the vicinity of the down-dip end of the stream. Dashed green line was contact between fresh and brackish water. Grey line was trace of the contact with the upper confining unit. White rectangle was a reference location and scale for the upper row. The stream was 10m wide for scale in the lower row. .......................................................... 115
CHAPTER I. INTRODUCTION

Geological carbon storage is being considered as a possible approach to reduce greenhouse gases in the atmosphere (USEPA 2013). Injecting dissolved or supercritical phase CO$_2$ into deep saline aquifers is designed to isolate the CO$_2$ and limit its detrimental effects on climate. For geological storage to be a viable option, however, it must be cost effective and have negligible environmental impact (USEPA 2013). One consequence of geologic storage is the pressurization effects in the host formation. The footprint area of the elevated pressure can be much larger than the CO$_2$ plume. Zhou et al. (2010) estimated that for a CO$_2$ plume of 100 km$^2$ area the elevated pressure area should be several 100,000 km$^2$. The pressurization may also displace saline water and encroach on overlying freshwater aquifer systems (Cavanagh 2011), which could reduce the quality of both ground water and surface water.

Salt water encroachment is common in coastal areas, where the shoreward movement of sea water displaces fresh water (Lee and Cheng 1974; Bakker 2003; Hutchings 2003; Lin et al. 2009). Encroachment may also occur as the upconing of saltwater beneath pumping wells in areas where fresh water aquifers are underlain by more saline water (Birkholzer et al. 2011; Celia et al. 2011). Upward flow along permeable faults or abandoned wells may exacerbate this process. Factors that could increase the upward flow of saline water are a concern because two-thirds of the freshwater aquifers used for water supply in the United States are underlain by highly saline aquifers (Fairchild 1987).
The distribution of salt and fresh water in an aquifer can result from many processes integrated through the geologic history of the parent formation, but the same basic process is likely important early in the formation of fresh water aquifers in many areas. Aquifer materials are commonly deposited in saline water, for example, when sands are deposited during a transgression. At some point, uplift or sea-level drop exposes the region sub-aerially where it is exposed to rainfall. Fresh water infiltrates during rainfall and begins to flush out the connate salt water. A similar process could occur when sea level falls after a period of seawater inundation—not necessarily when the aquifer material was deposited. Continued recharge forms a thin layer of fresh water that deepens with time. Mixing of fresh and salt water forms a transition zone that widens and deepens as recharge continues to flush salt from the aquifer. This process results in a fresh water aquifer that transitions to saltier water at depth. Myriad processes, including fluctuations in sea level, variations in recharge, glacial loading and ice melting (Siddall et al. 2003), interaction between water and rocks (Webster 1994), and hydrostratigraphy can modify the distribution of salt in ground water (Korus 2013).

Fluctuations in sea level have played a role in the development of fresh water aquifers, particularly in coastal areas. During the last interglacial period, sea level rise submerged the coastal plain and seawater intruded unconsolidated sediments. Similarly, sea level dropped during glacial advances, and the average sea level during the past 900,000 years has been estimated as more than 150 ft lower than present (Meisler 1985). As sea level declines during glaciation, the land surface is exposed to freshwater recharge, flushing out salt water and pushing the fresh/salt transition downward and toward the sea.
In some areas where groundwater circulation was relatively slow, seawater has remained trapped in the sediments and bedrock (Tepper 1980; Snow 1990). For example, in the Lake Okeechobee area, Florida where the flow system in the Upper Floridian aquifer is tightly confined, a saline aquifer was discovered. This may be due to incomplete freshwater flushing of residual seawater left behind during high sea level stands in the Pleistocene (Johnston 1988; Sprinkle 1989; Reese 1994; Reese 2000).

In coastal areas, the fluctuations of sea level produced a broad zone where the salt content of the groundwater is variable (Barlow 2003). Water density increases with salt concentration and concentration-induced variations in density are large enough to affect flow in ground water. Density differences cause seawater to intrude beneath fresh water, for example. Saltwater predominates in the deeper and seaward region and freshwater predominates in the shallower and landward region of northern Atlantic Coastal Plain (Meisler 1985). The fresh/salt water transition may be either sharp or dispersed majorly depending on density difference and hydraulic head distribution (Kim et al. 2007).

The importance of the density difference between fresh and salt water has long been recognized. According to Konikow and Reilly (1999), the principle of static equilibrium between fresh and salt water can be attributed to Du Commun (1828), who used this principle to explain water levels in wells in Coastal Plain sediments in New Jersey. Despite the early work by Du Commun, it is Ghyben and Herzberg (Mahendra 2013) who are generally recognized as identifying the basic relationship between water
density and piezometric height. By equating the pressures in two columns of water with
different densities, the Gyben-Herzberg relation shows that

$$\Delta h = h_1 \left( \frac{\rho_s - \rho_f}{\rho_f} \right)$$

(1)

where $\Delta h$ is the head in a freshwater aquifer measured relative to sea level, $h_1$ is the depth
to the fresh/salt interface below sealevel, $\rho_s$ is the density of salt water and $\rho_f$ is the
density of fresh water. The density of seawater is approximately 1025 kg/m$^3$, and using
$\rho_f = 1000$ kg/m$^3$ gives 1/40. As a result, the Ghyben-Hersberg relation (1) implies that for
every foot of fresh water in an unconfined aquifer above sea level, there will be forty feet
of fresh water in the aquifer below sea level (Herzberg 1901). This difference in water
level is independent of horizontal changes in head and is solely due to changes in density.
The depth from ground surface to saline water layer is not only affected by surface recharge but is also dominated by factors like regional structure, subsurface drainage patterns, and hydrogeologic properties in regional study. Typical fresh/salt interface naturally forms under regional groundwater circulation, as is schematically shown in Figure 1 (Barlow 2003).

![Figure 1 Generalized ground-water flow patterns in a multilayer, regional aquifer system. Groundwater discharges into surface discharge areas; blue arrows show groundwater flow directions (Barlow 2003).](image)

An example of regional interface distribution was taken around Jessamine Dome and the downdip regions away from the dome (Hopkins 1966). As part of the Mississippian Plateau region the fresh/salt interface is mostly under the influence of
surface/subsurface drainage pattern. The regional interface gradient from beneath the upland to beneath nearby major streams as the Salt, Kentucky and Licking Rivers and their tributaries was approximated as the dip of rocks away from the Jassamine Dome (Hopkins 1966).

Salt water intrusion is certainly important in coastal areas, but salt water also underlies much of the United States. Saline water occurs commonly at depths less than 150 m, and over half of the continent is underlain by saline water within a 500 m depth (Figure 2) (Feth 1965). For example, in Mississippian Plateau of Kentucky, the normal depth to the fresh/salt interface is no more than about 300 m. The Western Coal Fields region of Kentucky has an average of 180 m depth to fresh/salt interface (Hopkins 1966).

Many of the areas in Figure 2 where saline water is relatively shallow are sedimentary basins being considered for CO₂ storage. The shallow occurrence of saline water makes the fresh water resources in these areas vulnerable to contamination if CO₂ storage increases the upward flux. Certainly limiting the extent of basin pressurization is an important component of the design of CO₂ storage projects, but the consequences of basin pressurization and increased upward flux have primarily focused on effects from leaking wells or faults (Rutqvist et al. 2007; Zhou et al. 2008; Birkholzer et al. 2011). While these leakage paths certainly present risks, the details of how upwardly flowing saline water would interact with fresh water remain incompletely known. As a result, it
is difficult to evaluate how pressurizing a basin may affect risks of contaminating overlying aquifers with salt.

Figure 2 Depth to saline ground water, generalized by National Research Council (2008) from Feth (1965).
Objective

The objective of this study is to evaluate how an increase in upward flux of saline water from the basin could affect water quality in freshwater aquifers and surface waters. Particularly the objective is to estimate the changes in salt concentration that result from a pulse-like change in upward flux, which could result from pressurization during CO$_2$ storage.

Approach

The approach used for this investigation includes:

- Analyze benchmark problems to verify the performance of COMSOL Multiphysics code;
- Characterize the development of a freshwater aquifer by flushing of salt water in idealized, but representative aquifer geometries;
- Evaluate the effects of a pulse of upward flux of saline water on the distribution of salt concentration in shallow ground water and surface water;
- Evaluate environment impacts to ground water and surface water.

Background: Numerical Models

Numerical models have been important tools to explore flow dynamics and saline water encroachment during CO$_2$ injection into deep saline aquifers, and they will be an important tool in this research. Simulations range from simple one-dimensional,
homogenous conditions (Kumar 2007) to strongly heterogeneous geologic formations (Doughty and Pruess 2004). Most of the previous studies have been devoted to investigating the transport phenomena at the plume scale, which is typically on the order of less than 100 km$^2$ (Zhou et al. 2010; Hussain 2013). In plume-scale models, CO$_2$ gas saturation and pressure buildup distribution (Rutqvist et al. 2007; Birkholzer et al. 2009; Mathias et al. 2009; Nicot 2009; Birkholzer et al. 2011) was studied in vicinity of the CO$_2$ injection well. However, increased attention is being paid towards the basin-scale migration of formation water.

Conceptualized regional groundwater flow models were developed to evaluate possible impacts brought by geologic CO$_2$ injection and storage. Site specific study cases were applied to the Texas Gulf Coast Basin (Nicot 2008), Illinois Basin (Person et al. 2010) in the United States and Tokyo Bay in Japan (Yamamoto et al. 2009). Numerical models serve to support decision making. For example, in United States a certification framework (CF) (Oldenburg 2009) was developed to ensure the potential impact of pressurization effects at geologic carbon sequestration sites was within safety thresholds. Yet other than water table rise and CO$_2$ plume migration/well leakage as a result of pressurized injection (Nordbotten et al. 2004; Nordbotten et al. 2005), rarely have any regional studies paid specific attention to density-dependent flow exchange between saline and freshwater system.

Internal fluid density variance is one of the notable driving forces on regional groundwater flow patterns (Celia et al. 2011) (Gupta and Bair 1997). Previous research on
seawater (NaCl concentration at ~30 g/L) encroachment (Huyakorn et al. 1987) initiated the governing equation of variable density flow in terms of reference hydraulic head. Numerical method was examined and improved (Voss and Souza 1987) to come up with solutions of density-dependent groundwater flow with sharp transition zone, followed by more innovated methods to simplify the density implementation (Bakker 2003).

To solve complex density-dependent groundwater flow problems numerical models are used to compute flow and transport at discrete temporal and spatial points. In this study three numerical code COMSOL Multiphysics (COMSOL 2012) was evaluated. COMSOL Multiphysics is a finite element code designed to analyze a wide range of processes, including fluid flow, mass and heat transport, elasticity, electromagnetism, and related modules.

**Background: Benchmark Problems**

Even though numerical codes have been highly developed, different constructions of computational schemes embedded in numerical codes come with variation in numerical accuracy and computation speed. Computational efficiency also depends on the way that physics modules are internally coupled. Therefore it is crucial to compare and verify the performance for specific applications (i.e. density-dependent flow in this study). Voss and Souza (1987) stated that using Henry’s (Henry 1964) problem for verification of density-dependent transport simulators is inadequate to check for consistency of velocity approximations, and for the accuracy of simulating flow driven by buoyancy forces. Therefore in addition to Henry’s problem, 2D benchmark problems
described by (Elder 1967) and (Cole 1986) as Elder’s and HYDROCOIN Case 5 problems were used in this study for code assessment. The semi-analytical Henry solution assumes a linear relationship between dissolved salt concentration and fluid density, constant dispersion coefficient and maximum fluid density that is not significantly larger than freshwater density (Simpson and Clement 2004). The Elder problem was modified into a solute transport problem from an experimental heat transport problem performed in a Hele-Shaw cell (Hogan 2006). There is currently no analytical solution to the Elder problem. It is difficult to identically reproduce the Elder solution because the results are sensitive to model parameters and mesh discretization (Diersch and Kolditz 2002). In a previous benchmark problem study described by Dausman (2009), a simulation of Elder problem using A Computer Program for Simulation of Three-Dimensional Variable-Density Ground-Water Flow and Transport (SEAWAT) was compared with 1) the original numerical results from Elder (1967), 2) results from a previous version of SEAWAT (Guo 2002), and 3) results from Saturated-Unsaturated Transport (SUTRA) (Voss 2010). The HYDROCOIN Case 5 problem is a theoretical analysis applicable for inter-code testing (Dausman 2009). It was designed to represent freshwater flowing across the top of a salt formation under both a hydraulic head gradient and density-driven diffusion. Details of benchmark problems will be stated.
**Importance of this study**

As transport-incorporated groundwater flow problems are applied to real-world cases, numerous site specific studies have been implemented based on local aquifer properties and observations. For example, previous research on geologic carbon sequestration impacts on groundwater resources in United States mainly focused on the Illinois Basin (Person et al. 2010) and Texas Gulf Coast area (Nicot 2008). However, it is recognized that in many of the study areas where the density-dependent groundwater flow problem is occurring, data is not available to parameterize complex models. The lack of model training data calls for relatively simple and robust methodologies based on commonly obtained data (Filfedder 2002).

In summary, density-dependent groundwater flow and its related benchmark problems have been widely discussed for decades. Yet still there are aspects that can be further emphasized. Firstly, few evaluations has been placed using finite element COMSOL Multiphysics code on classic benchmark density-dependent flow problems. Moreover, previous studies explored regional-scale carbon sequestration driving groundwater flow problems in either idealized geometry (Birkholzer et al. 2009) or with constant regional salinity (Nicot 2008; Yamamoto et al. 2009). Rarely has any dimensionless-scale analysis of flow and transport in porous media been compared to regional environmental regulations. This study aims to assess environmental impacts due to CO$_2$ sequestration introduced density-dependent salt water encroachment. The
ultimate purpose is to increase the model flexibility and robustness in applying to
different field study cases.

**Thesis Outline**

Chapter Two starts with an overview of research methodology. The second part
introduces the theoretical background of numerical modeling used in this study. The
governing equations of groundwater flow, transport and density-dependent features will
be discussed.

Chapter Three Analysis of Benchmark Problems evaluates COMSOL
performance on benchmark problems where the density is a function of concentration.

Chapter Four Analysis of Salt Transport at Shallow Depths presents a conceptual
model with model geometry and boundary conditions. A numerical model is used to
simulate flushing of salt water to produce a freshwater aquifer, followed by a pulse of
upward flux of saltwater. Results of both two-dimensional and three-dimensional models
are presented.

Chapter Five identifies the environmental impacts associated with increases in
upward flux from a basin. Regional regulations will be concerned to support the risk
assessment framework, and determine how much effect the conceptualized encroachment
will place on surface water system and freshwater aquifer.
CHAPTER II. RESEARCH METHODOLOGY

Study Workflow

The overall study workflow consisted of five elements (Figure 3).

1. **Code verification** The code COMSOL Multiphysics was initially verified by analyzing benchmark problems.

2. **Evaluate flushing of connate salt water** COMSOL Multiphysics performed well during the benchmark tests, and it was then used to simulate flushing of connate saline water to form a freshwater aquifer system. The development of the freshwater aquifer defines the distribution of salt at the onset of the pulse of flux from the basin, and this initial salt distribution is an important control on the impact to streams.

3. **Evaluate scaling** To better understand the development of the freshwater aquifer, the process was analyzed to determine the controlling scales. This results in a characterization of the flushing of connate saltwater governed by dimensionless variables.

4. **Evaluate effects of flux from basin** The effects of a pulse-like increase in upward flux of salt water were characterized with the results from element 2 as initial conditions. Parameter sensitivities were evaluated over 2D and 3D domains.
5. Evaluation The impacts to ground water and surface water resulting from an increase in basin flux were assessed by comparing to current regulations and research results.

![Diagram](image_url)

**Figure 3 Overview of research methodology**
Governing Equations

Equations governing the computation process are derived from conservation of mass and momentum using dependent variables of hydraulic head or pressure, and solute concentration. The concentration effect on fluid density and viscosity, that the flow/transport coupling will be discussed in the following sections.

Conservation of mass

Mathematical representation of groundwater flow requires considering a mass balance on the water stored within, and crossing the boundaries of a control volume (Figure 4). The rate of increase of water mass within the control volume equals the sum of inward mass flux integrated over each face of the control volume and the rate of mass produced by sources within the control volume.

\[ \rho q_x + \frac{d}{dx}(\rho q_x) \Delta x \]

Figure 4 Mass flux through a control volume in the x direction.

Assuming a 1D flow in the x direction for the purposes of illustration, Figure 4 shows that integrating the inward mass flux over the surface of the control volume gives
the net mass rate entering the control volume as \( \frac{d}{dx}(\rho q_x)\Delta A \) where \( \rho \) is fluid density, \( q_x \) is the volumetric flux \([L^3 T^{-1}]\), and \( \Delta A = \Delta y\Delta z \). It follows that the mass conservation principle outlined above can be expressed as

\[
\nabla \cdot (\rho \bar{q}) + \rho Q_s = \frac{\partial (n\rho)}{\partial t}
\]

where \( Q_s \) is a volumetric rate of water produced by a source per unit volume \([T^{-1}]\), and \( n \) is porosity. Expanding the right hand side gives,

\[
\frac{\partial (n\rho)}{\partial t} = \rho \frac{\partial n}{\partial t} + n \frac{\partial \rho}{\partial t} = \rho \frac{\partial n}{\partial P} \frac{\partial P}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t}
\]

Fluid density is a function of fluid pressure and solute concentration under isothermal conditions. Therefore, the last term in Equation (2) can be written as:

\[
\frac{\partial \rho}{\partial t} = \frac{\partial \rho}{\partial P} \frac{\partial P}{\partial t} + \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t}
\]

where \( P \) is pore pressure \([ML^{-1}T^{-2}]\), and \( C \) is solute concentration \([ML^{-3}]\).

Substituting (3) into (2) gives

\[
\frac{\partial (n\rho)}{\partial t} = \rho \frac{\partial n}{\partial t} + n \frac{\partial \rho}{\partial t} = \rho \frac{\partial n}{\partial P} \frac{\partial P}{\partial t} + \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} + \frac{\partial \rho}{\partial P} \frac{\partial P}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t}
\]

Introducing the definition of bulk aquifer pore compressibility \([M^1LT^2] \) (Bear 1979)
\[ \beta_p = \frac{1}{(1 - n)} \frac{\partial n}{\partial P} \]  \hspace{1cm} (5)

also water compressibility \([\text{M}^{-1}\text{LT}^2]\) is

\[ \beta_w = \frac{1}{\rho} \frac{\partial \rho}{\partial P} \]  \hspace{1cm} (6)

Taking (5) and (6) into (4) gives

\[ \frac{\partial(n \rho)}{\partial t} = \rho \beta_p (1 - n) + \beta_w n \frac{\partial P}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} \]  \hspace{1cm} (7)

where \( S_s = \beta_p (1 - n) + \beta_w n \) is the volume of water released from storage per unit volume of an aquifer per unit change in pressure \([P^{-1}]\).

Therefore Equation (7) becomes

\[ \frac{\partial(n \rho)}{\partial t} = \rho S_s \frac{\partial P}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} \]  \hspace{1cm} (8)

and Equation (1) becomes

\[ \nabla \cdot (\rho \bar{q}) + \rho Q_s = \rho S_s \frac{\partial P}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} \]  \hspace{1cm} (9)

**Equation governing head or pressure**

The general form of Darcy’s law for groundwater flow is typically written as

\[ \bar{q} = -\frac{k}{\mu} (\nabla P + \rho g \nabla z) \]  \hspace{1cm} (10)
where $\vec{q}$ is the volumetric flux vector, $\vec{k}$ is the intrinsic permeability tensor [$L^2$], $\mu$ is dynamic viscosity [$ML^{-1}T^{-1}$], $P$ is pressure, $\rho$ is fluid density, $g$ is gravitational acceleration, and $z$ is the upward elevation coordinate.

It follows by substitution that the equation governing the pressure in an aquifer is governed by

$$
-\nabla \cdot \left( \frac{\rho \vec{k}}{\mu} (\nabla P + \rho g \nabla z) \right) + \rho QT = \rho S_t \frac{\partial P}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t}
$$

(11)

A slightly different form of governing equation is used by density dependent flow codes. This occurs because a form of Darcy’s law is used which is based on freshwater head instead of pressure (Guo 2002). Equivalent freshwater head (Luschynski 1961) is

$$
h_f = \frac{P}{\rho_f g} + z
$$

(12)

Where freshwater head is the elevation above an arbitrary datum of the water surface in a piezometer filled with freshwater. Note $\rho_f$ is the density of fresh water [$ML^{-3}$] and $P$ is the pressure in the aquifer. The hydrostatic pressure in water whose average density is $\rho$, and is given by

$$
P = (h - z) \rho g
$$

(13)

Rearranging (12), equating to (13) gives the total freshwater head in terms of the total hydraulic head, $h$, as
Darcy’s Law can be written in terms of hydraulic head by introducing freshwater hydraulic conductivity computed from freshwater density and viscosity \( \tilde{K}_f \) [LT\(^{-1}\)]

\[
h_f = h \frac{\rho_f}{\rho_f} + z \frac{\rho_f - \rho}{\rho_f}
\]  \hspace{1cm} (14)

Substituting into (10)

\[
\tilde{q} = -\tilde{K}_f \frac{\mu_f}{\mu} \rho_f g \left[ (\nabla h_f - \nabla z) \rho_f + \rho g \nabla z \right]
= -\tilde{K}_f \frac{\mu_f}{\mu} \left[ (\nabla h_f + (\frac{\rho}{\rho_f} - 1) \nabla z \right]
= -\tilde{K}_f \frac{\mu_f}{\mu} \left[ (\nabla h_f + (\frac{\rho - \rho_f}{\rho_f}) \nabla z \right]
\]  \hspace{1cm} (16)

(Voss and Souza 1987; Langevin and Guo 2006; Zidane 2012)

The governing equation follows by substituting (14) into (9)

\[
-\nabla \cdot (\tilde{\rho} \tilde{K}_f \frac{\mu_f}{\mu} [\nabla h_f + (\frac{\rho - \rho_f}{\rho_f}) \nabla z]) = \rho S \frac{\partial P}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} - \rho_s Q_s
\]  \hspace{1cm} (17)

\[
-\nabla \cdot (\tilde{\rho} \tilde{K}_f \frac{\mu_f}{\mu} [\nabla h_f + (\frac{\rho - \rho_f}{\rho_f}) \nabla z]) = \rho S g \rho_f \frac{\partial h_f}{\partial t} + n \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} - \rho_s Q_s
\]
where \( S_j = S_j \rho_j \) is the specific storage in terms of freshwater head; \( \rho_j \) is the fluid density of source/sinks \([\text{ML}^{-3}]\).

When pressure is treated as the dependent variable for Darcy’s flux the conservation of mass is:

\[
\nabla \cdot \left( \rho \mathbf{v} \frac{\mu}{\mu} \left[ \nabla h_j + \left( \frac{\rho - \rho_f}{\rho_f} \right) \nabla z \right] \right) = \rho s \frac{\partial h_j}{\partial t} + n \frac{\partial \rho}{\partial t} \frac{\partial C}{\partial t} - \rho, Q,
\]

\( \text{(18)} \)

**Solute transport**

Mass transport of solute in porous media with groundwater flow includes groundwater advection, dispersion, source/sinks and production/decay rate. It can be expressed as (Langevin and Guo 2006):

\[
\frac{\partial n C}{\partial t} = \nabla \cdot (n \mathbf{D} \cdot \nabla C) + \nabla \cdot (\bar{q} C) + R_s
\]

\( \text{(19)} \)

Where \( \mathbf{D} \) is the dispersion tensor \([\text{L}^2\text{T}^{-1}]\); \( C \) is solute concentration \([\text{ML}^{-3}]\); \( R_s \) is the source production or decay rate \([\text{ML}^{-3}\text{T}^{-1}]\) and \( n \) is porosity.

**Effect of concentration on fluid density**

The density of a solution that contains a single solute can be calculated using a density correction factor (SysCAD 2013).

\[
\rho = a + bX + cX^2 + dX^3 + eX^4
\]

\( \text{(20)} \)
where $X$ is the mass fraction of the solute of a species.

Specifically for the density of sodium chloride (NaCl) solution, the terms in (Eqn. 20) are

\begin{align*}
a &= 1 \quad (21a) \\
b &= 0.7085 \quad (21b) \\
c &= 0.1214 \quad (21c) \\
d &= 0.3702 \quad (21d)
\end{align*}

The first-order form of (Eqn. 19) is adequate for small mass fractions and is assumed to be adequate for groundwater problems (Langevin and Guo 2006).

Converting the concentration to units of mol/m$^3$, which were used in the analysis, the water density is given in units of kg/m$^3$ as

$$
\rho = 1000 + C f_\rho
$$

(22)

where $C$ is the salt concentration in unit of [mol/m$^3$] and the density coefficient $f_\rho$ is 0.058 kg/mol. It follows that the term in (3), (7)-(11) and elsewhere is

$$
\frac{d\rho}{dC} = 0.058 \frac{kg}{mol}
$$

(23)

**Viscosity and temperature**

The viscosity of water increases with the concentration of sodium chloride solution (Ozbek 2010). Experimental data (Nickels 1937) was used to correlate viscosity with temperature and concentration as

$$
\eta = c_1 + c_2 \exp(\alpha_1 T) + c_3 \exp(\alpha_2 C) + c_4 \exp[\alpha_3 (0.01 T + m)] + c_5 \exp[\alpha_4 (0.01 T - m)]
$$

(24)
where

\( \eta \) - Dynamic viscosity (mPa s)

T - Temperature (°C)

M - Concentration, molality (mol/kg)

c_1 = 0.1256735 \quad \alpha_1 = -0.04296718

c_2 = 1.265347 \quad \alpha_2 = 0.3710073

c_3 = -1.105369 \quad \alpha_3 = 0.4230889

c_4 = 0.2044679 \quad \alpha_4 = -0.3259828

c_5 = 1.308779

The viscosity data used to develop (Eqn. 24) were spanned temperatures varying from 0 °C to 150 °C (Figure 5). In our study salt concentration in groundwater varied from 0 mol/m³ (freshwater) to 1000 mol/m³ (saline); the corresponding molality varied from 0 mol/kg to 0.94 mol/kg. On Figure 5 at fixed temperature, for example 20°C, viscosity for 0 mol/kg salt concentration is 1.05 mPa S; for 0.94 mol/kg is 1.10 mPa S. Therefore viscosity variation with changes in molality was less than \( 10^{-4} \) Pa s, which is 10% of dynamic viscosity of freshwater as \( 10^{-3} \) Pa s. As temperature increases, the effect of concentration on viscosity is reduced.
Figure 5 Viscosity of NaCl solutions as a functions of concentration and temperature using Eqn. 24 (Ozbek 2010)

According to (Guo 2002), viscosity can be assumed essentially the same as that of freshwater for many hydrogeological applications, even where concentration variations are large enough to cause important differences in density. Variations in viscosity caused by variations in temperature can be much larger than variations caused by concentration.
changes. Where substantial temperature variations are absent and where hydraulic conductivity has been measured at the same water temperature for which velocity is to be calculated, the viscosity correction usually can be neglected (Guo 2002).

**Coupling between density and concentration**

The analysis of fluid pressure and mass transport are coupled through the fluid density, \( \rho \). The fluid density depends on the solute concentration through Eqn. 20 and 21 or 22, and the solute concentration depends on the fluid flow, which depends on the density (e.g. through Eqn. 10 and 11).

In cases where the solute concentration is low, the change in density with concentration is negligible and fluid density can be regarded as constant. This is the case for many contaminant plumes where solute concentrations are in the ppm range. However, the concentration of salt in seawater is 35,000 ppm and some brine has salt concentration larger than 200,000 ppm. The density of seawater is several (2.5) percent greater than fresh water, and that the density of brines is even greater. This change in density can significantly alter the pattern and rate of a groundwater flow system compared to a system where the density is assumed to be constant and uniform.

Solute concentrations similar to seawater appear to be common and the effects of these fluids on overlying freshwater aquifers are of primary interest to this investigation. As a result, I will assume that it is necessary to include the effect of solute concentration on fluid density in the analyses. This results in a pair governing equations that are coupled through the fluid density. This type of coupled problem requires specialized
solution methods to simultaneously satisfy both governing equations. One approach solves first for pressures and then concentrations at a new timestep, and then the updated concentrations are used to solve for the pressures, and the new pressures are used to update the concentrations. This sequence is repeated iteratively until the solutions converge. An alternative approach is to solve for both the pressures and the concentrations at a new time step simultaneously.
Solution

The equations outlined above were solved numerically using three different codes. Each code discretizes the governing equations over a mesh or grid on the problem domain. The numerical approach for solving the resulting system of equations differs among the codes, however. Each code was set up using specific packages or modules to solve the problems required for this investigation.
Numerical Method

Numerical methods are chosen for solving partial differential equation (PDE). Different spatial and temporal discretization schemes break down complex models into parameter matrix, which are solved through numerical iterations. The choice of proper numerical methods depends on model geometry, accuracy requirement, and computational resources.

COMSOL uses the finite-element method (FEM), which solves partial differential equation using continuous piecewise linear approximating functions based on triangulations adapted to the geometry of the domain (Thomee 2001). The physics of one element is approximately described by a finite number of degrees of freedom (DOFs). In COMSOL each element is assigned a set of characteristic equations (describing physical properties, boundary conditions, and imposed forces), which are then solved as a set of simultaneous equations to predict the object’s behavior (COMSOL 2013).

In COMSOL the finite element analyses described here used the Darcy interface to solve (Eqn. 10) and the Species Transport through Porous Media interface to solve (Eqn. 8). Meshes were developed for each problem to achieve sufficient accuracy and stability while minimizing the number of elements. This was done by setting some of the mesh dimensions manually and using the mesh generator to determine the other dimensions. Some problems used irregular meshes with triangular elements, whereas others used mapped meshes with rectangular elements.
Quadratic elements were used in all cases. Experiments were conducted with linear elements, which resulted in fewer degrees of freedom and faster analyses. However, the linear elements resulted in solutions that differed significantly from those generated by quadratic, and in many cases the solutions from the linear elements were noisier than those with quadratic elements.

All the problems were solved using the MUltifrontal Massively Parallel sparse direct Solver (MUMPS). This is a public domain solver developed to solve large sparse systems of linear algebraic equations on distributed memory parallel computers (Amestoy et al. 2000). It uses the multifrontal method, which is a version of Gaussian elimination for large sparse systems of equations such as those resulting from the finite element method. MUMPS was released to the public in 1999 and it continues to be refined. More information is available at http://mumps.enseeiht.fr/index.php?page=home

Fluid density was determined using a variant of (Eqn. 22)

\[
\rho = 1000 + Cf_p \ast (C > 0)
\]

(25)

where the inequality in parenthesis should be taken as a Boolean expression that essentially sets \(f_p\) to 0 where \(C\) is negative. Negative values of \(C\) can occur due to numerical anomalies, and the Boolean expression assumes these values are zero so they don’t become buoyant and affect the flow. A similar Boolean expression was used so
numerical overshooting of the concentration did not cause the fluid density to be anomalously large and perturb the flow.
CHAPTER III. ANALYSIS OF BENCHMARK PROBLEMS

Verification of COMSOL Multiphysics used for the research involved experiments on benchmark problems (Henry, Elder, HYDROCOIN Case 5). The code was run on the benchmark problems and the results were compared.

A major focus in this study was to evaluate the results of coupling between fluid density and salt water concentration.

**Henry Problem**

The Henry problem describes steady state seawater encroachment into inland freshwater through an isotropic porous media. (Henry 1964) developed a semi-analytical solution for the steady-state distribution of salt concentration within this system.

In the Henry problem, freshwater enters an idealized 2 m length and 1 m depth rectangular simulation domain. The domain was discretized according to different numerical methods that were selected for solving governing equations. Flux from the inland freshwater (left) boundary enters the study domain at a constant rate and flows towards saltwater on the right boundary (Figure 6). No mechanical dispersion but only molecular diffusion is assigned with the flow.

The density difference causes saltwater to sink and form a wedge that extends under freshwater along the right side of the model (Fig 6). The fresh and salt water mix
my diffusion, forming a transition zone.

Boundary conditions for the analysis were specified as:

- No-flow/mass flux condition along the top and bottom boundaries
- Uniform freshwater ($C_{in} = 0$) inflow at inland boundary ($q = 6.6E-04$ m/s)
- Hydraulic head of 0 m, hydrostatic boundary assigned to seawater boundary
- Uniform concentration at seawater boundary ($C_s = 35.0$ kg/m$^3$)
COMSOL Multiphysics model uses Darcy’s Law (dl) and Species Transport in Porous Media (chpm) modules to solve Henry’s problem. Flow and mass flux boundary condition in Henry’s problem was assigned to the boundary interface.

**Discretization**

The study domain was discretized into finite number of triangular meshes. Boundary refined mesh was built with 229 edge elements and a growth rate of 1.284, expanding from the saltwater source and bottom boundaries toward the inland and aquifer upper surface. Initial test of the mesh density ran with total number of elements of 6943. The concentration contours were plotted as mesh size was increased in a parametric sweep. The final mesh construction was determined with minimized computation time, but still, provided results that were close enough to the previous set of experiments without numerical blow-up (i.e. extremely high/negative concentration values in the study domain). The final number of elements was determined as 2629 (Figure 7).

**Results**

Three contour lines of 25%, 50% and 75% of the original saltwater concentration (8.75 kg/m³, 17.5 kg/m³, 26.25 kg/m³) were compared with semi-analytical results that (Henry 1964) provided (Figure 8). Steady state simulation showed good correlation with Henry’s analytical solution. There was slightly more dispersed transition zone where the width of transition zone increases with increased vertical depth. The intermediate 50% concentration contour has the best correlation with the analytical results. The saltwater front propagated slightly faster into the freshwater as more diluted dispersion pattern shows up using COMSOL finite element simulator.
Figure 7 COMSOL mesh construction for Henry problem

Figure 8 COMSOL simulation of Henry's problem with 25%, 50% and 70% saltwater concentration contours.
COMSOL produced concentration contours that were similar in shape and quite close (within approximately 0.1m) of the semi-analytical results from Henry (1964). It generally indicates that the correct behavior is represented.
Elder Problem

The Elder problem is a product of experiments described by Elder (1967). The experiment was set up in a closed rectangular box, where the flow pattern across the cross-section was characterized. Elder set this problem to flow in porous media which was driven by a density gradient (Elder 1967). Denser saltwater was supposed to flow from the top of the experiment downward toward the bottom driven by gravity and molecular diffusion. The problem we simulated should be referred to as the Elder salt-convection problem (Voss and Souza 1987; Oldenburg and Pruess 1995; Woods 2003).

The salt concentration increased as a uniform layer during the beginning of Elder’s experiment, but soon lobes of high concentration descended from either end of the saltwater source (Figure 11). Three more lobes then began to grow near the middle of the layer, and salt water descended through these five lobes. Then the middle three lobes coalesced so there was one central and two outer lobes. The two outer lobes reached the base of the experiment first and started to spread laterally while the middle lobe lagged behind. However, with time, the middle lobe grew at the expense of the outer two lobes and eventually all the saltwater descended through the middle lobe. At the end of the experiment, relatively high concentration water was flowing downward and spreading across the bottom through the central lobe (Figure 11).

In the conceptual model (Figure 9), a section of constant concentration (285.7 kg/m$^3$) was assigned to the middle of the uppermost boundary. The bottom layer was defined as constant concentration of 0 kg/m$^3$. A fixed pressure head of 150 m was
maintained at the two upper corners providing an outlet or inlet. Flow and mass flux are allowed to enter/leave the upper corners. Initially the domain was filled with freshwater before solute convection started to perform in the study domain.

![Conceptual model of Elder problem](image_url)

Figure 9 Conceptual model of Elder problem (side view of vertical plane)
Darcy’s Law (dl) and Solute Transport (esst) modules in COMSOL were used for simulating Elder problem. Transient model were run up to 20 years and results were compared to previous published benchmarks from Elder experiments (Elder 1967) and later simulation using SUTRA (Voss and Souza 1987) and from SEAWAT manual (Guo 2002).

**Discretization**

The COMSOL simulation was set up with an unstructured mesh of 25748, uniformly sized triangular elements (Figure 10). Specifying an even finer mesh near the upper boundary's midpoint helps to resolve the sharp concentration gradient resulting from the specified boundary conditions (COMSOL 2012).

**Results**

Results from the simulation show the development of two peripheral lobes, then three central ones, followed by coalescence to a single, central lobe (Figure 11). The dynamics of lobe development and coalescence predicted by COMSOL is essentially the same as observed by Elder. Details of the size and timing of the lobes predicted by COMSOL are slightly different than those observed by Elder. For example, simulation results (Figure 11) showed more rapid downward saltwater convection in the first ten years of time window. The five plume fingers occurred at the end of second year and the middle plume propagated slowly afterwards. Comparatively, the major plumes at both sides grew much faster from the end of third year until the tenth year. After the ten years simulation time a noticeable downward plume with high concentration formed through the centerline of the domain and sunk towards the bottom boundary. At the end of
simulation (Figure 12) COMSOL generated a larger horizontal plume expansion compared to Elder experiments. However, COMSOL provided very close outputs with previous study using SUTRA (Voss and Souza 1987). Compared to SUTRA, COMSOL predicted that the center plume was deeper vertically and spread more horizontally towards both sides. In addition, two small downward plumes were observed at the both sides of the major center plume close to the salt water source. It took 294s for the transient model to run until reaching 20 year of simulation.

![Figure 10 COMSOL mesh construction for Elder problem (two symmetric half planes each representing either side of the plume)](image)

Figure 10 COMSOL mesh construction for Elder problem (two symmetric half planes each representing either side of the plume)
Figure 11 COMSOL simulation of Elder problem in time series (Left: COMSOL simulation (color legend is normalized concentration); Right: previous published benchmark problems using SEAWAT, SUTRA and Elder experiments)
Figure 12  20% and 60% source concentration contours measured by Elder and simulated by COMSOL and in other published studies.

COMSOL simulations, along with published results from SUTRA and SEAWAT manual, were able to predict the essential details of the Elder problem with reasonable accuracy. They all predicted downward flow through two lateral lobes at early time. Then they showed how several other lobes developed and coalesced, and soon all the lobes coalesced to form a central lobe that dominated the downward flow. In general, COMSOL predicted concentration contours that were within $0.2L_c$ of the experimental results, where the characteristic length $L_c$ is the half-width of the source of saltwater at the top of the experiment.
HYDROCOIN Case 5 Problem

The purpose of the Hydrologic Code Inter-comparison (HYDROCOIN) project was to evaluate the accuracy of selected ground-water modeling codes. One of the problems used for testing is the HYDROCOIN Case 5 problem. The HYDROCOIN Case 5 problem describes a scenario where density is a function of concentration and freshwater flows across the top of a salt dome formation. The general geometry and boundary conditions for the HYDROCOIN Case 5 problem are shown in Figure 13. Along the base of the middle part of the model, a constant-concentration condition is applied to represent the top of a salt dome. As ground water flows along the bottom boundary and over the salt dome, salt disperses into the system and collects in the lower right corner of the model domain.

No-flow/no-mass flux boundary conditions were assigned to the left and right boundaries. The middle interval of the bottom boundary was specified with constant concentration of 280 kg/m³ (salt mass fraction as 0.233). Constant hydraulic heads of 10.080 m and 0.113 m were set at the upper left and upper right corners of the domain forming a constant gradient head boundary. Longitudinal dispersivity was defined as 20 m and transverse dispersivity as 2 meters (Figure 13).

The finite element mesh has almost uniform resolution within the domain and was refined with narrow rectangular elements at the boundaries. This was done to improve resolution of the concentration gradients at the boundaries. The upper boundary was defined as a flux outflow boundary with constant hydraulic head and gradient. The
COMSOL simulation was compared with SEAWAT and MOCDENSE outputs from previous research.

**Discretization**

The mesh consisted of 7612 elements (Figure 14).

---

**Figure 13** Conceptual model of HYDROCOIN Case 5 problem.

**Figure 14** COMSOL mesh for Hydrocoin problem
The hydrodynamic dispersion tensor, $D_{ij}$, is defined by Bear (1979). The definition used in COMSOL fluid transport numerical scheme follows the dispersion rule that (Burnett and Frind 1987) proposed for anisotropic porous media. The standard isotropic definition is modified and introduced by a horizontal and vertical transverse dispersivity $\alpha_{TH}$ and $\alpha_{TV}$ (COMSOL 2011) as:

\[
D_{xx} = \alpha_L \frac{u^2}{|U|} + \alpha_{TH} \frac{v^2}{|U|} + \alpha_{TV} \frac{w^2}{|U|} + D^* \\
D_{yy} = \alpha_L \frac{v^2}{|U|} + \alpha_{TH} \frac{u^2}{|U|} + \alpha_{TV} \frac{w^2}{|U|} + D^* \\
D_{zz} = \alpha_L \frac{w^2}{|U|} + \alpha_{TV} \frac{u^2}{|U|} + \alpha_{TV} \frac{v^2}{|U|} + D^* \\
D_{xy} = D_{yx} = (\alpha_L - \alpha_{TH}) \frac{uv}{|U|} \\
D_{xz} = D_{zx} = (\alpha_L - \alpha_{TV}) \frac{uw}{|U|} \\
D_{yz} = D_{zy} = (\alpha_L - \alpha_{TV}) \frac{vw}{|U|}
\]

where $|U| = \sqrt{u^2 + v^2 + w^2}$ – magnitude of the velocity vector [LT$^{-1}$]

$D_{ij}$ – hydrodynamic dispersion tensor [L$^2$T$^{-1}$]

$\alpha_L$ – longitudinal dispersivity [L]

$\alpha_{HT}$ – horizontal transverse dispersivity [L]

$\alpha_{VT}$ – vertical transverse dispersivity [L]

$D^*$ – effective molecular diffusion coefficient [L$^2$T$^{-1}$]
u, v, w – components of velocity vector in x, y and z directions [LT\(^{-1}\)] (porosity effect included)

**Results**

The model 51 seconds to run until of the simulated time reached 5000 years. This time was long enough for the system to reach steady state.

The concentration contours predicted by COMSOL were in good fit to those predicted by SEAWAT and MOCDENSE (Figure 15). The 0.05 contour predicted by COMSOL was between the contours from the other codes, and the other contours were essentially coincident.

![Concentration contours](image)

Figure 15 Concentration contours simulated by COMSOL (dash-dot), MOCDENSE (red dash) and SEAWAT (Langevin 2001); Concentration contours were in magnitude of 0.05, 0.1, 0.2 and 0.3 from top to bottom.
In summary, the performance of COMSOL was able to simulate the benchmark problems with sufficient accuracy to conclude the code was valid for solving this type of problem. The runtimes were faster or similar to analyses of the same problems conducted using SEAWAT (Guo, 2002). COMSOL used many more elements than SEAWAT for similar runtimes and accuracies. Details of the performance of COMSOL is mesh dependent. The graphics and post-processing capabilities available in COMSOL were particularly useful in evaluating results of analyses.
CHAPTER IV. ANALYSIS OF SALT TRANSPORT CAUSED BY PRESSURE CHANGES AT DEPTH

When CO$_2$ is injected into a deep saline formation, the pressure will increase and this may induce flow in the vicinity. In some cases, the change in pressure may reach shallow depths and this could affect flows in freshwater aquifers. One possibility is that this would affect the elevation of the fresh/salt interface (the surface where $C = 8.54$ mol/m$^3$), thus degrading the ground water quality. Raising the fresh/salt interface will also increase the risk that the salt content is increased in the shallow ground water circulation system. This would increase the composition of ground water discharging to surface water, and may therefore present a risk to aquatic ecosystems and surface water quality.

Conceptual Model

An analysis was conducted to evaluate the potential for increases in risk caused by pressurizing deep formations during CO$_2$ storage. The conceptual model consists of an aquifer system that extends from a shallow water table to depth in a sedimentary basin. The aquifer units are assumed to be shallowly dipping sediments that include permeable sands or sandstones, and lower permeability clays or shales. The bottom of the region is connected to a basin of large lateral extent and the injected CO$_2$ is assumed to be a considerable distance away so the only effect is a change in pressure or flow. The bottom of the region is deep enough so the water is saline. The upper boundary of the region receives freshwater recharge that is uniformly distributed. Evenly spaced streams are
assumed to cross the outcrop roughly perpendicular to strike, and they are the discharge points for the recharge. It will be assumed that the region is dominated by regional ground water flow systems.

The distribution of salt when the near-surface region becomes pressurized will play an important role on the resulting risks. If the fresh/salt interface is relatively deep, then a pulse of increased upward flow may have negligible impact. However, if the fresh/salt interface is relatively shallow, then even a modest displacement of the interface may have a significant effect on wells and streams (Figure 16).

The distribution of salt in the subsurface will reflect the composition of the connate water, the magnitude, distribution, and composition of recharge, permeability structure, geochemical interaction with wall rocks, and other effects. However, the essential process controlling the development of a fresh water aquifer is assumed to be the flushing of connate water by fresh water entering as recharge. In the following analysis, this flushing process will be assumed to create the initial distribution of salt.
Figure 16 Conceptual model showing a shallowly dipping aquifer receiving recharge with streams crossing perpendicular to strike. Freshwater occurs at shallow depths and is underlain by saline water. Brown layer is an aquitard which is assumed to perfectly seal the groundwater flow within lower formation. Injection of CO$_2$ deep within the basin increases the pressure and causes upward flow, displacing the fresh/salt interface upward and increasing the risk of contaminating shallow aquifers with salt. Dashed line shows a location of the 2D model.
Numerical Model

The conceptual model was analyzed by formulating representative numerical models in 2D and 3D with appropriate geometry, boundary conditions, and properties. The 2D model was a rectangular region 2km in lateral dimension and 3km deep. The plane was assumed to be perpendicular to the ground surface in the 2D study. The upper boundary represented the ground surface. There were two zones 20m wide and spaced 1km apart that represented streams.

The spacing between streams is an important scale in the model. It was taken as 1000 m based on the typical drainage density of in the midwestern and eastern U.S (Charlston 1963; Elmore 2013). The head in surface streams was uniform and constant. The concentration gradient normal to the stream boundaries was set to zero so diffusion was prevented, but advective transport out the streams was allowed. Between the streams, the inflow rate was uniform and constant and set equal to the recharge rate. The concentration of salt in the recharging water was set to zero.

The lower boundary was assumed to be in contact with a saline formation, so the concentration was set equal to a standard value, either 600 mol/m$^3$ or 1000 mol/m$^3$. The water flux across the bottom boundary ranged from zero during early stages to a positive value when pressurization caused by CO$_2$ injection was occurring.

Both sides of the domain were defined as no-flow and no-mass-flux boundaries because it was assumed there were additional streams that created a symmetry condition at the lateral boundaries.
The permeability was assumed to be homogeneous, and both isotropic and anisotropic conditions were evaluated. When the permeability was isotropic, the rectangular region could approximately represent a plane parallel to the contacts of a dipping regional aquifer (Figure 17), or a vertical section through a thick, uniform aquifer. Alternatively, it could represent a section through inter-bedded strata of varying permeability when anisotropic conditions were assumed.

Figure 17 Geometry and boundary conditions for the 2D problem. Numbers are dimensions in meters.
**Initial conditions and boundary sequence**

The problem was analyzed in two stages, one to simulate the flushing of connate water by fresh recharge, and another to simulate a pulse-like increase in the pressure or upward flow from the underlying basin. The first stage, called the *Freshwater Flushing* Stage, was used to create a distribution of fresh and saline water. This was followed by the *Basin Pulse* Stage.

**Initial condition**

The initial condition assumes that the formation is saturated with salt water of uniform concentration. This could be connate water, or it could be water that infiltrated when the area was inundated. Some simulations assumed an initial concentration of 600 mol/m$^3$, the current concentration of seawater, whereas other simulations assumed a somewhat greater concentration of 1000 mol/m$^3$.

**Stage 1 Freshwater flushing**

The Freshwater Flushing stage was a run for $10^{15}$ s (approximately 31.7 million years). This the same scale as the time since aquifers in the Midwestern U.S. were inundated with seawater during the Cretaceous Period (65- 144 million years ago) (USGS 2004; USGS 2011). Conditions at the end of this stage were assumed to represent the result of the maximum duration of flushing. The simulation that assumed isotropic conditions and $10^{15}$ s resulted in a fresh/salt interface at a depth of 500m, which is deeper than many locations in the Midwest (Figure 2). Results from the simulation from shorter
durations of flushing were used to create initial conditions for cases with a shallower fresh/salt interface.

**Stage 2 Basin pulse**

This stage consists of a transient simulation where the upward flux or the pressure along the bottom of the model was increased for a period of time and then returned to ambient conditions. The magnitude of the upward flux was scaled to the recharge, Re, and magnitudes of 0.1Re, Re and 10Re were considered in the model. The pulse of increased basin flux was evaluated for durations of 5, 20, and 50 years for each flux magnitude.

With major constants defined in Table 1 and Table 2, the conditions and parameters were input for different modeling stages in sequence.
Table 1 Model conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inter stream distance</td>
<td>1000 m</td>
</tr>
<tr>
<td>Recharge</td>
<td>$10^{-9}$ m/s</td>
</tr>
<tr>
<td>Basin flux</td>
<td>0 during stage 1</td>
</tr>
<tr>
<td></td>
<td>Scaled to Re during stage 2</td>
</tr>
<tr>
<td>Initial Concentration</td>
<td>1000 mol/m$^3$ - 58 mg/L</td>
</tr>
<tr>
<td>Concentration in recharge</td>
<td>0</td>
</tr>
<tr>
<td>Concentration from basin</td>
<td>1000 mol/m$^3$ (58 mg/L)</td>
</tr>
<tr>
<td></td>
<td>600 mol/m$^3$ (35 mg/L)</td>
</tr>
<tr>
<td>Basin pulse simulation</td>
<td>Up to 1.58e9(s) - 50 years</td>
</tr>
<tr>
<td>Recovery simulation</td>
<td>Pulse 1.58e9(s) - 50 years</td>
</tr>
<tr>
<td></td>
<td>Release 4.73e9(s) - 150 years</td>
</tr>
</tbody>
</table>

Table 2 Model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability</td>
<td>$10^{-14}$ m$^2$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.05</td>
</tr>
<tr>
<td>Water viscosity</td>
<td>0.001 Pa s</td>
</tr>
<tr>
<td>Water density</td>
<td>$1000 + f_\rho C$ kg/m$^3$</td>
</tr>
<tr>
<td>Density coefficient, $f_\rho$</td>
<td>0.058 kg/mol</td>
</tr>
<tr>
<td>Water Compressibility</td>
<td>$4 \times 10^{10}$ Pa$^{-1}$</td>
</tr>
<tr>
<td>Aquifer Compressibility</td>
<td>$1 \times 10^{10}$ Pa$^{-1}$</td>
</tr>
<tr>
<td>Dispersivity, long=tran</td>
<td>10 m</td>
</tr>
<tr>
<td>Salt Diffusion in water</td>
<td>$2 \times 10^{-8}$ m$^2$/s</td>
</tr>
</tbody>
</table>
1. Mesh evaluation

The performance of numerical models can depend strongly on the design of the mesh, with a tradeoff between accuracy and run-time occurring as the size of the mesh changes. To evaluate this effect, the study domain was initially meshed with an unstructured mesh system consisting of 14019 finite elements (Figure 18). The mesh was divided into the upper ¼ and lower ¾ of the domain. The upper domain was built with a swept rectangular mesh. The minimum element size was 0.7 m across under the stream (20 elements). The element size increased with horizontal and vertical distance from the stream, and reached a maximum size of 15 m at the bottom of the upper domain, which was at 800 m depth (elevation of 2200 m in Figure 18). The lower domain was constructed with larger triangular elements. The size of triangular elements increased with depth and reached a maximum size of 80 m at depth about 1250 m (elevation of 1750 m). The size of the mesh was uniform below 1250 m. This design provided a high resolution of where the more complex processes occurred in the upper domain, particularly where the streamlines converged beneath the streams (Figure 19).
Figure 18 Baseline finite element mesh used for the analysis
Figure 19 Mesh in vicinity of stream, blue line, minimum element width is 0.7 m
A parametric sweep model was set up to evaluate the effects of mesh density. The same domain geometry and mesh configuration were used. The mesh size was controlled by setting the maximum element size and the maximum element growth rate scaled to a Mesh Coefficient $\chi$. The maximum element size in the upper $\frac{1}{4}$ domain was set to

$$M_{uu} = 15m / \chi$$

The maximum element size in the lower $\frac{3}{4}$ domain was set to

$$M_{ul} = 80m / \chi$$

and the element growth rate was set to

$$M_{gr} = 1 + 0.3 / \chi$$

The number of elements across the streams was set to

$$N_{str} = 20 \chi$$

The parameter $\chi$ was adjusted from 0.3 to 2.0 to change the size of the mesh. When $\chi=0.3$, the mesh consisted of 1742 elements and the minimum size of the elements at the ground surface along the stream was approximately 2.2 m, whereas when $\chi=2.0$ the mesh consisted of 52077 elements and the size of the minimum element along the stream was approximately 0.4m (Figure 20). The total number of elements in the study region, as a function of mesh coefficient, was generally fit in a second-order polynomial or simplified in a linear relationship as:
The simulation was conducted by running the Freshwater Flushing Stage to $10^{10}$ s (300 yrs). The effect of the mesh size was evaluated by repeating the transport analysis for different values of $\chi$ and comparing the results.

The simulation started with a uniform concentration ($C=1000$ mol/m$^3$) filling the pore volume. The recharge swept out curved regions of freshwater that were thickest beneath the upland. By the end of the simulation at 300 yrs, the freshwater region extended downward to a depth of 500m beneath the upland, and there were cusp-like ridges of high concentration beneath the streams.

The basic distribution of concentration was independent of the mesh, with results from the coarsest mesh generally resembling those from the finest mesh (Figure 21).
The most significant effect of mesh density was in the width of the transition from low to high concentration below the upland. The width of this zone decreased with the mesh size. Moreover, there were local bands of negative concentration above this transition and bands of concentration greater than 1000 mol/m$^3$ below the transition (Figure 21).

Negative concentrations have no physical meaning and concentrations greater than the initial concentration cannot be created by physical processes in the model. Therefore these anomalous concentrations were created from numerical artifacts. The magnitude of these artifacts was reduced with the mesh size decrease, although they were still present when even the finest mesh was used. This could be confirmed by noting the range of the legend, which was set to the maximum and minimum values in the domain.

The width of the transition zone below the upland was roughly 100m for $\chi=0.3$, and it decreased to 80 m for $\chi=0.5$. The width was approximately 50m and appeared to be independent of $\chi$ for $\chi>=1$.

The anomalous concentration ranged from -231 to -50 mol/m$^3$ for $\chi<1$ in the low concentration region. These anomalous variations in concentration were less than a few percent for $\chi>1$. Similarly, the highest concentrations exceeded 1000 mol/m$^3$ by a few percent for $\chi>1$.  


Figure 21 Concentration distribution after Freshwater Flushing Stage of 300 yrs (Top to bottom: 
\( \chi = 0.3, 0.5, 1, 1.5, 2.0 \) )
The concentration distribution was mostly affected by the mesh in the vicinity of the upland region. Thus vertical profiles of concentration at this location served to highlight the mesh effect (Figure 22). Results showed profiles generated by all the meshes intersected at depth = 500m. In other words the depth beneath upland to concentration iso-surface where \( C = 500 \text{ mol/m}^3 \), was essentially independent of the mesh. The magnitude of the anomalous concentrations along the vertical profile diminished with increasing mesh density. The profile of the transition from fresh to salt was smooth with the width of about 50 m (Figure 22).
Figure 22 Concentration profile beneath the upland with different mesh density
The concentration discharging to the stream was zero on the edge of the stream and increased to 37 mol/m$^3$ at the center. The distribution of concentration was essentially independent of the mesh, although the maximum concentration decreased slightly from the coarsest mesh to finest. The decrease in maximum concentration was small enough to be neglected when $\chi>1$. The maximum concentration converged at approximately 37 mol/m$^3$ with $\chi$ increasing up to 2.0 (Figure 23).

Figure 23 Concentration profile across the stream with different mesh density
Results indicated that even the coarsest mesh might give useful results for some applications, such as the distribution of concentration at the streams. However, there were differences in the concentration distribution that could be potentially significant below the upland. The width of the transition zone from fresh to saline and the appearance of spurious concentrations (negative or greater than unity) appeared to be the most significant effects of the mesh. The evaluation indicates that $\chi=1$ results in a mesh (Figure 18) with sufficient accuracy and execution time for most applications.
Characterization of Stage 1 Freshwater Flushing

The development of a freshwater aquifer occurs first at the area around the streams with the downward movement of the interface between saline and fresher water. Later the interface depth grows faster under upland than under streams. As freshwater flushing continues, the denser saline particles were wiped away from the saline layer surface and discharge into the surface stream, the fresh water was underlain by a transition zone where concentrations graded from fresh to saline conditions. The fresh/salt interface is shaped with upward cusps beneath the streams. During the flushing stage the depth to salt/fresh interface ($D_L$) beneath upland area was taken as a characteristic parameter for the aquifer development (Figure 24). $D_L$ is the depth to $C = 8.54 \text{ mol/m}^3$. The magnitude of $D_L$ increases with the flushing duration. In field cases $D_L$ is represented by the depth from the ground surface where high salt content indicates the location of saline formation. In this study $D_L$ was recorded in time series as the freshwater aquifer developed.
Figure 24 Representative cross section concentration distribution (color, in mol/m$^3$) created when freshwater flushes salt water. White line is 8.55 mol/m$^3$ (500 ppm), indicating fresh/salt interface; blue lines are streamlines indicating flow paths; yellow arrow shows how $D_L$ is defined.
The simulation was conducted by investigating two scenarios: 1) a baseline scenario where the effect of groundwater concentration ($C$) change on fluid density ($\rho$) was ignored. In other words, it assumes constant fluid density under varying concentration condition; 2) test scenario where fluid density ($\rho$) is a function of groundwater concentration (Eqn. 22).

During the first 3,000 yrs, the width of the fresh/salt transition was approximately 50 m, and this was underlain by a narrow transition front. As $D_L$ increased, the width of transition band increased. After 300,000 yrs flushing, the width of transition band grew up to 300 m. The width of transition zone also varied at different locations. For example, at the end of 30,000 yrs it was about 200 m thick beneath the uplands and it is nearly 500 m thick beneath the streams. This difference in transition zone width beneath the stream and upland area became even more significant with time. The bottom diffused into the saline layer and leveled off until 30,000,000 years flushing and the system generally reached steady state.

We run the same analysis again with fluid density dependent of salt concentration, and found that the results were affected. The test scenario used an initial concentration of $C=1000[\text{mol/m}^3]$.

In either scenario, three periods of fresh/salt development were identified: Advection dominated period, when surface recharge flushing salt from the interface dominated the advective transport, Diffusion dominated period, when diffusive transport
of salt from the constant concentration saline basin dominated concentration distribution, and Transition period in between of the former two.

The qualitative progression indicated, during the first 3,000 yrs of Advection dominated period, the width of the fresh/salt transition zone was approximately 10 m, and this was underlain by a narrow transition front. During Transition period, the transition zone width increased from beneath the uplands to beneath the surface streams. As $D_L$ increased, difference in transition zone width beneath the stream and upland area became larger. For vertical profile at each location (Figure 25), the average width of transition band also increased. The cusp-shaped transition beneath the streams gradually collapsed over time; the bottom of transition zone progressed from parallel (end of 3,000 yrs) to the cusp-shaped interface to a lateral front (30,000 yrs). At steady-state, concentration gradient was uniformly distributed below the fresh/salt interface. After 30,000,000 years of flushing, diffusion effect started to dominate the flushing when transition zone continued to grow until steady-state.

The qualitative progression indicated, at the same simulation time, shallower and more uniform freshwater/brackish interface was observed in the case of involving concentration into density function. The significant difference occurred starting from the end of 3,000 yrs flushing. The interface in baseline scenario reached at depth of about 200 m. Yet the same interface had a depth of 500 m in constant density scenario. At the end of 30,000,000 yrs, where the background scenario had a depth to salt water of 600 m and the constant density scenario had that for 900 m. It was also noticeable to point out
that the cusp-shaped fresh/salt transition zone changed much faster when the density was variable compared to the baseline case (Figure 25).
Figure 25 Cross sections of the development of a fresh water aquifer by flushing salt water at five simulation time spot. (Upper Row: background scenario with constant density; Lower Row: test scenario with dependent density)
**Evaluation of lower boundary condition**

In previous analysis of freshwater flushing salt water stage the lower boundary condition was assumed as no flow. This assumed that flow at shallow depth had no interaction with conditions at depth. In order to evaluate this assumption, two scenarios were compared, one with a no-flow and another with a constant head bottom boundary.

Hydraulic head distribution and vertical flux component were first examined in the baseline case with the no-flow bottom boundary (permeability $k=10^{-14}$ m$^2$, recharge rate $R=10^{-9}$ m/s, simulation time $t=8\times10^{11}$ s). At the end of simulation the maximum vertical flux occurred at the surface stream with magnitude of $3.04\times10^{-7}$ mol/m$^2$ s. Flux rate as low as zero beneath upland area indicated little effect that near-surface fresh/salt circulation placed upon this region (Figure 26).

![Hydraulic head (m) and salt flux (mol/m$^2$ s) distribution (no-flow bottom boundary)](image)

Figure 26 Hydraulic head (m) and salt flux (mol/m$^2$ s) distribution (no-flow bottom boundary)
Another way to represent the lower boundary was with a constant head. This could represent a case where there were mass flux exchanges at time. In the other scenario where the model was setup with a constant head lower boundary, an increased flow entered the lower aquifer by the end of simulation. This increased upward flow with raised maximum flux rate for $4.4 \times 10^{-8}$ mol/m$^2$ s within the domain (difference between Figure 26 and Figure 27). This system went to steady state when the upward flow balanced the downward flow, which was driven by surface recharge and gravity force.

Figure 27 Hydraulic head (m) and salt flux (mol/m$^2$ s) distribution (constant head bottom boundary)

Increase of flux due to the constant head boundary also had an effect on the concentration distribution and location of fresh/brackish interface. A slightly elevated interface occurred with the constant head boundary condition. The greatest change in the position
of the interface was observed below the divide with an increase of approximately 10 m after $8 \times 10^{11}$ s flushing (Figure 28).

Figure 28 Fresh/brackish interface with no-flow boundary (white) and constant head boundary (cyan) after $8 \times 10^{11}$ s flushing
The averaged normal convective flux through the bottom boundary was also evaluated under two types of boundary conditions. During the first 6300 yrs (2x10^{11} s) of freshwater flushing, the constant head boundary condition resulted in downward flux of as much as 1.8x10^{-7} mol/m^2 s flux rate. This occurred because surface recharge caused the head to increase in the shallower region, resulting in a net downward head gradient. However the downward component of the flow decreased and eventually changed sign. This occurred in response to flushing of the salt at shallow depths, which dropped the head. The upward flux gradually reached steady-state with magnitude of 10^{-8} mol/m^2 s (Figure 29).

Figure 29 Normal convective flux (mol/(m^2 s)) through bottom boundary during freshwater flushing stage (positive: outward domain; negative: inward domain)
Even though bottom boundary conditions resulted in changes of concentration, the difference in the position of the freshwater interface was small and difficult to detect at the scale of the model (Figure 28). As a result, although the lower boundary conditions clearly have an effect on the results, it appears that this effect is relatively small so only no-flow lower boundary condition will be evaluated in the following analysis.

**Viscosity effect**

In order to verify the assumption that molarity places a negligible effect on viscosity, a freshwater flushing analysis with the viscosity effect included was tested. Three cases with dynamic viscosity of 1.01mPa s, 1.04mPa s and 1.09mPa s respectively were used to represent salt concentration of 0 mol/m$^3$, 600 mol/m$^3$ and 1000 mol/m$^3$ (Kestin 1981; Ozbek 2010). In general, the viscosity of the fluid stiffens with concentration.

The change in the freshwater/brackish interface is barely noticeable under the three viscosity situations. Generally the fresh/salt interface with stiffer viscosity is lower ($D_L$ is greater) than the case with a thinner viscosity. The maximum difference in interface elevation occurred below the upland area with the magnitude of approximately 10 m. The difference was even smaller beneath the streams (Figure 30, 31). Considering the model scale, the effect of concentration changed on viscosity is small and this effect was neglected in our research. Viscosity was assumed to be constant and equal to that of fresh water.
Figure 30 Freshwater/brackish interface with viscosity of 1.01mPa s (red), 1.04mPa s (green) and 1.09mPa s (yellow).

Figure 31 Freshwater/brackish interface with viscosity of 1.01mPa s (red), 1.04mPa s (green) and 1.09mPa s (yellow). Close up view beneath the upland in Figure 30.
**Problem scaling**

The previous analyses used representative material properties and dimensions, but these values can vary with location. These variations will affect the results, for example, by altering in the development of $D_L$ over time. One approach to generalizing the results of analyses is to normalize them using characteristic scales of the problem. This strategy also normalizes parameters using characteristic scales to develop dimensionless groups that are important to the problem.

The characteristic length scale for this problem is assumed to be the average spacing between streams, $L$.

$$L_c = L \quad (32)$$

For anisotropic conditions caused by stratigraphic layering, the characteristic length parallel to layering is $L_{ch} = L$. However, the characteristic length scale in the $y$ direction is shortened by the layering and is given by

$$L_{cy} = L \sqrt{\frac{k}{k_y}} \quad (33)$$

The vertical characteristic length will be important for scaling $D_L$, for example.

The characteristic time scale follows from assuming the characteristic ground water flow velocity is based on the recharge, so

$$v_c = \frac{R}{n_e} \quad (34)$$
In this case, the characteristic time is

$$t_c = \frac{L}{v_c} = \frac{n_e L}{R}$$  \hspace{1cm} (35)

It follows that the dimensionless time is

$$t^* = \frac{tR}{n_e L}$$  \hspace{1cm} (36)

The regional Peclet number, $Pe_R$, is assumed to be defined in terms of characteristic scales, so

$$Pe_R = \frac{RL}{n_e D}$$  \hspace{1cm} (37)

where $D$ is the diffusion coefficient. The regional groundwater flow Peclet number characterized two key procedures as described in previous contents of dimensionless scaling. Recharge rate ($R$) indicated the surface recharge flushing salt from the interface dominated by advective transport. Diffusion ($D$) indicated the diffusive transport of salt from the constant concentration saline basin due to the concentration gradient.

Verification

In order to verify the assumption of the problem scaling, we tested the simulations under constant concentration condition using different combinations of $R$, $D$, and $\frac{k_h}{k_v}$. The baseline parameters were $R = 10^{-9}$ m/s, $D = 2 \times 10^{-8}$ [m$^2$/s], $\frac{k_h}{k_v} = 1$. Anisotropy and $R/D$ ratio and were tested respectively in the following analysis to evaluate the validation.
of dimensionless scaling. Baseline parameters were kept constant when varying the other(s).

On varying anisotropy, \( \frac{k_h}{k_v} \) values of 1, 5, 10 and 20 were implemented in the test cases. \( R \) and \( D \) were kept as baseline cases.

Figure 32 indicate that \( D_L \) decreases as \( \frac{k_h}{k_v} \) increases. \( D_L \) is reduced to less than half when \( \frac{k_h}{k_v} \) increases from 1 to 5, for example. When \( \frac{k_h}{k_v} \) increased from 5 to 20, \( D_L \) also decreased by roughly half.

Using the scaling relationships given in (Eqn. 33) and (Eqn. 36), the same output data generally merged onto the same line (Figure 32). The largest discrepancies were approximately 0.2 and occurred at early times. Values of \( D_L \) were determined manually from profiles of concentration, and the discrepancies probably were largely due to variations in identifying \( D_L \) at any particular time. In general, these results appeared to confirm the scaling of \( D_L \) using anisotropy \( \frac{k_h}{k_v} \).
Figure 32 Dimensioned and dimensionless configuration with varying anisotropy
Variations of $R$ and $D$ were evaluated using $R=10^{-10}, 10^{-9}, 10^{-8}$ [m/s]; $D=2\times10^{-9}, 2\times10^{-8}, 2\times10^{-7}$ [m$^2$/s]. $R$ and $D$ were paired in providing fixed regional groundwater flow Peclet number (Eqn. 37). Anisotropy was kept as baseline value of 1. Dimensioned/dimensionless $D_L$ was plotted over dimensioned/dimensionless time (Figure 33).

$D_L$-t relationship showed distinguishing difference in interface development pattern (Figure 33). The dimensionless configuration, however, works effectively merges all three cases into one characteristic curve, errors also lying within satisfactory threshold.
Figure 33 $D_l$ as a function of time for different values of R and D using dimensioned (a.) and dimensionless (b.) axes. R/D is held constant at R/D=0.05 m$^{-1}$.
D as a function of time

The depth to the fresh/salt interface, $D_L$, was determined for a variety of properties to evaluate the scaling outlined above. The objective was to identify the dimensionless configuration applied to our sensitivity analysis of flushing stage under various concentration and parameter combinations. It was firstly applied to the background group where constant fluid was assumed with varying salt concentration.

Three case studies were examined with different permeability and surface recharge rates ($k=1e^{-15}, 1e^{-14}, 1e^{-13} [m^2]$, $R = 1e^{-10}, 1e^{-9}$ and $1e^{-8} [m/s]$). For each permeability and recharge rate combination the corresponding $D_L$ value was recorded in time series and plotted on both $D_L-t$ (Figure 34) and $D_L^*-t^*$ (Figure 34) relationship. The same procedure was repeated with the density-dependent flushing groups where salt concentration is 600 [mol/m$^3$] and 1000 [mol/m$^3$]. The 600 [mol/m$^3$] density group represented normal seawater density. The 1000 [mol/m$^3$] density group represented typical salt concentration in underground brine formation, which was generally denser than seawater density due to mineral reaction and rock dissolution (Figure 34, 35).

The dimensionless depth of the interface increased linearly on the semi-log plot until $t^* \approx 2$. The slope gradually flattens and is roughly constant when $t^* > 200$. The steady state depth of the interface varied according to groundwater flow. It was determined in terms of the modified Peclet number involving surface recharge and diffusion.

Therefore the saline density determined the fresh/salt interface depth during advective development stage. In the diffusion dominated stage where interface
development is slow enough to be close to steady-state and under a typical saline density this depth was determined by the regional groundwater Peclet number.

In case of involving concentration into the density function, two significant patterns were further confirmed with the previous qualitative analysis. 1) At the same dimensionless time, concentration-density coupling groups generally had the interface shallower than the non-coupling group. It indicated that it takes longer time to flush denser fluid and discharge into the upper streams. 2) The difference in $P_{e_R}$ characterized development was much smaller than the non-coupling group.

Generally the larger the concentration, the shallower the interface would be located after the same duration of freshwater flushing. Still the development pattern with salt concentration of 600 [mol/m$^3$] was similar to that in the case when density function involving salt concentration of 1000 [mol/m$^3$]. In future studies more variations in salt concentration could be tested to evaluate this effect. This study provided a general trend how freshwater aquifer was developed in three typical cases.
Figure 34 Dimensioned salt-fresh interface depth below upland with/without density-dependent coupling (fixed k/R ratio).

Figure 35 Dimensionless characteristic salt-fresh interface depth below upland with/without density-dependent coupling (fixed k/R ratio).
k/R ratio

In previous analysis, k and R were varied, but their ratio was fixed. To test the effect of k/R ratio on DL, the k/R ratio was varied while density was held constant. The fundamental strategy of varying one parameter while fixing the other parameters during a sensitivity analysis was used here.

Three case studies were first examined with the same recharge rate of R=$10^{-8}$ m/s, but different permeability $k$ as $10^{-14}$, $10^{-13}$ and $10^{-12}$ m$^2$. The corresponding k/R ratio ranged from $10^6$, $10^5$ to $10^4$. Results from the simulation (Figure 36) showed little difference in interface propagation with varying k/R ratio. Although at initial condition small offsets existed for about 0.12 dimensionless depth between the maximum and minimum value, later development of dimensionless depth merged into the same line after $t^* = 30$ (Figure 36).

It should be noted that the low sensitivity to permeability $k$ was found only in the case where concentration was assumed to have no influence on fluid density. In the constant density scenario, the flow paths were constant and the flow rate was only dependent on surface recharge R. Changing permeability $k$ will change the head along the flow path, but not the flow rate between any two points. Because the fluid density and concentration had no direct relationship to each other, it was reasonable that the change in head had little effect on the distribution of concentration.
Figure 36 k/R ratio change with fixed R of 10^{-8} m/s, permeability = 10^{-14} m^2 (Blue), 10^{-14} m^2 (Red), 10^{-14} m^2 (Green) under constant concentration condition.
In the following experiments, three tests were implemented with fixed permeability of \( k = 10^{-14} \text{ m}^2 \) but different recharge rate \( R \) as \( 10^{-10}, 10^{-9} \) and \( 10^{-8} \) m/s, giving \( k/R \) ratio of \( 10^4, 10^5 \) to \( 10^6 \) respectively. The outputs at dimensioned scale showed almost parallel and equal difference \( D_L \) on the semi-log chart between three cases, with largest \( D_L \) occurring in the case of largest recharge rate \( R \) of \( 10^{-8} \) m/s. When rescaling into dimensionless form, the dimensionless depth over dimensionless time merged into the same characteristic curve. Similar to the background case where fluid density and \( k/R \) ratio was fixed, the steady state dimensionless depth to brackish water was determined by regional groundwater flow Pelet number (Figure 37).

Therefore, the characteristic curve configured in this study for dimensionless \( D_L \) development was unique for different concentration scenarios during advective progressing stage. The following diffusive growth and steady state dimensionless depth was determined according to \( \text{Pe} \) which was directly proportional to \( R \) and an inversely proportional to \( D \).
Figure 37 k/R ratio change with fixed k. (Upper: dimensioned scaling; Lower: dimensionless scaling)
Characterization of Stage 2 Basin Flux

The analysis included an upward flux from the basin for a period of 50 yrs. The upward flux from the basin, $q_b$, was scaled to the recharge with three cases, $q_b=0.1Re$, $q_b=1.0Re$, and $q_b=10Re$. The case where the upward flux was equal to the recharge was used as a baseline.

The distribution of pressure and concentration from three different times during the Freshwater Flushing stage were used as the initial conditions. These datasets were selected so the initial fresh/salt transition was located at 200 m, 300 m and 400 m below the ground surface of the upland area. This range of depth to the fresh/salt transition is typical of the Midwestern U.S., according to Figure 2. It should be noted that the time for freshwater aquifer development in the simulation was much shorter than the time of exposure of the aquifers in the midwestern U.S.. This occurred because the analyses were conducted assuming isotropic aquifer material, but the flat-lying rocks in the Midwest are expected to be anisotropic with a relatively low vertical permeability that would have slowed the flushing of salt water.

Comparing three different initial conditions, the largest increase in the interface occurred during the case with the deepest initial interface at 400[m] (Figure 38). The largest increase in surface water concentration happened to the case with shallowest initial interface at 200[m]. While comparing three cases with different basin flux rates, the largest magnitude of concentration increase, as well the largest increase in the elevation of the interface occurred with largest basin flux rate of $q_b=10Re$. In the
background case where \( q_b = Re \), and the initial \( D_L = 300 \) m depth, the increase in maximum stream concentration between 5-year and 50-years of basin flux is 67 [mol/m\(^3\)]. The same parameter was evaluated as 4 [mol/m\(^3\)] and 180 [mol/m\(^3\)] for \( q_b = 0.1 Re \) and \( q_b = 10 Re \), respectively (Figure 38).

In the case where \( q_b = 10 Re \) the change in the fresh/salt transition reached as much as 350 m. When \( q_b < 0.1 x Re \), however, the change in the fresh/salt transition is much smaller than the thickness of the freshwater layer. The magnitude of the flux during the pulse is an important control on the impact on the fresh/salt interface (Figure 38).
Figure 38 Upper: Salt concentration across stream for pulses lasting 5 years (red), 20 years (green), and 50 (blue) years. Columns are for different magnitudes of $q_b$. Lower: Cross sections of concentration (color) and the fresh/salt interface (lines) before and after pulse of basin flux).

Column 1: initial $D_L = 200$ m; Column 2: initial $D_L = 300$ m; Column 3: initial $D_L = 400$ m.
In order to quantify the change in fresh/salt transition zone, vertical concentration profiles were plotted (Figure 39) beneath the upland area and the stream for a pulse duration of 100 years. Results indicated in Figure 39, for a fixed concentration level (e.g. fresh/salt interface concentration), the corresponding depth before and after the pulse. A concentration profile beneath the uplands showed the freshwater/brackish contact \((C = 8.54 \text{ mol/m}^3)\) at a depth of approximately 300m initially. It rose to 250m by \(t = 100\text{yrs}\) when the basin flux was equal to the recharge and to 180m when basin flux was 10Re.

The concentration profile beneath the stream showed a much wider and smoother transition zone compared to the profile beneath the upland, which extended from the ground surface where concentration was 0 to 500 m depth where concentration was 1000 mol/m\(^3\) (Figure 39). The increased flux raised the concentration profile toward ground surface and generally followed the shape of the initial profile. However, in the case where basin flux was 10Re, the concentration was raised significantly, with the profile forming a sharp transition zone at 80 m depth where concentration was about 990 mol/m\(^3\). The concentration profiles quantitatively locate concentration distribution in previous qualitative cross-sectional profile beneath the stream and upland area in Figure 38.
Figure 39 Vertical profile of salt concentration measured up to 500 m beneath upland/stream before and after 50 year basin pulse
The average concentration of water discharging to the stream increased with time throughout the basin pulse, and then decreased when the pulse stopped (Figure 40). The average concentration discharging to the streams increased with the magnitude of the basin flux, and with the initial depth to the fresh/salt transition.

The change in average concentration was essentially negligible when basin flux<0.1Re. The maximum concentration increased by 30 and 140 mol/m$^3$ where $q_b=1Re$ and $10Re$ for $D_L=200m$ (Figure 40). When the basin pulse occurred for $D_L=400m$, its effect was minor $q_b=1Re$. When $q_b=10Re$, the increase in average stream concentration was over 60 mol/m$^3$ with the initial fresh/salt interface as deep as 400 m.
Figure 40 Average concentration of water discharging to streams during and following a 50-yr-long pulse of increased flux from the basin (basin flux=0.1Re (upper), 1.0Re (middle) and 10Re (lower); Initial concentration =1000[mol/m$^3$]). Pulse ends at t=50 yrs (1.58e9[s]).
Other than magnitude and duration of the basin flux, the average concentration discharging to the streams was also dependent on the initial salt concentration. Therefore the following study explored whether, under the same magnitude and duration of pulse, a lower concentration would have a larger impact on surface water system due to lower gravity force. To test this, the simulations were repeated where the initial concentration was set to 600 mol/m$^3$, which is equal to the salt concentration in seawater. This concentration was also used for the lower boundary condition.

Results showed (Figure 41) maximum decrease of stream concentration due to the concentration reduction occurred in the case where $q_b=10Re$ and initial saline depth was 200 m. The peak concentration reduced 60 mol/m$^3$ from roughly 170 mol/m$^3$ to 110 mol/m$^3$ (e.g. compare the blue curve in the lower plot in Figure 40 to the blue curve in the same plot in Figure 41). Generally the smaller the peak concentration, the smaller decrease in stream concentration. In the case where basin flux=0.1Re and initial $D_L=400$ m there was hardly any averaged salt concentration change in stream (Figure 41). Therefore, magnitude of the impact on stream concentration decreases with the concentration of the underlying water.

There were fluctuations in concentration around $t = 2 \times 10^9$ s (65 yrs) where $q_b=10Re$ and smaller fluctuations where $q_b=Re$ (Figure 40 and 41). This appears to be a numerical artifact resulting from the relatively rapid change in flux at the boundary and it likely has limited relevance to the salt transport.
The concentration decreases after the basin pulse in all cases. The decrease is sharp when the pulse ends, but then the rate of change diminishes (Figure 41). For example, with initial $D_L = 200 \text{ m}$ and $q_b = 0.1Re$, the average concentration in the stream took two times the pulse period to come back to background level. The deeper the initial transition was located (larger initial $D_L$), and the larger $q_b$, the longer the system took to recover to its background concentration. With initial $D_L = 400 \text{ m}$ and $q_b = 10Re$, the average concentration in the stream took more than six times the pulse period to come back to background level.
Figure 41 Average concentration (mol/m$^3$) of water discharging to streams during and following a 50-yr-long pulse of increased flux from the basin (basin flux=0.1, 1 and 10 recharge flux; c=600[mol/m$^3$]). Peak concentration occurs at t=50 yrs (1.58x10$^9$[s]).
Mass rate of salt discharging to the stream was determined as the product of the concentration and the volumetric flux integrated over the width of the stream. This gives the average mass discharging per unit length in the direction of flow. The results show that the mass rate resembles the history of concentration in Figures 40 and 41 in that it increases during the pulse and decreases afterward. When \( C = 1000 \text{ mol/m}^3 \), the largest effect occurred for \( q_b = 10\text{Re} \) and \( D_L = 200\text{m} \), and this resulted in \( J = 2 \times 10^{-3} \text{ mol s}^{-1} \text{ m}^{-1} \).

This peak value dropped off markedly with \( q_b \), however. It is \( 4 \times 10^{-5} \text{ mol s}^{-1} \text{ m}^{-1} \) for \( q_b = 1.0\text{Re} \) and \( 8 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-1} \) for \( q_b = 0.1\text{Re} \). Smaller fluxes occurred for larger values of \( D_L \) (Figure 40 and 41).

These mass flux values are important because regulations are written in terms of the mass rate discharging to a stream reach (BARR 2010). The mass flux values given here can be used to estimate the total mass discharging to a stream reach of a particular length.
3D Numerical Analysis

The effects of basin pressurization were evaluated in 3D to determine the extent to which geometric factors associated with the 2D analysis may have controlled the response. The problem consists of a permeable layer that forms an unconfined aquifer at the ground surface, but that dips shallowly and forms a confined aquifer at depth (Figure 42). The layer was assumed to be 100m thick, to dip 5°, and to be sandwiched between low permeability confining units. As such, this idealized geometry could represent a sandstone cropping out at the periphery of a basin (the Mt. Simon on the northwestern periphery of the Illinois Basin, for example (Gupta and Bair 1997; Person et al. 2010; Zhou et al. 2010)). It could also represent a sand formation along the Atlantic or Gulf Coast (Nicot 2008).

The region is 2.5km long in the dip direction, so only a small portion of the lateral extent of the represented region is included. The downdip extent is truncated and either a constant head or no-flow boundary condition is used to represent interactions between the shallow formation and the deep aquifer. The no-flow condition represents a case where the permeability decreases significantly with depth, whereas the constant head condition represents a case where head in the basin is unaffected by changes in head at shallow depths. This could be approximated, for example, if the down dip formation had a large hydraulic diffusivity and lateral extent. The lower boundary of the simulation is assumed to remain saturated with salt water at the initial concentration, so regardless of whether it is held at constant head or is no-flow, the concentration is fixed at the lower boundary.
The model is 0.5 km wide and is bounded by no-flow conditions. Streams traverse the outcrop perpendicular to strike, and the concept is that there are many such streams spaced 1 km apart. The symmetry of this configuration creates no-flow boundaries beneath the streams and the uplands, and these are the lateral no-flow boundaries in the model. The outcrop length perpendicular to strike is approximately 1100m.

The bottom and top boundaries and a short boundary on the up-dip side are all assumed to be no-flow because the aquifer is bounded by confining units.

The outcrop area is assumed to receive a recharge flux of $10^{-9}$ m/s that is constant, nearly uniformly distributed, and the salt concentration in the recharge is zero. The stream was represented as a rectangular region, 10m wide and extending along one side of the outcrop. One half of the stream is represented in this model, so the total width of the stream is 20m because of symmetry, which is the same as used in the 2D model. The head in the stream was held constant and was assumed to be uniform, ignoring a hydraulic gradient along the length of the stream. The recharge was assumed to be uniformly distributed everywhere except within 20m of the stream where it was set to zero.

The permeability of the formation was assumed uniform, constant, and equal to $10^{-13}$ m$^2$. Porosity was 0.3. The rate at which pressure equilibrated within this system was much faster than the rate of change of concentration, so the effects of water and aquifer compressibility were ignored. Density was assumed to be a function of the
concentration according to Eqn. 24. The viscosity was assumed to be constant and uniform, in keeping with the earlier analysis.

The initial concentration was assumed to be uniform and equal to 600 mol/m$^3$, the concentration of modern seawater. The initial pressure was assumed to be hydrostatic based on the initial density. This pressure was assumed to be held constant when the constant head condition was used on the lower boundary. The pressure at the stream was set to zero initially and held constant.

Figure 42 Hydraulic head and flow vectors early in the flushing stage (t = 0.5Gs, 15.9yrs).

Dark red is +4m. Dark blue is 0m.
The problem was discretized using a swept mesh of hexahedral elements approximately 25 m on a side (Figure 42) and 16m high. The stream was discretized with rectangular elements 10m x 25m. This resulted in a mesh with 12k hexahedral elements. Many different mesh designs were evaluated while setting up this model and most of them used small elements where the flow converged in the vicinity of the stream and larger elements near the divide. However, numerical instabilities were more common with meshes that had a range of element sizes than they were with meshes with uniform sizes for this problem. The mesh-dependent instabilities occurred when concentration variations resulted in density changes of a few percent. These instabilities were absent, and the run times were significantly shorter, when the variations in density were a few tenths of a percent or less. The mesh that was used for the problem (Figure 42) gave the best performance among the meshes evaluated for this problem.

Analysis

The analysis was conducted in two stages following the approach used in 2D. The run time for the 3D model was much longer than in 2D and this restricted the total time of the Freshwater Flushing stage to 2000Gs, which is approximately 63.4k yrs. The model that used the constant head for the lower boundary condition will be described first.

Stage 1 Freshwater flushing

The hydraulic head mounded in the outcrop area and reached a maximum of approximately 4m in the up dip corner (Figure 43). This gave an average horizontal head gradient of slightly less than 0.01, which is a typical value for unconfined aquifers.
The pressure head in the unconfined part of the aquifer increased abruptly at the start of the analysis as a result of recharge \((h=0\) initially\), but then it decreased with time during flushing. For example, the pressure head dropped by approximately 1.2m at a depth of 50m (Figure 43). This occurred as the relatively dense salt water that was present initially was flushed out and replaced with fresh water of lower density. This drop in pressure causes the hydraulic potential in the unconfined region to decrease with time.

![Figure 43 Change in pressure head as a function of time at 50m depth in unconfined part of the aquifer (x=250m, y=1000m).](image)

The process of freshwater flushing to create the shallow aquifer was driven by ground water flow that radiates from a mound along the divide and then converged on the stream (Figure 44). This created relatively short, fast flowpaths in the vicinity of the stream and along the updip edge of the aquifer. The length of the flowpaths increased and the velocity diminished with distance from the stream. The longest and slowest paths
start where the upper contact of the aquifer was exposed. Recharge entering the aquifer in this area flowed downward under the confining unit, and then it curved around and converged on the down-dip end of the stream (Figure 44). Particle traces that started in the confined part of the aquifer are nearly static at early time, but they flowed up dip at later times. This caused salt water to flow upward and discharge to the stream (Figure 44).

Figure 44 Development of a dipping freshwater aquifer by flushing of connate salt water, $C_i = 600 \text{mol/m}^3$ (35 kg/m$^3$). Case 1, c.h. boundary on downdip side. Color on vertical sections is concentration, blue = 0.1$C_i$, dark red > 0.5$C_i$. Particle traces are colored with log($t_{\text{max}}$), where $t_{\text{max}}$ is the maximum time in that frame. Green balls are the current position of a particle. Stream is the double yellow line. Confining unit is grey.
Flow in the confined part of the aquifer was in the down dip direction at early times, but it reversed direction and flowed upward later in the simulation. This resulted in a reversal of the volumetric flux across the lower boundary (Figure 45). The down-dip flow occurred because recharge caused the head in the unconfined part of the aquifer to increase relative to the head on the lower boundary, which was held constant and equal to the initial head. However, the change in concentration resulting from fresh water flushing drops the pressure in the unconfined aquifer and this affected the flow at depth in the aquifer. The down-dip component of the flow decreased and eventually changed sign in response to flushing of the unconfined aquifer (Figure 45).

![Figure 45 Volumetric flux of water out of lower boundary as a function of time normalized to the recharge flux.](image)

The concentration changed at shallow depths soon after recharge of fresh water starts (Figure 44). The fresh/salt transition moved downward and down dip with time, and after 10Gs dilution occurred in the confined part of the aquifer. The rate at which the concentrations dropped in the confined aquifer was slow, however. The concentration
reached a steady state after approximately 200 Gs (6.34k yrs) as the downward circulation rate from recharge balances the upward flow caused by the drop in head in the outcrop area. There was a region of fresh water that extended 100m or so into the confined aquifer at steady state, and the larger region where the water was diluted to 0.5 of the initial concentration was limited to within several 100m from the outcrop. Brackish or saline water underlay the fresh water in this region, and it was replenished by upward flow from depth (Figure 44, 46).

Water discharging to the stream was mostly fresh, but the salt concentration increased in the down-dip direction and brackish water with a maximum concentration of 28 mol/m$^3$ discharged at the contact between the aquifer and the overlying confining unit (Figure 47a). Most of the discharge to the stream was fresh, and the average concentration was approximately 1 mol/m$^3$. The overall mass flow rate into the stream decreased with time from several 10s of kg/day to approximately 2.3 kg/day at steady state (Figure 47b).
Figure 46 Conditions after 2000Gs of flushing connate salt water with fresh water in recharge area.  a.) Particle traces with relative velocity in as color (red=fast, blue=slow). Green isosurface bounds freshwater zone (C<1000mg/l).  b. Concentrations at surface

Figure 47a. Maximum (green) and average (blue) concentration of salt in ground water discharging to stream during fresh water flushing. b. Mass rate of salt discharging to stream during fresh water flushing.
**Stage 2 Basin pulse**

A pulse of flow from the basin was represented by increasing the hydraulic head at the bottom boundary by 10m over a duration of 3Gs (approximately 100yrs). The head was dropped back to original conditions and the simulation was continued for a total of 10 Gs (317yrs) (Figure 48). This elevated the pressure throughout the region, but the change was less than at the boundary. For example, the change in head was 1.8m at a location in the unconfined aquifer (Figure 48). Even though the head was significantly less, the head within the aquifer changed roughly in proportion to the change at the boundary. Nearly 2m of change in head is more than expected in outcrop regions during CO$_2$ storage (Nicot 2008), but it seems plausible that the head could change by this much under some unplanned scenario.

Figure 48 Pressure head at the lower boundary (green) and at 50 m depth in the unconfined aquifer at (250m, 1000m) the same location as in Figure 43 (blue).
The pulse from the basin increases the maximum and average concentration of salt discharging to the stream (Figure 49). The maximum concentration increases from 27 mol/m$^3$ to nearly 44 mol/m$^3$. This results in a 30 percent increase in the average concentration, but the initial concentration is low (1.0 mol/m$^3$) and the increased value, 1.3 mol/m$^3$, is well below the USEPA chloride MCL in primary drinking water regulation as 250mg/L, which is equivalent of 4.27 mol/m$^3$ (USEPA 2009). The total mass rate of salt discharging to the stream increases by several fold from 2.5 kg/day to more than 7 kg/day (Figure 50).

All of these measures suggest that the effect of the basin pulse is mild, but it is worth pointing out that none of these measures returns to background values after the pulse is over (Figures 49 and 50). The maximum concentration is the most notable. It drops to approximately 33 mol/m$^3$ after the pulse and decreases slowly for the next 6 Gs (200 yrs).

However, while this also occurs with the mass rate, the magnitude is small, with the rate at the start of the pulse being 2.3 kg/day and the rate at the end of the pulse 2.6 kg/day.

The changing distribution of salt (Figure 51) is also important because it could cause contamination of fresh ground water and it shows how the effect on surface water is manifested. The transition from fresh to salty water contains the 17 mol/m$^3$ isosurface, which bounds the region of fresh water (Figure 51). This surface occurs near the edge of the outcrop area, where it is inclined and underlays a 200-m-wide band that straddles the
confined and unconfined regions of the aquifer (Figure 51). This surface moves in the up-dip direction during the basin pulse. The total displacement horizontal displacement is less than 50 m. This results in an upward displacement of roughly 20 m in the 200-m-wide band underlain by the iso-surface. After the pulse, the isosurface recedes by approximately 10 m during the next 200 years, although this change is barely discernable on Figure 58. The small change in the isosurface after the pulse is consistent with the persistent increase in maximum concentration discharging to the stream (Figure 49).

Figure 49 Maximum and average concentration of groundwater discharging to stream as a function of time. Pulse of increased pressure from basin from 2000 to 2003 Gs.
The effect of the basin pulse on the stream is best illustrated by the lower row of images in Figure 58, which show the distribution of concentration in ground water discharging to the stream. Before the basin pulse, water originating at depth within the confined part of the aquifer was upwelling and discharging to the down-dip end of the stream. This resulted in a localized zone approximately 10m long where brackish water discharged to the stream (Figure 51a). Increasing the head from the basin for 100 years (3Gs) caused the region of brackish discharge to grow to approximately 30m long. This is where the high concentration indicated in Figure 49 was discharging. At the end of the simulation, 200 years after the pressure at the lower boundary returned to ambient conditions, the length of the zone of brackish water discharging to the stream had decreased to approximately 20m (Figure 51c bottom row).
Figure 51 Concentrations on boundaries at different times using same color scheme and perspective view as Figure 56. The top surface of the outcrop and above the fresh water isosurface (green) was transparent to show the position of the isosurface. The blue surface was fresh water at the bottom of the aquifer. Elevated pressure occurred as a pulse $2000Gs < t < 2003Gs$. Bottom row was enlargement of the vicinity of the down-dip end of the stream. Dashed green line was contact between fresh and brackish water. Grey line was trace of the contact with the upper confining unit. White rectangle was a reference location and scale for the upper row. The stream was 10m wide for scale in the lower row.
CHAPTER V. IDENTIFICATION OF IMPACTS

The analyses outlined above show that increased upward flux from a basin can affect the distribution and fluxes of salt in shallow aquifers. This can cause risks because salt can be a serious contaminant. It can kill crops and ruin the fertility of soil (Page 1926), cause diarrhea or other health problems in humans (Alderman 2000), and alter the species that inhabit freshwater aquatic ecosystems (Hart 2003). However, the impact depends on a variety of factors ranging from the concentration and mass flux of salts to how they are distributed in the subsurface. The effects of exposure to salt can be less severe than with compounds like chlorinated solvents and radionuclides, so the framework for evaluating impacts is incomplete compared to that associated with more toxic compounds. As a result, I have developed a 3-tiered system for evaluating impacts that is consistent with current regulations. This system considers impacts associated with increases in concentration, and increases in mass loading to surface water, as well as reduction in the thickness of freshwater aquifers. This system will form the basis for evaluating the impacts associated with increases in basin flux.

Impacts to Surface Water Based on Concentration

A baseline impact associated with surface water is exceeding concentrations identified by the Maximum Contaminant Limit (MCL). For total dissolved solids the MCL is 500 ppm (8.55 mol/m$^3$), and it is 250 ppm for chloride (USEPA). Concentrations are slightly greater than this in some drinking water sources. For example, TDS values
were up to 1000 ppm in water supplies from the Irondogenese aquifer in New York (Olcott, 1995, Figure 40).

EPA regulations identify the maximum acceptable chloride concentration for chronic exposure in aquatic ecosystems as 230 ppm, and 860 ppm for acute exposure (USEPA). Recent investigations have shown that chloride toxicity in aquatic ecosystems depends on the concentrations of calcium, magnesium and sulfate (USEPA). New guidelines issued by the EPA adjust the acceptable acute and chronic concentrations using a function that depends on hardness and sulfate. As an example, a hardness of 200 mg/l and a sulfate concentration of 63 mg/l, average values in Iowa, give an acceptable concentration for chronic exposure of 389 mg/l and for acute exposure it is 629 mg/l. Scaling these values to concentrations of a NaCl solution gives 633 mg/l and 1025 mg/l for chronic and acute concentrations, respectively.

Crops vary in susceptibility to salts, but TDS concentrations in excess of 2000 mg/l are unsuitable for virtually any crop. Sodium will damage soil structure and reduce permeability, which will reduce crop yields. Acceptable concentrations of Na\(^+\) for agricultural applications depends on concentrations of Ca\(^{2+}\) and Mg\(^{2+}\), but in general acceptable Na\(^+\) concentrations are in the range of several hundred ppm (Warrence 2002).

Freshwater aquatic ecosystems are vulnerable to elevated salt contents, and the impacts vary depending on the organism and the degree to which it has evolved salt tolerance (Hart 2003). Significant effects, ranging from loss of vigor to death, occur
when freshwater plants and invertebrates are exposed to water concentrations in the range of 1000-2000 mg/l, according to (Hart 2003).

Adult freshwater fish may tolerate salt concentrations up to 10000 mg/l (Hart 2003), although considerable variability exists depending on species and duration of exposure. For example, Bringolf et al. (2005) found that the median lethal concentration for flathead catfish was 10,000 ppm in NaCl and 14,000ppm in synthetic seawater for 96 hrs of exposure. The salt tolerance of cutthroat trout was in the range of 20,000 ppm, according to 96-hr-exposure mortality tests reported by Wagner et al. (2001).

An important consequence of increased salt content is that it reduces the resiliency of an ecosystem, which can alter the community structure at concentrations less than those required to result in direct mortality. Fish eggs and juveniles are less tolerant to salt than adults (Hart et al. 2003), for example, so elevated salt content can impose a stress that favors shifts to more tolerant species even at relatively low concentrations (Hart et al. 2003; Davis et al. 2003). The salt tolerance of some macro-invertebrates is relatively low, whereas other can tolerate higher concentrations (Zinchenko and Golovatyuk, 2013). The ability of Salt Cedar or Tamarisk to tolerate high salinities is one factor behind its ability to displace Cottonwood and other native species in the western U.S. (Lovich and deGouvenain, 1998). As a result, it seems likely that even subtle changes in salinity will have an environmental impact by shifting populations in aquatic and hyporheic ecosystems toward more salt tolerant species.
Increasing the salt flux to surface water causes risks by limiting the beneficial water use and reducing ecosystem services. These factors can be grouped to define three levels of impact based on the resulting concentration of salt in surface water.

*Low Impact (≤500 mg/l)* These concentrations are within the MCL, and should be within the guidelines for chloride in most cases.

*Significant Impact (500-3000 mg/l)* These concentrations exceed the MCL, but some municipal supplies use water in the low end of this range. Impacts on agriculture become severe at the upper end of this range. 1000 mg/l is a threshold for detrimental effects on aquatic plants and some invertebrates.

*Severe Impact (>3000 mg/l)* Significant health problems caused by drinking this water. Agriculture is severely impacted. Some invertebrates can survive, along with some adult freshwater fish. Expect significant changes in ecosystem diversity.

**Impacts to Surface Water Based on Mass Loading Rate**

Evaporation is perhaps the most common process that increases salt concentration in surface waters, but human activities are a close second. This has led to regulations that limit these activities in order to protect surface water quality. Runoff of salt used to melt ice during snowstorms is a common activity that increases the concentration of chloride in surface water, and several of the northern states have regulations that limit the use of chloride. These regulations are typically based on the total mass of chloride that be released to a watershed on a daily basis, to Total Maximum Daily Load (TMDL).
An example of this type of regulation is the one that applies to Nine Mile Creek, Minnesota (BARR 2010). Nine Mile Creek (AUID 07020012-518) is located in southwest Hennepin County in the lower portion of the Minnesota River Basin. It is 5 to 10 miles southwest of Minneapolis and it covers an area of 44.5 square miles. There are various urban land uses, several large open areas, as well as lakes and wetland complexes. The creek was first listed on the Minnesota Pollution Control Agency’s (MPCA)’s 303(d) list in 2004 after data indicated chloride levels in excess of the MPCA’s state water quality chronic standard of 230 mg/L. Nine Mile Creek was again listed on the MPCA 2008 303(d) Impaired Waters List because of high chloride contents. Regulations for developed in 2010 limit the annual total load to 2543 tons/yr (2010). Distributing this load over the 25 km of stream reach gives a load of 102 tons/yr-km. This value is larger than other loadings and it may be because the stream drainage density in the Ninemile Creek watershed is unusually low. There are many small, isolated ponds and lakes in the watershed, but I only used the length of streams for normalizing the loading rate.

For comparison, the TMYL of West Branch DuPage River in the suburbs of Chicago is 6,600 tons/yr (CH2MHILL 2003), and this gives a normalized value of 77 tons/yr km using channel length of 85 km. The first order stream is not shown on the map (CH2MHILL 2003) so the stream length would be greater than estimated value, and the actual TMYL would be less than 77 ton/yr km. Chloride transport in streams in Massachusetts and New Hampshire were evaluated by Trowbridge (2007), who reports chloride loadings ranging from 100 to 250 tons/yr mi$^2$, with most of this from salt applied
as a de-icer. The assuming a drainage density of approximately 1/km, the normalized salt loads in these streams ranges from 35 tons/yr km to 87 tons/yr km.

TMDL regulations scale the acceptable mass load to the flowrate in the stream. For example, the Total Maximum Daily Load in Porcupine Brook, NH, ranges from more than 10 tons/day when the flow is high (20% exceedance) to less than 1 ton/day when the flow is low (80% exceedance (Currier 2009)). Normalizing these loads as a mass rate per year gives 13 tons/yr km to 130 tons/yr km for Porcupine Creek (assuming the drainage density is 1/km and using 28 km² as the drainage area). A similar flow-duration analysis was done for Shingle Creek in Minnesota (WENCK ASSOCIATES 2006), and this loadings that range from 6 tons/yr km to 30 tons/yr km after normalization.

These results indicate three levels of impact for total mass loading of chloride to surface water

*Low Impact (<5 tons/km yr)*. This is less than the TMDL values for streams impacted by chloride from de-icing.

*Significant Impact (5 tons/km yr to 100 tons/km yr)*. This rate includes the loading reported for streams affected by salt from de-icing.

*Severe Impact (>100 tons/km yr)*. This exceeds the published data for chloride loading to streams.
Impacts to Ground Water

Fresh ground water is a critical resource for consumptive use, and most applications can be impacted by increases in salt concentration. Regulations on impacts to ground water are based on MCLs of the produced water. This has limited value in assessing effects of increased basin flux where the primary result appears to be a reduction in the thickness of the freshwater layer. Reducing the thickness by a small amount will reduce the volume of stored freshwater and this may affect the long-term availability of the resource. Reducing the thickness by a larger amount could cause wells to produce salt water, which would significantly impact the value of the ground water supply.

We propose to evaluate the severity of impact based on the fractional change in volume of water stored per unit area of the aquifer. This amounts to a fractional change in the thickness of the freshwater layer forming the aquifer, $\Delta b_i = \Delta b/b_i$, where $\Delta b$ is the reduction in thickness and $b_i$ is the initial thickness of the freshwater layer. We expect that natural variations in recharge will cause the fresh/salt transition to vary seasonally and perhaps with longer periods as well. We expect that it will be challenging to distinguish small fluctuations in the fresh/salt transition from background. So, while any change in aquifer volume is a concern, a reduction by 5% ($\Delta b_i < 0.05$) would probably be difficult to detect, so the impacts associated with this change are assumed to be low.

Water quality from aquifers underlain by salty water are prone to damage by upconing, so they are typically designed with their screens significantly above the
expected upper limit of the fresh/salt transition. This is accomplished by designing the location of the screen and the magnitude of pumping so the top of the upcone of salt water is a safe distance below the bottom of the well. Guidelines from several investigators recommend that the height of the upcone is 0.25 to 0.33 of the distance from the bottom of a well to the original position of the fresh/salt transition (Motz, 1992 and references therein). The ideal depth a well penetrates the freshwater layer would likely vary with the hydrogeology, but here I will assume the well penetrates half the thickness of the freshwater layer, which is similar to the dimensions of a well in the Floridan aquifer described by Motz (1992). Assuming the well is pumped so the height of the upcone is 0.33 of the distance from the bottom of the well to the fresh/salt interface leaves a distance of 1/3 of the original thickness of the freshwater layer between the bottom of the well and the top of the fresh/salt transition mounded beneath the operating well.

In this scenario, reducing the thickness of the freshwater layer by 1/3 ($\Delta b_r = 0.33$) would move the fresh/salt transition to the bottom of the screen, presumably significantly degrading or ruining the utility of the well. This leads to the following impact categories:

*Low Impact ($\Delta b_r < 0.05$)*. Reduction is the freshwater thickness is small and will likely be difficult to identify above background variations.

*Significant Impact ($0.05 < \Delta b_r < 0.33$)*. The volume of freshwater stored in the aquifer is reduced. Water quality affected in wells operating at drawdowns that are larger than guidelines.
Severe Impact ($Ah > 0.33$) Large reduction in volume of stored water. Water quality in properly designed wells degraded by upconing.
CHAPTER VI. CONCLUSIONS

Aquifers provide fresh ground water for beneficial use and they supply baseflow to aquatic ecosystems, but in many locations throughout the U.S the presence of underlying salt water poses a potential contamination threat if it is mobilized by pressure increases during CO₂ storage. The potential for contamination was evaluated by developing simulations of transport processes that could occur in shallow aquifers when the upward flux of salt water is increased. A first step in the analysis was to evaluate the performance of COMSOL Multiphysics code during the simulation of benchmark problems that involve the flow and transport of water where the density depends on the concentration. COMSOL Multiphysics was capable of simulating the benchmark problems.

The simulation of basin pressurization was conducted in two stages, where the first stage was designed to create a freshwater aquifer by flushing out water that was initially at a uniform concentration similar to seawater. The purpose of the Freshwater Flushing stage was to create a fresh water overlying a salt water aquifer with a distribution of salt that was in a dynamic equilibrium with the boundary conditions. These were the initial conditions for the second stage where the effects of CO₂ injection were represented by increasing either the flux or the pressure as a temporary pulse at the bottom boundary of the model. The effects of the pulse on the position of the fresh/salt transition zone and on the discharge to a stream were then evaluated.
**Freshwater Flushing**

The results of 2D simulations show that the depth to the fresh/salt transition increases with time and is greater under the uplands than the streams. This gives the transition zone a scalloped shape with cusp-like ridges of relatively salty water under the streams. The average depth to the fresh/salt transition increases, but the rate of increase diminishes with time and stabilizes as the system goes to a steady state (Figure 35).

**Effect of Concentration on Density**

Simulations were conducted with and without the density as a function of concentration. These results show that the average depth to the fresh/salt transition becomes shallower when the density is a function of concentration. Moreover, the cusp-like ridges beneath streams diminish more quickly when this effect is included (Figure 25), presumably because the ridges collapse by gravity.

**Lower Boundary Condition and Steady State**

Salt transport goes to a steady state with either no-flow bottom boundary or constant head bottom boundary. But there are different mechanisms involved that depend on the lower boundary condition for the fluid flow problem. When the lower boundary is assumed to be no-flow (Figure 25), the depth to the fresh/salt transition increases until diffusion from the lower boundary (where $C = \text{constant}$) to the upper boundary ($C = 0$) dominates. At this time, the salt mass flux is controlled by steady upward diffusion from depth. This is indicated by a linear distribution of concentration with depth (Figure 25) in the region below the freshwater aquifer.
In contrast, a different mechanism occurs when the hydraulic head at the lower boundary is assumed to be constant (Figure 27). In this case, flushing dense salt water reduces the head in the shallow aquifer and this causes upward flow from the lower boundary. The system becomes steady when the upward advective flux limits the downward migration of the fresh/salt transition. Thus, assuming the lower boundary condition is no-flow causes the system to go to steady state where the mass flux is dominated by upward diffusion, whereas assuming the lower boundary condition is constant head also results in a steady state, but in this case it is controlled by upward advection.

The time required for the system to equilibrate by upward diffusion scales as 

\[ t_{cd} = \frac{d_s^2}{D} \]

where \( d_s \) is the depth to the lower boundary and \( D \) is the diffusion constant. This time is on the order of millions of years when typical values are used. By contrast, the time required for the system to equilibrate by advection is several orders of magnitude faster.

The distribution of salt at the start of the basin pulse is an important control on the impact of the pulse, so salt distributions resulting from the two different lower boundary conditions were compared. Results prior to steady state (Figure 28) show that the salt distributions are remarkably similar for the two lower boundary conditions. Thus, even though the lower boundary condition plays an important role in the long-term hydrologic behavior, it has a minor effect on the development of the salt distribution in our 2D study.
**Scaling**

The stream spacing, $L$, was used as a characteristic length, and the recharge rate, $R$, and effective porosity, $n_e$, were used to determine a characteristic time as $t_c = n_e L / R$. These basic scales, along with formation anisotropy were used to define a dimensionless depth to salt water ($D_L \sqrt{k_h} / L \sqrt{k_v}$) as a function of dimensionless time ($tR/n_e L$) (Figure 32 and 33).

Numerical experiments were conducted using a variety of different parameters and the results confirm the basic scaling outlined above for the case of low concentrations and negligible density change (Figure 35). Additional scaling is required to account for the shallower depth to fresh/salt transition that occurs when density is a function of concentration and the concentration change is on the order of several percent.

The analysis also defined an aquifer-scale Peclet number, $P_{e_a} = \frac{RL}{n_e D}$ that determines the relative importance of advective and diffusive transport. The basin-scale Peclet number is important at steady state when the lower boundary is no-flow. In this case, the depth to fresh/salt transition at steady state is characterized by Figure 35.

**Basin Pulse**

The Basin Pulse stage of the analysis used the distribution of salt and hydraulic head from the Freshwater Flushing stage as initial conditions. Results from different times during the Freshwater Flushing analysis were used to generate freshwater aquifers
with thicknesses ranging from 200 m to 400 m. Effects of pulses of upward flux were evaluated using sensitivity analyses of key parameters.

**2D analysis**

Results from the 2D analyses indicated that the effect of basin flux was to raise the fresh/salt transition and the stream salt content (Figure 38). The most extreme case that was considered was a 50-yr-long basin pulse with the initial fresh/salt interface at 200 m below upland area. The upward flux from the basin pulse was 10 times recharge rate. The results show that the depth of the fresh/salt transition would be reduced by 150 m. The maximum stream concentration was increased from 20 to 170 mol/m$^3$. This effect would seriously disrupt the ground water resources and it would likely damage a freshwater ecosystem with the discharge of saline water.

The magnitudes of the effects appeared to be small for basin fluxes less than the recharge rate. For example, when the upward flux was equal to the recharge rate, the depth to the fresh/salt transition increased by 50 m and when the upward flux was 0.1Re, the transition only changed by 5 m. Similarly, the average concentration in the stream was raised from 14 to 16 mol/m$^3$ when the upward flux was equal to the recharge. The average concentration in the stream was raised from 20 to 50 mol/m$^3$ when the upward flux was 0.1Re. The salt concentration in surface stream, and change in the fresh/salt transition was sensitive to the depth to the transition at the beginning of the pulse. The increase in the salt concentration in the surface stream was greatest when the fresh/salt transition was shallowest. The greatest increase in the fresh/salt interface, however, occurred in the case of deepest initial interface. For example, when basin pulse was
scaled equal to recharge rate, the interface raise with 200 m initial location was approximately 20 m. The same value was approximate 80 m with 400 m initial interface location.

The effect of changes in the concentration field was found to persist long after basin pressurization diminished. For example, with initial fresh/salt interface at 200 m and basin flux = 0.1R, the average concentration in the stream took 2 times the pulse period to come back to background level. This recovery time increased with increasing initial interface depth and pulse magnitude. The deeper the initial transition was located, and the larger the pulse was, the longer the system would take to recover to its background concentration. With initial fresh/salt interface at 400 m and basin flux scaled to 10R, the average concentration in the stream took more than 6 times the pulse period to come back to background level.

The effects were also sensitive to the initial concentration. By lowering the saline concentration from 1000 to 600 mol/m$^3$ the stream salt content was reduced by roughly 30% with salt water density as a function of salt concentration.

**3D Case**

Three-dimensional analysis with concentration dependent density in a dipping aquifer suggested pattern of fresh/salt transition development that resembled some effects observed in the 2D analyses. During the flushing stage the average concentration dropped to approximately 1.0 mol/m$^3$ (58 ppm) as equivalent to 2.3 kg/ m$^3$, which is very fresh water. Hydraulic head was raised for 10m at the lower boundary to simulate the
basin pulse, which continued for 3Gs (100 yrs) and for the analysis was continued for another 7 Gs (230 yrs).

The pulse from the basin increased the maximum and average concentration of salt discharging to the stream (Figure 51), just as in the 2D case, but the magnitudes were much smaller than in 2D. For example, the average concentration increased from 1.0 mol/m$^3$ to nearly 1.3 mol/m$^3$, which is well below the USEPA chloride MCL in primary drinking water regulation as 4.27 mol/m$^3$. The total mass rate of salt discharging to the stream increases from 2.3 kg/day to more than 7 kg/day.

The effects of the basin pulse in 3D resemble those in 2D, but their magnitude is less. This can be explained by the position of the fresh/salt transition in the dipping aquifer used in the 3D analysis. Freshwater flushing removed all the salt in the unconfined portion of the aquifer and the transition zone migrated to the vicinity of the up-dip edge of the confined part of the aquifer.

**Impact Assessment**

Results from the analyses outlined above suggest that increasing upward flux from a basin could cause problems in freshwater aquifers. The impacts of these problems occurring can be evaluated within the framework outlined in Chapter V, where impact categories were established for three different measures of salt transport (Table 3).

Results of the analysis based on the 2D data (Table 3) show that the level of impact varies with magnitude of the increased flux and the depth to the salt transition at
the start of the pulse, $D_L$. Initial conditions of maximum salt concentration in the stream and mass loading rate to the stream are ignored in Table 3 assuming salt in the stream is fully flushed by freshwater recharge. However they are going to be considered in future study. The impact is low when the change in the upward flux is small ($q_b=0.1Re$) and $D_L$ is relatively large ($D_L>300m$). There is significant risk of streams being affected when $D_L$ is shallow, even when the upward flux is small ($q_b=0.1Re$), according to the analyses.

As the upward volumetric flux is increased to equal recharge, the effect on the streams is minor for the deeper values of $D_L$, but there is significant impact of reducing the thickness of the freshwater aquifer. There are significant impacts to both the streams and the aquifer when $D_L$ is relatively shallow (200m) for the intermediate flux case ($q_b=1.0Re$).

Increasing the flux to $q_b=10Re$ causes severe impact to the thickness of the freshwater aquifer and the water quality in the streams, according to the analysis (Table 3).
Table 3 Maximum concentration, and mass loading rate discharging to stream and the fractional change of the thickness of the freshwater layer predicted from 2D analyses at the end of a 50-year-long pulse for various basic fluxes and transition depths. Impact levels from Chapter 5, green=Low impact; Yellow = significant impact; red= severe impact.

<table>
<thead>
<tr>
<th>Basin Flux, $q_b$</th>
<th>Transition Depth $D_t$ (m)</th>
<th>Max Conc. in NaCl (mg/L)</th>
<th>Mass Loading Rate in NaCl (tons/yr km)</th>
<th>Fractional change in freshwater thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1$Re$</td>
<td>200</td>
<td>1300</td>
<td>15</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>180</td>
<td>0.89</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>58</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>1.0$Re$</td>
<td>200</td>
<td>4.4E+03</td>
<td>76</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.1E+02</td>
<td>5.8</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.2E+02</td>
<td>1.4</td>
<td>0.17</td>
</tr>
<tr>
<td>10$Re$</td>
<td>200</td>
<td>1.4E+04</td>
<td>3.7E+03</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.2E+04</td>
<td>2.7E+03</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>5.3E+03</td>
<td>1.0E+03</td>
<td>0.88</td>
</tr>
</tbody>
</table>

The 3D simulation, compared to 2D, has much lower average concentration and mass load to the stream. This occurs because the discharge of salt in 3D is localized to a small interval where the stream crosses the upper contact between the aquifer and confining unit (Figure 51), but in 2D the discharge is assumed to occur uniformly along the stream reach. Under the conditions we used for the 3D example, a minor effect would be expected on the surface stream salt content.

The effect on the aquifer in 3D is also more localized than in 2D. The fresh/salt transition is a sloping zone that only underlies a small fraction of the freshwater aquifer, so much of the freshwater aquifer is unaffected by the basin pulse in the 3D case. This
result shows how the structure of the ground water flow system in a hydrogeologic setting can influence the severity of an increase in flux from a basin.

**Implications to CO₂ Storage**

A motivation for this work was to evaluate how an increase in upward flux resulting from CO₂ storage may affect the shallow freshwater hydrologic system. The results of the analysis show that increasing the upward flux has the potential to significantly affect freshwater aquifers, but the magnitude of this effect depends on the magnitude of the upward flux and the thickness of the freshwater layer. When the upward flux is a fraction of the recharge flux, the effect on the streams and aquifer may be small. For example, the concentration may be less than the MCL, the mass loading less than current TMDLs, and the change in the freshwater thickness within the resolution of monitoring methods.

The current design strategy for CO₂ storage sites is that there should be no interaction with the freshwater system. This is an appropriate design goal and no interaction with the freshwater system would certainly be ideal. However, this work shows that the effects of a small increase in flux (relative to recharge), may have little effect on the freshwater system. However, if allowed to grow, the upward flux could lead to significant contamination problems that persist long after the storage operation and upward flux has ceased. This puts an extra level of importance on developing monitoring methods that can detect increases in upward flux early while there is still an opportunity to take corrective action.
The results of this work show that the severity of impacts depends on details of the hydrogeologic conditions assumed in the analysis. For example, results for the 3D analyses were milder than for the 2D analyses, and the results from analyses that considered density as a function of concentration were significantly different than those assuming uniform density. This underscores the importance of understanding details of the hydrogeology when evaluating impacts that CO₂ storage may impose on shallow freshwater aquifers.
REFERENCES


(2010). Decision Document For the Nune Mile Creek Watershed Chloride TMDL, Hennepin County, Minnesota. M. Hennepin County.


Feth, J. H., and others (1965). Preliminary map of the conterminous United States showing depth to and quality of shallowest ground water containing more than 1,000 parts per million dissolved solids. *Hydrologic Investigations Atlas* U.S. Geological Survey HA-199.


