AEROSOL DELIVERY AS A METHOD FOR ENHANCING REMEDIAL APPLICATION IN CONTAMINATED VADOSE ZONES

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AEROSOL DELIVERY AS A METHOD FOR ENHANCING REMEDIAL APPLICATION IN CONTAMINATED VADOSE ZONES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Environmental Engineering

by
Richard J. Hall
May 2013

Accepted by:
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Dr. Fred J. Molz
Abstract

Remediation of contaminated vadose zones is often hindered by an inability to effectively distribute liquid- or solid-phase amendments. Many amendment-based approaches, such as bioremediation, chemical oxidation, and reactive barriers have been successful in saturated formations. However, these remedial approaches have seen limited application in unsaturated materials, largely because of difficulties delivering amendments.

Aerosol delivery is a promising approach for distributing amendments in contaminated vadose zones. The amendments are aerosolized, creating a cloud of micron to sub-micron-scale liquid droplets held suspended in a gas by Brownian motion. During injection into porous media, the aerosol particles are transported along with the gas until they are deposited on the surfaces of soil grains. The process is continued until appropriate amendment concentrations are achieved, ideally resulting in a radially and vertically broad distribution. Such a distribution could not be achieved by injecting pure liquid-phase solutions.

The objectives of this work were A) to characterize transport and deposition of aerosols in unsaturated porous media, B) to develop capabilities for predicting results of aerosol injection scenarios at the field scale, and C) to evaluate biodegradation of trichloroethene (TCE) under partially saturated conditions when amendments and/or microbes are delivered as aerosols. Aerosol transport and deposition processes were investigated by conducting lab-scale injection experiments. These experiments involved injection of aerosols through sand in columns or in a wedge-shaped apparatus that creates
a radial flow geometry. A particle-size analyzer was used to measure aerosol particle size distributions along gas flow paths through the sand-filled geometries with time, and sand samples were taken following injection for amendment content analysis. Predictive capabilities were obtained by developing a numerical model capable of simulating aerosol transport and deposition in porous media. Stimulation of TCE biodegradation using aerosolized amendments (electron donor, nutrients, and bioaugmentation culture) was investigated by constructing anaerobic microcosms in 160 ml serum bottles. Headspace samples were analyzed for TCE, cis-dichloroethene (cDCE), vinyl chloride (VC), and ethene to determine the rates and extent of biodegradation within each bottle. Multiple sets of microcosms were created to determine differences based on water saturation, electron donor, and amendment delivery method.

According to particle analysis, aqueous aerosols used during experimentation tended to occur over a 0 to 2 micron particle size range, whereas soybean oil and salt water aerosols tended to occur over a 2 to 6 micron range. Results of aerosol injection tests show that aerosol transport and deposition depend on the liquid used. Results from tests involving soybean oil aerosols show that oil saturations greater than 0.5 g oil/kg sand could be achieved throughout the sand-filled laboratory cells. Lab-scale tests conducted with aqueous (fresh water) aerosols show that liquid accumulation only occurs near the point of injection. Tests conducted using 200 g/L salt water (NaCl) confirm that changes in water saturation were small and limited to the vicinity of the injection region. However, aerosol particles were measured, and salt was deposited throughout the lab-
scale apparatuses, even though liquid accumulation was negligible. Apparently, solid particles of salt were created and transported as the water evaporated.

A numerical model was developed based on a fully coupled transient analysis of gas and liquid in a porous medium. Aerosols were assumed to be advected in the gas and deposited as an irreversible sorption process governed by a collector efficiency. Changes in saturation resulting from aerosol deposition altered the relative permeability and mobility of the liquid and gas phases in the fully coupled system. The numerical model was calibrated using results from the laboratory test, and then used to evaluate aerosol injection at the field-scale. Modeling results suggest that gas injection rates and aerosol particle size are the most important factors in determining amendment distribution. Liquid saturations from field-scale simulations suggest that effective radii of influence on the scale of 3-4 meters around a well screen could be achieved in partially saturated sand.

Microcosm results show that anaerobic reductive dechlorination of TCE can occur in unsaturated systems. Significant differences in degradation activity were not observed based on whether amendments in aqueous solution were added directly or as an aerosol. Addition of a chloroethene bioaugmentation as aerosols resulted in complete conversion of TCE to ethene, however, initial reaction rates were typically slower than when culture was added directly. Delivery of culture in an oil-based mixture was tested as an alternative to overcome potential limitations with water aerosol delivery. Direct inoculation of microcosms with the mixture resulted in dechlorination of TCE, however, aerosol delivery of the same mixture resulted in little activity.
The aerosol delivery process appears to be capable of distributing oil amendments over considerable volumes of formation at concentrations appropriate for remediation purposes. Evaporation of water limited liquid accumulation when using aqueous aerosols. However, results from salt water experiments suggest that solid-phase aerosols created during the evaporation process can effectively distribute water soluble amendments (electron donor, pH buffer, oxidants, etc.). Successful implementation at the field-scale will require site-specific optimization of injection parameters and aerosolizers that are specifically designed to produce preferentially small particles. Utilization of aerosol delivery could considerably expand treatment options for contaminated vadose zones at a wide variety of sites.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xv</td>
</tr>
</tbody>
</table>

## CHAPTER

1 INTRODUCTION .................................................................................. 1

1.1 Aerosols ........................................................................................ 3
1.2 Objectives and Approach ............................................................ 7

2 AEROSOLIZERS AND PARTICLE MEASUREMENT ........................................ 10

2.1 Aerosolizer Construction and Operation ......................................... 10
2.2 Particle Analyzer .......................................................................... 14
2.3 Methods .......................................................................................... 18
2.4 Results ............................................................................................ 26
2.5 Discussion ....................................................................................... 51
2.6 Conclusions ..................................................................................... 57

3 COLUMN INJECTION TESTS .................................................................. 59

3.1 Test Methods .................................................................................. 62
3.2 Results ............................................................................................ 72
3.3 Discussion ....................................................................................... 102
3.4 Conclusions .................................................................................... 118
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Wedge Injection Tests</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>4.1 Wedge Apparatus</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>4.2 Aerosol Supply System</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>4.3 Test and Analysis Procedures</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>4.4 Test Methods</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>4.5 Results</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>4.6 Discussion</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>4.7 Conclusions</td>
<td>144</td>
</tr>
<tr>
<td>5</td>
<td>Theoretical Analysis of Aerosol Transport</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>5.1 Methods</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>5.2 Results</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>5.3 Discussion</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>5.4 Conclusions</td>
<td>178</td>
</tr>
<tr>
<td>6</td>
<td>Microcosm Experiments</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>6.1 Methods</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>6.2 Results</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>6.3 Discussion</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>6.4 Conclusions</td>
<td>225</td>
</tr>
<tr>
<td>7</td>
<td>Conclusions</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td>7.1 Conceptual Model</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td>7.2 Controlling Factors</td>
<td>229</td>
</tr>
<tr>
<td></td>
<td>7.3 Solid Aerosols</td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>7.4 Application for Enhanced Bioremediation</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>7.5 Field-Scale Applications</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>237</td>
</tr>
<tr>
<td></td>
<td>Appendix A</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>Appendix B</td>
<td>244</td>
</tr>
<tr>
<td></td>
<td>Appendix C</td>
<td>248</td>
</tr>
<tr>
<td></td>
<td>Appendix D</td>
<td>251</td>
</tr>
<tr>
<td></td>
<td>Appendix E</td>
<td>254</td>
</tr>
<tr>
<td></td>
<td>Appendix F</td>
<td>256</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Pore-scale conceptual model of aerosol particle transport and deposition</td>
<td>2</td>
</tr>
<tr>
<td>1.2 The three mechanisms by which aerosol particles are deposited</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Classes of experiments conducted to achieve research objectives</td>
<td>9</td>
</tr>
<tr>
<td>2.1 3-D and cross-section views of aluminum aerosolizer blocks</td>
<td>12</td>
</tr>
<tr>
<td>2.2 Diagram showing aerosolizer block installation into one side of flange</td>
<td>12</td>
</tr>
<tr>
<td>2.3 Diagram showing aerosol generation system</td>
<td>13</td>
</tr>
<tr>
<td>2.4 Repeat particle analyzer measurements taken using Live and Real settings</td>
<td>16</td>
</tr>
<tr>
<td>2.5 Repeat measurements taken of 3 aerosol clouds to show repeatability</td>
<td>16</td>
</tr>
<tr>
<td>2.6 Diagram showing the testing configuration used during dilution tests</td>
<td>22</td>
</tr>
<tr>
<td>2.7 Particle distributions of polystyrene spheres before and after calibration</td>
<td>27</td>
</tr>
<tr>
<td>2.8 Size distributions of diluted veg. oil aerosols created w/ and w/o impact plate</td>
<td>29</td>
</tr>
<tr>
<td>2.9 Soybean oil size distributions scaled by dilution factor</td>
<td>29</td>
</tr>
<tr>
<td>2.10 Ratio of calculated to measured mass rate as a function of dilution factor</td>
<td>31</td>
</tr>
<tr>
<td>2.11 Results of 3-3 and 3-5 A and B aerosolizer block tests</td>
<td>37</td>
</tr>
<tr>
<td>2.12 Results of 5-5 and 3-7 A and B aerosolizer block tests</td>
<td>38</td>
</tr>
<tr>
<td>2.13 Results of 5-7 and 7-7 A and B aerosolizer block tests</td>
<td>39</td>
</tr>
<tr>
<td>2.14 Number vs. size of particles from 3-3 block based on operating conditions</td>
<td>42</td>
</tr>
<tr>
<td>2.15 Number vs. size of particles from 3-5 block based on operating conditions</td>
<td>43</td>
</tr>
<tr>
<td>2.16 Number vs. size of particles from 3-7 block based on operating conditions</td>
<td>44</td>
</tr>
<tr>
<td>2.17 Particle samples from 3-3, 3-5, and 5-5 blocks based on operating conditions</td>
<td>47</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.18</td>
<td>48</td>
</tr>
<tr>
<td>2.19</td>
<td>49</td>
</tr>
<tr>
<td>3.1</td>
<td>61</td>
</tr>
<tr>
<td>3.2</td>
<td>66</td>
</tr>
<tr>
<td>3.3</td>
<td>68</td>
</tr>
<tr>
<td>3.4</td>
<td>69</td>
</tr>
<tr>
<td>3.5</td>
<td>73</td>
</tr>
<tr>
<td>3.6</td>
<td>74</td>
</tr>
<tr>
<td>3.7</td>
<td>75</td>
</tr>
<tr>
<td>3.8</td>
<td>78</td>
</tr>
<tr>
<td>3.9</td>
<td>79</td>
</tr>
<tr>
<td>3.10</td>
<td>80</td>
</tr>
<tr>
<td>3.11</td>
<td>81</td>
</tr>
<tr>
<td>3.12</td>
<td>83</td>
</tr>
<tr>
<td>3.13</td>
<td>85</td>
</tr>
<tr>
<td>3.14</td>
<td>85</td>
</tr>
<tr>
<td>3.15</td>
<td>86</td>
</tr>
<tr>
<td>3.16</td>
<td>87</td>
</tr>
<tr>
<td>3.17</td>
<td>90</td>
</tr>
<tr>
<td>3.18</td>
<td>91</td>
</tr>
<tr>
<td>3.19</td>
<td>91</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.20 Liquid content as a function of column distance during Extreme case tests</td>
<td>93</td>
</tr>
<tr>
<td>3.21 Particle distributions along column from water and salt water aerosol tests</td>
<td>94</td>
</tr>
<tr>
<td>3.22 Liquid and salt mass along column after 2 hour salt water aerosol injection</td>
<td>96</td>
</tr>
<tr>
<td>3.23 Liquid mass along initially wet column after salt water aerosol injection</td>
<td>96</td>
</tr>
<tr>
<td>3.24 Salt mass along initially wet column after salt water aerosol injection</td>
<td>98</td>
</tr>
<tr>
<td>3.25 Equivalent liquid content of salt mass measured for salt water injection tests</td>
<td>98</td>
</tr>
<tr>
<td>3.26 Oil content measured following veg. oil injection for Fine and Medium sand</td>
<td>101</td>
</tr>
<tr>
<td>3.27 Aerosol test data and assumed processes responsible particle count decreases</td>
<td>112</td>
</tr>
<tr>
<td>3.28 TCE mass dechlorinated to ethene based on soybean oil content</td>
<td>117</td>
</tr>
<tr>
<td>4.1 Wedge test apparatus with the lid and aerosol delivery system in place</td>
<td>124</td>
</tr>
<tr>
<td>4.2 Apparatus filled with sand without the lid installed</td>
<td>125</td>
</tr>
<tr>
<td>4.3 Gasket at the apex of the wedge apparatus for delivery system attachment</td>
<td>126</td>
</tr>
<tr>
<td>4.4 Exhaust compartment of the wedge apparatus with the lid in place</td>
<td>127</td>
</tr>
<tr>
<td>4.5 Design of single and double aerosolizer blocks</td>
<td>128</td>
</tr>
<tr>
<td>4.6 Grain size distributions for the Coarse and Fine sand used during wedge tests</td>
<td>129</td>
</tr>
<tr>
<td>4.7 Locations of sand sampling points for liquid content analyses</td>
<td>131</td>
</tr>
<tr>
<td>4.8 Oil content in wedge following Injection Duration Tests with Coarse sand</td>
<td>134</td>
</tr>
<tr>
<td>4.9 Oil content in wedge following Injection Duration Tests with Fine sand</td>
<td>135</td>
</tr>
<tr>
<td>4.10 Oil saturation as a function of radial distance from Injection Duration Tests</td>
<td>136</td>
</tr>
<tr>
<td>4.11 Oil saturation as a function of radial distance from Injection Intensity Tests</td>
<td>138</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4.12</td>
<td>Oil content in wedge following Injection Intensity Tests with Coarse sand</td>
</tr>
<tr>
<td>4.13</td>
<td>Oil content in wedge following Injection Intensity Tests with Fine sand</td>
</tr>
<tr>
<td>5.1</td>
<td>Mesh used for field-scale simulations</td>
</tr>
<tr>
<td>5.2</td>
<td>Steady-state water saturation distributions from Comsol and T2VOC.</td>
</tr>
<tr>
<td>5.3</td>
<td>Pressure distributions from Comsol and T2VOC gas injection simulations.</td>
</tr>
<tr>
<td>5.4</td>
<td>Water distributions from Comsol and T2VOC column-filling simulations.</td>
</tr>
<tr>
<td>5.5</td>
<td>Water distributions from Comsol and T2VOC multiphase flow simulations.</td>
</tr>
<tr>
<td>5.6</td>
<td>Assumed particle size characterization for wedge simulations.</td>
</tr>
<tr>
<td>5.7</td>
<td>Oil distribution fits from duration wedge tests and calibrated model.</td>
</tr>
<tr>
<td>5.8</td>
<td>Oil distributions along centerline from long duration wedge simulations.</td>
</tr>
<tr>
<td>5.9</td>
<td>Oil distributions along cross-sections from Long-Duration simulations.</td>
</tr>
<tr>
<td>5.10</td>
<td>Oil saturation distributions from coarse sand injection intensity simulations.</td>
</tr>
<tr>
<td>5.11</td>
<td>Sorption coefficients with radial distance for Injection Intensity simulations.</td>
</tr>
<tr>
<td>5.12</td>
<td>Oil saturations resulting from one month aerosol injection simulations.</td>
</tr>
<tr>
<td>5.13</td>
<td>Oil saturations along centerline for field-scale, 1-month injection simulations.</td>
</tr>
<tr>
<td>6.1</td>
<td>Serum bottle microcosm containers</td>
</tr>
<tr>
<td>6.2</td>
<td>Bottom of ultrasonic aerosolization chamber</td>
</tr>
<tr>
<td>6.3</td>
<td>Diagram of aerosol generation and delivery system</td>
</tr>
<tr>
<td>6.4</td>
<td>System used to deliver liquids to microcosms and collect liquid inoculate</td>
</tr>
<tr>
<td>6.5</td>
<td>Various containers used for aerosol delivery microcosms</td>
</tr>
<tr>
<td>6.6</td>
<td>Mass content results from Serum Bottle Loss Test</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>Chlorinated compound concentrations from No Donor microcosms</td>
<td>201</td>
</tr>
<tr>
<td>6.8</td>
<td>Chlorinated compound concentrations from Hydrogen Inclusion Tests</td>
<td>203</td>
</tr>
<tr>
<td>6.9</td>
<td>Chlorinated compound concentrations from Donor/Saturation Tests</td>
<td>205</td>
</tr>
<tr>
<td>6.10</td>
<td>Chlorinated compound concentrations from Lactate Tests</td>
<td>207</td>
</tr>
<tr>
<td>6.11</td>
<td>Chlorinated compound concentrations from Veg. Oil Survivability Tests</td>
<td>209</td>
</tr>
<tr>
<td>6.12</td>
<td>Chlorinated compound concentrations from Aerosolization Survivability Tests</td>
<td>211</td>
</tr>
<tr>
<td>6.13</td>
<td>Typical results PVC and Metal aerosol delivery containers</td>
<td>212</td>
</tr>
<tr>
<td>6.14</td>
<td>Chlorinated compound concentrations from Aerosol Delivery Tests</td>
<td>214</td>
</tr>
</tbody>
</table>
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Gas flow rates based on velocities and gas orifice diameter</td>
</tr>
<tr>
<td>2.2</td>
<td>Aerosol mass rates measured experimentally and calculated from particle data</td>
</tr>
<tr>
<td>2.3</td>
<td>Calculated and measured mass flow rates from dilution tests</td>
</tr>
<tr>
<td>2.4</td>
<td>Gas pressure required to generate gas flow rates for A &amp; B aerosolizer blocks</td>
</tr>
<tr>
<td>2.5</td>
<td>Aerosol liquid water volume integrations from humidifier stack tests</td>
</tr>
<tr>
<td>2.6</td>
<td>Peal particle sizes measured during soybean oil experiments</td>
</tr>
<tr>
<td>3.1</td>
<td>Grain sizes used to define sands used during column experiments</td>
</tr>
<tr>
<td>3.2</td>
<td>Salt aerosolized and deposition during Liquid/Salt Content tests</td>
</tr>
<tr>
<td>5.1</td>
<td>Porous material properties used for wedge simulations</td>
</tr>
<tr>
<td>5.2</td>
<td>Fluid properties used for wedge simulations</td>
</tr>
<tr>
<td>6.1</td>
<td>Volumes of liquid components used to construct non-aerosol microcosms</td>
</tr>
<tr>
<td>6.2</td>
<td>Volumes of liquid components used to construct aerosol microcosms</td>
</tr>
</tbody>
</table>
**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROI</td>
<td>Radius of Influence</td>
</tr>
<tr>
<td>cDCE</td>
<td>cis-1,2-Dichloroethene</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>MNA</td>
<td>Monitored natural attenuation</td>
</tr>
<tr>
<td>NAPL</td>
<td>Non-aqueous phase liquid</td>
</tr>
<tr>
<td>PCE</td>
<td>Tetrachloroethene</td>
</tr>
<tr>
<td>SRS</td>
<td>Savannah River Site</td>
</tr>
<tr>
<td>TCE</td>
<td>Trichloroethene</td>
</tr>
<tr>
<td>TEA</td>
<td>Terminal electron acceptor</td>
</tr>
<tr>
<td>VC</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>SVE</td>
<td>Soil Vapor Extraction</td>
</tr>
<tr>
<td>M</td>
<td>Meter(s)</td>
</tr>
<tr>
<td>Cm</td>
<td>Centimeter(s)</td>
</tr>
<tr>
<td>Mm</td>
<td>Micrometer(s)</td>
</tr>
<tr>
<td>Pa</td>
<td>Kilopascal(s)</td>
</tr>
<tr>
<td>Kg</td>
<td>Kilogram(s)</td>
</tr>
<tr>
<td>L</td>
<td>Liter(s)</td>
</tr>
<tr>
<td>Scms</td>
<td>Standard cubic meters per second</td>
</tr>
</tbody>
</table>
List of Symbols

- $t$ .......................................................... Time (s)
- $\phi$ .......................................................... Porosity
- $\phi_e$ ......................................................... Effective porosity
- $h$ ............................................................ Head (m)
- $S$ ............................................................. Storage term ($m^1$)
- $S_\beta$ ......................................................... Saturation of phase $\beta$
- $\rho_\beta$ ....................................................... Density of phase $\beta$ ($Kg/m^3$)
- $\rho_p$ ......................................................... Particle density ($Kg/m^3$)
- $v_g$ ........................................................... Gas velocity (m/s)
- $\beta$ .......................................................... Denotes phase (g-gas, w-water, n-NAPL)
- $q$ ............................................................. Source, sink term ($Kg/(s \ m^3)$)
- $C$ ............................................................. Aerosol concentration (particles/m$^3$)
- $D$ ............................................................. Diffusion coefficient ($m^2/s$)
- $d_g$ ........................................................... Grain diameter (m)
- $d_p$ ........................................................... Particle diameter (m)
- $n$ ............................................................. Fitting parameter
- $S_m$ .......................................................... Minimum water saturation
- $K$ ............................................................. Intrinsic permeability ($m^2$)
- $k_{\beta}$ ....................................................... Relative permeability of phase $\beta$
- $k_s$ .......................................................... Sorption coefficient ($m^{-1}$)
- $P_{c\beta\beta}$ .................................................. Capillary pressure between phases (Pa)
- $G$ ............................................................. Acceleration due to gravity ($m/s^2$)
- $\Psi_{\beta\beta}$ ................................................ Fitting parameter for capillary pressure
- $\eta_{tot}$ ...................................................... Total collector efficiency
- $\eta_{k,s,d}$ ................................................ Collector efficiencies
- $\alpha$ ........................................................ Collision efficiency
- $N_{Pe}$ ....................................................... Peclet Number
- $\mu_\beta$ ..................................................... Viscosity of phase $\beta$ (Pa⋅s)
- $B$ ............................................................ Boltzmann’s constant ($1.38x10^{-23} J\cdot K^{-1}$)
- $P_\beta$ ....................................................... Pressure of phase $\beta$ (Pa)
- $T$ ............................................................. Absolute temperature (K)
Chapter 1-Introduction

There are many contaminant remediation methods available for addressing saturated zones, and most require the delivery of some type of amendment. Some example methods include biostimulation, in situ oxidation or reduction, solubilization, and sequestration (Glaze and Kang, 1988; Fountain et al., 1991; Hopkins et al., 1993; Cantrell et al., 1995). Distributing amendments in the saturated zone is typically accomplished by injecting them as aqueous solutions, which follow groundwater flowpaths (Lendvay et al., 2003). This technique is capable of distributing amendments through the saturated zone, which is sufficient to effectively remediate some subsurface scenarios. In some cases an amendment solution is injected and then flushed away from the well to disperse in the formation (Borden, 2007). Amendments have been added as pure phase NAPL (Hunter, 2001), dissolved in water (Lendvay et al., 2003), or as an emulsion in water (Newman and Pelle, 2006; Borden, 2007).

Despite the success of some applications, delivery of remedial amendments remains a challenge. Low permeability materials or heterogeneities with strong contrasts in permeability either limit mass rates of delivery or cause remedial amendments to avoid contaminants that have diffused into low permeability regions (Murdoch et al., 1994; Abriola et al., 1995). These processes cause difficulties in the saturated zone, but problems with amendment delivery are much worse in the vadose zone. Liquid injections in the vadose zone are dominated by multi-phase flow effects that cause amendments to be localized, and to flow preferentially downward instead of spreading laterally between
injection points. The result is that remediation methods that require amendment delivery currently have limited application to the vadose zone.

Delivering amendments as aerosols could be a method for overcoming distribution limitations in vadose zones. The conceptual model for a field application involves injecting aerosol-laden gas into the vadose zone where the particles are transported and deposited on the walls of pore spaces (Figure 1.1). The flow paths of the particles would follow the flow paths of gas from a well, which are radially outward and upward in the vadose zone (Falta et al., 1992; Bradner and Murdoch, 2005). Thus it appears that this process could distribute amendments further laterally than injection as a liquid phase, but this approach has received scant attention in the literature, so the details remain unclear.

Figure 1.1 - Pore-scale conceptual model of aerosol particle transport and deposition in porous media.
The aerosol deposition process will cause changes in phase saturations, which could affect gas-phase relative permeability, effective porosity, and the subsequent deposition rate (Yao et al., 1971). This will cause coupling between the gas flow and aerosol transport processes, which makes resulting amendment distributions difficult to anticipate without experiments and theoretical analysis. It is also not clear how the effectiveness of amendments delivered as aerosols compares to that of amendments delivered as neat liquids. Delivery of electron donor, nutrients, buffers, and microbes for the purpose of enhancing biological reductive dechlorination appear to be feasible, but their effectiveness remains unknown.

1.1 Aerosols

Aerosols are suspensions of micron to sub-micron-scale liquid droplets or solid particles in gas. Aerosol droplets are retained in suspension by Brownian motion, which decreases the settling effect of gravity (Tien and Payatakes, 1979). Naturally occurring aerosols exist as smoke, dust, fog, and sea-spray, which play important roles in meteorological processes (Henningson and Ahlberg, 1994; Satheesh and Moorothy, 2005; Rotstayn et al., 2009). Aerosols are also produced by man and used extensively in medical, industrial, and consumer product applications (Burkholz, 1982; Hickey, 2003; Kleinstreuer et al., 2008). The three most commonly used methods for producing aerosols are: 1) Jet aerosolization, which involves injecting fluids into a high velocity gas stream; 2) ultrasonic aerosolization, which utilizes a plate vibrating at high frequencies; and 3) misting nozzles, through which fluids are passed at high velocities (McCallion et al., 1995; Steckel and Eskandar, 2003).
1.1.1 Aerosol Generation

Devices designed for producing liquid aerosols are called aerosolizers, nebulizers, and/or atomizers. Jet aerosolizers introduce a fluid into a high velocity gas jet. The fluid is dispersed into small droplets due to the turbulence within the jet and/or upon impact with a solid surface (Wright, 1958). Ultrasonic aerosolization uses a piezoelectric crystal that vibrates when subjected to an alternating electric field (Dennis and Hendrick, 1992). The piezoelectric crystal is attached to a plate at the bottom of a liquid reservoir, which in turn oscillates at high frequency. Energy is transmitted to the surface of the liquid where capillary waves are formed. Aerosol droplets are formed at the crests of the capillary waves (Dennis and Hendrick, 1992).

Jet aerosolization requires a relatively large gas to liquid ratio; therefore, evaporative losses are to be expected (Dennis et al., 1990). Evaporative tendencies affect the resulting aerosol particle size distribution. Aerosol particle size distributions are also affected by aerosolizer properties and operating parameters. For example, according to Mercer (1981) the average aerosol particle diameter produced by a jet aerosolizer is

\[
D = D_L 0.64 \left[ 1 + 0.011 \left( \frac{G_L}{G_g} \right)^2 \right] \times \left( \frac{2\gamma}{9\rho_g v_g^2 D_L} \right)^{0.45}
\] (1-1)

where \(D_L\) is liquid inlet orifice, \(G_L\) is the mass flow rate of liquid, \(G_g\) is the mass flow rate of gas, \(\gamma\) is the surface tension of the liquid, \(\rho_g\) is gas density, and \(v_g\) is gas velocity.

One consequence of creating a high velocity gas jet is that the expansion of the jet cools the gas and condenses the water vapor in the gas. The condensate may itself make aerosols, but the carrier gas becomes drier and this may increase the evaporation rate of
the aerosols. As a result, the dynamics controlling aerosol size can be affected by competing processes of condensation and evaporation.

By contrast, ultrasonic techniques create aerosols mechanically, so the complicated jet dynamics are avoided. A carrier gas is typically used to remove the aerosols, but the characteristics of this gas can be controlled to avoid evaporation of aerosols. Evaporative losses are significantly less or non-existent when using ultrasonic aerosolizers (Dennis et al., 1990). Aerosol particle size distributions produced during ultrasonic aerosolization are a function of the wavelength of surface capillary waves, which decreases as the frequency of ultrasonic vibrations increase (Mercer et al., 1968).

1.1.2 Aerosol Transport

Aerosol transport through porous media has been studied in the context of understanding filtration of particles from gas (Gutfinger and Tardos, 1979; Lee and Gieseke, 1980; Tien and Payatakes, 1979; Dietz, 1981; Chang and Chan, 2008). The conceptual model is that aerosols are advected and dispersed in a flowing gas (Tien and Payatakes, 1979). Aerosols are deposited on pore walls in a process similar to irreversible sorption. The deposition of an individual particle occurs when the transport processes causes it to collide with a solid surface within a porous medium.

There are at least six recognized processes that can lead to aerosol particle deposition on solid surfaces, and several of them typically occur simultaneously to account for total deposition rates. These processes include 1) Interception, 2) Gravity Settling, 3) Brownian Diffusion, 4) Inertial Impaction, 5) Electrostatic Forces, and 6) Straining (Tien and Ramarao, 2007). Mechanisms 1, 2, and 3 can account for the majority
of particle deposition under typical flow conditions, and therefore are commonly used to represent deposition when analyzing filtration systems (Yao et al., 1971).

Particle filtration processes have primarily focused on quantification of individual deposition mechanisms such as interception (Yao et al., 1971; Rajagopalatan and Tien, 1976; Lee and Gieseke, 1979; Gutfinger and Tardos, 1979; Tardos et al., 1979; Dietz, 1981), gravity settling (Yao et al., 1971; Rajagopalatan and Tien, 1976; Tardos et al., 1979; Lee, 1981), and Brownian diffusion (Yao et al., 1971; Lee and Gieseke, 1979; Tardos et al., 1978; Lee, 1981) (Figure 1.2).

---

**Figure 1.2** - The three mechanisms by which aerosol particles are deposited in granular materials: A- Interception, B- Gravitational Force, and C- Diffusion.

During transport analyses the effect of each depositional mechanism is characterized by a collection efficiency ($\eta$), which is a factor defining the ratio of suspended particles that will contact a collector surface (Tien and Ramarao, 2007). Collection efficiencies are functions of gas flow velocity ($v_g$), aerosol particle diameter
(\(d_p\)), and formation grain diameter (\(d_p\)) and other factors. For example, the method originally proposed by Yao et al., (1971) gives collection efficiencies as:

\[
\eta_D = 4.04A_s^{\frac{1}{3}} \left( v_g \phi_e \frac{d_p}{D} \right)^{\frac{2}{3}}
\]

(1-2)

\[
\eta_I = \frac{3}{2} A_s \left( \frac{d_p}{d_g} \right)^2
\]

(1-3)

\[
\eta_G = \frac{\rho_p - \rho_g}{18 \mu_g v_g} g d_p^2
\]

(1-4)

where, \(A_s = \frac{2(1-\gamma^5)}{2 - 3\gamma + 3\gamma^5 - 2\gamma^6}\) and \(\gamma = (1 - \phi_e)^{\frac{1}{5}}\)

\[
\eta_{tot} = \eta_D + \eta_I + \eta_G
\]

(1-5)

where \(\eta_D, \eta_I, \text{ and } \eta_G\) are the diffusion, interception, and gravitational settling collection efficiencies respectively, \(\phi_e\) is effective porosity, \(D\) is particle diffusion coefficient, \(\rho_p\) is particle density, \(\rho_g\) is grain density, \(\mu_g\) is gas viscosity, and \(g\) is gravity. Summation of individual collection efficiencies provides a total collection efficiency that can be used to represent overall aerosol depositional behaviors (\(\eta_{tot}\)) for a system (Equation 1-5).

1.2 Objectives and Approach

The overlying objective of this research is to evaluate the feasibility of using aerosol delivery technology to enhance or enable remediation approaches in vadose zones. Secondary objectives are to characterize processes of aerosol transport and deposition in unsaturated materials, and to evaluate the effects of selected aerosols on bioremediation reactions in the vadose zone.
The objectives of this study were achieved by conducting three interrelated investigations: 1) Bench-scale aerosol injection experiments; 2) Theoretical transport and deposition analysis; and 3) Aerosol delivery microcosm experiments (Figure 1.3). The methods, results, and findings of this work are presented in the following chapters:

**Chapter 2-** Injection experiments involved the use of custom built aerosolizers for generating aerosols and a particle analyzer for measuring particle size distributions. This chapter presents results of experiments designed to characterize the effect of aerosolizer design, operating parameters, and aerosolized liquid on resulting aerosol particle size distributions. The operation, repeatability, and accuracy of the particle analyzer are also discussed.

**Chapter 3-** Experiments were designed to characterize transport and deposition behaviors of aerosols during linear transport through porous media. Experiments involved injection of aerosols through 2.5-cm and 1.5-m, sand-filled columns. Aerosol particle size distributions along the columns were measured during injection and liquid contents along the columns were measured following injection.

**Chapter 4-** Experiments were designed to characterize transport and deposition behaviors of aerosols during radial transport through porous media. Experiments involved injection of aerosols through a 2-m-radius, 36°, 7.6-cm-thick, sand-filled wedge. Aerosol particle size distributions along the wedge were measured during injection and liquid contents along the wedge were measured following injection.

**Chapter 5-** A numerical model was constructed that is capable of simulating transport and deposition of aerosol particles in porous media with two mobile phases (gas
and aerosolized liquid). The model was calibrated by reproducing results observed during wedge injection experiments. The calibrated model was used to make predictions about liquid distributions that could be achieved during field-scale injection through a conventional well.

Chapter 6- Microcosm experiments were designed to characterize degradation of TCE that can be induced when delivering nutrients, electron donor, and/or microbes as aerosols. Electron donors investigated included hydrogen, lactate, and soybean oil, and microbe delivery as aerosols was attempted using water and soybean oil bases. TCE degradation activity was monitored by analyzing gas headspace samples on a gas chromatograph (GC).

<table>
<thead>
<tr>
<th>Bench-Scale Injection Tests</th>
<th>Modeling</th>
<th>Microcosms</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Bench-Scale Injection Tests Image" /></td>
<td><img src="image2.png" alt="Modeling Image" /></td>
<td><img src="image3.png" alt="Microcosms Image" /></td>
</tr>
</tbody>
</table>

**Figure 1.3-** Major classes of experiments conducted to achieve objectives of this research project.
Chapter 2-Aerosolizers and Particle Analysis

Bench-scale aerosol injection and microcosm experiments (Chapters 3-6) required generation of aerosols using aerosolizers. Preliminary tests were carried out to determine the effectiveness of commercially available jet, ultrasonic, and misting nozzle aerosolizers with water or soybean oil. Jet aerosolization successfully produced water and soybean oil aerosols, ultrasonic aerosolization produced water aerosols but had no effect on soybean oil, and misting nozzles produced relatively large droplet sprays with water and solid liquid streams when using soybean oil. Jet aerosolization was pursued as the aerosol production method for injection tests because it gave the most promising results during the preliminary tests.

Investigations involved making comparisons between aerosols created using different aerosolizers, as well as characterizing aerosol transport behavior through porous media. Accomplishing these goals required the ability to measure aerosol particle count and size distributions in gas samples. A Climet Model CI-226 particle analyzer was used for all particle size distribution analyzes.

2.1 Aerosolizer Construction and Operation

Jet aerosolizers were created by drilling two holes in rectangular plates or blocks of aluminum approximately 2-in. x 2-in. x 0.5 in. A small, through going hole along the long axis of the rectangular block was intersected by a transverse hole (Fig. 2.1). Gas was injected into the axial hole, and it will be called the “gas orifice,” whereas liquid was injected into the transverse hole, which will be called the “liquid orifice” (Figure 2.1).
Aerosolizer blocks were fabricated using several different sizes and shapes of holes in order to evaluate characteristics that created aerosols with useful transport characteristics. The aerosolizer blocks are described using a two number designation (Example: 3-3). The first number refers to the liquid orifice diameter in hundredths of an inch and the second number refers to the gas orifice diameter in hundredths of an inch. Six different variations of orifice diameter combinations were constructed: 3-3, 3-5, 5-5, 3-7, 5-7, and 7-7. Two examples of each variation were constructed for repeatability testing. The duplicates of each type are designated A and B (Example: 3-3A and 3-3B).

The aerosolizer blocks were shaped like a square plate with the gas orifice at the center of the block. A liquid orifice of diameter 0.03, 0.05, or 0.07 inches was drilled from a side of the block such that it was perpendicular to, intersected, and terminated at the gas orifice (Figure 2.1). The liquid orifice hole was tapped with 10-32 threads so that tubing from a peristaltic pump could be attached. A 1/8-in-deep, cone-shaped hole (bevel) was created on the outlet end of each gas orifice to act as an expansion cone on a venturi (Figure 2.1).

During operation, the aerosolizer block is sandwiched between ¾-inch NPT steel flange fittings. Square slots matching the dimensions of the aerosolizer blocks were milled into the centers of the flanges around the inlet/outlet holes (Figure 2.2). Rubber gaskets are inserted into the slots with the aerosolizer block between them and the flanges are then bolted together. A quick-connect fitting for attaching the gas supply is installed on outside of the inlet flange. A 2-inch-PVC slip fitting is attached to the outside of the outlet flange. Two variations of the slip fitting are used. One variation is open and the
Figure 2.1- 3-D and cross-section views of aluminum aerosolizer blocks.

Figure 2.2- Diagram showing aerosolizer block installation into one side of flange.
other variation holds an impact plate that is located 2 inches from the aerosolizer outlet. The slip fitting allows the flange assembly to be connected to 2-inch PVC pipe (Figure 2.3).

A compressed gas source is used to feed the aerosolizer during operation. The gas flow rate is controlled with a pressure regulator and monitored with a variable area flow meter (Figure 2.3). A peristaltic pump is used to control the rate of liquid flow to the aerosolizer. Aerosols are created as the gas shears the liquid flowing from the liquid orifice. The aerosols flow through the slip fitting and into a 2-ft-long section of 2-inch-PVC that is mounted at a 45 degree angle (Figure 2.3). The 2-ft-long section of PVC pipe intersects a vertically oriented section of 2-inch-PVC pipe that is 1-ft-long above and below the point of intersection. Liquid that is not transported as aerosols accumulates in the lower portion, which serves as a liquid overflow reservoir (Figure 2.3). A valve is

![Diagram showing aerosol generation system.](image)

**Figure 2.3-** Diagram showing aerosol generation system.
installed at the base of the reservoir to allow drainage of liquid during and/or following testing. The aerosols flow upward from the point of intersection and exhaust out of the upper section. The upper section terminates at a threaded fitting that allows attachment of sand filled columns, microcosms, etc. (Figure 2.3).

**2.2 Particle Analyzer**

A Climet Model CI-226 particle analyzer was used for all particle size distribution analyzes. The device uses a vacuum to obtain the gas sample, which enters through a port and flows into a chamber were it passes through a beam of light. Particles entrained in the gas refract light, which is detected by a photomultiplier tube. The photomultiplier tube converts the detected light into electrical signals, with the amplitude of the signals being proportional to particle size. The electrical signals are compiled using a multichannel data acquisition system, and these data are analyzed with software built into the device. The resulting data set consists of the number of particles counted for 256 particle size intervals during the sampling duration.

**2.2.1 Particle Measurement Procedure**

The particle analyzer was set to obtain gas samples at a rate of 5 standard cubic feet per hour (scfh). Sample durations were always set to 10 seconds. However, the actual duration of each measurement interval depended on which of two multichannel analyzer settings were used, “Live” or “Real”. According to the manual describing the functioning of the device, the multichannel analyzer is only capable of measuring voltage pulses at a certain rate. If this rate is exceeded then signal analysis is discontinued while
data is uploaded. When using the “Live” setting the analyzer will continue to sample until 10 seconds of active collection has been achieved. Under these circumstances the actual test interval will be greater than 10 seconds because the analyzer is inactive during some of the time. When using the “Real” setting the test duration lasts for 10 seconds, however, the actual time during which samples are analyzed is less than 10 seconds. In this case the duration over which the system was active is provided and can be used to scale the data.

Both settings were used during testing for this research. The Live setting was typically used when the process was essentially steady, so the time interval between sample measurements was unimportant. The Real setting was used when characterizing a transient behavior. Samples needed to be taken at predetermined time intervals under these conditions; therefore, each sampling event had to be restricted to 10 actual seconds. Samples of the same aerosol clouds were taken using both settings for three different aerosolizer configurations to confirm consistency between the two measurement methods. Results show good agreement between Live setting and scaled Real setting data sets (Figure 2.4).

Investigations into transient behaviors required rapid measurements, so data sets from transient tests are typically representative of one particle distribution measurement. Multiple subsequent measurements (typically 3) would be taken when measuring aerosols under steady state conditions. In these instances the data set presented represents the average of measurements taken. These repeat measurements were taken while all aerosolizer operating conditions such as aerosolizer block, gas pressure, and liquid feed rate are held constant.
Figure 2.4- Results of particle analyzer tests using five aerosolizer configurations (Case 1-5). Solid lines are converted Real setting data and dashed lines are Live setting data.

Figure 2.5- Sets of three repeat particle size distribution measurements taken during 3 cases where all aerosolization parameters were held constant.
Particle size distributions obtained under constant aerosolizer operating conditions were repeatable (Figure 2.5). Sample repeatability was reliable unless the device had been sampling for a long period of time from a dense aerosol cloud. The inlet port of the particle counter narrows down to approximately 1 mm before entering the detection chamber. Aerosol particle deposition within the inlet could cause liquid to accumulate and cause intermittent clogging. This was avoided by cleaning the inlet valve often during testing.

2.2.2 Uncertainty in Particle Analyzer Data

Liquid mass aerosolization rate estimates made based on particle count and size distributions differed from physically measured rates. Another apparent discrepancy was discovered when sampling aerosols that had been injected through sand. The “filtered” aerosols exhausting from the sand produced particle size distribution measurements that suggested the presence of particles in numbers and sizes that differed from those measured in unfiltered samples.

The data sets obtained from individual sampling events are composed of numbers of particles counted within 256 size categories. Summing the total number of particles counted during preliminary sampling events revealed that 700k particles was an upper limit, with nearly all data set totals ranging from 600-700k. This indicated that some aspect of the particle analyzer and/or multichannel analyzer was limiting the number of particles that could be detected to 700k over a ten second period. A limit to the number of particles that could be counted would prevent accurate aerosolization rate estimation if the number of particles per gas volume exceeded that value. Aerosolization rates are
consistently underestimated and the number of particles are at maximum values, which indicates that the particle concentrations in sampled aerosol clouds may exceed the systems capabilities.

2.3 Methods

Experiments are divided into two broad categories. One category includes tests pertaining to characterization of the particle analyzer itself, whereas the other includes tests pertaining to characterization of aerosols produced as functions of aerosolizer block design and operating parameters.

Aerosolizer operation during all experiments involved liquid and gas supplied at predetermined rates. A peristaltic pump was used to deliver liquid to the aerosolizer blocks. The liquid flow rate (LFR) is provided in units of ml/min for all test descriptions and data presentations. A pressure regulator and variable-area flow meter were used to control and measure gas flow rate during all tests. The gas flow rate (GFR) is described as “Low” or “High” (a few cases involve a “higher” GFR). The gas flow rates were selected to produce desired gas velocities through the aerosolizer blocks based on gas orifice diameter (Table 2.1). Gas velocity through aerosolizer blocks was selected as the setting standard because it controls average aerosol particle size according to Equation 1-1. Using consistent gas velocity settings allowed effects of other aerosolizer design parameters to be characterized. The flow rates were selected to provide gas velocities as follows: “Low” flow rate = velocity of 250 m/s; “High” = 300 m/s, and “Higher” = 350 m/s (Table 2.1).
Air used to create aerosols was bubbled through two, 10-ft-long columns of water to raise the humidity before it was injected into the aerosolizers. This caused the relative humidity to be essentially 100 percent at the pressure and temperature conditions upstream from the aerosolizers during all tests designed to create water aerosols. The water-filled columns will be termed “humidification stacks.”

<table>
<thead>
<tr>
<th>Gas Orifice Diam. (inch)</th>
<th>Gas Orifice Diam. (m)</th>
<th>X-Sectional Area (m²)</th>
<th>GFR Description</th>
<th>Flow Rate (scms)</th>
<th>Vel (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>For Blocks</td>
<td>0.031</td>
<td>0.00079</td>
<td>4.867E-07</td>
<td>Low</td>
<td>0.00012</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High</td>
<td>0.00015</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Higher</td>
<td>0.00017</td>
</tr>
<tr>
<td>For Blocks</td>
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<td>0.00132</td>
<td>1.3694E-06</td>
<td>Low</td>
<td>0.00034</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High</td>
<td>0.00041</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Higher</td>
<td>0.00048</td>
</tr>
<tr>
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<td>0.07</td>
<td>0.00178</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>High</td>
<td>0.00074</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Higher</td>
<td>0.00086</td>
</tr>
</tbody>
</table>

Table 2.1- Gas flow rates based on velocities and gas orifice diameter.

2.3.1 Particle Analyzer Tests

The particle analyzer was calibrated for particle size. Aerosolization Rate Tests were conducted to quantify errors in aerosolization rate estimates made based on particle distribution measurements. Dilution Tests were designed to investigate whether high aerosol particle concentrations could be the cause of apparent inaccuracy in particle count data obtained using the particle analyzer.
2.3.1.1 Particle Analyzer Calibration

The particle counter was calibrated for particle size using 1, 3.65, and 5 μm polystyrene microspheres obtained in powder form from microspheres-nanosperes.com (Corpuscular Inc.). The microspheres were aspirated into a 100 ml syringe and injected into tubing connected to the particle analyzer inlet port. Each microsphere particle size was sampled three times and averaged to obtain a calibration factor.

2.3.1.2 Aerosolization Rate Tests

Aerosolization Rate Tests were designed to characterize liquid aerosolization rate estimates using particle size and particle count values obtained using the particle counter. Rate estimates were determined by calculating the volume of particles within each individual size range, and then integrating over the entire particle size range to obtain the volume of liquid sampled during the 10 second sampling event. The sample rate used by the particle analyzer (5 scfh) is less than the volumetric gas flow rate used to produce the aerosols; therefore, the volume of liquid sampled is up-scaled by this ratio to obtain liquid aerosolization rate estimates in ml/hr.

Actual liquid aerosolization rates were obtained by direct measurement. Measurement involved creating aerosols for one hour while holding all operating parameters constant. The liquid volume delivered to the aerosolizer was monitored, and the volume of liquid in the overflow reservoir was measured after the test was complete. The difference was assumed to represent the volume of liquid that was aerosolized and exhausted from the system.
Calculated and measured aerosolization rates were obtained for tests using three different aerosolizers (3-3, 3-5, 3-7). Tests were completed for each aerosolizer while operating at a Low and a High GFR, and while using LFRs of 4 and 8 ml/min. Each variation was completed while using water as the liquid without an impact plate and with an impact plate. For comparison purposes selected tests were also conducted while using soybean oil.

### 2.3.1.3 Dilution Tests

Dilution Tests were designed to determine whether dilution of aerosol clouds would produce data sets that better predicted actual aerosolization rates. Soybean oil was used for the dilution tests to avoid evaporative losses. Block 3-3 aerosolizer blocks, High GFR, and an LFR of 8 ml/min were used. Two different sets of tests were conducted under these operating conditions; without an impact plate and with an impact plate.

Lower dilutions (5-30X) were created by injecting clean air into a dilution chamber along with aerosols (Figure 2.6). The dilution chamber was constructed using a 4-ft-long piece of 6-inch PVC pipe. The aerosols entered through the bottom center of the chamber, and ambient air was injected through a port installed in the bottom corner (Figure 2.6). A variable-area flow meter was used to measure the rate of ambient air injection, which was some multiple (desired dilution factor) of the gas flow rate used to produce the aerosols (Figure 2.6). The aerosols and ambient air would mix within the chamber before being sampled through a port at the top. To create higher dilutions (40+), some of the pre-diluted aerosols would be pumped out of the flow stream before entering the chamber (Figure 2.6). The extraction flow rates were measured using a variable-area
flow meter, and would represent 0.5, 0.75, or 0.875 of the gas flow rate used to produce the aerosols. A filter was placed in line before the flow meter and vacuum pump to prevent fouling due to aerosol deposition (Figure 2.6).

Figure 2.6- Diagram showing the testing configuration used during dilution tests. Black arrows represent gas flow direction.

2.3.2 Aerosolizer Block Tests

Each aerosolizer was tested under different operating conditions. The parameters that could be adjusted include the orifice sizes (aerosolizer blocks), the liquid flow rate, the gas flow rate, use or non-use of an impact plate, and the liquid aerosolized (water,
soybean oil). The aerosols produced were sampled using the particle analyzer. The results of these tests were then compared to determine whether trends in particle size could be observed based on operational parameters.

Analysis of Aerosolizer Block Test data involved correlating the average particle size created by an aerosolizer block with liquid orifice diameter, liquid mass flow rate, gas mass flow rate (gas orifice diameter, gas pressure), and liquid surface tension. Investigation of these parameters was used to evaluate the reliability of models such as Equation 1-1. However, there are other factors affecting the jet aerosolization process that could affect average particle size that are not included in such models. These factors include use of an impact plate and/or pre-humidifying the carrier gas. Test subsets were conducted to isolate and characterize these parameters.

2.3.2.1 Comparison of Similarly Constructed Blocks

Duplicates of each aerosolizer block configuration were constructed and designated blocks A and B (ie. Blocks 3-3 A and 3-3 B). Duplicate blocks were tested to determine whether unintentional variations resulting from the construction process could influence the particle size distribution produced during liquid aerosolization. Tests were also designed to investigate the effects using a humidifying stack during water aerosolization.

2.3.2.1.1 A&B Block Comparisons

The A and B blocks for each aerosolizer orifice combination were fabricated at the same time using the same processes in a professional machine shop. If the A and B
blocks were functionally similar, then they would create particle size distributions that were identical within the variability expected for the system when using the same LFR-GFR settings. Sets of tests were conducted using water with the A and B blocks of each configuration. The test configurations included LFR settings of 4 or 8 $\text{ml}/\text{min}$ in combination with Low and High GFR settings.

2.3.2.1.2 Use of Humidifying Stack

Evaporation can potentially play a significant role during delivery of aqueous aerosols. A humidifying stack was designed and tested as a potential method for minimizing the effects of water evaporation during aqueous aerosol delivery. The humidifying stack was constructed using three 10-ft-long pieces of 6-inch-PVC pipe. Each section of pipe was capped on top and bottom, and threaded fittings were installed in all of the caps to allow the attachment of gas hoses. Porous polyethylene diffusers were installed on the inside of the bottom cap for each section. Each section was filled with 8 ft of water and plumbed together in series. The humidifying stack was placed in line between the compressed gas source and the gas regulator (Figure 2.3). During operation, the gas would flow through each of the three sections, bubble through a total of 24 ft of standing water before being supplied to the aerosolizers.

Tests were designed to characterize the effect of using a humidifying stack. The aerosolizer blocks used during the tests were 3-3, 3-5, and 3-7 (same liquid orifice size, different gas orifice size). Sets of tests were conducted with each aerosolizer using Low, High, and Higher GFRs. Each test configuration was conducted with and without the humidifying stack.
2.3.2.2 Block Characterizations

Block Characterization Tests involved measurement of aerosol particle size distributions produced from different aerosolizer blocks under different operating conditions. According to Equation 1-1, the average particle size of aerosols produced are expected to decrease as liquid orifice decreases, liquid flow rate decreases, gas flow rate-velocity increases, and liquid surface tension decreases. Experiments were designed to characterize these operating parameters.

The particle size production behaviors of individual aerosolizer blocks were characterized by producing aerosols using combinations of Low and High GFR’s along with LFR settings of 4 and $8 \text{ ml/min}$ (termed Low and High LFR in results). All tests were conducted using water, and oil was tested with the 0.03-0.05-inch-diameter gas orifice blocks.

Selected variations were repeated with or without an impact plate. The intended purpose of the impact plate is to remove a portion of the particles from the aerosols that are produced from the aerosolizer. It is expected that the momentum of the larger particles will make them more likely than smaller particles to impact the plate and be removed from the aerosol stream.
2.4 Results

2.4.1 Particle Analyzer Tests

2.4.1.1 Particle Analyzer Calibration

An average particle analyzer response was obtained from three sampling events for each of three different polystyrene sphere sizes (1, 3.65, and 5 μm). In each case a calibration factor was calculated by dividing the actual particle size by the measured particle size. The average calibration factor from the three particle sizes was 2.5. The measured particle size was multiplied by the calibration factor to estimate the actual size (Figure 2.7).

2.4.1.2 Aerosolization Rate Tests

Calculating aerosolization rates from particle analyzer data consistently underestimated actual (measured) mass rates (Table 2.2). This is quantified by dividing the measured rate by the calculated rate (result represents the factor by which actual aerosolization rate is underestimated)(Table 2.2). When water was used without an impact plate the error ratios ranged from 48 to 833, with an outlier of 3534. The error ratios calculated for water tests using an impact plate tended to be much larger (Table 2.2).

The calculated aerosolization rates for soybean oil tests predicted actual aerosolization rates more closely than those for water tests; however, actual rates were still underestimated by factors ranging from 17 to 42. The measured aerosolization rates for water tests were larger than those for oil tests by an order of magnitude.
The data show that mass of liquid injected into the aerosolizer is one to several orders of magnitude greater than the mass of aerosols measured by the particle analyzer. This is probably because the particle analyzer underestimates the number of particles, particularly when the number is large and exceeds the counting capacity of the device. It
also occurs because some of the liquid is lost due to evaporation. Water and oil were used at roughly the same rates, so the larger discrepancy between the injected rate of water and the rate of production of water aerosols likely occurs because water evaporates at a higher rate than soybean oil.

**Table 2.2**- Aerosol mass flow rates measured experimentally and calculated from particle size distribution for different orifice sizes, flow rates and plate configurations.

**2.4.1.3 Dilution Tests**

Tests conducted with and without an impact plate produced similar patterns with respect to dilution (Figure 2.8). In both cases the data obtained by sampling undiluted soybean oil aerosol tend toward larger particle sizes. When the sample is slightly diluted (5 to 1) the data shifts toward the smaller end of the scale (Fig. 2.9). In both sets of tests the data representing dilutions between 80 to 1 and 240 to 1 produce similar plots with respect to particle size distribution. The highest dilution attempted was 450 to 1 for the impact plate case, which also showed a decrease in particle size from the fairly constant
distribution observed for 80, 120, and 240 to 1 (Figure 2.8). However, total particle
counts never dropped below approximately 550k even at the highest dilution, suggesting
that the maximum particle count rate of the particle analyzer system was still being
exceeded.

Figure 2.8- Particle size distributions for various dilutions of soybean oil aerosols
created with and without an impact plate.

Figure 2.9- Particle size distributions scaled based on dilution factor for soybean oil
aerosols created with and without an impact plate.
Calculating aerosolization rates from dilution data involved the same method used for undiluted data, except that the numbers of particles acquired during dilution tests are multiplied by the dilution factors. The raw data from each test (Figure 2.8) multiplied by the dilution factor produces converted data that were used to calculate aerosolization rates (Figure 2.9). These data are approximations of the number of particles that would be measured if the sampling system was not limited by the number of counts.

Aerosolization rates were calculated for the results of each dilution test (Table 2.3). Calculated and measured aerosolization rate discrepancies were quantified by dividing the calculated rate by the measured rate (Table 2.3). The calculated value underestimates the measured rate when this number is less than 1, predicts the measured rate “correctly” when this value is 1, and overestimates the measured rate when the value is greater than 1.

The undiluted or slightly diluted test results underestimate the measured value (Table 2.3). The calculated rate increases as the dilution factor increases; therefore, the calculated to measured ratio also increases and actually exceeds 1 in both cases (Table 2.3). With no impact plate the measured rate is exceeded at a dilution of 240 to 1 with a value of 1.21. For impact plate tests the measured rate is exceeded at a dilution of 80 to 1 with values of 1.89, 4.02, and 8.41 for dilutions of 80, 120, and 240 to 1 respectively (Table 2.3). The calculated to measured ratio increases at a greater rate with respect to dilution factor when an impact plate is used (Figure 2.10).
Table 2.3- Mass flow rates from dilution tests with calculated/measured aerosolization rate ratios.

<table>
<thead>
<tr>
<th>Dilution Factor</th>
<th>No Plate Data</th>
<th>Plate Data</th>
<th>Accurate Rate Approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>100</td>
<td>0.33</td>
<td>0.21</td>
<td>0.17</td>
</tr>
<tr>
<td>200</td>
<td>0.50</td>
<td>0.29</td>
<td>0.22</td>
</tr>
<tr>
<td>300</td>
<td>1.55</td>
<td>2.43</td>
<td>1.89</td>
</tr>
<tr>
<td>400</td>
<td>2.50</td>
<td>5.17</td>
<td>4.02</td>
</tr>
<tr>
<td>500</td>
<td>5.18</td>
<td>10.81</td>
<td>8.41</td>
</tr>
<tr>
<td>600</td>
<td>11.68</td>
<td>11.68</td>
<td>9.09</td>
</tr>
</tbody>
</table>

Figure 2.10- Ratio of calculated to measured mass rate as a function of dilution factor for tests conducted with and without an impact plate. Black line represents “correct” value based on measured rate.
2.4.1.4 Particle Analyzer Summary and Implications for Application

Lab tests show that the Clement Model CI-226 produces data that are useful for some applications, but they are of limited utility in other cases. Measurements of particle size distributions can be repeatable and have been calibrated to known particle sizes. For example, repeat samplings from a continuous stream of water aerosol produced size distribution curves with the same shape and the magnitudes deviate by a maximum of 20% (Figure 2.5).

The device was calibrated for particle size using latex particles with known diameter (Figure 2.7). Capability to characterize relative particle size changes is confirmed by comparing the mode particle size (peak on the distribution plot) from tests using different aerosolizer operating parameters. The relative changes are consistent with Equation 1-1, which describes the expected change in particle size as a function of operating parameters, according to Mercer (1981).

These results indicate that the particle size data are useful for making comparisons between the general particle size distribution for different tests, or different times within the same transient test. Another application involves comparison of data sets to determine whether particles have been removed, which would produce changes similar to dilution in some instances (Figure 2.8). This type of observation is used to confirm the action of an impact plate, or as an indication of particle deposition in porous media during injection tests (Chapters 3-5).
2.4.1.4.1 Effects of high concentrations

Operational conditions resulted in aerosol concentrations that far exceeded concentrations created during calibration, and this appears to affect the accuracy of the measurements. Integrating the number of particles of different sizes measured by the analyzer underestimated the mass of aerosols produced during a test. This appears to occur because the analyzer is only capable of measuring approximately 700k particles over a 10 second period. This indicates that the relative distribution of particle sizes is representative, but the data are only capable of estimating the lower bound on the total number of particles in each size category.

Dilution tests were conducted in an effort to reduce the number of particles to below the 700k maximum and improve the accuracy with which the numbers of particles were counted. The calculated mass rate increased with the magnitude of dilution. However, the calculated mass rate exceeded the actual rate at large values of dilution, suggesting that dilution was not a viable way of improving the accuracy of the total mass of aerosols in the relatively dense clouds created for this investigation.

The dilution tests also showed that the distribution of aerosol size was affected by dilution. In general, the mode particle size decreased as the amount of dilution increased. For example, the modal size is 5 µm for an undiluted sample, but it decreases to 4 µm for 5 to 1 dilution and to ~2 µm for 450 to 1 dilution (Figure 2.8).

It is possible that the size distribution measured by the aerosolizer is affected by the concentration of aerosols. The particle counter estimates particle size based on the angle of refraction caused by individual particles. It seems feasible that light that is
successively refracted by one small particle and then another one would be miscounted as being refracted from one large particle. Alternatively, smaller particles may also pass through the chamber without being detected due to masking by larger particles.

The particle analyzer was used to characterize particle size distributions from aerosolizers, and at different points along sand-filled apparatuses during bench-scale injection tests (Chapters 3,4). Larger aerosol particles preferentially deposit earlier during transport, therefore, particle size distributions should tend toward smaller particles with transport distance. This type of behavior is supported by particle measurement data (Figure 3.5A,B). However, in many cases the number of small particles measured along the flow path are greater than that measured in the original aerosol (Figure 3.5A,B). This seeming discrepancy is due to the fact that both samples are limited to ~750,000 counts. The particle size distribution is assumed to represent the actual distribution in both cases, but the total mass represented by each sample cannot be directly compared.

2.4.1.4.1 Summary

The assessment of the particle analyzer indicates that the device is capable of measuring distributions of particle sizes within the range of 1 to 10 µm. This size range is important because the mobility of aerosols larger than 10 µm is expected to be limited. The particle analyzer is unable to distinguish particle sizes smaller than 1 micron. The characteristic spikes in particle count that occur in data sets near 1 µm are believed to be representative of these undistinguished particles (Figure 2.8).

The large concentrations of aerosols created during this work rapidly fill the available memory in the particle analyzer, so the number of measured particles
underestimates the actual number in the aerosol cloud. This makes the data from the analyzer poorly suited to estimating the total mass concentration, and it was never used for this application.

In the following applications it is assumed that the particle size distributions measured by the analyzer are representative of the actual distributions to within uncertainties that are at least equal those estimated by the repeatability tests (+/- 20%). It is possible that high aerosol concentrations cause the number of large aerosols to be overestimated relative to the number of smaller particles, according to results from dilution tests. This effect likely increases the uncertainties in the particle size distributions. The data are insufficient to quantify this effect, although it could be significantly larger than the uncertainty resulting from repeat testing. The result of the un-quantified uncertainty resulting from measuring large aerosol concentrations is that qualitative assessment and comparison of the particle size distributions will be used instead of detailed, quantitative evaluations in many of the following applications.

2.4.2 Aerosolizer Block Tests

2.4.2.1 A&B Block Comparisons

Block B created particle size distributions that were shifted toward the smaller end of the scale as compared to Block A for 3-3 aerosolizer tests (Figure 2.11A-D). The 3-5 Blocks A and B produced distributions that are similar in shape, however, Block B tends to produce aerosols in greater number over the entire range of particle sizes (Figure 2.11E-H). Block 5-5A produces slightly greater numbers of aerosol particles with
distributions shifted slightly toward the larger sizes as compared to Block B (Figure 2.12A-D). The 3-7 Block A produced measurable results under Low GFR operating conditions (Figure 2.12E,F), however, for the High GFR settings no response was measured for 4 \( \text{ml/min} \) LFR and only a slight response was measured for the 8 \( \text{ml/min} \) LFR setting (Figure 2.12G,H). Sampling of aerosols produced from Block 3-7B produced indications of particles only at the smallest end of the measureable range for all operating conditions (Figure 2.12E-H). Agreement was good between A and B blocks for 5-7 and 7-7 aerosolizers (Figure 2.13A-H), and the overall behavior of these aerosolizers was similar. In each case the 4 \( \text{ml/min} \) LFR settings produced aerosols that created little to no response in the particle analyzer (Figure 2.13A,C,E, and G). However, operating 5-7 and 7-7 aerosolizer blocks with an 8 \( \text{ml/min} \) LFR always produced measureable particle distributions (Figure 2.13B,D,F, and H).

The gas pressure required to produce the appropriate GFRs was measured during A&B Block Comparison Tests (Table 2.4). Increased pressure is required to increase the GFR, and data also show that increases in gas pressure are required to maintain GFR when LFR is increased (Table 2.4). Noticeable differences are observed in the pressure required to produce given operating conditions for Blocks A and B of similar aerosolizer constructions (Table 2.4). However, the pressure differences do not necessarily change systematically with the differences in particle distributions measured during testing (Table 2.4)(Figures 2.11-2.13). Block 3-3B required less pressure than Block 3-3A to produce the appropriate GFR and created greater numbers of aerosol particles shifted toward the smaller range (Table 2.4)(Figure 2.11A-D). However, Block 3-5B required
Figure 2.11: Number of particles versus particle size measured during 3-3 and 3-5 A & B aerosolizer block tests under different operating conditions.
Figure 2.12: Number of particles versus particle size measured during 5-5 and 3-7 A & B aerosolizer block tests under different operating conditions.
Figure 2.13: Number of particles versus particle size measured during 5-7 and 7-7 A & B aerosolizer block tests under different operating conditions.
more pressure than Block 3-5A while also creating greater numbers of aerosol particles across the entire particle size range (Table 2.4)(Figure 2.11E-H). The 3-7 blocks showed the most variation between A and B particle size distribution results (Figure 2.12E-H), however, there was basically no difference in the pressure required to produce appropriate GFR values (Table 2.4).

One block (A or B) was selected for use in subsequent tests. The block selection was made based on visual comparison of particle size distribution data (Figures 2.11-2.13). In each case the block was selected that produced the most detectable aerosol particles and/or particles that were shifted toward the smaller end of the size spectrum. The blocks selected were 3-3B, 3-5B, 5-5A, 3-7A, 5-7B, and 7-7B.

<table>
<thead>
<tr>
<th></th>
<th>GFR 3-3 LFR Low</th>
<th></th>
<th>GFR 3-5 LFR Low</th>
<th></th>
<th>GFR 3-7 LFR Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4 15.5 (B) 29 (E)</td>
<td>A</td>
<td>4 16.5 (B) 31 (E)</td>
<td>A</td>
<td>4 22 (B) 47 (E)</td>
</tr>
<tr>
<td>8</td>
<td>18 (C) 31.5 (F)</td>
<td>8</td>
<td>17 (C) 31.8 (F)</td>
<td>8</td>
<td>22 (C) 47 (F)</td>
</tr>
<tr>
<td>B</td>
<td>4 13 (B) 22 (E)</td>
<td>B</td>
<td>4 18.8 (B) 36.5 (E)</td>
<td>B</td>
<td>4 22.3 (B) 47 (E)</td>
</tr>
<tr>
<td>8</td>
<td>13.8 (C) 23 (F)</td>
<td>8</td>
<td>19.8 (C) 37.5 (F)</td>
<td>8</td>
<td>22.5 (C) 47 (F)</td>
</tr>
</tbody>
</table>

Table 2.4- Gas pressure in psi required to generate appropriate gas flow rate values for A and B aerosolizer blocks with 0.03-inch-diameter liquid orifices. Letters in parenthesis indicate corresponding plots in Figures 2.11, 2.12, and 2.13.
2.4.2.2 Use of Humidifying Stack

Utilizing the humidifying stack consistently resulted in more particles counted (Figures 2.14-2.16). With few exceptions, an increase in particle count is observable over the entire range of particle sizes for each test. While the numbers of particles counted differs for each set of test conditions, the general shape of the particle size distribution curves remained similar (Figures 2.14-2.16). The effect of pre-humidifying the carrier gas increased as GFR and LFR decreased for Block 3-3 tests (Figure 2.14). The overall behaviors for 3-5 and 3-7 aerosolizer blocks were similar (Figures 2.15,2.16). These blocks produced little to no detectable aerosols under any GFR and LFR setting when ambient gas was used. Use of a humidifying stack did, however, increase detectable aerosol production in some of the cases. Particle count increases became more prevalent as GFRs decreased and as LFRs increased (Figures 2.15,2.16).

Humidifying Stack Test data were further quantified by integrating the total liquid volume represented by the particles measured (Table 2.5). The liquid volume integrations tended to be less when humidifying stacks were not used, and the percent increase from using the humidifying stacks was calculated for each case (Table 2.5). The percent increase in liquid volume values ranged from 0% to 1376% with an average value of 320% (Table 2.5). Zero values represent a decrease in liquid volume detected when using the humidifying stack, which occurred for three sets of tests associated with the Block 3-3 aerosolizers (Table 2.5). Each example is characterized by greater numbers of particles measured in the larger particle size range during tests for which the humidifying stacks were not used (Figure 2.14A,E, and F).
**Block 3-3 Tests**

**Low GFR**

- LFR = 2 ml/min
- LFR = 4 ml/min
- LFR = 8 ml/min

**High GFR**

- LFR = 2 ml/min
- LFR = 4 ml/min
- LFR = 8 ml/min

**Figure 2.14:** Number of particles vs. particle size measured using a 3-3 aerosolizer block, different operating conditions, with and without humidifying stack.
Figure 2.15: Number of particles vs. particle size measured using a 3-5 aerosolizer block, different operating conditions, with and without humidifying stack.
Figure 2.16: Number of particles vs. particle size measured using a 3-7 aerosolizer block, different operating conditions, with and without humidifying stack.
Table 2.5- Liquid water volume integrations from humidifier stack tests along with volume percent increase when stack is used. Letters in parenthesis correspond to plots in Figures 2.14, 2.15, and 2.16.

### 2.4.2.3 Block Characterizations

Average particle size produced based on GFR and LFR for tests involving water are similar (Figures 2.17-2.19). The general shapes of particle distribution curves measured for aerosolizer block-impact plate combinations are independent of fluid feed rates. The typical distribution is that the particle counts for the small particle sizes are relatively large and the size distribution tails off as particle size increases. Regardless of magnitude, curves with similar shapes represent similar average particle sizes.

The few instances where average particle comparisons can be drawn include results from 3-3 and 5-5 blocks (Figure 2.17A,C). The high GFR results from 3-3 aerosolizer blocks have distributions that are typical of water aerosols, however, the low GFR plots show a shift towards a larger average particle size (Figure 2.17A). A similar effect can be observed in 5-5 block results, however, the shift is based on LFR as
opposed to GFR (Figure 2.17C). The low LFR plots follow the typical particle size
distribution for water aerosols, whereas use of the high LFR setting causes the
distributions to shift toward the larger end of the scale (Figure 2.17C).

The size distribution of water aerosol plots are similar in shape, however, they
vary in particle count magnitude. The particle counts for individual aerosolizers tend to
increase as LFR increases and/or GFR decreases. In every case (except for block 3-3) the
largest particle counts were measured when operating at Low GFR-High LFR and the
smallest particle counts were measured when operating at High GFR-Low LFR. The
remaining operating conditions (Low GFR-Low LFR, High GFR-High LFR) represented
the second and third particle count totals, however, rank was not consistent from
aerosolizer to aerosolizer (Figures 2.17, 2.18).

Unlike the plots for water experiments, the plots for soybean oil experiments are
characterized by peaks that occur away from the smallest particle size end of the
measureable range (Figure 2.19). Blocks 3-3, 3-5, and 5-5 were tested with soybean oil,
the particle sizes at which peaks occurred for each test variation are shown in Table 2.6.
The peak particle size values range from 5.03 to 12.93, however, most occurred between
5 and 6 microns (Table 2.6). Use of Low GFR settings with the 5-5 block produced a
bimodal particle size distribution (Figure 2.19C), resulting in particle size values for two
different peaks (Table 2.6).

Peak particle size consistently increased with increases in GFR when using
soybean oil (Table 2.6). The volumetric gas flow rate is larger for the 3-5 and 5-5 blocks
as compared to the 3-3 Block (Table 2.1), however, particle size values are similar for
**Figure 2.17:** Number of particles versus particle size measured using water with 3-3, 3-5, and 5-5 aerosolizer blocks, different operating conditions, with and without an impact plate.
**Figure 2.18:** Number of particles versus particle size measured using water with 3-7, 5-7, and 7-7 aerosolizer blocks, different operating conditions, with and without an impact plate.
Figure 2.19: Number of particles verses particle size measured using soybean oil with 3-7, 5-7, and 7-7 aerosolizer blocks, different operating conditions, with and without an impact plate.
Blocks 3-3 and 3-5 while they are larger for Block 5-5 (Table 2.6). This observation is consistent with what would be expected based on liquid orifice properties (Equation 1-1), with the 3-3 and 3-5 Blocks having smaller liquid orifices than Block 5-5.

Table 2.6- Particle sizes (micron) at peak points for soybean oil experiments. Letters in parenthesis correlate to plots in Figure 2.19.

<table>
<thead>
<tr>
<th></th>
<th>Block 3-3 (A)</th>
<th>Block 3-5 (B)</th>
<th>Block 5-5 (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low GFR</td>
<td>5.33</td>
<td>5.5</td>
<td>6.08-10.35</td>
</tr>
<tr>
<td>High GFR</td>
<td>5.88</td>
<td>5.88</td>
<td>5.7-10.35</td>
</tr>
</tbody>
</table>

The number and size of water aerosols created when using an impact plate was typically less than those created when not using an impact plate (Figures 2.17, 2.18). In most cases the number of particles is reduced to a point that registers little response with the particle analyzer (Figures 2.17A and 2.18D-F). Some registering aerosol particle size distributions were produced from blocks 3-3 and 5-5 when using an impact plate (Figure 2.17D,F).

Impact plate aerosols that were measurable consistently corresponded with test configurations that produced the most particles and/or largest particles when an impact plate was not used (Figure 2.17A,C,D, and F). In particular the Low GFR settings produced aerosols that retained high numbers of particles, however, the particle sizes shifted toward the smaller end of the scale in all instances (Figure 2.17D,F). Tests involving High GFR settings registered measurable aerosols with an impact plate in only one instance (Figure 2.17F). However, the reduction in number of particles measured was greater when High GFR as opposed to Low GFR was used (Figure 2.17F).
Impact plate tests involving soybean oil were only conducted using Low LFR settings with the 3-3 Block (Figure 2.19D). In both cases the peak particle size was reduced; from 5.88 to 4.85 μm under High GFR conditions and from 5.33 to 2.75 μm under Low GFR conditions (Figure 2.19D). Particle sizes decrease with use of an impact plate, however, the number of smaller particles measured increased (Figure 2.19D). This behavior also occurred under Low GFR conditions when using water with Block 5-5 (Figure 2.17F).

2.5 Discussion

2.5.1 Comparison of Similarly Constructed Blocks

Duplicates (A and B) of aerosol blocks were constructed at the same time using identical methods. Identical blocks should create identical aerosol clouds under similar operating conditions; however, testing has revealed differences between similarly constructed blocks are observed in particle size distribution data collected using the particle analyzer (Figures 2.11-2.13). These differences are represented by a shift toward more or less particles and/or a shift toward the larger or smaller end of the particle size range (Figures 2.11-2.13).

GFR was increased or decreased by changing the gas feed pressure. Increases in gas feed pressure were also typically required to maintain desired GFR when LFR was increased. The increased gas pressure is presumably required because of the resistance produced by increasing the liquid flow rate (Figure 2.1). The A and B blocks of a given aerosolizer configuration require different pressure feeds when using the same LFR
(Table 2.4), which is more prevalent as the gas orifice size becomes smaller. Smaller gas orifice size means that the pressure drop across the aerosolizer for a given GFR will be greater; a condition that would likely magnify subtle differences between A and B blocks.

The most likely explanation for A and B block test result discrepancies is differences generated during the machining process. Particularly, inconsistencies could occur at the point where the gas and liquid orifices intersect. Attempts were made to ensure that the liquid orifice intersected at a right angle directly in the center of the gas orifice; however, the degree to which these was achieved varied. Metal wire was used to clean debris from the orifices following machining. It is possible that small burrs could have remained within the orifices that would partially account for some inconsistencies that were observed.

2.5.2 Use of Humidifying Stack

Use of a humidifying stack increased the number of particles detected for all test variations compared to using ambient air (Figures 2.14-2.16). Shapes of the humidified and non-humidified plots were similar, but the number of particles varied. The humidified to non-humidified trends observed in these tests could result either from a decrease in the numbers of particles of each particle size, or from a shift in particle size from larger to smaller (Figures 2.14-2.16). It is assumed that the use of a humidifying stack would decrease evaporation rates of aerosol particles; therefore, a shift in particle size would be a likely explanation for the trends observed in test data.

Due to larger surface area to volume ratios, the volumetric evaporation rate will be inversely proportional to particle size. When a humidifying stack is not utilized the
evaporation rates are increased, which preferentially causes the loss of smaller particles. Evaporation of larger particles causes them to shrink in size. The particle distributions measured during humidified experiments are characterized by large numbers of small particles and lesser numbers of larger particles. In this case a shift in particle size (due to evaporation) appears to be a shift toward smaller numbers of particles (Figures 2.14, 2.16).

The impact of evaporation should depend on the ratio between the masses of gas and water used during the aerosolization process. A high gas to water ratio will increase the volumetric evaporation rate of aerosol particles. This condition can be induced by increasing GFR and/or decreasing LFR. Comparisons can be made between tests using Low and High GFR settings for each aerosolizer block, however, when comparing results from different blocks the actual volumetric gas flow rate should be considered. GFR settings are determined based on desired velocity through the orifice (Table 2.1), therefore, volumetric gas flow rates will increase at a given setting for blocks with larger gas orifice diameters. The volumetric rate through the 3-5 blocks is 2.8 times, and through the 3-7 blocks is 5.4 times the volumetric rate through the 3-3 blocks (Table 2.1).

The effect of using a humidifying stack is determined by the aerosolizer operating conditions as they pertain to evaporation. Block 3-3 operation is characterized by relatively low volumetric gas flow rate and results suggest low evaporation rates. There is evidence of evaporation when humidifying stacks are not used with Block 3-3, but the effect is fairly subtle. Plot differences become more accentuated as LFR decreases, with
LFR= $2 \text{ ml/min}$ plots showing the greatest evaporative effects of the group (Figure 2.14 A,D).

Block 3-5 and 3-7 tests involved higher volumetric gas flow rates, and the results show evidence of increased evaporation rates. Intermediate evaporative effects are displayed by LFR= $4 \text{ ml/min}$ (Figures 2.15B,E and 2.16B) and LFR= $8 \text{ ml/min}$ experiments (Figures 2.15C,F and 2.16C,F). In these cases the particles that were created without use of a humidifying stack were evaporated to the point of non- or small detectability upon reaching the particle analyzer. However, use of a humidifying stack under the same operating conditions reduced evaporation rates enough to maintain detectable aerosols at the point of sampling. The greatest evaporative conditions are displayed by LFR= $2 \text{ ml/min}$ (Figures 2.15A,D and 2.16A,D). In these cases the small amount of water entering the aerosolizer likely resulted in evaporation rates that were too large to overcome even when using the humidification stack.

2.5.3 Block Characterizations

Trends in average particle size distribution based on operational conditions could be observed in two cases when using water as the aerosolization liquid. The particle size created by Block 3-3 increases as GFR decreases (Figure 2.17A). Average particle size should increase with decreases in gas mass flow rate and gas velocity according to Equation 1-1, making these results qualitatively consistent with predictions. Block 5-5 results show an increase in particle size as LFR increases (Figure 2.17C), which again is qualitatively consistent with Equation 1-1.
Observations consistent with jet aerosol particle size theory (Mercer, 1981) occurred in the Block Characterization Test results; however, it is likely that these water aerosol particle size distributions are dominated by evaporation (Figures 2.17-2.19). Nearly all water plots display a peak at the smallest particle size end of the scale, which could be a result of evaporation. Another indication of evaporation is provided upon examination of plot magnitudes. The Low GFR-High LFR experiments produced the largest particle counts in nearly every case (Figures 2.17A-C and 2.18A-C). Low GFR along with High LFR creates the smallest GFR to LFR ratios tested, a condition that is most likely to decrease the effects of evaporation and allow particles to reach the sampling port in the greatest numbers. Conversely, High GFR-Low LFR operating conditions represent the opposite extreme, thus producing the smallest particle counts obtained for every block (Figures 2.17A-C and 2.18A-C).

It is concluded that plots shown for water experiments in Figures 2.17-2.19 represent the particle distributions following evaporation that occurs between the aerosolizer and the gas sampling port located approximately 1 meter downstream (Figures 2.17A-C and 2.18A-C). The predominance of evaporation during water aerosolization is evident when comparing liquid aerosolization rate values of water and soybean oil (Table 2.2). Soybean oil has a lower vapor pressure than water; therefore, evaporation rates are smaller. The “loss” rates during soybean oil aerosolization are an order of magnitude less than those observed for water. The shapes of particle size distribution plots obtained during soybean oil tests may provide a better approximation of
the types of plots that would be observed for water if evaporation were not a factor (Figure 2.19A-C).

The particle size trends observable in soybean oil test results tended to be subtle. One consistent trend was an increase in particle size with increase in GFR, which is opposite of what would be expected according to Equation 1-1. The peak particle sizes under all operating conditions were similar for Blocks 3-3 and 3-5 (Figure 2.19A,B). The behavior of Block 5-5 differed in that the increase in particle size with increase in GFR was more exaggerated (Figure 2.19C). Liquid orifice diameter is the operating condition that can best be correlated to this trend, suggesting that liquid orifice may be the most important determining factor for particle size within the operating ranges tested.

Aerosols tended to be depleted to the point of non-measurability when using an impact plate during aqueous aerosol experiments (Figures 2.17D-F and 2.18D-F). Use of an impact plate is expected to remove a fraction of the aerosol particles from the flowing gas, with preferential effect on larger particles. This would produce an aerosol cloud with less liquid mass per gas volume, and liquid mass occurring as smaller particles. Both of these conditions would amplify the effect of evaporation. Aerosols were most likely not measurable because nearly all of the particles retained past the impact plate evaporated before reaching the gas sampling port. The High GFR aerosolizer configurations tended to be more effected by the presence of an impact plate than Low GFR configurations. This would be expected because the aerosols exit the aerosolizer nozzle at greater velocity under High GFR conditions. Under these conditions the individual aerosol
particles have greater momentum, which increases the likelihood of impacting the plate and being removed from the particle flow stream (Figure 2.17D-F).

2.6 Conclusions

Aerosolizer characterization experiments focused on determining effects of aerosolizer design, aerosolizer operating parameters, and aerosolized liquid on resulting particle size distribution. Repeatability of measurements between multiple samplings was demonstrated when using the particle analyzer, and particle size trends observed between different measurements consistently showed trends that were expected based on Equation 1-1. These observations provide confidence in the capability to draw conclusions based on comparison of different particle analyzer data sets.

Significant differences were consistently observed in particle analyzer data from measurements of water and soybean oil aerosols. In particular, the particle size correlating to the mode for water aerosols tended to be less than 1 micron (the smallest measurable value) (Figures 2.11-2.13), whereas modes for soybean oil aerosols are larger, in the range of 5 to 13 micron (Figure 2.19). Evaporation likely reduces the size of aerosols made from water more than those from oil.

Successful delivery of liquid mass as water aerosols during field implementation will require controls on evaporation rates. Pre-humidifying the carrier gas prior to aerosol production is a mechanism that could be implemented in the field. Use of humidifying stacks evidently prevented some evaporation during testing, resulting in a nearly 14x increase in liquid mass detected under some conditions (Table 2.5). Test results also indicate that aerosolizer operating conditions can have some effect on aerosol transport.
Increases in water aerosol particle counts were consistently observed with increases in liquid to gas feed ratio (Figures 2.11-2.13), which is accomplished by increasing LFR and/or decreasing GFR. Evaporation of water aerosols is likely enhanced by a decrease in gas humidity that occurs due to pressure drop during aerosolization. Increasing humidity of the gas prior to aerosolization and/or increasing the liquid to gas ratio used during aerosolization can partially alleviate, but not eliminate this effect.

According to particle filtration theory (Equations 1-2 through 1-5), decreasing aerosol particle size will increase average transport distance during injection into porous media. Use of an impact plate has been shown to be an effective mechanism for decreasing average particle size when using soybean oil (Figure 2.19A,D). Impact plates are useful for removing the largest particles; however, removal of these particles could result in significant decreases in total mass delivered as aerosols. This issue could be partially overcome by utilizing operating parameters that reduce average aerosol particle size that is produced from the aerosolizer. According to soybean oil aerosolization results, decreasing liquid orifice diameter is the most important controlling parameter for decreasing aerosol particle size (Figure 2.19A,D).
Chapter 3-Column Injection Tests

Column tests were designed to characterize one-dimensional aerosol transport and deposition in porous materials at the bench-scale. The tests involved generating and injecting aerosols through 2-inch-diameter PVC pipe filled with sand. Aerosol particle size distributions were measured as functions of transport distance and time during injection, and liquid content distributions in the sand were measured after injection was complete.

The porous materials used during column tests consisted of sand sold as filter pack for wells and obtained from a local driller supply. The sands were sieved to create well-sorted materials for use during testing. Three sand classifications were selected to represent fine-, medium-, and coarse-grained fill materials. The size classifications, which will be referred to as Fine, Medium, and Coarse for the remainder of this chapter, are defined by size ranges that are bracketed by mesh sizes through which grains will and will not pass. The grain diameters for Fine, Medium, and Coarse sand are 1.19 to 1.68 mm, 1.68 to 2.38 mm, and 2.38 to 3.36 mm respectively (Table 3.1). Unless otherwise stated, the sand was oven dried prior to use for all column tests.

The particle counter settings and 10 second sample durations used during block characterization tests were also used during column tests. Plots of particle distribution data collected during Block Characterization Tests (e.g. Appendices A-C) represent the average of three individual measurements; however, plots in this chapter represent a single sample because the tests were transient and particle distributions changed with time.
Aerosols injected during column tests were created with water, soybean oil, or salt water (NaCl). Water and soybean oil liquid contents were determined for selected sand samples following injection. These determinations were made by heating samples at 110 C° for two hours to evaporate water and/or 600 C° for 4 hours to evaporate oil. Samples were weighted between each step and liquid mass contents were calculated by dividing the mass loss by the mass of sand in each sample. Salt contents were determined by first drying the samples as described above. The sample was immersed in 100 ml of deionized water, which presumably dissolved the salt. The water was then filtered and 5 ml samples were analyzed using an ion chromatograph to determine concentrations.

A stainless steel mesh screen was installed at the base of columns during all column tests. The screen served to hold the sand pack in place while allowing aerosols to pass through. A 20x20 screen (20 wires per inch) was used in all Medium and Coarse sand experiments, whereas a finer 30x30 mesh was used in all Fine sand experiments. Preliminary experiments were conducted to characterize how the mesh alone affected water aerosol transport (Figure 3.1). The experiments involved first measuring aerosol particle size distribution produced from the aerosolizer (no screen). The corresponding screen was then installed on the outlet port of the aerosolizer housing so that the water

<table>
<thead>
<tr>
<th>Classification</th>
<th>Sieve Sizes</th>
<th>Grain Diam (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>16 to 12</td>
<td>1.19-1.68</td>
</tr>
<tr>
<td>Medium</td>
<td>12 to 8</td>
<td>1.68-2.38</td>
</tr>
<tr>
<td>Coarse</td>
<td>8 to 6</td>
<td>2.38-3.36</td>
</tr>
</tbody>
</table>

Table 3.1- Sieve and grain sizes used to define sand classifications used during column experiments.
aerosols would pass through. The process was continued for 10 minutes with aerosol particle size distributions measured at time intervals throughout the duration (Figure 3.1).

Passing water aerosols through wire mesh caused a noticeable change in resulting particle distributions. The change was characterized by a decrease in number of large particles and increase in number of small particles (Figure 3.1). These observed shifts were more extreme with the fine mesh than for the coarse mesh. The particle distribution data shows that the changes are transient (Figure 3.1). In both tests the majority of the change takes place in the first 30 seconds of the experiment, however, the trend continues up to approximately 3 minutes and is steady thereafter. In both experiments the 3, 5, and 10 minutes distributions are nearly identical, suggesting that a steady-state condition has been reached (Figure 3.1).

**Figure 3.1** - Transient particle size distribution effects from passing water aerosols through a coarser mesh (20X20) and a finer mesh (30X30).
3.1 Test Methods

Column injection tests are divided into two broad categories based on the length of sand through which aerosols were injected. One category involved the use of shorter columns with 2.54 cm of sand (1-inch Column Tests), whereas longer columns with 1.5-m of sand were used for the other category.

3.1.1 1-inch-Column Tests

1-inch-Column Tests were designed to characterize basic transport and deposition behaviors. These tests focused on comparing transportability of aerosols produced using different aerosolizer blocks (orifice sizes), aerosolizer operating conditions, fluids, and porous media. The tests involve placing 2.54-cm of sand into a 15-cm-long, 2-inch PVC pipe nipple that is fitted with a stainless steel mesh screen. The threaded ends of the nipple allowed direct attachment to the aerosolizer housing (Figure 2.3).

Aerosolizer operating conditions (gas pressure, liquid flow rate) were set and the aerosolizer was allowed to run prior to the beginning of each test. The particle analyzer was used to sample gas coming from the aerosolizer. The results of these samplings were assumed to represent the aerosol particle size distribution injected into the sand, and are termed “unfiltered” during data presentation. Following the unfiltered sampling, the column was installed onto the aerosolizer housing so that the aerosols flowed through the sand. Aerosol samples from the top of the column were subsequently taken at predetermined time intervals to characterize particle size distributions as a function of time. Particle measurements made while aerosols were injected through a column are called “column in place” measurements.
3.1.1.1 Block, GFR, LFR Variations

Sets of tests were conducted using water as the aerosolization liquid with different aerosolizer blocks, and GFR and LFR operating conditions. The LFRs used were 4 and 8 \( \text{ml/min} \) (Low and High LFR), and the Low and High GFR settings were used based on gas orifice diameter (Table 2.1). The tests were all 10 minutes in duration and used Medium sand as fill (Table 3.1). Aerosol gas samples were taken from the top of the column at 0s, 30s, 1m, 3m, and 5m following attachment to the aerosolizer housing.

3.1.1.2 Sand Size and Impact Plate Variations

Sets of 1-inch-Column Tests were conducted using water through Block 3-3 aerosolizers to determine the effects of using impact plates and injecting through sands of differing grain size. The sampling method and times were identical to those used for Block, GFR, LFR Variation Tests. Each sand grain size category was tested (Fine, Medium, Coarse) using different GFR and LFR settings with and without an impact plate installed.

3.1.1.3 Water-Surface Interaction Tests

Results from early 1-inch-Column Tests suggest the possibility that surface interactions were playing a role in deposition rates. The data suggest that the water aerosol particles have a stronger affinity for deposition on dry sand grain surfaces as opposed to wetted sand grain surfaces. 1-inch-Column Test variations were designed to investigate this phenomenon. One set of tests involved injection of fresh water aerosols through oil-coated sand grains (Oily Sand Tests), whereas the other involved injection of
aerosols created from partially saturated with salt water through dry sand (Salt Water Tests).

3.1.1.3.1 Oily Sand

Oily Sand tests involved wetting the sand with soybean oil prior to water aerosol injection, which was done with the intention of changing potential surface interactions. The hypothesis was that soybean oil would produce hydrophilic properties on the surfaces of sand grains, potentially effecting deposition of water.

Oil was mixed into the sand at a ratio of $5 \text{ ml/100 g}$, resulting in an oil saturation of approximately 0.2 (termed “oily sand”). Oily Sand 1-inch-Column Tests were conducted using Block 3-3 aerosolizers and Low GFR. The variations included Low and High LFR, with and without an impact plate. The sampling method and times were identical to those used for Block, GFR, LFR Variation Tests.

3.1.1.3.2 Salt Water

The ionic strength of water is increased by addition of solutes. Changes in the ionic strength of liquid particles can affect deposition resulting from surface properties associated with electrostatic forces (Elimelech and O’melia, 1990). Addition of solutes also decreases the vapor pressure of the solution, which could decrease evaporation rates. 1-inch-Column Tests were conducted for 10 minutes using Block 3-3 aerosolizers, Low GFR-Low LFR settings, and Medium sand. Test variations included use of fresh water and salt water with concentrations of 25 g/L, 100 g/L, and 300 g/L NaCl. The sampling method and times were identical to those used for Block, GFR, LFR Variation Tests.
3.1.1.4 Soybean Oil Tests

Variations of 1-inch-Column Tests were designed to characterize the transport behaviors of soybean oil aerosols. Soybean Oil Tests were conducted similarly to Block, GFR, LFR Variation Tests, which were performed using water aerosols. Soybean Oil Tests, however, only included the use of Block 3-3 aerosolizers, selected sets of GFR-LFR operating conditions, and included impact plate and no impact plate varieties. Low and High GFR and LFR varieties were completed using Medium sand and no plate. The remaining tests involved using an impact plate and low LFR settings while varying sand grain size as well as GFR settings.

3.1.2 1.5-meter-Column Tests

1.5-meter-Column Tests were designed to characterize aerosol transport as a function of distance, and to provide information about amendment content distributions during flow through a linear geometry. These tests focused on comparing transportability of aerosols produced using different fluids and injection through different porous media. The mesh screen was mounted on the inside of a threaded adaptor at the bottom a PVC column, which could be filled with sand to a depth of 1.5 m. The threaded adaptor allowed direct attachment of the column to the aerosolizer housing (Figure 2.3).

Block 3-3 aerosolizer blocks were used at High GFR-High LFR settings for all 1.5-m-Column Tests unless otherwise stated. As with 1-inch-Column Tests, “unfiltered” aerosol samples were taken from the aerosolizer before attaching the column. Aerosol gas samples along the column could be obtained during testing through mesh-backed sampling ports (termed “column in place” samples). The sampling ports were sealed with
gaskets and pipe clamps when samples were not being taken (Figure 3.2). 1.5-m-Column Tests are divided into four categories. One category is called Empty Column Tests, and the names of the other categories depend on the fluid that was aerosolized: Water, Salt Water, and Soybean Oil.

![Sampling port and gasket clamp for obtaining aerosol gas (screen backed) and sand samples along column.](image)

Figure 3.2- Sampling port and gasket clamp for obtaining aerosol gas (screen backed) and sand samples along column.

### 3.1.2.1 Empty Column Tests

Preliminary test results indicated that evaporation could have a significant effect during transport of water aerosols. Empty Column Tests were conducted by injecting aerosols through an empty (no sand) column. Gas samples were taken at 0.06 m, 0.5 m, 1 m, and 1.5 m along the column to determine aerosol particle distributions as a function of distance (and thus transport time). Tests were conducted with fresh water, salt water, and soybean oil. It was expected that particle size distributions would shift toward the smaller end of the scale if evaporation were occurring along the 1.5 m distance.
3.1.2.2 Water Tests

There were three categories of water aerosol 1.5-m-Column Tests. Categorical tests were designed to investigate the effects of evaporation (Empty Column Tests), of formation grain size (Sand Size Effects), and to characterize the resulting water contents along the column following injection (Column Water Contents). The humidifying stack was used during all water aerosol 1.5-m-Column Tests.

3.1.2.2.1 Sand Size Effects

Sand Size Effect experiments were conducted to characterize the transient arrival of water aerosols over a 1.5 m transport distance as a function of porous media grain size. Water aerosols were injected through columns filled with Fine, Medium, or Coarse sand (Table 3.1). In each case the test duration was 1 hour. Aerosol particle sizes were analyzed from the top of the column at 0 s, 2 min, 5 min, 10 min, 30 min, and 1 hr after aerosol injection was initiated.

3.1.2.2.2 Column Water Contents

Liquid content along columns were determined following injection of water aerosols during preliminary 1.5-m column tests. These tests included variations with different aerosolizer blocks operated under various GFR and LFR operating conditions. Results from all preliminary experiments were characterized by high water content near the end of the column where injection occurred with no measureable water content throughout the rest of the column. This differed significantly from distribution of soybean oil after it was injected as an aerosol (Figure 3.3). The observed water content
distribution was inferred to result from rapid deposition of large aerosols where they entered the column, and evaporation of the smaller fraction of aerosols within the column itself.

![Liquid Content Distribution](image.png)

**Figure 3.3**- Typical soybean oil and water liquid content distributions after 5 hours of injection during preliminary tests.

Sets of “extreme” water aerosol column tests were designed with the goal of achieving measurable water content values along the column away from the point of injection. These tests involved modifying the aerosol generation and delivery processes in attempts to decrease evaporation rates, average particle size, and particle concentrations of water aerosols delivered to the column.

Procedures designed to decrease evaporation included using Low GFR-High LFR settings (High LFR = 8 $\text{ml/min}$), and adding ice to the water in the humidifying column and aerosolizer water supply container (Figure 3.4). Two Block 3-5 aerosolizers were also installed in-line before the Block 3-3 aerosolizer with the intention of increasing the water content in the carrier gas before aerosolization (Figure 3.4). In-line installation
limited the GFR to the Block 3-5 aerosolizers to the Block 3-3 Low GFR setting (Table 2.1), but a High LFR was delivered to each block. Overflow water was allowed to accumulate in 2-inch PVC pipes installed between the aerosolizers (Figure 3.4). All methods designed to decrease evaporation were implemented for each extreme case test. Variations of extreme case tests involved methods designed to decrease average aerosol particle size and/or particle concentration within the gas stream. Impact plates were installed at different distances from the aerosolizer outlet in order to achieve this (Figure 3.4). Another method involved installing a 6-inch-long, 2-inch-PVC pipe nipple containing a 1-inch-thick layer of sand at the base of the column. The sand was intended to serve as a filter for larger particles prior to the aerosols entering the column proper (Figure 3.4). Extreme type tests each involved three hours of aerosol injection through columns filled with Medium sand.

Figure 3.4- Design components implemented to decrease evaporation and average particle size during extreme case 1.5-m water aerosol column tests.
3.1.2.3 Salt Water Tests

Results from 1-inch-Column Tests showed significant increases in the number of particles that penetrated 1 inch of sand when injecting aerosolized salt water as opposed to aerosolized fresh water. Variations of 1.5-m-Column Tests were designed to characterize salt water aerosol particle transport over longer distances (Column Particle Distributions), and to determine liquid/salt contents that could be achieved during salt water aerosol deposition (Column Liquid/Salt Contents).

3.1.2.3.1 Column Particle Distributions

Salt water aerosol Column Particle Distribution Tests were conducted by injecting through Medium sand-filled columns. Aerosols were created from 200 g/L salt water solution. The aerosols were injected into the bottom of the column for 3 hours, and the particle analyzer was used to take samples at ports located 6 cm, 0.75 m, and at the top of the column (1.5 m) at 0 s, 20 min, 1hr, 2hr, and 3 hr after aerosol injection was initialized. A similar test was conducted using fresh water for comparison purposes; however, the fresh water experiment was terminated at 1 hour due to non-registry of aerosol particles at the top of the column.

3.1.2.3.2 Column Liquid/Salt Contents

Column Liquid/Salt Content Tests were designed to determine distributions along the column resulting from salt water aerosol injection. The column was filled with Medium sand and aerosols were generated using 200 g/L salt water (Same parameters used during Particle Distribution Tests). Aerosols were injected into the bottom of the
column for 2 hours. Liquid water and salt contents along the column were measured upon completion of the test.

Alternative salt water aerosol injection tests were conducted to determine how water content affects salt deposition rates, and involved using columns filled with pre-wetted sand. A container holding the sand was filled with water. The sand was scooped out of this container using a sieve with a 1.68 mm mesh screen, water was shaken out of the sand for approximately 10 seconds, and then the sand was placed into the column. Upon filling the column the top was capped to prevent evaporation, and water was allowed to drain through the screen at the bottom of the column for 24 hours. This procedure was intended to create moist sand at water contents defined by gravity drainage. Three different salt water aerosol injection tests were completed using initially wet sand. The tests differed based on duration (1, 2, and 3 hours). Liquid water and salt concentrations were determined from sand samples upon test completion.

3.1.2.4 Oil Tests

These tests were designed to determine the effects of injection duration and sand grain size on resulting soybean oil contents along the column. Sets of tests were completed using columns filled with Fine sand or Medium sand, each set included 2-hour-long and a 5-hour-long injection duration tests.
3.2 Results

3.2.1 1-inch-Column Tests

3.2.1.1 Block, GFR, LFR Variations

The total number of counted particles decreased and the particle size distribution shifted toward the smaller end of the scale when the experimental conditions were changed to include flow through a 1-inch-thick layer of sand (Figure 3.5-3.7). In many cases the number of particles counted for smaller particle sizes are greater than the number of particles counted in the unfiltered case (the same experiment without the sand layer). The most extreme examples of this occurred for Low GFR tests conducted with Block 3-3 aerosolizers (Figure 3.5A,B).

The Low GFR Block 3-3 tests registered the largest column in place particle counts of the configurations tested (Figure 3.5A,B). The early sampling events (0 sec, 30 sec) produced relatively small particle counts for both tests. However, particle counts increased to maximums at the 3-5 minute samples, and then decreased as evidenced by 10 minute distributions (Figure 3.5A,B). By contrast, the High GFR Block 3-3 tests produced smaller particle counts with the column in place (Figure 3.5C,D). The Low LFR setting particle counts started relatively high and decreased consistently with time (Figure 3.5C), however, the High LFR setting (Figure 3.5D) produced an increasing-decreasing pattern similar to that observed for Low GFR tests (Figure 3.5A,B).
Figure 3.5 - Block, GFR, LFR variation particle count vs. particle size measurements for Block 3-3 and 3-5 tests.
Figure 3.6- Block, GFR, LFR variation particle count vs. particle size measurements for Block 5-5 and 3-7 tests.
Figure 3.7- Block, GFR, LFR variation particle count vs. particle size measurements for Block 5-7 and 7-7 tests.
Aerosolizer blocks with 0.05 and 0.07 inch diameter gas orifices (3-5, 5-5, 3-7, 5-7, and 7-7) all produced column in place particle counts that were relatively small (Figures 3.5E-H, 3.6, and 3.7). Similar transient trends in particle distribution measurements occurred during these tests, with the largest particle counts measured early and decreases in counts as the tests continued (Figures 3.5E-H, 3.6, and 3.7). The particle count distributions are similar, however, blocks with 0.05 inch gas orifices (3-5, 5-5)(Figures 3.5E-H and 3.6A-D) tended to produce slightly larger particle counts than blocks with 0.07 in gas orifices (3-7, 5-7, 7-7)(Figures 3.6E,F and 3.7) with the column in place. The High GFR setting for the 3, 5, 7-7 blocks produced a flow velocity great enough to disrupt the sand within the 1-inch-column, therefore, only Low GFR settings were used for these tests (Figures 3.6E,F and 3.7).

Increasing the transport distance before deposition would be beneficial for effective field-scale implementation. Greater numbers of aerosol particles exiting 1-inch of sand for prolonged periods of time indicates greater transportability. Based on this line of reasoning and results from Block, GFR, LFR Variation Tests, it was decided that all subsequent column tests should be conducted using Block 3-3 aerosolizers.

3.2.1.2 Sand Size and Impact Plate Variations

Emplacing the column caused the average particle size measured to shift toward the smaller end of the scale and a reduction in the total number of particles measured for all Fine and Medium sand tests (Figures 3.8, 3.9), whereas the average particle size and ultimate total particles measured remained comparatively consistent when using Coarse sand (Figure 3.10). No plate tests that included High GFR variations (Figures 3.8C,D and
3.9C,D) revealed a tendency for total particles exiting the sand to decrease as GFR increases. The initially increasing then decreasing particle count patterns observed during Block, GFR, LFR Variation Tests(Figure 3.8A,B) occurred during some Sand Size and Impact Plate Variation Tests.

Use of an impact during Fine sand experiments caused a slight shift toward smaller particles for the unfiltered distribution while also causing a significant increase in the number of penetrating particles during testing (Figure 3.8E,F). In both examples (Low LFR, High LFR) the maximum particle counts measured with the column in place were similar to the number of particles measured in unfiltered aerosols (Figure 3.8E,F). Particle counts increased and then decreased during the Low LFR test (Figure 3.8E), whereas particle counts continuously increased throughout the 10-minute duration during the High LFR test (Figure 3.8F). By contrast, use of an impact plate during Medium sand tests had minimal effect on resulting penetrating particle counts (Figure 3.9E,F); however, the number of penetrating particles during no plate, Fine sand tests was less than for Medium sand tests (Figure 3.8E,F and 3.9E,F).

Only Low GFR-Low LFR settings were used during tests involving Coarse sand (Figure 3.10). The patterns observed for tests with and without a plate are similar. The number of particles measured in the unfiltered case and at each time interval are decreased with the plate in place, however, the number of particles penetrating the sand increases with time and approaches the unfiltered particle distribution in both cases (Figure 3.10).
Figure 3.8 - Sand and Plate Variation particle count vs. particle size measurements at different times when testing Block 3-3 aerosolizers with Fine sand.
Figure 3.9- Sand and Plate Variation particle count vs. particle size measurements at different times when testing Block 3-3 aerosolizers with Medium sand.
Coarse Sand

Low GFR

3.2.1.3 Water Surface Interaction Tests

3.2.1.3.1 Oily Sand

The number of particles that penetrate 1 inch of sand is consistently increased when the sand grains are coated in oil (Figure 3.11) compared to when dry sand was used (Figure 3.9A,B,E, and F). The Low LFR, oily sand, column-in-place particle counts were similar to those from unfiltered measurements throughout the duration of the tests (Figure 3.11A,C). Column-in-place particle distributions measured during tests with an impact
plate were basically identical to the unfiltered distribution (Figure 3.11C). The column in place particle distributions measured when using an impact plate tended to shift toward smaller particle sizes with time (Figure 3.11A).

Increasing LFR to the aerosolizer caused a decrease in particle counts during early injection (Figure 3.11B,D). Particle counts increased throughout the 10-minute-duration when no impact plate was used (Figure 3.11B). Particle counts increased and then decreased to match the unfiltered distribution when an impact plate was used (Figure 3.11D). These behaviors are significantly different than those from dry sand tests, in which all distributions showed extreme shifting and particle counts were relatively small during the beginning and end of the tests (Figure 3.9A,B,E, and F).

**Figure 3.11**- Results from Block 3-3, Low GFR tests using oily Medium sized sand. The “compare” tags make reference to similar tests conducted with dry sand.
3.2.1.3.2 Salt Water

The shape of particle size distributions measured for unfiltered saltwater aerosols differ from those measured for fresh water aerosols. The maximum particle counts for unfiltered fresh water aerosol particle distributions always occur at the smallest measurable particle size (Figure 3.12A). By contrast, the maximums for salt water aerosol distributions fall within the size range of 2 to 5 microns (Figure 3.12B-D), which is similar to the distributions measured during soybean oil Block Characterization Tests (Figure 2.19). The shapes of the unfiltered aerosol particle distributions also differed based on salt concentration, with the maximum particle count decreasing and peak particle size increasing as salt content increased (Figure 3.12B-D). This effect is fairly subtle in the 25 and 100 g/L tests, but is more apparent when salt concentration is increased to 300 g/L (Figure 3.12B-D).

The numbers of particles that penetrate through the sand are significantly greater during salt water tests. All three salt water tests showed shifts toward smaller size particles and increases in the number of smaller particles once the columns were in place. However, the transient behaviors of the particle distributions were not consistent. Particle counts during the 25 g/L test started relatively low and increase with test duration, the 100 g/L test distributions started high and decreased with test duration, and the 300 g/L results stayed relatively consistent throughout the test (Figure 3.12B-D).

2-hour-long tests were conducted to characterize behaviors over longer injection durations (Figure 3.13). Fresh water was used in one test, and 200 g/L salt water was used for the other. The 200 g/L salt content value was not used during salt concentration
Figure 3.12- Results from 10-minute, 1-inch column tests conducted using fresh water and different salt concentrations.
aerosol tests (Figure 3.12). 200 g/l was selected because a relatively high salt concentration was desired and 300 g/L caused problems with precipitation that clogged the inlet of the particle analyzer during sampling.

The particle counts of sand-penetrating fresh water aerosols were greatest at the beginning of the test, but decreased to approximately zero within 30 minutes (Figure 3.13A). By contrast, penetration of particles in large numbers was detected throughout the duration of the salt water test (Figure 3.13B). Particle counts increased and particle sizes decreased during the first hour of the salt water test, followed by a decrease in the number of penetrating particles between 1 and 2 hours (Figure 3.13B).

Aerosol deposition was characterized by monitoring liquid and/or solid mass accumulation within the columns. The columns were weighed at time intervals throughout the test duration to determine mass change (Figure 3.14). Injection of fresh water aerosols caused an accumulation of 6.94 g in 2 hours, and injection of salt water caused an accumulation of 4.38 g. The total mass loss from the liquid reservoir during aerosolization was 35 ml for fresh water and 22 ml for salt water. The total mass accumulation observed for fresh water is larger than for salt water, however, the accumulation totals account for ~0.2 of the total liquid aerosolized in each case. The trends of the curves are also similar; suggesting comparable deposition behaviors for liquid aerosols produced using fresh and salt water (Figure 3.14).

The effect of sand size on the transportability of salt water aerosols was characterized with 10-minute-long, 1-inch-Column Tests with Fine and Medium sand (Figure 3.15). Particle sizes measured with the column in place tend to be smaller than
unfiltered measurements for both cases, but the number of particles measured when using Fine sand (Figure 3.15A) are less than those measured when using Medium sand (Figure 3.15B). These tendencies are similar, but less extreme than those that occurred when using fresh water (Figures 3.8B and 3.9B).

**Figure 3.13**- Particle distributions measured during 2-hour, 1-inch column tests when injecting fresh water and salt water aerosols (notice different y axis ranges).

**Figure 3.14**- Column mass change due to aerosol deposition during 2-hour, 1-inch, Medium sand tests with fresh water and salt water.

**Measured Water Loss**

- Fresh- 35 ml
- Salt- 22 ml
Figure 3.15 - Particle distributions measured during salt water aerosol, 1-inch column tests involving injection through A) Fine sand and B) Medium sand. “compare” tags make reference to similar tests conducted with fresh water.

3.2.1.4 Soybean Oil Tests

The transient particle distribution patterns are similar for all Medium sand-No plate tests regardless of the GFR and/or LFR settings (Figure 3.16A-D). The pattern involves an increase in number and decrease in size of particles in comparison to those measured with the column in place. Some tests produced indication of particle count decreases towards the end of the injection event (Figure 3.16B-D); however, systematic changes in penetrating particle distributions are not otherwise apparent in results from these tests (Figure 3.16A-D). A larger percentage of particles penetrate the sand when using soybean oil (Figure 3.16A-D) as compared to when using water and the same aerosolizer operating conditions (Figure 3.5A-D).

The Low LFR, Medium sand tests were repeated with an impact plate installed (Figure 3.16E,F). The effects of the impact plate are decreases in the number and size of
<table>
<thead>
<tr>
<th>Condition</th>
<th>LFR</th>
<th>Particle Size</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low GFR Med Sand-No Plate</td>
<td>4 ml/min</td>
<td>(micron)</td>
<td></td>
</tr>
<tr>
<td>High GFR Med Sand-Plate</td>
<td>4 ml/min</td>
<td>(micron)</td>
<td></td>
</tr>
<tr>
<td>Fine Sand-Plate</td>
<td>4 ml/min</td>
<td>(micron)</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.16** - Particle count vs. particle size measurements at different times when injecting soybean oil aerosols through 1-inch of sand under different aerosolizer operating conditions.
particles in the unfiltered and column in place samples. Besides a general decrease in particle counts, the overall penetration behaviors are similar to the no plate results (Figure 3.16A-C). One slight exception is that particle distributions from early time samples (up to 1 min) shift toward the larger size range, a pattern that resulted in a bimodal distribution during the High GFR test (Figure 3.16F).

Impact plate tests were also completed using Fine sand (Figure 3.16G,H). Increases in particle count and decreases in particle size resulted from emplacement of the column (Figure 3.16G,H), which is similar to what occurred during other soybean oil tests (Figure 3.16A-F). However, the decrease in sand size caused a more extreme shift toward the smaller particle size end of the scale (Figure 3.16G,H), with the peak position only slightly larger than the smallest detectable particle size. Particle counts increased slightly with test duration during the Low GFR test while the High GFR results were consistent throughout. An exception is the 0 second distribution that seems to represent a transition between the unfiltered and column in place results (Figure 3.16H).

3.2.2 1.5-meter-Column Tests

3.2.2.1 Empty Column Tests

There was an immediate decrease in average aerosol particle size as fresh water aerosols flowed into the empty column through the mesh (Figure 3.17A, 6cm). The particle counts for water aerosols continued to decrease as measurements were taken along the column up to a distance of 1.5 m. Decreases between subsequent measurements
were relatively large up to a distance of 1 m, however, the 1 m and 1.5 m distributions were similar (Figure 3.17A).

A comparatively slight shift toward smaller particle sizes occurred as salt water and soybean oil aerosols entered through the screen into the column (Figure 3.17B,C). The systematic decrease in particle count measured for fresh water aerosols along the column did not occur for these liquids. There was some indication of particle size and count decrease towards the top of the column, but the overall magnitude of the decrease for salt water and soybean oil aerosols were small relative to that of water aerosols (Figure 3.17A,B,C).

### 3.2.2.2 Water Tests

#### 3.2.2.2.1 Sand Size Effects

Regardless of sand size, the water aerosol particles measured at the top of the 1.5 m, sand-filled column consisted of only the smallest detectable particle sizes during Sand Size Effect Tests (Figure 3.18). This condition results in plots with steep peaks at ~0.95 microns and most measured particles falling within a 0.4 micron range (Figure 3.18). This range represents 8 particle size data intervals as provided by the particle analyzer.

The peaks measured are centered around the same particle size in every case, however, the number of particles arriving within this size range differed based on sand grain size. The largest numbers of particles were observed during the Coarse sand test, and particle counts decreased as sand grain size decreased (Figure 3.18). The particle size distribution plots are also characterized by a sloped region, or long tail, in the particle
Figure 3.17- Particle size distributions measured along empty columns while injecting fresh water, salt water, and soybean oil aerosols.
**Figure 3.18** - Particle distributions at top of a 1.5 meter column during injection through Coarse, Medium, and Fine sand. (Notice small x-axis range)

**Figure 3.19** - Comparison of the unfiltered aerosol particle distribution and the maximum particle penetration measured at the top of the column for Coarse, Medium, and Fine grained sand tests (Figure 3.12).
size range larger than the mode. These tails are more prominent for the Coarse sand test
and diminish as sand grain size decreases (Figure 3.18).

The overall transient behavior is characterized by small particle counts at the start
of the test, and then a rapid increase in particle counts during early times (2-5
minutes)(Figure 3.18). Particle counts then systematically decreased during the remainder
of the tests (Figure 3.18). Regardless of sand grain size, the particles measured at the top
of the column were only a small portion of the aerosols that were injected into the
bottom. This can be visualized by plotting the unfiltered aerosol distribution with the
largest particle number measurements from each test (Figure 3.19).

3.2.2.2.2 Column Water Contents

Three different Extreme Water Test variations produced measurable water
contents along the 1.5-meter-columns. These variations included installation of an impact
plate at 1 cm and 2 cm from the aerosolizer outlet (Figure 3.4). The third variation did not
use an impact plate, but involved installation of a sand filter at the base of the column
(Figure 3.4). The filters contained Medium sand, and were swapped out new every 10
minutes during the three-hour-long test.

Water contents along the column were similar for the three extreme case test
variations, with most values between 0.1 and 0.2 $\text{kg} / \text{kg}$ (Figure 3.20). Some increase in
water accumulation near the point of injection (0 m) was observable for all three tests;
however, accumulation was much greater for the 2 cm plate experiment as compared to
the 1 cm plate and filter experiments (Figure 3.20).
3.2.2.3 Salt Water Tests

3.2.2.3.1 Column Particle Distributions

Column Particle Distribution Tests were conducted with fresh water and saltwater. These tests involved particle sampling at 6 cm, 0.75 m, and 1.5 m, as opposed to only 1.5 m as was the case with fresh water Sand Size Effect Tests (Figure 3.18). The results show relatively large numbers of fresh water aerosol particles reaching 6 cm, and intermediate numbers reaching 0.75 m into the column early in the test (<10 min)(Figure 3.21). However, the particle distribution was roughly steady within the column after one hour of injection (Figure 3.21). Aerosols exhausting from the top of the column were never visible during the fresh water test.

Figure 3.20- Liquid content as a function of distance during Extreme case tests.
Figure 3.21- Particle distributions measured at 3 points along a 1.5 meter column while injecting fresh water and salt water aerosols.
Time zero measurements were made during the salt water experiment. For each monitoring port the time zero measurements consisted of large particle sizes and small particle counts as compared to measurements at other times (Figure 3.21). The 20 minute samples represented particle count maximums at the 6 cm and 0.75 m ports, where decreases in particle counts occurred throughout the remainder of the test. By contrast, particle counts measured at the top of the column increased for subsequent measurements up to 2 hours before then decreasing (Figure 3.21). The numbers of particles measured along the column decreased with distance, as was the case during the fresh water experiment. However, the numbers of particles within the column are significantly larger than those observed during the fresh water test (Figure 3.21). Aerosols exhausting from the top of the column were plainly visible throughout the duration of the salt water test.

3.2.2.3.2 Column Liquid/Salt Contents

Injection of salt water aerosols into a 1.5-m-tall, sand-filled column resulted in a liquid content distribution that was typical of tests conducted using fresh water. This distribution is characterized by large water content near the point of injection and effectively zero water content along the rest of the column (Figure 3.22). However, salt content changed along the entire length of the column, even though the change in water content was undetectable (Figure 3.22).

A column filled with pre-wetted and drained sand was sampled to obtain an initial water distribution for wet sand tests. The initial water distribution is plotted along with resulting liquid contents from 1, 2, and 3 hour wet sand and the 2 hour fresh water dry sand tests for comparison purposes (Figure 3.23). The initial water content for the wet
Figure 3.22- Liquid and salt contents measured along a column following a 2 hours of salt water aerosol injection.

Figure 3.23- Liquid contents measured along column after salt water aerosol injection through initially dry and initially wet sand.
sand tests was approximately 40 g/kg at the screen, decreased within the first 0.4 m of the column, and was 18 to 20 g/kg over the remaining length (Figure 3.23). Injection of salt water aerosols for one hour resulted in a water content decrease over the bottom half of the column and an increase in water content in the top half of the column (Figure 3.23). Water contents then decrease along the entire length of the column during the remainder of the test (Figure 3.23). These results reveal a transient behavior that involves water content near the inlet screen remaining high while water content along the rest of the column decreases starting from the bottom and going up (Figure 3.23). The water content results from wet sand tests actually approach the typical water content results from dry sand tests as injection duration continues (Figure 3.23).

Salt contents along the columns increased with injection duration during wet sand tests (Figure 3.24). Salt concentration was greatest near the point of injection and decreased along the column; however, deposition along the entire length of the column continued up to 3 hours of injection duration (Figure 3.24). Salt content results from the 2-hour dry sand test display a similar distribution to that observed for the wet sand test conducted for the same duration (Figure 3.24).

It appears that the salt was deposited and the carrier water evaporated when salt water was used to create aerosols. The water content that would have been required to deposit the observed salt mass was determined as the product of the observed salt concentration in the sand (Fig. 3.24) divided by the concentration of the salt initially in the water (200 g/L). These results (Fig. 3.25) indicate that the concentration of the water was greater than 4 g/kg on the upstream end of the column, and it decreased to 1 g/kg to
Figure 3.24- Salt contents measured along column after salt water aerosol injection through initially dry and initially wet sand.

Figure 3.25- Greatest actual liquid water distribution realized during water aerosol injection (Figure 3.13) and the estimated liquid content required to achieve maximum salt contents realized during salt water injection (Figure 3.17).
1.5 g/kg in the downstream half of the column (Fig 3.25). By comparison, the concentrations of water observed in the sand were less than 10% of these values.

Salt contents along the column are measured as grams of salt per kg of sand, and Medium sand packs into the column at a rate of 3.4 kg/m. This data was used to integrate along the length of the column to obtain the total mass of deposited salt (Table 3.2). The salt water aerosolized during each experiment contained 200 g/L NaCl, and the total volume of salt water lost during aerosolization was measured. Therefore, the total mass of salt aerosolized during each experiment could also be calculated (Table 3.2). The difference between the total salt aerosolized and the total salt deposited represents the mass of salt that exhausted out of the top of the columns during testing. The mass of total salt that was transported 1.5 m through Medium sand and out of the column during the Salt Water Column Tests ranged between 51% and 62% of the total injected mass (Table 3.2). Aerosols leaving the top of the column were observed during all salt water aerosol injection tests, and it appears that roughly half of the injected salt left the column.

<table>
<thead>
<tr>
<th>Sand</th>
<th>Duration</th>
<th>Salt Water Aerosolized</th>
<th>Salt Aerosolized</th>
<th>Column Salt Content</th>
<th>Salt Deposited</th>
<th>Salt Exhausted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>2 Hr</td>
<td>33 ml</td>
<td>6.6 g</td>
<td>3.0 g</td>
<td>45%</td>
<td>55%</td>
</tr>
<tr>
<td>Wet</td>
<td>1 Hr</td>
<td>12 ml</td>
<td>2.4 g</td>
<td>1.2 g</td>
<td>49%</td>
<td>51%</td>
</tr>
<tr>
<td>Wet</td>
<td>2 Hr</td>
<td>30 ml</td>
<td>6.0 g</td>
<td>2.9 g</td>
<td>48%</td>
<td>52%</td>
</tr>
<tr>
<td>Wet</td>
<td>3 Hr</td>
<td>45 ml</td>
<td>9.0 g</td>
<td>3.5 g</td>
<td>38%</td>
<td>62%</td>
</tr>
</tbody>
</table>

**Table 3.2**- Salt aerosolized and deposition during Liquid/Salt Content tests.
3.2.2.4 Oil Tests

Resulting liquid mass contents along Fine and Medium sand-filled columns were determined after injection of soybean oil aerosols for 2 and 5 hour durations. The oil distributions achieved after 2 hours of injection into Fine and Medium sand are similar (Figure 3.26). Both had mass contents of approximately 3.9 $g/kg$ at 6 cm, and a fairly linear decrease with distance to approximately 2 $g/kg$ at the end of the column (Figure 3.26). Mass content along the column increased with injection duration for both sand types. Both 5-hour test results covered approximately the same range of oil content over most of the columns (approx. 4 to 8 $g/kg$), however, the shapes of the curves differed (Figure 3.26). The 5-hour, Medium sand plots retained the fairly linear decreasing pattern observed in both 2-hour test results, whereas the Fine sand plot is characterized by spikes at the beginning and end of the column (Figure 3.26). Total oil mass in the columns was not determined because samples of high oil content at the inlet of the column were not taken.

Oil content values from the 2 hour tests (Figure 3.26) are similar to the equivalent water contents from salt water injection tests (Figure 3.25). Salt accumulation is assumed to occur due to deposition of solid aerosols. Therefore, similarities between oil and saltwater tests indicate that oil aerosols transport behavior is more similar to that of solids as opposed to liquid water. This could result because of the hydrophilic interaction that is present with water aerosols, but is lacking with oil and solid aerosols.
Figure 3.26- Oil content distributions measured following soybean oil aerosol injection through Fine and Medium sand.

3.3 Discussion

The effectiveness of aerosol delivery during field application will depend on transport distances of aerosol particles before deposition (transportability). Inferences pertaining to transportability for column tests are based on comparisons between particle analyzer data sets collected during injection and/or mass deposition measured along the column following injection. Particle size distribution measurements taken during column tests were used to characterize transient changes (same point sampled at different times) or to characterize changes over transport distance (samples taken along column at same time). In either case, particle deposition would be indicated by a decrease in number of particles and decrease in average particle size.

Deductions of deposition behaviors can consistently be made based on particle analyzer data. However, an understanding of particle analyzer operation is required during interpretation. For instance, measured particle size distributions indicate that water
aerosol particle concentrations are impacted while passing through thin, stainless steel, mesh screens (Figure 3.1). The change in particle distribution data is a function of mesh size, as fining the mesh decreases the open cross-sectional area through which the aerosols can flow. Deposition on the screen resulted in a particle size distribution shifted toward the smaller end of the scale as compared to the unfiltered data (Figure 3.1). This effect is expected based on the assumption that larger particles deposit at a higher rate than smaller particles. However, this does not explain the increases in the number of small particles measured in aerosols above the screen (Figure 3.1).

The changes in particle distributions measured during screen tests were similar to those observed during dilution tests (Figure 2.10). These changes do not necessarily include a decrease in overall number of particles measured, however, counts for larger particles are decreased and counts for smaller particles and increased. This presentation is assumed to be caused by preferential deposition of larger particles and/or an increase in particle analyzer sensitivity to smaller particles as larger particles are removed or aerosol concentration is diluted (Figures 2.10 and 3.1).

3.3.1 1-inch-Column Tests

3.3.1.1 Block, GFR, LFR Variations

The quantity and size distribution of measurable aerosol particles exiting the 1-inch sand pack varies widely for different aerosolizer block-operating condition combinations (Figures 3.5-3.7). The number of penetrating particles tended to be a function of gas orifice size, with penetration increasing as gas orifice size decreased.
Penetration was also greater during Low GFR tests as compared to High GFR tests for individual blocks (Figures 3.5-3.7). These results indicate that aerosol transportability through the column is strongly dependent on the volumetric gas flow rate that is used to feed the aerosolizers.

Increases in gas mass flow rate would increase evaporative losses; however, during 1-inch-Column Tests the subsequent measurements are made at basically the same point along the aerosol flow path (only differ by 1-inch). Considering the gas flow velocity and residence time within the column, evaporative effects during 1-inch-Column Tests was assumed to be negligible. Increasing gas volumetric flow rate increases gas flow velocities through the sand. Individual aerosol particles are more likely to deposit due to inertial impact as velocity increases. It is suspected that aerosol penetration trends observed in these tests result due to gas flow velocity influences on deposition behavior (Figures 3.5-3.7).

The largest particle counts measured for most Block, GFR, LFR Variation Tests were for early injection times, and particle counts typically decreased systematically as injection continued (Figure 3.5C-E-H, 3.6, and 3.7). However, tests representing more favorable conditions for aerosol penetration produced a different behavior. This behavior is characterized by fewer particles penetrating early, an increase in particle penetration up to approximately 5 minutes, followed by a decrease (Figure 3.5A,B, and D).

It is assumed that the low aerosol particle counts during the early portions of these tests occur because the majority of the particles are depositing upstream from the sampling port. Increasing particle penetration rates with time indicated that particle
deposition rates were decreasing, which is attributable to increases in water saturation due to previous deposition. The sand was dried prior to testing, and water particles seem to have a stronger affinity for the completely dry sand as compared to slightly wet sand. Aerosol penetration decreases after a maximum has been reached. This is most likely due to increasing liquid saturation resulting from aerosol deposition. Increases in liquid saturation cause decreases in effective porosity, which would cause an increase in particle deposition rates.

### 3.3.1.2 Sand Size and Impact Plate Variations

Decreasing sand size should increase aerosol deposition rates. This response was observed in Sand Size test results, and is especially evident in the no-plate results (Figures 3.8-3.10). As compared to the unfiltered distributions, the number of penetrating particles increases from Fine (Figure 3.8A-D) to Medium (Figure 3.9A-D) to Coarse sand tests (Figure 3.10A). The Coarse grained example is unique in that, while it exhibits constant increase in penetrating particles, the size distribution does not shift toward the smaller end of the scale with time (Figure 3.10A). This difference is likely attributable to a condition where the majority of particles across the entire size scale are penetrating the sand, as opposed to only smaller particles. Lack of preferential removal of larger particles results in measured particle distributions that differ from the typical “diluted” type patterns that are observed in other tests.

Impact plates decrease average aerosol particle size by preferentially removing larger particles from the flow stream, which should cause a decrease in particle deposition rates. In general, this behavior is observed in test data. The effect was more
prominent during Fine sand tests than during Medium or Coarse sand tests (Figure 3.9E,F and Figure 3.10B), however, use of a plate significantly increased aerosol penetration when Fine sand is used (Figure 3.8E,F). Aerosol particle deposition rates should increase as the average pore throat to particle diameter ratio decreases, and the pore throat diameters for the Fine sand must have values that fall within a range that makes a physical difference.

### 3.3.1.3 Oily Sand

Coating sand grains with soybean oil made a significant difference in results obtained during 1-inch-Column Tests. There was an overall increase in the number of aerosol particles measured for all times for each test (Figure 3.11). Shifts toward the smaller end of the particle scale that are observed in dry sand tests are also decreased or absent from oily sand data. Lack of shift also indicates that more of the original particles are penetrating the sand, as the shifts are partially explained by “dilution” effects and particle analyzer operation. An extreme case is presented by Low LFR-Plate test data in which column-in-place data never deviated significantly from the unfiltered example (Figure 3.11). Zero deviation would indicate that no measurable aerosol deposition was occurring in the column, allowing all particles to penetrate.

The aerosol particle distributions and gas flow rates entering the columns were the same for oily sand and dry sand tests. Therefore, the apparent decreases in particle deposition rates should only have occurred if the tendency of individual particles to impact solid surfaces was decreased, or the tendency to stick to the surface following impact was decreased. It is unlikely that the presence of soybean oil would decrease the
likelihood of particle impact, unless soybean oil affects the electrostatic properties of grain surfaces. The presence of soybean oil actually decreases the effective porosity of the sand, which should increase deposition. It is more likely that a thin layer of soybean oil alters the grain surfaces from hydrophilic to hydrophobic; creating a surface that some aqueous particles will bounce off of without sticking.

### 3.3.1.4 Salt Water Aerosolization

Using salt (NaCl) water to generate aerosols made a significant difference in results obtained during 1-inch-Column Tests (Figure 3.12). One of the more noticeable differences is that the particle distribution peaks are shifted away from the smallest measurable particle size when salt is added, which is similar to the distributions produced during soybean oil aerosolization (Figure 3.16). Aerosol distribution peaks typically occur at the smallest measurable particle size when using fresh water aerosols. Interpretation of Block Characterization Test results was based on an assumption that this was due to evaporation, and that the actual distributions would resemble those for soybean oil, which are not affected by evaporation.

The salt water aerosol distributions provide further indications of evaporative effects. Addition of salt decreases the vapor pressure of the solution, which presumably could decrease evaporation rates. This could result in production of aerosol particle size distributions that are more representative of the “actual” distributions that would be produced in the absence of evaporation. This does not explain the deposition behavior differences observed between fresh and salt water. Larger average particle sizes and greater numbers of particles are measured when using salt water, yet a larger majority of
these particles transport successfully through the sand (Figure 3.12). It is more likely that aerosol particle evaporation is taking place. Salt crystals would precipitate and remain entrained within the aerosol carrier gas as salt water aerosol particles evaporated. The majority of the particles measured during salt water aerosolization tests most likely consist of solid salt crystals. This could explain the decreases in deposition rate, as solid particles would be more likely than liquid particles to bounce off of solid surfaces. Evaporation of water aerosols with higher salt concentrations would also result in larger average solid particle sizes (Figure 3.12).

The total liquid lost during 2-hour-long, 1-inch-Column Test aerosolization was larger for fresh water than for salt water (35 vs. 22 ml) (Figures 3.13-3.14). All test parameters were identical while conducting these tests with the exception of the composition of the liquid aerosolized; therefore, these differences could be attributable to decreased evaporation rates caused by increasing salt content. However, less liquid accumulated within the column during the salt water tests than during fresh water tests, which suggests that fewer liquid particles reached the sand (Figure 3.14). Measurements of liquid loss during aerosolization were made based on the total volume fed to the aerosolizer and resulting accumulation in the liquid overflow reservoir (Figure 2.3). This difference may be due to the settling out of larger particles during salt water aerosolization. These particles may have otherwise remained entrained in the gas flow stream if diameters were decreased by evaporation.

The transportability of salt water aerosols appears to be superior to that of fresh water based on the results of 2-hour tests (Figure 3.13). Evidence of aerosol deposition
can only be observed near the point of injection for the fresh water example (Figure 3.13). This behavior is most likely due to deposition of water particles in the sand near the screen, which subsequently causes a decrease in effective porosity and further increase in particle deposition rates. The column mass change data collected during fresh and salt water testing is similar, indicating that this depositional scenario also takes place when injecting salt water aerosol (Figure 3.14). However, a greater number of particles penetrate the sand when using salt water, which supports the idea that salt water aerosols occur at least partially as solids. Particles measured during salt water tests represent particles that would have completely evaporated during fresh water tests, a condition that would be undetected by the particle analyzer (Figure 3.13).

### 3.3.1.5 Soybean Oil Aerosolization

A greater portion of injected particles penetrate the sand when creating aerosols from soybean oil (Figure 3.16A-D) than when creating aerosols from fresh water (Figure 3.5A-D). Transient changes in particle distributions with the column in place are also smaller or absent from soybean oil data (Figure 3.16A-D). Transient changes in particle distribution curves indicate changes in deposition rates, which occur due to liquid accumulation (changes in effective porosity) from aerosol deposition. This could represent a steady state type of condition where aerosol deposition rates stabilize while overall transportability is unaffected.

Use of an impact plate is presumed to decrease the average size and number of aerosol particles entering the sand column. Decreasing the average particle size of injected aerosols should increase the average distance transported prior to deposition, and
thus increase the ratio of particles that penetrate through the sand. This effect was not observed for Medium sand, impact plate tests (Figure 3.16E,F), nor did it occur for Medium sand, water aerosol tests (Figure 3.9E,F). This further supports the idea that the average pore size of the Medium and Coarse sand are large enough to nullify the effects of aerosol particle size reduction within the injection conditions tested. Reducing average sand size significantly decreased the ratio of penetrating aerosols (Figure 3.9E,F), which should be the case according to aerosol filtration theory.

3.3.2 1.5-Meter-Column Tests

3.3.2.1 Empty Column Test

Results from the Empty Column Tests provide a strong indication that significant water aerosol evaporation takes place over the 1.5-m-length of the column (Figure 3.17). The fresh water particle distributions show a systematic decrease in particle size and count along the length of the column. The largest difference is observed between the unfiltered distribution and the 6 cm measurement (Figure 3.17). Some portion of this difference is due to the 20X20 mesh screen installed at the base of the column, the presence of which has been shown to affect resulting particle distributions (Figure 3.1). Some of the change in particle count along the column is also likely due to aerosol deposition on the interior walls of the 2-inch PVC pipe. The rate of change in particle distributions decreases at around 1m into the column, suggesting that a pseudo-steady state has been reached (Figure 3.17). This would be expected because evaporation along
the column would increase the humidity of the carrier gas and decrease the rate of evaporation.

A dominant evaporative effect with respect to fresh water aerosols is further supported by the fact that particle counts were comparatively unaffected during salt water and soybean oil tests (Figure 3.17B,C). There was indication of a screen effect on salt water and soybean oil aerosols upon entry into the column, however, aerosol deposition on the screen had less impact than was observed for fresh water (Figure 3.17B,C). There are also indications of particle count decrease toward the top of the column, which most likely represent aerosol particle deposition along the inside column surfaces (Figure 3.17B,C).

3.3.2.2 Fresh Water Tests

3.3.2.2.1 Sand Size

Measureable particle distributions reached the top of Fine, Medium, and Coarse sand-filled, 1.5-m-columns during injection of water aerosols (Figure 3.18). The aerosols arriving at the end of the columns were dilute, and only represent a small portion of the aerosols injected (Figure 3.19), however, systematic behaviors can be observed. The number of particles exiting the sand decreases as particle size decreases, and the larger particle size “tails” increase with the grain size (Figure 3.18). These results indicate that coarser-grained sands are more conducive to aerosol transportability, as more particles and larger particles are getting through.
The initial measurements produced relatively small particle counts regardless of sand type used to fill the column (Figure 3.18). This condition could be partly due to the aerosols not yet reaching the end of the column at the beginning of the sampling interval. However, it mimics the early portions of some 1-inch-Column Test results in which particle counts increased with subsequent measurements (Figure 3.5B). A proposed theory for that behavior was that aerosol particles preferentially deposit on the dry sand during the early portion of the test due to a “wetting” phenomena, a condition that is likely responsible for low counts in 0 time measurements for these tests (Figure 3.18).

The results of column experiments involving injection of water aerosols have suggested multiple processes that can account for decreases in particle counts along a column.

1.) **Screen**- Injection through a screen alone causes an effect (Figure 3.1),
2.) **Evaporation**- Occurs during flow along an empty column (Figure 3.17), and
3.) **Deposition**- Injection through sand-filled columns demonstrates the effects of deposition in sand (Figure 3.18).

Plotting results of these tests along with the particle distribution measured for the original aerosol indicates particle loss magnitudes that are attributable to each process (Figure 3.27).

Most of the larger particle (>3 microns) are removed upon initial entry through the screen (Figure 3.27). The majority of the remaining water mass is lost due to evaporation, which leaves a relatively small portion (<1%) of the original aerosolized water for deposition on sand grains (Figure 3.27). Particle size distributions plotted for each sand size represent the maximums measured at the top of the column during sand-filled column tests (Figure 3.18). Particle penetration during these tests decreased with
time to nearly zero at 1 hour, suggesting an increase in deposition rates with time.

Therefore, within an hour of injection initiation the entire area under the blue line would represent deposition regardless of sand grain size (Figure 3.27).

Figure 3.27- Compilation of water aerosol test data and assumed processes that are responsible for aerosol particle counts.

3.3.2.2 Extreme Water Tests

All tests involving water aerosol injection using typical aerosol delivery methods resulted in a large accumulation of water near the point of injection and no measurable water content along the remaining length of the column. This condition is believed to be due to aerosol deposition near the screen and evaporation of water that penetrates into the column. Extreme test variations were attempted to achieve some measurable water
content along the column. Three different variations produced some measurable content (Figure 3.20).

The water contents were fairly evenly distributed along the columns for each test variation, with most values beyond 0.8 m falling between 0.1 and 0.15 g/kg (Figure 3.20). It would be expected that aerosol concentrations would decrease along the column during injection due to deposition, therefore, the rate of deposition and resulting water content would decrease along the column, which was not case during Extreme Water Tests (Figure 3.20). A water content value of approximately 0.1 must have represented a threshold during Extreme Water Tests. This threshold could possibly be a “field capacity” or “minimum water content” type of value, which is a function of gas flow rate, gas humidity, and aerosol concentration used during the tests.

Some preferential water aerosol deposition near the point of injection is evident in all three tests, indicated by high water contents near 0 m (Figure 3.20). The increase is relatively large for the 2 cm plate test as compared to the 1 cm plate and filter tests. This could indicate that the 1 cm plate and filter are effective at eliminating larger particles and/or decreasing the concentration of aerosol particles in the flow stream (Figure 3.20).

3.3.2.3 Salt Water Tests

Particle concentration profiles along the column during injection of fresh water and salt water aerosols are significantly different (Figure 3.21). Some appreciable particle counts were measured near the point of injection during early portions of fresh water tests, but as a whole the fresh water particle counts are negligible as compared to salt water test results (Figure 3.21). Aerosols could not be seen exhausting from the end of
the column when injecting fresh water aerosols; however, such could plainly be seen when using salt water. This observation relates the transport and deposition properties of salt water aerosols more closely to those of soybean oil as opposed to fresh water, as aerosols leaving the top of the column are also visible during soybean oil tests.

The effects of “wetting” can be seen during the early portions of the salt water injection test, and is represented by the relatively low particle counts obtained during 0 time sampling at each port (Figure 3.21). The wetting front takes time to work up the column, as indicated by the still low particle count measured after 20 minutes at the end of the column (Figure 3.21). Particle counts during the salt water injection test began to tail off after reaching a maximum at each port. This behavior would be expected because previous deposition would decrease effective porosity, and thus increase deposition rates. However, the rate of decrease over the three hour injection period is fairly slow, especially as compared to fresh water test results where particle counts at each port decreased to almost nothing within an hour (Figure 3.21).

Two hours of salt water aerosol injection through a dry sand-filled column produced little to no liquid accumulation, however, it did produce salt contents that could be measured over the entire length of the column (Figure 3.22). Tests were conducted using wet sand and 1, 2, and 3 hour injection durations. These tests showed that salt contents were achieved along the column using wet sand and that salt content increases with test duration (Figure 3.24).

The data collected from column tests support the theory that solids comprise a large component of salt water aerosols due to evaporation of aerosol particles and
crystallization of salt. It was assumed that using wet sand would increase salt deposition rate if this were the case, as salt micro-particles would be more likely to “stick” to a wet surface. However, the wet and dry sand 2-hour duration tests produced similar salt content distributions, which suggest that water content does not affect the rate of salt accumulation (Figure 3.24).

Injection of salt water aerosols through wet sand causes a decrease in column water content with time (Figure 3.23). The transient pattern involved a “drying front” that started near the point of injection and progressed through to the top of the column (Figure 3.23). This pattern is indicative of evaporative effects caused by aerosol gas injection, which would cause preferential liquid content decrease near the point of injection during early portions of the test. Initial evaporation along the remainder of the column would be comparatively small due to humidification of the gas early in the column. This process would progress up-column with time, which occurred during testing (Figure 3.23).

Drying of the column indicated that water within the sand was evaporating along with the liquid aerosols present in the gas. This amount of evaporation would limit water accumulation during water aerosol injection into dry sand, which accounts for the typical water content distributions observed for fresh water tests (Figure 3.3). The occurrence of significant evaporation during aerosol injection is further supported by the fact that water saturations required to produce achievable salt contents far exceeds any actual water contents that have been achieved (Figure 3.25). The salt is either being deposited as salt water that then evaporates, or is being deposited as solid particles.
Regardless of how the salt is transported, measurements of salt content and total salt aerosolized suggest that significant percentages are reaching the ends of the 1.5 m columns (Table 3.2). The penetration rates are fairly consistent regardless of test duration and/or whether the sand is wet or dry. Greater than 50% of the salt delivered consistently transports to the end of the column (Table 3.2). These results indicate that maximum potential transport distances could be much greater than 1.5 m, which bodes well for effective field-scale applications.

### 3.3.2.4 Oil Tests

Liquid contents were measured along the entire lengths of 1.5-m-columns following soybean oil injection, the magnitude of which increased with injection duration (Figure 3.26). It is expected that deposition rates should increase as sand grain size decreases; however, the oil content distributions for 2 hour tests into Fine and Medium sand are similar (Figure 3.26). A comparatively large spike in oil content was measured near the point of injection in Fine sand after 5 hours of injection, which does suggest higher deposition rates in this region. But as a whole, results indicate that the effect of porous media grain size on soybean oil aerosol transportability is limited within the range of parameters tested. All soybean oil test results show at least a slight tailing upward in oil content at the ends of the column, which may indicate accumulation due to liquid-phase flow (Figure 3.26).

The oil contents measured along the column could represent reasonable approximations of oil contents that would achievable within a field-scale treatment zone. Successful implementation of different remedial technologies would require achieving
amendment distributions at specific minimal concentrations. As an example, soybean oil could be delivered as an electron donor for enhanced bioremediation. Assuming a porosity of 0.3, bulk sand density of 2.7 g/cm³, complete oxidation of soybean oil with 2.5 g COD/g soybean oil, and absence of competing electron acceptors, the mass content of TCE that could be converted to ethene can be plotted as a function of oil content (Figure 3.28). During column tests an oil saturation corresponding to the complete reduction of 20 g/kg TCE (grams TCE per kg sand) was achieved at 1.5 m from the point of injection after only 30 minutes. After 5 hours of injection the resulting oil content at 1.5 m corresponded to >90 g/kg TCE, which would encompass the majority of contaminant concentrations in vadose zones at contaminated sites. These results suggest that aerosol delivery is capable of achieving appropriate amendment concentrations for enhanced bioremediation under some field conditions.

![Figure 3.28](image)

**Figure 3.28**- Mass content of TCE that can be reductively dechlorinated to ethene based on soybean oil content measured at the top of a 1.5-m-column after different aerosol injection durations.
3.4 Conclusions

Column tests provided results that could be used to characterize aerosol transport behaviors with respect to aerosolizer operating parameters, porous medium properties, and liquid aerosolized. It was assumed that aerosol particle distributions as a function of aerosolizer properties could be predicted by Equation 1-1, and that aerosol transport behaviors would correlate to predictions made by established colloid filtration theory (Equations 1-2 through 1-5). Observed aerosol transport behaviors are consistent with theory, while injection of fresh water, salt water, and soybean oil aerosols revealed consistent tendencies based on aerosol particle composition.

Aerosol delivery application will be more successful when the distance aerosol particles travel before depositing is increased (increased transportability). Interception and gravity settling collection efficiencies increase as aerosol particle size increases (Equations 1-3,1-4), therefore, transportability should increase as aerosol particle size decreases. Particle size of injected aerosols is a function of aerosol operating parameters. Aerosol transportability consistently increased with decreases in liquid and gas orifice sizes (Figures 3.5-3.7). This observation is consistent with predictions made by Equation 1-1, according to which average aerosol particle size decreases with decreases in orifice sizes. Another aspect of aerosolizer operation that can affect average aerosol particle size is an impact plate, the use of which also consistently increased particle transportability (Figures 3.5-3.7). These observations are consistent with predictions made by particle transport theory (Equations 1-2 through 1-5), and suggest that controlling aerosol particle size distribution will be a key factor for successful field application.
Aerosol transportability should increase with decreasing particle size, however, interception collection efficiency is actually a function of particle to formation grain size ratio (Equation 1-3). Therefore, aerosol transportability should also increase as formation grain size increases. A variation of this effect was apparent when injecting aerosols through only a mesh screen, with more particles penetrating the coarse than the fine screen (Figure 3.1). Particle penetration also tended to decrease with sand grain size. This effect was observed when using fresh water (Figure 3.1), salt water (Figure 3.15), and soybean oil (Figure 3.16E-G). Resulting liquid contents suggest that aerosol transportability in sand used for these experiments would be sufficient for field application (Figure 3.26). However, since collection efficiency is a function of aerosol particle to formation grain size ratio, and aerosol particle size distribution cannot be absolutely controlled, then formation grain size could represent a limiting parameter for aerosol delivery application.

Column test results suggest soybean oil aerosols can be transported further than fresh water aerosols. This tendency is observed as greater numbers of particles penetrating sand during 1-inch tests (Figures 3.8-3.10, 3.16), and as greater liquid content away from the point of injection during 1.5-m column tests (Figure 3.3). Oil mass contents appropriate for some field applications were readily achieved at up to 1.5 m from the point of injection (Figure 3.3), and these contents increased linearly with time over the durations tested (Figure 3.28). These results indicate great potential for aerosol delivery applications when using soybean oil in sand formations. Remedial applications
that could benefit include emplacement of sequestration barriers for prevention of vapor intrusion, and delivery of oil-phase electron donor for enhanced bioremediation.

The aerosol particle sizes for salt water occurred within the measurable range for the particle analyzer (2 to 5 micron) (Figure 3.12), which is similar to soybean oil (Figure 3.16). In contrast, water produces smaller aerosols that are at the lowest end of the measurable scale. The transport behaviors for salt water aerosols were also similar to those observed for soybean oil aerosols. These similarities include the number of particles that penetrate sand (Figure 3.12), and mass contents along columns following injection (Figure 3.25). The mass measured along columns following salt water aerosol injection occurs as solid salt, and deposited aerosol particles are assumed to have been solid salt crystals that precipitated from evaporated liquid particles. Generation of solid aerosols using this method presents a potential benefit in that resulting aerosol particle size can be controlled based on solution concentration (Figure 3.12). Ability to transport solids also expands the applicability of aerosol delivery. Injecting aerosols created by inducting powders or by precipitation of solutes could be used for a variety of in situ oxidation and biostimulation applications. Delivery of microbes themselves could also be accomplished assuming that they are capable of surviving for a period in dry air.

Transportability of fresh water aerosols is poor as compared to soybean oil or salt water aerosols. The difference is due in part to greater deposition rates of fresh water aerosols near the point of injection. This tendency can be observed in the form of limited aerosol particle penetration during 1-inch tests (Figure 3.16), and liquid accumulation only near the point of injection during 1.5-m tests (Figure 3.3). The average particle size
measured for fresh water aerosols are smaller than those measured for soybean oil or salt water, therefore, the increase in deposition rates must be due to a mechanism that is not considered in Equations 1-2 and 1-4. The nature of this mechanism is most likely a surface interaction such as water affinity or electrostatic forces. Evidence for surface type reactions are evident in results of tests that involved coating sand grains with soybean oil, where the treatment significantly increased fresh water aerosol penetration (Figure 3.11). Another example is the fact that, under ideal injection conditions, the penetration rate of fresh water aerosols actually increases during early injection times (Figure 3.5A,B), which suggests greater surface affinity for dry as opposed to wet sand.

Surface interactions certainly play a role in fresh water aerosol deposition, however, it has been determined that the more important process affecting mass accumulation rates is evaporation. Particle size distributions measured for fresh water aerosols always have a maximum count value at the smallest end of the measurable range (Figures 3.5-3.7), which represents evidence of evaporative effects before the aerosols even reach the sand-filled columns. Empty column tests have shown that significant evaporation of fresh water aerosols continues to occur over the 1.5 m transport distance (Figure 3.17). Another case of evaporation observed during this research was the drying of initially wetted columns by injection of salt water aerosols (Figure 3.23).

The evaporative effects observed in column test results would eliminate the possibility of achieving liquid accumulation within field-scale formations due to fresh water aerosol injection. Attempts were made to alleviate the effects of evaporation during extreme 1.5-m injection tests. While some improvement was achieved, the liquid contents
along the columns (Figure 3.20) following injection were still small in comparison to soybean oil and salt water tests (Figures 3.25, 3.26). The primary cause of evaporation rates observed during column tests is assumed to be dehumidification of carrier gas due to pressure drop during aerosolization. Therefore, a more efficient means of humidifying the carrier gas and high humidity in the subsurface could possibly improve evaporative effects, but not eliminate them completely.
Chapter 4-Wedge Injection Tests

Wedge Injection Tests were designed to characterize aerosol transport and deposition during radial flow through porous media, which represents the flow geometry that would occur during injection through a well screen under field conditions. These experiments have been termed “wedge tests” because the experimental apparatus is shaped like a wedge (or sector of a circle). The wedge-shaped apparatus is filled with sand during injection tests. Carrier gas and aerosols are injected at the apex of the wedge, flow through the sand, and then exhaust out of the distal end (Figure 4.1). The wedge apparatus was designed to create radial flow paths 2 meters long through the sand.

4.1 Wedge Apparatus

The apparatus was a wedge-shaped box constructed atop a 4 ft X 8 ft sheet of ¾ inch oriented strand board (OSB), which constituted the top of a table (Figure 4.1). A shape matching the dimensions of the wedge was cut from a 1/8 inch-thick sheet of PVC. The wedge-shaped sheet of PVC was glued to the center of the table and served as the bottom surface of the apparatus. The radially oriented sidewalls of the wedge were constructed using 3 inch-tall, ¾ inch-wide PVC rectangles, which were mounted atop the edge of the PVC sheet. The linear contacts between the PVC sheet and the sidewalls were sealed with silicone caulk. The angle between the side walls of the apparatus was 36°, representing 1/10th the circumference of a circle (Figure 4.2).

The lid of the apparatus was cut from a sheet of ¾ inch OSB board, and a sheet of ¼-inch-thick closed-cell rubber foam was adhered to the underside. The rubber foam
Figure 4.1- Apparatus used for wedge tests with the lid and aerosol delivery system in place.

served as a sealing gasket for contacts between the lid and the sidewalls of the wedge, and between the lid and the terminal screen. The rubber foam also served to prevent open voids along gas flow paths by pressing down and conforming to the upper surface of the fill sand.

The lid was secured using 14 lag bolts. The bolts extended through the top of the lid, center of the PVC sidewalls, PVC basal sheet, and the table top. The bolts were emplaced through ¼-inch-diameter holes in the top of the lid and nuts were tightened on the underside of the table top. The distal end of the lid covered the exhaust compartment (Figure 4.4), and a port in the lid was used to divert aerosol-laden gas out of the building.
(Figure 4.1). The exhaust lid was also sealed with closed-cell, foam rubber gaskets, and was held closed using toggle clamps (Figure 4.4).

Figure 4.2- Apparatus filled with sand without the lid installed (looking down).

An aerosol supply system delivered carrier gas and aerosols to the wedge during testing (Figure 4.1). The terminus of the aerosol supply system was a length of 2-inch PVC pipe with a hole cut out of one side. The apex of the apparatus terminated in a vertical, cylindrical cut with a 2.3-inch radius of curvature (matching the outside of a 2-inch PVC pipe). This allowed installation of a closed-cell, foam rubber gasket (Figure 4.3A), which created a gas-tight seal when the PVC pipe was clamped into place (Figure 4.3B). The center of the PVC pipe represented the zero radius point of the wedge (Figure 4.2).
A fine wire mesh screen was mounted between the sidewalls of the wedge at a radial distance of 16 cm (Figure 4.2). This screen served as the inner boundary for the sand-fill, and approximated an effective well screen diameter of 12 inches. Another screen located at a radial distance of 2.16 m served as the outer sand-fill boundary (Figure 4.2). This terminal screen was composed of the same wire mesh; however, it was supported by a 1/8-inch-thick sheet of PVC. There were 13, equally-spaced, 2.5-inch-diameter holes cut across the length of the PVC sheet to allow gas flow out of the sand (Figure 4.4). The gas exited from the sand into an exhaust compartment (Figure 4.2), and finally exited the apparatus through an exhaust port installed through the lid (Figure 4.1).

**Figure 4.3** - A) the gasket at the apex of the wedge apparatus and B) the aerosol delivery system clamped in place.
4.2 Aerosol Supply System

Two different aerosolizer variations were used during wedge tests. One variation is the same design used during Block Characterization Tests and Column Injection Tests. This variation is termed “single” aerosolizer, and was constructed with one set of gas and liquid orifices (Figure 4.5). The other variation is termed a “double” aerosolizer, and was constructed with two sets of liquid and gas orifices (Figure 4.5). During operation the aerosolizer blocks were sandwiched between ¾-inch NPT steel flanges, as was the case during previous tests (Figure 2.2).

An air compressor was used to supply pressurized gas to the inlet side of the aerosolizer housings during operation. The gas flow rates were controlled with pressure regulators and monitored with variable-area flow meters (Figure 4.1). Peristaltic pumps were used to provide and control the liquid flow rates to the aerosolizers. The aerosols flowed from the aerosolizer housing into 3-ft-long sections of 2-inch-PVC that were mounted at 45-degree angles (Figure 4.1). Aerosols flowed downward through this
section, allowing larger aerosol particles and/or unaerosolized liquid to settle out. The V-shaped configuration created by the 2 settling sections came together into a vertically oriented length of PVC. At this point the aerosols and carrier gas flowed vertically upward before curving around to feed the inlet of the wedge apparatus, whereas the liquid flowed vertically downward into a liquid reservoir. The liquid reservoir was the supply for peristaltic pumps that feed the aerosolizers (Figure 4.1).

![Image](image_url)

**Figure 4.5** - Design of single and double aerosolizer blocks.

4.3 Test and Analysis Procedures

Two different varieties of sand were used as the porous media during wedge tests. Both sand varieties were fairly coarse-grained; however, they are referred to as “Fine” and “Coarse” for differentiation purposes. Both sand varieties were well-sorted, with 96% of grains between 0.85 and 1.68 mm for the Fine sand, and 87% of grains between 1.68 and 3.36 mm for the Coarse sand (Figure 4.6). The average grain size values were 1.2 mm and 2.6 mm and porosities were 0.35 and 0.4 for the Fine and Coarse sand, respectively.
Figure 4.6- Grain size distributions for the Coarse and Fine sand used during wedge experiments.

The sand was dried before use in the apparatus. Drying was achieved by spreading the sand out on a tarp, which was placed in the sun and mixed periodically for at least 12 hours. The wedge was filled by incrementally increasing the depth of the dry sand. Between each addition a hammer was used to vibrate the sand to promote packing. The wedge was filled until sand heaped past the top, then a screed board was used to level the top surface with the sidewalls of the wedge. The lid was then positioned atop the sand-filled wedge and bolted in place. The aerosol delivery system was installed on top of the lid and the terminal end was clamped into place on the foam rubber gasket at the inlet of the wedge (Figure 4.1).

There were two positions on the aerosol delivery system where an aerosolizer housing could be installed (Figure 4.1). The number and type of aerosolizers installed were dependent upon the type of test being conducted. Tests for this work used 1, 2, or 4
aerosolizers. The 1 aerosolizer setup involved a single aerosolizer (Figure 4.5) installed in one housing while the other housing was plugged. The 2 aerosolizer setup involved a single aerosolizer installed in each housing, and the 4 aerosolizer setup was achieved by installing double aerosolizers in each housing. A known volume (typically 2.5 L) of soybean oil was poured into the liquid reservoir portion of the aerosol delivery apparatus (Figure 4.1). Attachment of the pressurized gas hoses and liquid feed tubing culminated the pre-test preparation sequence.

The tests were initiated by supplying gas and liquid flow to the aerosolizers. The gas and liquid flow rates supplied to each individual aerosolizer during all tests were 8.76 X 10^{-3} scmm and 4 ml/m respectively. Aerosols were injected through the wedge at a constant rate over the predetermined test duration.

The volume of soybean oil remaining in the liquid reservoir was measured after completion of the injection test, which allowed calculation of the total volume of soybean oil that was aerosolized. The lid was then removed, and sand samples are taken at 25 points (Figure 4.7). The samples were obtained at a depth of approximately 1.5 inches (half the total depth) using a spoon. The sand samples were then analyzed for liquid content by measuring the weight change after heating at 600 C° for 6 hours.
4.4 Test Methods

The general wedge test procedure involved injection of aerosols in a carrier gas for a predetermined period of time, and characterization of resulting liquid content distribution. Individual aerosolizers were always operated using the same combination of gas and liquid feed rates (8.76 × 10⁻³ scmm and 4 ml/m). Therefore, it is assumed that the number of aerosol particles and particle size distribution produced from each aerosolizer remained constant. Variables that could change between tests were the type of sand used, the number of aerosolizers used, and/or injection duration. An experiment variation was designed to serve as a base for comparison. The base variation involved injection using 2 aerosolizers for a period of 2 days, and was conducted using each type of sand.
Subsequent tests were designed to characterize the effect of test duration and/or aerosol injection intensity on resulting liquid content distributions.

4.4.1 Injection Duration Tests

Injection Duration Tests were designed to characterize the transient change in liquid content distribution with injection time. The 2 aerosolizer setup was used for each test, with variations involving injection for 1, 2, and 4 days. In this case the aerosol delivery rate remained constant between each test. Therefore, in comparison to the baseline, the total volume of soybean oil delivered as aerosol particles is half as much during the 1-day test and twice as much during the 4-day test.

4.4.2 Injection Intensity Tests

Injection Intensity Tests were designed to characterize the effect of injection rate and aerosol concentration on resulting liquid content distribution. Injection intensity was adjusted by changing the number of aerosolizers used. One intensity variation involved using 1 aerosolizer over a 4 day duration (low intensity), and another involved using 4 aerosolizers over a 1 day period (high intensity). The gas and liquid supply to each aerosolizer was maintained regardless of the number of aerosolizers used. Therefore, it was assumed that doubling the number of aerosolizers doubled the soybean oil volumetric delivery rate and total gas flow rate, and halving the number of aerosolizers had the inverse effect. The injection durations for each intensity setting were selected with the intent of delivering the same total soybean oil aerosol volume for each test.
4.5 Results

All wedge injection tests resulted in liquid contents that were relatively high near the point of injection and decreased along the direction of flow (Figures 4.8, 4.9, 4.12, and 4.13). The maximum mass content ranged from 35 to 40 g/kg for Coarse sand tests and 45 to 50 g/kg for Fine sand tests. This corresponds to oil saturations of 0.15 to 0.17 for Coarse sand and 0.22 to 0.25 for Fine sand. The liquid content decreased in the direction of flow to undetectable values in some tests, which required extrapolation of a zero contour line (Figures 4.9 and 4.13). In other tests, detectable values were obtained from samples taken all the way to the exit screen of the wedge (Figures 4.8 and 4.12).

4.5.1 Injection Duration Tests

Liquid content throughout the wedge consistently increased with injection time during Coarse sand Injection Duration Tests (Figure 4.8). There was some variability in liquid contents at given radii, but an average value at each sampling radius was calculated and plotted in terms of oil saturation (Figure 4.10A). The saturation along the wedge increased with injection duration, although the general shape of the radial profile remained the same. The radial profile is characterized by saturations that decrease with distance as roughly a negative exponential function (Fig. 4.10A).

The oil saturation near the point of injection reached 0.17 (39 g/kg) after one day and changed little thereafter (mass content reached a maximum of 40 g/kg after 4 days) (Figure 4.8) (Figure 4.10A). The oil saturation near the exit was approximately zero (0.03 g/kg) after one day of injection and reached approximately 0.002 (0.4 g/kg) after 4 days. Average saturation increased roughly linearly with injection time (Figure 4.10A).
Figure 4.8- Interpolated contours of oil content in grams oil/kg sand from Injection Duration Tests with Coarse sand.
Figure 4.9- Interpolated contours of oil content in grams oil/kg sand from Injection Duration Tests with Fine sand.
For example, saturation at \( r = 0.5 \text{m} \) was approximately 0.025 (5.88 g/kg) after 1 day, 0.045 (10.48 g/kg) after 2 days, and 0.082 (19 g/kg) after 4 days of injection, which amounts to a saturation change rate of roughly 0.02/day. By contrast, the average saturation change at \( r = 1.0 \text{m} \) was approximately 0.01/day.

![Figure 4.10- Oil saturation as a function of radial distance from Injection Duration Tests using A) Coarse sand and B) Fine sand.](image)

A mass balance on the experiment was conducted by integrating oil contents over the volume of the apparatus to determine the total mass of oil deposited. The mass of oil injected was measured directly from the apparatus. The injection rate varied slightly with time between 13 ml/h and 16 ml/h, resulting in volumes of 380 ml, 720 ml, and 1230 ml injected after 1, 2, and 4 days, respectively. The mass of oil deposited is 0.95 of the injected mass after 1 day and it decreases to 0.85 after 2 and 3 days. This suggests that most of the injected oil was deposited in the sand, although it is possible that up to 15% exited the apparatus.
The trends observed during Fine sand Injection Duration Tests (Figure 4.9) were generally similar to those observed during Coarse sand tests, but there were some important differences. The oil saturation near the point of injection was 0.23 (45.6 g/kg) after 1 day and increased to 0.25 (50.5 g/kg) after 2 days of injection (Figure 4.10B), which is approximately 47% greater than the oil saturation at the same location when using Coarse sand (Figure 4.10A). The oil saturation increased to a maximum of 0.26 at $r = 0.1$ m, which is the largest saturation measured during the tests. The general shape of the radial profile at 4 days of injection was unique among Injection Duration Tests in that saturation increased over the first 0.1 m of transport distance (Figure 4.10B).

The oil saturations increased roughly linearly with injection duration, as they did when using Coarse sand. The saturation rates in the vicinity of the injection point were greater than they were when using Coarse sand, however, with rates of 0.03/day at $r = 0.5$ m and 0.015/day at $r = 1$ m. This trend changes where $r > 0.5$ m because the deposition rate for Fine sand falls off and is less than that for Coarse sand. The oil saturation at the exit remained at zero after 4 days of injection into the Fine sand, whereas it reached small detectable values when using Coarse sand (Figure 4.10A). The maximum radius at which aerosol deposition was detectable was approximately 1.9 meters in Fine sand (Figure 4.9F). The oil content integrated over the volume of the apparatus was essentially the same as the injected volume during the Fine sand tests.

4.5.2 Injection Intensity Tests

The distribution of oil along the wedge was essentially independent of the injection intensity, however, did differ between Coarse and Fine sand (Figure 4.11). The
differences between Coarse and Fine sand distributions were consistent with tendencies observed during Injection Duration Tests. Liquid contents measured near the point of injection were greater for the Coarse sand tests while those measured near the exit were greater for the Fine sand tests.

![Graph](image)

**Figure 4.11** - Oil saturation as a function of radial distance during Injection Intensity Tests using A) Coarse sand and B) Fine sand. All tests injected the same volume of oil.

There was little difference in oil content along the wedges as a function of injection duration; however, there were systematic changes in radius of penetration. Radius of penetration increased with injection intensity during Coarse sand Injection Intensity Tests (Figure 4.12). The maximum radial penetration achieved while injecting with 1 aerosolizer for 4 days was approximately 1.5 meters, with 2 aerosolizers for 2 days was approximately 2 m, and with 4 aerosolizers for 1 day was beyond the radius of the wedge (Figure 4.12). Radius of penetration also increased with injection intensity during Fine sand tests (Figure 4.13). The maximum radial penetration from injecting with 1 aerosolizer for 4 days was approximately 1.2 meters, with 2 aerosolizers for 2 days was
Figure 4.12- Interpolated contours of oil content in grams oil/kg sand from Injection Intensity Tests with Coarse sand.
Figure 4.13 - Interpolated contours of oil content in grams oil/kg sand from Injection Intensity Tests with Fine sand.
approximately 1.6 m, and with 4 aerosolizers for 1 day was approximately 2 meters (Figure 4.13).

Injection Intensity Tests were designed to deliver the same total oil volume over the duration of each test; however, there were inconsistencies in total mass delivered. The volumes delivered during the 2 and 4 aerosolizer Coarse Sand tests were similar at 720 and 740 ml respectively, but only 415 ml were delivered during the 1 aerosolizer test (Figure 4.12). The total oil volume delivered during Fine sand tests was 515, 680, and 785 ml for the low, mid, and high intensity tests respectively (Figure 4.13).

Variations in mass balance within the wedge were similar to those observed during Injection Duration Tests. The percentage of injected oil deposited in the wedge during Coarse sand tests decreased with injection intensity, from approximately 100% to 85% to 75% for low, mid, and high intensity tests respectively (Figure 4.12). Approximately 100% of the injected oil was deposited during each Fine sand test variation (Figure 4.13).

Some general visual observations were made during the wedge tests that may indicate of transport and deposition behavior. Aerosols exiting the wedge through the terminal screen could be visually observed throughout the duration of all Coarse sand tests, whereas few to no aerosols were observable at the terminal screen during Fine sand tests. These observations are consistent with the mass balance calculations that suggest 10 to 15 percent of the oil injected into the Coarse sand flowed out of the apparatus. The mass balance for the Fine sand was closed, suggesting no aerosol particle transport out of the device. The fill-sand was cleaned out of the wedge after sampling was completed.
While cleaning the wedge, there typically was a thin layer of oil pooled near the point of injection on the PVC sheet lining the bottom. Pooling was more extreme when Fine grained sand was used, and when greater volumes of soybean oil aerosol had been injected.

4.6 Discussion

A consistent behavior was observed near the point of injection for all wedge test results. The oil content near the point of injection would increase quickly to a value, but then remain constant with continued aerosol injection (Figures 4.10, 4.11). Aerosol deposition rates are expected to be greatest near the point of injection, where aerosol concentrations, aerosol particle sizes, and liquid contents are greatest. However, in a flowing gas field the liquid content can only increase to a certain threshold value. Liquid relative permeability increases as liquid content increases, and the threshold represents the point at which the liquid flow rate along the wedge equals the aerosol deposition rate. This value should vary based on porous media properties. In a gas-oil system the oil is the wetting phase, therefore smaller pore spaces will promote greater liquid saturation due to capillary effects. This tendency is observed in test data; with the apparent threshold occurring at an oil saturation of approximately 0.17 for Coarse sand and at approximately 0.22 for Fine sand (Figures 4.10, 4.11).

Additional effects of liquid flow can be observed in two different Fine sand test data sets. This effect is characterized by an increase in liquid content with distance near the point of injection, before the characteristic decrease along the remaining radius of the wedge (Figures 4.10B, 4.11B). The liquid flow/aerosol deposition threshold should
depend on gas flow rate, with a greater liquid content threshold at lower gas flow rates, and less at higher gas flow rates. The flow within the wedge is radial; therefore, gas flow rate decreases with radius. This causes a subsequent increase in oil saturation threshold value with radius.

According to wedge test results, injection intensity (mass rate of aerosol injection) has limited control on resulting liquid distribution in porous material. Injection of high mass rates at high gas injection rates for short durations produced distribution patterns that were similar to those obtained while injecting lesser mass rates at low gas flow rates for longer durations. Assuming that total liquid mass delivered over the injection duration is the same, the aerosol mass delivery rate maintained over the duration is assumed to have little impact on resulting liquid content with radius. This assumption is based on the fact that deposition rates occur as a ratio of gas concentration (which was constant for all tests)(Equations 1-2 through 1-5). Mass delivery rate and aerosol concentration also are not factors in the total collection efficiency value (Equations 1-2 through 1-5).

Another parameter affected by injection intensity is gas flow velocity, which is a factor in collection efficiency value (Equations 1-2 through 1-5). Collection efficiency increases as gas flow velocity increases, which in turn should increase aerosol deposition rates and increase near screen liquid contents. However, increasing gas injection rates also should increase liquid flow away from the screen, decrease the maximum liquid threshold value, and decrease near screen liquid contents. Injection intensity was expected to affect resulting liquid content distributions based on these competing effects.
Similar liquid content distribution results may indicate these effects are offset for the injection intensity gas flow conditions that were selected.

### 4.7 Conclusions

Oil is readily transported as aerosols through sand, with radial transport distances after 4 days of injection greater than 2 m through dry sand with a mean grain size of 2.6 mm, and 1.9 m through finer sand (1.2 mm mean grain size). Deposition of oil aerosols rapidly increases the saturation at the injection face, and the saturation remains roughly constant (approximately 0.2 in sand). Oil saturation decreases with radial distance in most cases. The radial saturation profile resembles a negative exponential, with sharp decreases in saturation near the well flanked by a broad zone of gradually decreasing saturation.

The type of aerosol transport and deposition behaviors observed during wedge tests would be capable of achieving effective amendment distributions under some field-scale conditions. Some particles will tend to deposit near the screen during aerosol injection, whereas particles will tend to transport some distance before depositing. It is the transport distance that ultimately makes aerosol injection a worthwhile pursuit, as increasing liquid content near the screen is easily achieved by other means.

An aspect that would prevent successful implementation would be liquid contents near the screen increasing to the point that would prevent further transport of any aerosol particles. However, these tests indicate that saturations at the well screen rapidly increase and are maintained at a roughly constant value. This is encouraging for field application because it suggests that pores will remain open to gas flow. However, oil saturation
increased at the bottom of the apparatus, apparently because it drained downward. This suggests that oil drainage may have also contributed to maintaining partially open pores at mid-height in the apparatus. Presumably the thickness of the zone that is saturated in oil would increase with time and this may affect injection. Additional testing for longer than 4 days would be required to evaluate this effect.
Chapter 5-Theoretical Analysis of Aerosol Transport Through Porous Media

A numerical analysis was developed and used to investigate the effects of aerosol injection methodologies on resulting amendment saturation distributions in porous media. The model simulates aerosol transport and deposition in a partially saturated system with two mobile phases. The mobile phases are one gas (the carrier for the aerosol particles) and one liquid (used to create the aerosol particles).

5.1 Methods

The model was developed based on traditional multiphase flow and particle filtration theories (Yao et al., 1971). The multiphase flow components were validated by comparing results to a pre-existing multiphase flow simulator. Aerosol transport components were included in the validated model, which was calibrated by reproducing observations made during bench-scale experiments. The calibrated model was then utilized to make predictions about aerosol transport and deposition behavior during field-scale injection.

5.1.1 Fluid Flow

The dependent variable used for phase flow equations is pressure. The pressure distribution of each phase satisfies mass continuity. Derivation of governing equations is accomplished by analyzing phase mass flux through an elementary representative volume. This mass balance establishes a relationship between divergence of flux and change in mass stored:
\[ -\nabla q_i = -\nabla \left[ -\frac{kk_r}{\mu} \nabla (P_i + \rho_i gz) \right] = \frac{d\theta_i \rho_i}{dt} \]

\[ -\nabla q_i = \theta_i \frac{d\rho_i}{dt} + \rho_i \frac{d\theta_i}{dt} \]

\[ -\nabla q_i = \theta_i \frac{d\rho_i}{dP_i \, dt} + \rho_i \left( \frac{d\theta_i}{dP_i \, dt} \right) + \rho_i \frac{d\theta_i}{dP_c \, dt} \]  \hspace{1cm} (5-1)

where \( q \) is mass flux, \( k \) is permeability, \( k_r \) is relative permeability, \( \mu \) is viscosity, \( g \) is acceleration due to gravity, \( z \) is elevation, \( \theta \) is volume of fluid per total volume, \( \rho \) is density of the fluid, \( P \) is pressure, \( P_c \) is capillary pressure, \( t \) is time, and subscript \( i \) is phase designation (\( g \)=gas, \( l \)=liquid). Fluid compressibility \( \beta_i \) and capillary pressure are defined as:

\[ \frac{d\rho_i}{dP_i} = \beta_i \rho_i \]

\[ P_c = P_g - P_l \]

and substituting into (5-1) gives:

\[ -\nabla q_i = \theta_i \beta_i \rho_i \frac{dP_i}{dt} + \rho_i \frac{d\theta_i}{dP_i \, dt} \left( \frac{dP_g}{dt} - \frac{dP_i}{dt} \right) \] \hspace{1cm} (5-2)

Capillary pressure-phase volumetric content relationships are characterized using \( (\text{van Genuchten}, 1980) \):

\[ \theta_i = \phi S_r + \phi (1 - S_r) \left[ 1 + (\alpha P_c)^n \right]^{-m} \] \hspace{1cm} (5-3)

\[ \theta_g = \phi - \theta_l \]

\[ \text{where, } m = 1 - \frac{1}{n} \]
where $S_r$ is irreducible liquid saturation, $\phi$ is porosity, and $n$ and $\alpha$ are curve fitting parameters. Phase volumetric content as a function of capillary pressure is obtained by taking the derivative of Equation 5-3:

\[
\frac{d\theta_l}{dP_c} = -\frac{m\phi}{P_c} (1 - S_r)[1 + (\alpha P_c)^n]^{-m-1}(\alpha P_c)^n
\]  

(5-4)

\[
\frac{d\theta_g}{dP_c} = -\frac{d\theta_l}{dP_c}
\]  

(5-5)

Combining Equations 5-2, 3, 4, and 5 gives:

\[
\rho_l \left( \frac{d\theta_l}{dP_c} - \theta_l \beta_l \right) \frac{dP_l}{dt} + \nabla q_l = -\rho_l \frac{d\theta_l}{dP_c} \frac{dP_l}{dt}
\]  

(5-6)

\[
\rho_g \left( \frac{d\theta_g}{dP_c} - \theta_g \beta_g \right) \frac{dP_g}{dt} + \nabla q_g = -\rho_g \frac{d\theta_l}{dP_c} \frac{dP_l}{dt}
\]  

(5-7)

Liquids are assumed to be incompressible during simulation. Gas compressibility is derived from the ideal gas law:

\[
V_g = \frac{M_g RT}{P_g}
\]

\[
\frac{dV_g}{dP_g} = \frac{-M_g RT}{P_g^2}
\]

Compressibility is defined as: $\beta_g = -\frac{1}{V_g} \frac{dV_g}{dP_g}$

So: $\beta_g = \frac{1}{P_g}$

where $V$ is volume, $M$ is mass, $R$ is the ideal gas constant, and $T$ is temperature.

Relative permeabilities for each phase are characterized using (van Genuchten, 1980):
\[ k_{rl} = \bar{S}_l^{1/2} \left[ 1 - \left( 1 - \bar{S}_l^{1/m} \right)^2 \right] \]

\[ k_{rg} = (S_g)^{1/2} \left( 1 - \bar{S}_l^{1/m} \right)^{2m} \]

\[ \bar{S}_l = \frac{S_l - S_r}{1 - S_r} \]

where \( \bar{S} \) is scaled liquid saturation.

Average velocity is determined using:

\[ v_g = -\frac{k k_{rg}}{\mu_g \Phi_e} \nabla P_g \]

where \( \Phi_e \) is effective gas phase porosity.

5.1.2 Aerosol Transport

The spatial distribution of oil particle concentration can be characterized using an advection-diffusion equation with irreversible sorption,

\[ \frac{dC_g}{dt} = D \nabla^2 C_g - v_g \nabla C_g - k_s C_g \quad (5-8) \]

where \( C_g \) is concentration of aerosols in the gas given as particles per volume, \( D \) is the particle diffusion coefficient, \( v_g \) is gas phase velocity, and \( k_s \) is the sorption coefficient.

The particle diffusion coefficient was estimated using the Stokes-Einstein equation (Einstein, 1956),

\[ D = \frac{B_s T}{3\pi \mu_g d} \]
where $B_c$ is Boltzmann’s constant ($1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$), $T$ is absolute temperature, $\eta$ is viscosity of the suspending fluid, and $d$ is the diameter of the particles.

5.1.3 Aerosol Deposition

According to colloid filtration theory (Yao et al., 1971), the sorption coefficient can be described as,

$$k_s = \frac{3}{2} \frac{(1-\phi_e)}{d_g} \alpha_c \eta_{tot} v_g$$

(5-9)

where $d_g$ is grain diameter, $\alpha_c$ is collision efficiency (ratio between particles that stick and particles that impact collectors), and $\eta_{tot}$ is total collection efficiency.

The model considers three possible mechanisms for particle capture: diffusion, interception, and gravitational settling (Figure 1.2). Therefore, the collection efficiency has diffusion, interception, and gravitational settling components, each of which can vary with space and time. The method used to estimate collection efficiency was originally developed for water filtration (Yao et al., 1971); however, it has been shown to work well for aerosol filtration (Chang and Chan, 2008). Application involves summing collection efficiencies for diffusion, interception, gravitational settling components to give a total collection efficiency. Yao et al. (1971) introduced a method for calculating collection efficiencies based on a solution to the advection-diffusion equation for flow towards a single spherical collector. The current model uses the method originally proposed by Yao et al., 1971:

$$\eta_{tot} = \eta_D + \eta_I + \eta_G$$
\[ \eta_D = 4.04A_s \left( v_g \phi_e \frac{d_g}{D} \right)^2 \] (5-10)

\[ \eta_I = \frac{3}{2} A_s \left( \frac{d_p}{d_g} \right)^2 \] (5-11)

\[ \eta_G = \frac{\rho_p - \rho_g}{18 \mu_g \rho_g} g d_p^2 \] (5-12)

where, \( A_s = \frac{2(1-\gamma^5)}{2-3\gamma+3\gamma^5-2\gamma^6} \) and \( \gamma = (1 - \phi_e)^{\frac{1}{3}} \) (5-13)

where \( \eta_D, \eta_I, \) and \( \eta_G \) are the diffusion, interception, and gravitational settling collection efficiencies respectively, and \( d_p \) is aerosol particle diameter.

The deposition rate \( \frac{dC_i}{dt} \) is calculated as particles per volume of gas per time.

Aerosol deposition affects liquid saturation, which in turn affects effective porosity. Change in liquid saturation as a function of aerosol deposition rate is calculated using:

\[ \frac{ds_l}{dt} = -\frac{dc_g}{dt} \left( \frac{4\pi(0.5d_p)^3}{3\phi} \right) \]

Effective gas phase porosity is calculated using:

\[ \phi_e = \phi - \phi(S_l) \]

5.1.4 Modeling Approach

The coupled equations for fluid flow and aerosol transport in a partially saturated porous medium outlined above are solved using Comsol Multiphysics. This code uses the finite element method to solve partial differential equations (Equations 5-6,7,8) subjected to boundary and constitutive relationships. The beginning of the transport process is solved by uncoupling fluid flow (Equations 5-6,7) from transport (Equation 5-8). This
allows steady state pressure and flow conditions to be established prior to aerosol injection. This is numerically convenient, but steady state flow conditions were established before introducing aerosols in the bench-scale experiments, so it is also physically relevant. In general, the gas flow and aerosol transport are strongly coupled because deposition of aerosol droplets reduces relative permeability of the gas phase and decreases the effective porosity, which in turn affect aerosol advection and deposition rates. Liquid saturations may also increase to the point where liquid flow occurs.

Three model geometries are assumed. A 1-D geometry is used to represent a vertical 1.5-m-long column configuration. The 1-D model was used for verification of the multiphase flow simulation by comparing results to those obtained from T2VOC (Falta et al., 1995). A 2-D, thin, axisymmetric geometry was developed to simulate injection during the bench-scale wedge tests. Data from the wedge tests are used to calibrate the aerosol deposition properties using 2-D axisymmetric model. A thicker axisymmetric geometry was created to simulate injection at the field-scale. This simulation consists of a gas injection well screened at depth below a surface at atmospheric pressure. Parameter values obtained from wedge model calibration were used to simulate field-scale injection.

The boundary conditions during aerosol injection for the 1-D models are:

\[
\frac{dP_l}{dz} = 0; (z = 0 \text{ and } z = 1.5)
\]

\[
P_g = 0; (z = 1.5)
\]

\[
q_g = q_{g-inj}; (z = 0)
\]

\[
q_a = q_{a-inj}; (z = 0)
\]
Where \( q_{g-\text{inj}} \) and \( q_{a-\text{inj}} \) are the gas and aerosol mass fluxes used during the injection tests (units of kg/m\(^2\)/s and particles/m\(^2\)/s respectively). The boundary conditions during aerosol injection for the wedge test simulations are:

\[
\begin{align*}
\frac{dP_l}{dz} &= 0, \quad \frac{dP_g}{dz} = 0, \quad \frac{dC_g}{dz} = 0 \\
\frac{dP_l}{dz} &= 0, \quad P_g = 0
\end{align*}
\]

and for the field-scale simulations are:

\[
\begin{align*}
\frac{dP_l}{dz} &= 0, \quad P_g = 0 \\
\frac{dP_l}{dr} &= 0, \quad q_g = q_{g-\text{inj}} \\
q_a &= q_{a-\text{inj}}
\end{align*}
\]

The 1.5-m-long geometry of the 1-D simulations was divided into 150 x 1 cm elements for numerical simulations and 100 x 1.5 cm elements for T2VOC simulations. A rectangular grid consisting of 10, 0.76-cm-high cells in the z-direction and 200, 1-cm-long cells in the r-direction was used for the wedge test simulations. The mesh used for
field-scale simulations was created by subdividing the 2-m-long well screen boundary into 40 x 5 cm intervals and then discretizing the remainder with the free triangular mesh generator in Comsol (Figure 5.1). Controlling parameters used during triangular mesh generation were minimum element size = 0.05 m, maximum element size = 5 m, and maximum element growth rate = 1.02. This resulted in a mesh consisting of 31,736 elements.

![Figure 5.1- Mesh used for field-scale simulations. Red line represents well screen location.](image)

### 5.1.4 Model Validation

The multiphase fluid flow simulating capabilities of the model were validated by comparing results to those obtained by simulating the same problem using T2VOC, an established multiphase flow simulator (Falta et al., 1995). The simulations were 1-D, and the domains represented a 1.5 m-long, sand-filled column. The sand was assigned a permeability of $10^{11}$ m$^2$ and a porosity of 0.35. Air and water were the phases used during validation simulations.
A total of five different simulation variations were conducted and compared. The variations differed based on the flow and/or fluid saturation conditions that were represented. The variations are:

1) Phase saturation distribution under equilibrium conditions,
2) Water saturation while increasing gas pressure in a closed system,
3) Transient gas flow through a dry column,
4) Filling a partially saturated column with water, and
5) Two phase flow induced by gas injection through partially saturated column.

5.1.4.1 Equilibrium Phase Saturation

Phase saturations at steady state were characterized with no flowing phases. Two scenarios were simulated with each model. The first scenario (High Sat) established steady state conditions when the top of the column was set to $S_w = 0.05$ while the bottom was set to $S_w = 0.95$ ($S_w = \text{water saturation}$). The second scenario (Low Sat) used $S_w = 0.01$ and $S_w = 0.2$ for the top and bottom of the column respectively. The steady state phase distributions predicted by the two models are essentially identical (Figure 5.2).

5.1.4.2 Mass Conservation

Mass conservation simulations were used to verify that initial water mass would be conserved within a sealed column while increasing gas pressure. This was required to ensure that capillary pressure was independent of changes in pressure of a single phase. The initial conditions used for the simulations were the High Sat conditions from the Equilibrium Phase Saturation simulations (Figure 5.2). Pressure was increased from 0 to 100,000 Pa over a period of 1000 seconds for each simulation. Phase saturations were unaffected with both models (water was assumed incompressible).
5.1.4.3 Transient gas pressure

These simulations involved characterizing transient gas pressure distribution along the column while injecting at constant gas pressure. Initial conditions were static gas pressure with 0.01 water saturation along the entire column, and gas was injected at 70 kPa. The transient pressure profiles differ by a maximum of 7%, which occurs between the 1s data sets (Figure 5.3). The maximum deviation between the steady state pressure profiles is less than 1% (Figure 5.3), which is most likely due to subtle differences in the numerical procedures.
5.1.4.4 Filling a column

The initial conditions for the column-filling simulations were the “low sat” conditions from the Equilibrium Phase Saturation simulations (Figure 5.2). One meter of water head was applied at the base of the column, which caused the column to fill with water. The transient filling behavior for the two models was similar, with the results from Comsol lagging slightly behind those from T2VOC (Figure 5.4). This occurred because the wetting front in the Comsol simulation was slightly sharper than the one simulated by T2VOC. The maximum lag occurred at the leading edge and is roughly 5 cm. This difference is most likely due to subtle differences in the numerical procedures (Figure 5.4). A larger difference occurs with the phase saturation distribution at steady state (Figure 5.4).
5.1.4.5 Two-phase flow induced by gas injection

This simulation involved inducing multiphase flow by injecting gas through a partially saturated column. The initial conditions used for these simulations were the High Sat conditions the Equilibrium Phase Saturation simulations (Figure 5.2). Gas was injected at the lower boundary at 70 KPa, and water saturation at the lower boundary was maintained at 0.95. This caused a wetting front at approximately 0.95 water saturation to move along the column until a steady-state distribution was reached. Both simulations show a sharp wetting front where the position of the front differs by less than 1 cm (Figure 5.5). The wetting fronts simulated by Comsol were slightly steeper than those simulated by T2VOC, but the overall behavior and magnitudes are similar (Figure 5.5).
5.1.4 Wedge Simulations

Wedge simulations were used to calibrate the numerical models by reproducing results from physical experiments. The calibrated wedge simulations were then used to make predictions about liquid content distributions that would occur for longer injection durations and for different injection intensities.

5.1.4.1 Model Calibration

Coarse and Fine sand duration test oil saturations were the data sets used for calibration (Figure 4.7). The porous material properties used for the fill-sands are provided in Table 5.1. Permeabilities were estimated by fitting gas flow rate/gas injection pressure relationships that were measured during injection through packed columns, and
porosity was measured by filling voids with measured volumes of water. Average grain size was determined by sieve analysis, whereas capillary pressure and relative permeability parameters were typical values given for sand in literature (Parker et al., 1987). Fluid properties used were based on typical values (Table 5.2); wedge simulations involved only soybean oil aerosols.

<table>
<thead>
<tr>
<th>Porous Material Properties</th>
<th>Coarse Sand</th>
<th>Fine Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability (m$^2$)</td>
<td>3x10$^{-10}$</td>
<td>8x10$^{-11}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.4</td>
<td>0.35</td>
</tr>
<tr>
<td>Van Genuchten n</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>Van Genuchten α (Pa$^{-1}$)</td>
<td>9.9x10$^{-4}$</td>
<td>9.9x10$^{-4}$</td>
</tr>
<tr>
<td>Grain Size (mm)</td>
<td>2.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Minimum Liquid Sat</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluid Properties</th>
<th>Gas</th>
<th>Veg. Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (Pa s)</td>
<td>1.818x10$^{-5}$</td>
<td>6.8x10$^{-3}$</td>
</tr>
<tr>
<td>Density (kg/m$^3$)</td>
<td>$\frac{P_g}{(R*T)}$</td>
<td>922</td>
</tr>
<tr>
<td>Compressibility (Pa$^{-1}$)</td>
<td>$\frac{1}{P_g}$</td>
<td>4.6x10$^{-10}$</td>
</tr>
</tbody>
</table>

**Table 5.1** Porous material properties used for wedge simulations.

**Table 5.2** Fluid properties used for wedge simulations.

Block 3-3 aerosolizers without impaction plates were used during wedge injection experiments. It is assumed that the most accurate aerosol particle size measurements made during this research were from dilution tests, for which block 3-3 aerosolizers were also used (Figures 2.9, 2.10). The dilution factor that produced the best approximation of actual mass aerosolization rates during no plate dilution tests was 240:1 (Figure 2.11); therefore, the data from that test was used to describe the aerosol particle size distribution during wedge simulations. Particle counts on the lower particle size end of the spectrum are assumed to be artificially inflated due to the presence of a large number of particles that were smaller than the lower detection limit (0.75 micron). A normal distribution curve was fit to the larger particle size end of the measured distribution (Figure 5.6).
model was designed to include three different aerosol particle sizes; therefore, the normal distribution was subdivided into three regions with a representative particle size and ratio of total aerosolized mass value assigned to each (Figure 5.6).

The aerosolization rate estimates for each Coarse and Fine duration test were used to generate the simulated 1, 2, and 4 day saturation distributions (Figures 4.8 and 4.9). Collection efficiency ($\alpha_c$, Equation 5-9) was the lone parameter used to fit saturation distribution data. Separate collection efficiencies were determined for Coarse and Fine sand.

![Diagram of particle size distribution](image)

**Figure 5.6** Assumed particle size characterization for wedge simulations.

### 5.1.4.2 Duration and Intensity Simulations

The calibrated wedge simulations were used to make predictions about aerosol transport and deposition behaviors during longer duration injections. This was done by extrapolating calibrated Coarse and Fine sand wedge injection experiments for durations...
of 1, 2, 3, and 4 weeks. The gas flow rate used during the experiments (0.623 scmh) was used for the simulations along with an aerosolization rate of 15 g/hr.

The calibrated simulations were also used to determine the theoretical influence of injection intensity on resulting oil content distributions. The simulations used the gas flow rate and intended aerosolization rate conditions used for the Coarse sand, Intensity, wedge injection experiments (Appendix H, WT7-9). Results from these experiments were compared to the results from physical experiments, which displayed no discernible liquid distribution tendencies with respect to injection intensity (Figure 4.9).

5.1.4 Field-Scale Simulations

Models were scaled-up to represent aerosol injection through a conventional well with a 2-m-long screen (9 to 11 m bgs) under field conditions. The parameters obtained during calibration were used to predict resulting oil saturation distributions after two months of Mid-intensity injection under conditions that existed during wedge experiments (Tables 5.1, 2). Simulations were also constructed to characterize the effects of gas injection rate and aerosol particle size on resulting liquid distributions. One set of simulations assumed that gas injection rates were increased by 4x, another assumed that all aerosol particles were 0.8 microns (smallest size category used, Figure 5.6), and yet another assumed both increased gas injection rate and decreased aerosol particle size. Each simulation was done for Coarse and Fine sand, and area of influence was assumed to be delineated by the 0.01 saturation contour for each case.

Another field-scale simulation was designed to investigate the effect of an alternative injection methodology. The methodology involved injection for a total of one
month while injecting aerosols under Mid-intensity conditions for 23 hours of each day and injecting clean gas at 100 times the normal rate during the 24th hour of each day. Effect of gas flow rate was further investigated by determining the maximum radius along the well screen centerline at which sufficient particle deposition rates occurred at early injection time (when aerosol penetration distance is at a maximum). The minimal early-time deposition rate was selected as 1.524x10^{-6} \text{ kg/m}^3 \text{s}, which, assuming that deposition rates remained constant, would produce 0.01 oil saturation over a month’s time. Aerosol deposition near the well screen leads to decreasing aerosol penetration; therefore deposition rates at the selected radius were expectedly not sustained. However, the corresponding radius was assumed to represent a limiting maximum radius of influence that could be achieved under the given injection conditions. Alternative injection methodology and maximum radius simulations were conducted for Coarse sand only.

5.2 Results

5.2.1 Model Calibration

Coarse and fine sand duration wedge test results were characterized by a general increase in saturation values along the wedge with time (Figure 4.10). Saturation values at \( r = 0 \) were exceptions to this tendency, as a maximum value was reached within 1 day of injection and maintained as roughly constant thereafter (Figure 4.10). Adjustment of collision efficiency \( (\alpha_c, \text{Equation 5-9}) \) did not enable reproduction of this behavior over
the measured saturation range. Alternatively, the simulated saturations increased continuously with injection duration at $r = 0$ (Figure 5.7).

The primary purpose of the model was to determine maximum radius of influence that is achievable when injecting aerosols at the field-scale. Therefore, focus was placed on more closely fitting the large radius saturation data as opposed to the small radius saturation data. The collision efficiencies that best achieved these fits were 0.3 for Coarse sand and 0.2 for Fine sand (Figure 5.7).

![Figure 5.7- Oil saturation distribution fits along the centerline from duration wedge tests and the calibrated model.](image)

The general shape of the saturation distribution curves at small $r$ values differs for coarse sand experimental and simulated data. The saturation values decrease sharply with radius for the 1, 2, and 4 day, Coarse sand tests (Figure 5.7). The simulated saturation values near the injection point remain fairly constant by comparison, and even increase slightly in the 4 day case (Figure 5.7). These simulated patterns likely represent a
transition towards the behavior that was observed for the 4 day duration, Fine sand test, where saturation increased with radius near the point of injection (Figure 5.7).

An extremely confined approach was utilized to calibrate the model. Collision efficiency was the only fitting parameter, however, it is expected that better fits could be achieved if calibration was allowed to be more flexible. Including the Van Genuchten curve fitting parameter \(n\) and minimum liquid saturation \(S_r\) (Equation 5-3) as fitting parameters could improve reproduction of saturation distributions observed near the point of injection during bench scale tests (Figure 5.7).

5.2.2 Long Duration Wedge Simulations

Aerosol injection for up to 4 weeks was simulated for Coarse and Fine sand-filled wedges. Saturation distribution results produced from these simulations follow a continuation of trends observed in calibration simulation results. The 4 day Coarse and Fine sand calibration simulation results produced saturation distributions that increased initially and then decreased sharply with radius (Figure 5.7). Continued injection produces an increase in maximum oil saturations, as well as an increase in radial distance to the point where the maximum occurs (Figure 5.7).

The oil saturation along the centerline of the wedge at \(r = 0\) for Coarse sand simulations increases over the entire 4 week injection duration, however, the rate of saturation increase slows with time (Figure 5.8). The \(r = 0\) saturation along the centerline reaches a maximum value within 1 week of injection in Fine sand with no further increases over the remainder of the injection period (Figure 5.8).
The 2, 3, and 4 week injection saturation distribution curves can be subdivided into two regions. One region starts at $r=0$ and is characterized by an increase followed by a decrease in saturation (Figure 5.8). The second region begins at a point marked by a deflection in the saturation profile and is characterized by a relatively slow decrease with radius over the remainder of the affected distance (Figure 5.8). The 2, 3, and 4 week deflections occur at approximately 1.4 m, 1.7 m, and 1.95 m for Coarse sand simulations and approximately 1.25 m, 1.6 m, and 1.8 m for Fine sand simulations (Figure 5.8).

![Figure 5.8](image)

**Figure 5.8** - Oil saturation distributions along centerline from long duration wedge simulations.

Generating saturation contour plots with time over two-dimensional, vertical slices of the wedges reveals a vertical distribution component that is not observable in centerline plots (Figure 5.9). Two-dimensional plots reveal saturation contours that advance along the wedge with time for Coarse and Fine sand (Figure 5.9), which is consistent with what was observed in centerline plot results (Figure 5.8). Vertical saturation distributions along the wedge for both types of sand are characterized by lesser saturations at the top and greater saturations at the bottom, a pattern that increases with
injection durations (Figure 5.9). The radius at which the maximum saturation occurs also
increases with injection duration. Maximum simulated saturations within the wedges
after 4 weeks of injection were approximately 0.35 for Coarse sand and 0.44 for Fine
sand (Figure 5.9).

**Figure 5.9**- Oil saturation distributions along vertical, radial cross-sections from
Long-Duration wedge simulations for A) Coarse sand and B) Fine sand.
5.2.3 Intensity Wedge Simulations

Oil saturation distribution seemed to be relatively insensitive to injection intensity during physical wedge injection experiments (Figure 4.9). However, according to simulation results, injection intensity could influence oil saturation distribution following injection through Coarse sand (Figure 5.10). The Low intensity simulations (1 aerosolizer over 4 days; Lesser oil mass and gas flow rates, greater duration) produced greater saturation near the point of injection and lesser saturations at greater radii than Mid (2 aerosolizers over 2 days; Intermediate oil mass rates, gas flow rates, and duration) and subsequently High intensity (4 aerosolizers over 1 days; Greater oil mass and gas flow rates, Lesser duration) simulations. The final oil saturations at 2 m were 0.003, 0.004, and 0.006 for Low, Mid, and High intensity simulations respectively.

![Figure 5.10- Oil saturation distributions from coarse sand injection intensity simulations.](chart.png)

Aerosol deposition rates are a function of the sorption coefficient ($k_s$, Equation 5-9), which in turn is a function of collection efficiencies (Equations 5-10,11,12). Sorption coefficients at the initiation of injection intensity simulations (Time = 0) increase with
aerosol particle size (Figure 5.11), which would be expected according to Equations 5-11,12. Sorption coefficients are highest at the point of injection and decrease with radius for all Time = 0 plots (Figure 5.11). This behavior is correlated with gas velocity, which

![Figure 5.11](image)

**Figure 5.11**- Sorption coefficients for three particle sizes as a function of radial distance at the beginning and end of low, mid, and high intensity injection simulations using the wedge geometry. Notice that y-axis ranges differ.
is greatest near the point of injection and logarithmically decreases with radius. Sorption coefficient should increase with velocity according to Equations 5-9,10. Time = 0 sorption coefficients also increase with injection intensity for each aerosol particle size (Figure 5.11). The only difference between intensity simulations that would affect sorption coefficient magnitude is gas velocity (increased gas velocity with increased intensity). Considering the effect of gas velocity on sorption coefficient, this behavior is consistent with Equations 5-9,10.

By the end of injection, sorption coefficients had increased for Low, Mid, and High intensity simulations. Sorption coefficient increases were largest at small radial distances and lower injection intensity (Figure 5.11). Smaller radial distances are characterized by greater liquid saturation (Figure 5.10). This effect is greatest in the 5.5 μm particle size, Time = End results, where the magnitude rankings of intensity sorption coefficients actually invert near the point of injection (Figure 5.11). This behavior also correlates to liquid saturation (Figure 5.10) and is expected according to Equations 5-10,11,12, which suggest that sorption coefficient should increase with decreasing effective porosity.

5.2.4 Field-Scale Simulations

The ROI as measured from the center of the well screens reached 1.9 m and 1.6 m respectively for Coarse and Fine sand after one month of injection when using parameters obtained during model calibration (Fit)(Figure 5.12). Increasing gas injection rate by 4 times resulted in a ROI increases to 2.7 m (142% of Fit simulation) and 2.4 m (150% of
Figure 5.12- Oil saturations resulting from one month of aerosol injection in Coarse and Fine sand under different conditions. Red lines represent well screens, dash line marks ROI at centerline.
Fit simulation) for Coarse and Fine sand respectively (Figure 5.12). ROI increase from decreasing aerosol particle size was greater than that of increasing gas injection rate when simulating Coarse sand (3 m, 158% of Fit), whereas the effect of the two condition alterations were the same when using Fine sand (2.4 m, 150% of Fit). The greatest ROI predictions were produced by simulations that assumed increased gas injection rate and decreased aerosol particle size. These simulations resulted in an ROI of 3.8 m (200% of Fit) when using Coarse sand and 2.9 m (181% of Fit) when using Fine sand (Figure 5.12).

Plotting oil saturation along the centerline (horizontal from center of screen) indicates that larger ROI consistently correlate with lesser oil saturation near the screen (Figure 5.13). The extremes for near-screen saturations were obtained for the Fit (greatest saturation) and Both (least saturation) for Coarse and Fine sand simulations (Figure 5.13). Near-screen saturation values were affected differently based on sand type when implementing either increase gas injection rate or decrease in particle size. Implementing the two conditions in Coarse sand resulted in similar saturations at 0 radius, greater near screen saturations with increased gas flow, and increased distal saturations with decreased particle size (Figure 5.13). For Fine sand, increasing gas flow had a greater effect in decreasing 0 radius oil saturation than did particle size (Figure 5.13). The near screen saturation values still reach nearly the same value; however, the maximum is shifted slightly downstream for the increased gas flow case (Figure 5.13). Oil saturation distribution at distal radii are similar for the two conditional cases in Fine sand (Figure 5.13).
There are also differences in resulting oil saturations with respect to vertical symmetry about the well screen (Figure 5.12). This asymmetry is most evident in Fit simulation results, as a high oil saturation (0.46) at the base of the oil bearing zone for the Coarse sand simulation and a general increase in average oil saturation with downward distance from the well screen (max of approximately 0.35) for the Fine sand simulation (Figure 5.12). Indications of saturation asymmetry can also be observed when only gas flow is increased, or when only aerosol particle size is decreased during Fine sand simulations (Figure 5.12). However, comparatively symmetrical distributions occurred for all remaining simulations (Figure 5.12).
5.3 Discussion

5.3.1 Wedge Simulations

The effect of liquid phase flow is evident in transient plots of oil saturation along the wedge centerline during long duration wedge simulations (Figure 5.8). Increasing oil saturation with radius near the point of injection was observed for physical wedge tests after 4 days of injection through Fine sand (Figure 4.8B), which was determined to result due to a maximum saturation threshold that decreases as gas flow velocity (pressure gradient) increases. The maximum simulated oil saturation along the centerline of the wedge in Coarse and Fine sand migrates along the column with time (Figure 5.8). Saturations up to the radius where the maximum saturation have reached the threshold value, therefore, at these locations oil flows as a liquid along the column at the same rate that it is deposited. Oil flowing along the column with time causes points at more distal radii to reach the flow velocity-based saturation threshold, therefore, the radius corresponding to maximum oil saturation increases with time (Figure 5.8).

Saturations decrease with radius at radii greater than the point of maximum saturation (Figure 5.8). The slope is relatively high and then it abruptly flattens and saturations decrease gradually beyond this point (Figure 5.8). The region between the saturation maximum and the slope change is characterized by saturation that is increasing, but is less than the saturation threshold. The oil in this region, however, was largely deposited from an aerosol at smaller radial distance and then flowed as a partially saturated liquid to its current location. The slope change represents a transition point where the rate of unsaturated flow of oil decrease sharply. Oil saturations beyond this
point are affected largely by deposition from aerosols (Figure 5.8). The saturations in this region are relatively small, but they extend a relatively large distance from the injection point (Figure 5.8).

A vertical component to the flow during long duration simulations become evident when plotting saturation contours across 2 dimensional wedge slices with time (Figure 5.9). The highest saturations occur along the bottom of the wedge, which is due to gravity-driven, vertically downward liquid flow. The general behaviors observed in the centerline plot (Figure 5.8) hold for the two dimensional transients (Figure 5.9). One aspect in two dimensional plots is a saturation decrease with depth in the deposition dominated region, which is most evident in the 0.01, 3 week, Fine sand contour (Figure 5.9B). This occurs because the aerosol particle concentrations decrease with depth in this region, which is due to greater deposition rates with depth at lesser radii (deposition rates increase with saturation).

Simulations suggest that injection intensity should effect saturation distribution following injection of a given aerosol mass (Figure 5.10). The results obtained for High intensity injection show oil spreading to further radial distances than those obtained for Low intensity injection (Figure 5.10). These results are apparently not due to initial sorption coefficient values (Figure 5.11), which indicate that initial deposition rates near the point of injection are greater for higher intensity injection scenarios. These results indicate that at long injection times the oil saturation near the point of injection is less a function of aerosol particle deposition rate, and more a function of maximum saturation threshold based on gas flow velocity. Greater gas velocities that occur during higher
intensity injections cause increased liquid flow along the column, and thereby keep liquid saturations down. Lower liquid saturations have a greater effect on sorption coefficient than does gas flow velocity under the conditions simulated; therefore, deposition rates near the point of injection are ultimately lower for higher injection intensity scenarios (Figure 5.11).

5.3.2.1 Field-Scale Simulations

The ROI’s predicted by 4-week duration, Fit simulations were 1.9 m and 1.6 m for Coarse and Fine sand respectively (Figure 5.12). These ROI are less than those predicted during long duration wedge simulations (Figure 5.8). Greater ROI’s during wedge simulations were due to a combination of strict radial flow (field-scale gas flow pattern has vertical component), and a lower barrier that prevented vertical liquid migration to greater depths. Gas flow patterns that radiate outward from the injection well cause flow velocity to drop, which in turn decreases mass deposition rates at given points. The gas flow velocity along the centerline (midpoint of well screen) is also decreased under spherical flow conditions and lesser liquid saturations occur due to vertical flow. These aspects decrease horizontal liquid flow, and thus decrease the ROI along the centerline (Figure 5.12).

Gravity-driven, vertical liquid flow caused asymmetrical oil distribution patterns in field-scale simulations. The Coarse-Fit simulation results show the greatest influence of downward flow, which resulted in oil pooling at the base of the oil bearing zone (Figure 5.12). By contrast, the vertical liquid flow during the Fine-Fit simulation resulted in decreasing oil content with depth below the well screen but not pooling (Figure 5.12).
This difference resulted from a combination of greater effective permeability in Coarse sand and greater gas flow rates in Fine sand. Gas flow velocities were greater during Fine sand simulations because the assigned porosity was less (0.35 as opposed to 0.4). Increased gas flow velocity induced oil flow along the gas flow direction, which prevented accumulation of oil to saturations where gravity-driven flow would be dominant (Figure 5.12).

Decreasing the particle size of injected aerosols should increase average transport distances according to Equations 5-11,12. Results of injection intensity simulations also suggest that injecting at greater gas flow rates could increase average aerosol transport distances (Figure 5.10). Adjustment of simulation parameters to represent one or both of these conditions resulted in increased ROI’s for Coarse and Fine sand (Figure 5.12). The ROI increase due to increased gas injection rates was greater than the ROI increase from decreasing aerosol particle size when simulating Coarse sand (Figure 5.12). By contrast, the effect of the two conditions on ROI was the same for Fine sand. The reason for this difference is that, while decreasing aerosol particle size will always increase particle transportability, the magnitude of the effect is a function of particle to formation grain size ratio (Equation 5-10). Implementing both changes simultaneously resulted in ROI that were 200% and 181% of Fit Coarse and Fine sand simulations respectively (Figure 5.12), which correspond to zones of influence that are approximately 300% of Fit results in each case. These improvements are promising with respect to condition-specific tuning of injection parameters to optimize aerosol delivery under field conditions.
Increases in ROI consistently correlate with lesser oil saturation near the screen (Figure 5.13). This would be expected because aerosol deposition rates increase as effective porosity increases (Equations 5-9 through 5-13). Injection parameters such as average aerosol particle size and gas injection rate affect ROI because they determine resulting liquid saturations near the screen. Decreasing aerosol particle size causes a decrease in near screen liquid saturation by decreasing the sorption coefficient (Equation 16). Increasing gas injection rate reduces near-screen liquid content by inducing liquid flow in the gas flow direction. Increasing flow velocity also increases the sorption coefficient (Equation 5-9,10), which in turn increases deposition rates. However, increasing sorption does not necessarily increase deposition near the well screen. The units of the sorption coefficient are 1/s (Equation 5-9), and increasing velocity will increase the distance covered with time. If the distance covered with time increases are greater than the deposition rate increases, then actual deposition near the well screen can decrease with increasing velocity.

5.3 Conclusions

The validation tests indicate that the analysis outlined above and described in Equations 5-1 through 5-7 produces results that are essentially identical to those of T2VOC when implemented using Comsol Multiphysics. Relative errors of less than one percent were obtained in all cases except those that involved sharp fronts. In these cases, the fronts predicted by Comsol were slightly sharper and lagged slightly behind those of T2VOC. This apparently is a result of differences in the numerical methods and is small enough to be ignored. The approach used to represent aerosol deposition processes is
based on the assumption that mass balances are maintained. The approach was validated by comparing model results to data from physical injection tests (Figure 5.7). Validation provides strong grounds for confidence in subsequent simulations.

Aerosol particle size and gas injection rate are the injection parameters that 1) Affect aerosol deposition process and, 2) Can be at least partially controlled during injection. Adjustments that would result in ROI increases were evaluated, as increases in ROI would be beneficial during field application. The results indicate that the maximum ROI depends on the number of aerosol particles that will flow along with gas and deposit at a given radius. This depends on near-screen saturations, because effective porosity affects deposition rates at lesser radii. Decreasing aerosol particle size directly increases average aerosol transport distances according to Equations 5-10 through 5-13. Whereas, according to simulation results, increase in gas injection rate indirectly increases average aerosol transport distances by reducing near screen saturations (Figure 5.12). This occurs because injection of gas also causes liquid flow in the direction of gas flow.

There are two transport mechanisms that achieve radial distribution of aerosol mass away from the well screen; 1) Transport and deposition as aerosols, and 2) Flow as a liquid phase deposited from aerosol. The occurrence of each of these processes are evident in data sets from long duration wedge simulations (Figure 5.8), where the liquid flow and aerosol deposition dominated regions are easy to differentiate based on the slope of the saturation profile. Gravity-induced, vertically-downward liquid flow was limited in these simulations due to an impermeable baseplate, however, the effect occurs and is evident in some field-scale simulation results (Figure 5.12).
The occurrence of gravity-induced flow indicates that liquid saturations are reaching and exceeding a relative-permeability threshold value. Symmetrical distribution about the well screen is preferred, as this condition would create a greater volume of influence. Therefore, limiting liquid accumulation and gravity-induced drainage would be ideal. This can be achieved by decreasing aerosol particle size and/or increasing gas injection rates. Implementing these conditions results in a more symmetric zone of influence such as that obtained during Coarse sand-“Both” simulation (Figure 5.12). These injection parameters limit liquid accumulation near the well screen, however, the boundary between liquid flow and aerosol deposition-dominated regions becomes blurred (Figure 5.13). This makes it difficult to determine the actual effect of aerosol transport and deposition on resulting saturations.

Using the fit simulation parameters, ROI’s of 1.9 m and 1.6 m were predicted for 4-week injection into Coarse and Fine sand respectively (Figure 5.12). The resulting zones of influence represented volumes that would suffice for some field applications in sandy formations. However, results suggest that adjustment of a few injection parameters could increase radii of influence by up to 100% and increase zone of influence by up to 200% (Figure 5.12). These results are promising with respect of site specific injection optimization capabilities.

Results of modeling indicate that aerosol delivery technologies could serve as a viable tool for enhancing contaminant remediation technologies under some site conditions, particularly at sites characterized by coarse-grained, well-sorted sediments. A relatively even, vertically and horizontally symmetrical distribution of effective
saturations can be obtained by optimizing and controlling aerosol injection parameters (Figure 5.12).
Chapter 6-Microcosm Experiments

Microcosm studies were used to characterize biostimulation and bioaugmentation using aerosol delivery techniques. The basic approach was to create microcosms representing various environmental and nutrient conditions, and then periodically analyze samples for contaminant degradation products. The parameters that were varied include water saturation, type of electron donor, presence of a bioaugmentation culture, and method for delivering various components (direct addition or aerosol delivery). Delivery of microbes in soybean oil aerosols was evaluated as a potential remedy for aqueous aerosol delivery limitations. The assumption is that enhanced biodegradation at the field-scale can be achieved if the following requirements are met using aerosol delivery:

1) The culture is capable of degrading TCE under partially saturated conditions,
2) Amendments can be delivered as aerosols, and
3) Microbes can be delivered as aerosols and remain viable.

The objective of this chapter is to evaluate the feasibility of meeting these requirements.

6.1 Methods

Microcosms were prepared in 160 mL serum bottles sealed with Teflon-coated rubber septum and crimp-on caps (Figure 6.1). Each microcosm contained 20 g fine-grained, quartz sand purchased from Driller Supply. The mineral medium used to construct microcosms is henceforth referred to as “nutrient water.” Nutrient water was prepared by amending deionized water with P, N, Mg, Ca, Fe, B, Zn, Ni, Mn, Cu, Co, Se,
Al, buffer (NaHCO$_3$), and yeast extract (growth factors)(Appendix A). The representative contaminant was TCE, which was added as a saturated aqueous solution (~1100 mg/L). Electron donors used during microcosm construction included hydrogen (5% by volume in N$_2$), sodium lactate (60% solution), EOS$®$ (emulsified soybean oil with lactate and other proprietary amendments), and soybean oil (neat). A Dehalococcoides enrichment culture characterized by Eaddy (2008), Elango et al., (2010) and Shan et al., (2010) was used as inoculum.

Microcosms were constructed to represent one of three different states of liquid saturation, termed oversaturated, saturated, and undersaturated. The total liquid added (nutrient water + inoculum + electron donor solution + TCE solution) to each microcosm was 50 ml for “oversaturated,” 5 ml for “saturated”, or 2.5 ml for “undersaturated” conditions. TCE solution was added to achieve 66 mg/L liquid concentration (ignoring
phase partitioning) and bioaugmentation was achieved by adding the inoculum at 1% by liquid volume. Electron donor was added at a mass concentration equal to at least 100 times that needed to stoichiometrically reduce TCE to ethene. Lactate was mixed directly into the nutrient water at the appropriate concentration, whereas soybean oil was added by direct injection into the microcosm with a syringe.

Nutrient water, electron donor, and/or inoculum was added to microcosms either directly as a liquid stream (by pouring or injecting with a syringe), or as an aerosol. A standard procedure was followed when preparing microcosms that involved only direct delivery. The first step was to add appropriate volumes of sand, nutrient water, and electron donor to a serum bottle. The bottle was purged with nitrogen that had been bubbled through TiCl$_3$ solution for 5 minutes to remove oxygen from the headspace and then sealed with a crimp cap and septum. Preliminary tests conducted using the redox indicator reazurin indicated that an $E_h$ below -110 mV was typically established within 4 to 5 days following nitrogen purging. Therefore, the bottles were incubated for 7 days to ensure that reducing conditions had been established. A syringe was used to inject the TCE solution following incubation, after which the bottles were allowed to stand for another day to allow TCE phase distribution to occur. The final step in microcosm construction was to augment with culture using a syringe. Following construction the oversaturated microcosms were stored upside-down to put the septum in contact with liquid. There was no standing liquid in the saturated and undersaturated variations; therefore, they were stored right-side-up.
Microcosm experiments are divided into two broad categories. The experiments are divided based on whether the intent is to investigate the effect of environmental conditions, or the effect of aerosol delivery on TCE biodegradation activity. The categories are named accordingly: Non-Aerosol Microcosms (NA) and Aerosol Microcosms (AER). Each category contains test subsets that differ based on construction methods and microcosm components. Each category also included associated, non-microcosm experiments, which are referred to as control tests.

6.1.1 Non-Aerosol Microcosms

Direct addition was used to deliver all components during the construction of Non-Aerosol Microcosm experiments, which were designed to investigate the effects of environmental conditions on reductive dechlorination of TCE. Two sets of control experiments were conducted; one to investigate compound mass loss rates from serum bottles and another to characterize compound degradation in the absence of added electron donor. Hydrogen Inclusion Tests characterized TCE dechlorination activity in the presence of hydrogen, whereas Donor/Saturation Tests investigated the effect of indirect electron donors and liquid saturation without addition of hydrogen. Lastly, Lactate Tests were designed to characterize the effect of creating lactate solution with powder as opposed to more expensive laboratory grade syrup.
6.1.1.1 Non-Aerosol Control Tests

Results from preliminary microcosm tests indicated that chlorinated compound mass loss occurred in some serum bottles. A Serum Bottle Loss test was designed to determine chlorinated compound losses in the absence of biological activity. The serum bottle was autoclaved and filled with 5 ml of DI water. The headspace in the bottle was purged with nitrogen, and then the bottle was sealed with a septum and crimp-cap. A syringe was then used to add 0.15 ml of TCE saturated solution, 0.05 ml of cDCE saturated solution, and 0.06 ml of VC as a gas. Samples were taken every 2 weeks over a 7 month period to characterize chemical concentrations. The bottle was stored upside-down for the first 2 months and right-side-up for the remainder of the test.

No Donor Tests were designed to serve as baseline cases for other microcosm experiments. Two different variations were constructed. The variations differed based on whether they were inoculated or not, but no electron donor was added in either case (Table 6.1, NA-CT-1 through 6). Each variation was constructed using oversaturated, saturated, and undersaturated conditions in duplicate. The purpose of No Donor control tests was to determine whether degradation would take place in the absence of intentionally added electron donor.
### Table 6.1 - Experimental design for non-aerosol microcosms

<table>
<thead>
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<th>Treatment&lt;sup&gt;a&lt;/sup&gt;</th>
<th>n</th>
<th>Amounts Added Per Bottle&lt;br&gt; (ml)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Nutrient Water</th>
<th>TCE Sat Water</th>
<th>Lactate Syrup Sol.</th>
<th>Lactate Powder Sol.</th>
<th>Soybean Oil</th>
<th>EOS</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Culture&lt;br&gt; (ml)</th>
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<sup>a</sup>NA = non-aerosol; CT = control tests; HIT = H<sub>2</sub> inclusion test; DST = donor/saturation test; LT = lactate test

<sup>b</sup>Treatments with >46 ml nutrient water = oversaturated; 4.6-4.7 ml = saturated; 2.25-2.35 = undersaturated

<sup>c</sup>Stock solution of 70% Na-Lactate syrup, 30% DDI water

<sup>d</sup>Stock solution of 560 g/L Na-Lactate (created from powdered form)

6.1.1.2 Hydrogen Inclusion Tests (HIT)

The aerosol delivery process involves gas injection, of which hydrogen can be a component. Hydrogen Inclusion Tests (Table 6.1, NA-HIT-1 through 6) were designed to investigate whether the presence of indirect electron donors (Lactate, Soybean oil, EOS) affected the biodegradation process in the presence of hydrogen. Hydrogen Inclusion Tests (HIT)
Tests were all oversaturated, bioaugmented, and contained 5% by volume hydrogen in the headspace. Each experiment was constructed in triplicate with the exception of Test NA-HIT-3 (soybean oil as electron donor), which was constructed in sextuplicate (6)(Table 6.1).

Test NA-HIT-1 served as the baseline case for this set of experiments. Hydrogen was the only electron donor added (Table 6.1). Test NA-HIT-2 differed in that lactate was added. In Test NA-HIT-3 soybean oil was added, and in Test NA-HIT-5 EOS was added (Table 6.1). Tests NA-HIT-4 and NA-HIT-6 contained combinations of indirect electron donors; soybean oil and lactate in Test NA-HIT-4 and EOS and lactate in Test NA-HIT-6 (Table 6.1).

### 6.1.1.3 Donor/Saturation Tests (DST)

Donor/Saturation tests involved two groups of microcosms defined by the type of electron donor added (Table 6.1, NA-DST-1 through 6). Lactate was used in one group (Tests NA-DST-1 through 3) and soybean oil was used in the other (Tests NA-DST-4 through 6)(Table 6.1). Oversaturated, saturated, and undersaturated variations were constructed for each group; all of these microcosms were inoculated (Table 6.1). Each Donor/Saturation experiment variation was constructed in duplicate.

### 6.1.1.4 Lactate Tests (LT)

Lactate is universally accepted as an effective electron donor for stimulating reductive dechlorination. Laboratory-grade lactate is typically supplied as a 60% by volume syrup, whereas cosmetic grade lactate is supplied as a powder. The ability to
utilize the powdered form under field settings could provide many benefits, including: 1) Significant cost savings, 2) Ability to deliver by aerosolizing powdered form, and 3) Delivery as mixture in soybean oil aerosols. Lactate Tests were designed to characterize the potential differences in microbial activity when biostimulated with lactate powder as opposed to lactate syrup.

Lactate Test microcosms were designed to create the most ideal conditions possible for reductive dechlorination of TCE. They were all constructed under oversaturated conditions and were directly inoculated with aqueous culture (Table 6.1, NA-LT-1,2). The tests involved two variations that differed based on whether liquid (NA-LT-1) or powdered (NA-LT-2) lactate was used. Each variation was constructed in triplicate (Table 6.1).

6.1.2 Aerosol Microcosms

Jet and ultrasonic aerosolizer technologies were evaluated. A 3-3 aerosolizer block (Figure 2.1) operated at $1.5 \times 10^{-4}$ scms gas flow rate and $8 \text{ ml/min}$ liquid flow rate was used for all jet aerosolization. The ultrasonic aerosolizers were constructed using piezoelectric plates removed from commercially available humidifiers (Sunbeam SUL495-UM). The jet aerosolizer was capable of aerosolizing aqueous solutions and soybean oil. The ultrasonic aerosolizer was able to aerosolize aqueous solutions, however, was incapable of aerosolizing soybean oil.

The ultrasonic aerosolizer was mounted in an apparatus that allowed a carrier gas to be supplied under pressure, which was required during aerosol delivery. The piezoelectric plate from the humidifier included a protruding, circular, plastic lip
mounted on the top-side (Figure 6.2). A hole equal in size to the diameter of the lip was cut through the center of a 2-inch-PVC cap. This allowed the piezoelectric plate to be mounted onto the underside of the cap (Figure 6.2). The plate was attached using mounting screws and sealed using silicone caulk. Operation of the ultrasonic plate required a power supply and control box. Carrier gas was injected through brass tubing installed through the PVC cap (Figure 6.2). The tubing was installed using a method that allowed the cap to be attached to a 2-inch-PVC pipe nipple. The capped nipple configuration served as an aerosolization chamber and liquid reservoir during operation. The chamber was designed to allow use with multiple aerosol delivery systems.

**Figure 6.2-** Bottom of ultrasonic aerosolization chamber constructed by mounting a piezoelectric plate through a PVC cap.

The apparatus was designed to facilitate the creation and delivery of aerosols into microcosms. An aerosolizer (jet or ultrasonic) was enclosed within an aerosolization chamber (Figure 6.3). The aerosolization chamber also served as a recirculating reservoir
for the liquid to be aerosolized (Figure 6.3). Aerosols were generated and flowed through the top of the aerosolization chamber into a 30-cm-long, horizontally oriented length of 2-inch PVC pipe (Figure 6.3). The opposite end of the pipe entered a vertically oriented fitting attached to a 1-m-long length of ½ inch flexible tubing (Figure 6.3).

Jet aerosolization requires a pressurized gas feed that also provides the gas flow to carry the aerosol particles. Ultrasonic aerosolization does not utilize pressurized gas; therefore, gas was fed through the brass tubing to provide gas flow (Figure 6.2). Liquid droplets splash around in the chamber during aerosolization with either type of aerosolizer technology. The inverted “Z” shape of the system eliminates the possibility of these droplets splashing into the tubing, ensuring that only aerosol particles are delivered to the intended target (Figure 6.3).

**Figure 6.3**- Diagram of aerosol generation and delivery system.
Preparation of microcosms involving aerosol delivery required slight modification to the procedure used for the non-aerosol microcosms. The initial step in delivery of components as aerosols was to place the component liquid into the aerosolization chamber (reservoir) of the apparatus (Figure 6.3). Inducing aerosol production and gas flow caused aerosols to flow through the flexible tubing (Figure 6.3). The end of the flexible tubing was placed on top of the sand within the serum bottles (Figure 6.4A). This configuration allowed aerosols to enter the sand under the flexible tubing, flow radially out through the sand depositing particles, exit the top of the sand, and then exhaust out through the top of the bottle (Figure 6.4A). The serum bottle was placed on a digital scale to monitor the liquid mass deposited.

**Figure 6.4**- Diagram of system used to A) Deliver component liquids to microcosms and B) Collect liquid inoculum following aerosolization.
Aerosol delivery of nutrient water was accomplished using air as the carrier gas, which then required a nitrogen purge to remove oxygen. Nitrogen gas was always used during aerosol delivery of inoculum. With the exception of delivery method, the construction process for aerosol delivery microcosms only differed in that TCE was the last component added. This deviation was required to maintain mass control of TCE. Losses would have occurred during aerosol delivery of inoculum due to volatility. The implications of this are that TCE was not given time to reach phase concentration equilibrium prior to inoculation and initial sampling.

Solute retention tests were conducted to characterize the effect of jet and ultrasonic aerosolization on resulting aerosol solute concentration. Microcosm experiments were designed to test the survivability of microbes during submersion in soybean oil and during aerosolization, which are termed Soybean Oil and Aerosolization Survivability Tests, respectively. Aerosol Delivery Tests were performed to characterize the effect on TCE dechlorination when components were delivered to microcosms as aerosols.

**6.1.2.1 Aerosol Supplemental Test**

Delivery of soluble amendments as aerosolized solutions requires that solute concentrations are retained in aerosol particles. A Solute Retention Test was designed to characterize solute conservation during jet and ultrasonic aerosolization processes. The liquid reservoir in the aerosolization chamber was filled with sodium sulfate solution (Figure 6.3). The exit end of the flexible tubing was packed full of compressed glass wool (Figure 6.4B). Inducing aerosol production and gas flow caused aerosols to flow
through the flexible tubing, the end of which was placed into a serum bottle (Figure 6.4B). The glass wool was used to facilitate aerosol liquid deposition in the tubing, which was then collected in the serum bottle (Figure 6.4B). The sodium sulfate concentration of the initial solution and concentrations of solutions collected in the serum bottles were then determined using ion chromatography.

6.1.2.2 Soybean Oil Survivability Tests (SST)

The method for producing inoculum for the Soybean Oil Survivability Tests involved centrifuging 500 ml the Dehalococcoides culture. In an anaerobic glovebox, the centrate was decanted and the moist solids were then mixed into 250 ml neat soybean oil by shaking vigorously. The soybean oil inoculum was added directly to microcosms with a syringe.

Soybean Oil Survivability microcosms involved 2 groups. Soybean oil was the only electron donor used in one group whereas soybean oil and lactate were used in the other. Oversaturated and undersaturated variations were constructed for each group. The 2 variations within 2 groups constituted 4 tests (Table 6.2, AER-SST-1 through 4), each of which was prepared in triplicate. The volume of TCE saturated solution added to the saturated variations is half of that added to saturated variations of other experiment categories (Table 6.2, AER-SST-2,4). This deviation was unintentional, and resulted in a 33 mg/L liquid TCE concentration as opposed to the intended 66 mg/L concentration.
### Table 6.2: Experimental design for aerosol delivery microcosms

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- SST = soybean oil survivability test; ADT = aerosol delivery test; SAT = aerosol survival test
- Contains 0.15 ml lactate solution per 2.3 ml nutrient water
- Stock solution of 70% Na-lactate syrup, 30% DDI water
- Treatments with >46 ml nutrient water = oversaturated; 2.3 = undersaturated
- Stock solution of 70% Na-Lactate syrup, 30% DDI water
- Contains 0.15 ml Lactate solution per 2.3 ml nutrient water

195
6.1.2.3 Aerosol Survivability Tests (AST)

Aerosolization Survivability tests included 3 different variations (Table 6.2 AER-AST-1 through 3). All were constructed using oversaturated conditions and lactate as the electron donor. One test variation (AER-AST-1) was designed to serve as a baseline and involved inoculation with the un-aerosolized culture. The remaining two variations involved inoculation with liquid collected from aerosols (Table 6.2). The previously described method of packing glass wool into the flexible tubing and collecting liquid in a serum bottle was used to obtain aerosolized liquids (Figure 6.4B). The process was utilized to collect aerosolized culture from jet and ultrasonic aerosols, which were then used to inoculate microcosms via syringe (AER-AST-2,3). Each of the 3 variations was prepared in triplicate.

6.1.2.4 Aerosol Delivery Microcosms

6.1.2.4.1 Alternative Aerosol Delivery Containers

The ideal design for aerosol delivery microcosm tests would have been a container that allowed aerosol to flow unidirectionally through the porous medium. This type of configuration would most closely reproduce the transport and deposition conditions that would occur in a field setting. The original containers designed for this purpose involved construction with threaded PVC components (Figure 6.5A). The filter sand was emplaced upon a screen within the microcosm container. Aerosol laden gas was injected through a valve on the bottom-side, and exhaust passed through a valve on the top-side (Figure 6.5A)
Other variations were constructed using the same basic design, but were modified in an attempt to eliminate chlorinated compound leakage or diffusion from the container. One variety involved elimination of pipe threads, and was constructed using 2-inch, glue-on PVC fittings (Figure 6.5B). Containers were constructed and left open in a running ventilation hood for 3 days to allow flushing of PVC cement vapors. The other variation was designed to eliminate PVC from the container. This container was constructed using all threaded metal parts (Figure 6.5C).

Figure 6.5- Various containers used for aerosol delivery microcosms, A) Threaded PVC, B) Glued PVC, C) Metal.
6.1.2.4.2 Aerosol Delivery Tests (ADT)

Aerosol Delivery tests included 4 different variations (Table 6.2, AER-ADT-1 through 4), all of which were constructed using undersaturated conditions (Table 6.2). The first three variations utilized aerosol delivery of aqueous components and lactate as the electron donor. One involved aerosol delivery of nutrient water and direct addition of inoculum (AER-ADT-1), another involved direct addition of nutrient water and aerosol delivery of inoculum (AER-ADT-2), and another involved addition of all components as aerosols (AER-ADT-3)(Table 6.2). These test variations were prepared in quadruplicate.

The final variation involved direct addition of nutrient water and aerosol delivery of soybean oil inoculum (AER-ADT-4). The soybean oil inoculum was created using the method outlined for Soybean Oil Survivability tests, and the soybean oil served as the electron donor (Table 6.2). A total of 7 replicates were prepared for this variation.

6.1.3 Chemicals and Analytical Methods

TCE (99.5%, Fisher) and cDCE (99%, TCI America) were neat liquids and VC (99.5%, Fluka) was a neat gas. Sodium lactate syrup (EM Science) was obtained as a 60% solution with specific gravity of 1.31. Soybean oil (Cargill) was industrial grade soybean oil. Sodium sulfate was reagent grade.

A syringe was used to periodically take 0.5 ml gas samples from microcosm headspaces. TCE, cDCE, VC, and ethene mass concentrations in headspace samples were analyzed using a Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector and 2.44 m x 3.175 mm column packed with 1% SP-1000 on 60/80 Carbopack B (Supelco). Sodium sulfate solution concentrations were analyzed
using a Dionex ICS2100 ion chromatograph with a AS-9HC column with a AG-9HC guard.

Biological activity in microcosms was characterized based on amounts of TCE, cDCE, VC, and ethene in headspace gas. Fugacity relationships were used to convert gas concentration to total moles within the microcosm container for each compound. These values were then scaled to the total moles of TCE added to the bottle, therefore, the range for scaled data values is 0 to 1 (Figures 5-8). The conversion ratio along each step of the degradation chain is 1:1, therefore, mass conservation at any given time is indicated when compound ratios sum to unity. Data from a representative test are plotted as an example of activity within a particular group of microcosms (Figures 6-8, 9, 11, 12, and 14). The plotted data set was selected to represent an average; however, the plotted data represents the lone replicate in which activity was measured in some cases. Results from all microcosm replicate tests are provided in Appendixes B-D.

6.2 Results

6.2.1 Non-Aerosol Microcosms

6.2.1.1 Non-Aerosol Control Tests

TCE and cDCE decreased at roughly 0.007 μmol/d during the first two months of the Serum Bottle Loss Test, while VC concentrations remained constant (Figure 6.6). The bottle was stored right-side-up after the first 2 months. Following this change TCE and cDCE concentration decreased at a greater rate (~3 μmol/100 days), while VC concentration decreased slightly (Figure 6.6).
A relatively small amount of biodegradation occurred over the first 10 to 15 days in No Donor Test microcosms that were inoculated, after which point the process stalled (Figure 6.7). Reductive dechlorination was not observed under any saturation conditions when microcosms were not bioaugmented (Figure 6.7).
Figure 6.7 - Scaled chlorinated compound concentrations with time from No Donor microcosms.
6.2.1.2 Hydrogen Inclusion Tests

Reductive dechlorination of TCE to ethene tended to occur during Hydrogen Inclusion Tests, however, microcosms containing EOS were the exception. Test NA-HIT-5 microcosms contained hydrogen and EOS, while Test NA-HIT-6 microcosms contained hydrogen, EOS, and lactate (Table 6.1). There was no evidence of reductive dechlorination observed for any of these cases (Figure 6.8E,F).

Test NA-HIT-1 (Hydrogen), NA-HIT-2 (Hydrogen and Lactate), and NA-HIT-3 (Hydrogen and Soybean Oil) exhibited similar results; complete dechlorination occurred over a period of approximately 50 to 70 days (Figure 6.8A-D). Results from replicates were fairly consistent. One exception was Test NA-HIT-3F, in which reductive dechlorination was initiated but then stalled after approximately 30 days (Appendix B).

Test NA-HIT-4 contained hydrogen, lactate, and soybean oil. As compared to Tests NA-HIT-1, 2, and 3, the tendency in NA-HIT-4 microcosms was a slower rate of dechlorination and/or a stall in the dechlorination process (Figure 6.8D). Results from Test NA-HIT-4A were approaching complete dechlorination, however, the rate was slow compared to treatments in which lactate and soybean oil were not added together (Appendix B). The dechlorination process stalled at approximately 50 days during Tests NA-HIT-4B,C (Figure 6.8D).
Figure 6.8- Scaled chlorinated compound concentrations with time from Hydrogen Inclusion Tests (NA-HIT-1-6). Activity in alternates: ↑ (greater); = (similar); ↓ (lesser); 0 (none).
6.2.1.3 Donor/Saturation Tests

With one exception (NA-DST-3B, Appendix C), complete reduction of TCE to ethene occurred under all saturation conditions when lactate was the lone electron donor (Figure 6.9A-C). Oversaturated microcosms were designed to represent ideal conditions for biodegradation, and complete reduction to ethene occurred over a period of ~ 60 days. Complete reduction in saturated and undersaturated microcosms was faster, occurring over periods of 30 to 50 days. A notable trend in the lactate test results is that mass balance was satisfied while oversaturated, whereas apparent losses of 40 to 80% were incurred when saturated or undersaturated (Figure 6.9B,C). This result is related to storage orientation, and was typical of all microcosms evaluated during this research.

TCE concentration dropped upon initiation of tests that contained soybean oil, an effect that occurred in Donor/Saturation tests where soybean oil was the lone electron donor (Figure 6.9D-F). TCE degradation was induced under all saturation conditions, however, the pattern and completeness of the reduction process differed from examples in which lactate was used (Figure 6.9A-C). There was an initial lag time of 30 to 40 days before significant dechlorination started, whereas degradation started immediately when using lactate. The rate of dechlorination increased significantly following initial lag periods, but abruptly stalled after 50-60 days (Figure 6.9D-F). The extent of dechlorination in Donor/ Saturation soybean oil experiments generally decreased with decreasing water saturation. There was also variability between the duplicate tests for each of the three saturation conditions, with significantly less activity having occurred for a duplicate from each case (Figure 6.9D-F).
Figure 6.9- Scaled chlorinated compound concentrations as a function time, e− donor, inoculation, and liquid saturation during Donor/Saturation Tests (NA-DST-1-6). Activity in alternates: ↑ (greater); = (similar); ↓ (lesser); 0 (none).
6.2.1.4 Lactate Tests

Complete reduction of TCE to ethene was achieved in every test from both lactate experiment variations (Figure 6.10). Evidence of reductive chlorination was observed immediately following inoculation in all of the tests in the form of daughter product formation. However, a feature that was prevalent in both experiment variations was a period of fairly constant daughter product concentrations while TCE concentration decreased. This period tended to last from 50-75 days during the early portions of the tests (Figure 6.10). This period tended to be followed by a fairly rapid generation and decrease in cDCE and VC concentrations along with a rapid accumulation of ethene (Figure 6.10).

Differences in daughter product production patterns for some of the tests are noteworthy. These differences were characterized by whether cDCE or VC accumulated to high levels (Figure 6.10). However, these differences were not patterned on the type of lactate used. Differences in overall reaction rates also could not be discerned based on lactate used. Complete dechlorination was achieved within 150 to 180 days in all cases (Figure 6.10).
Figure 6.10 - Relative TCE concentrations as a function time for Lactate Test microcosms.
6.2.2 Aerosol Microcosms

6.2.2.1 Aerosol Solute Retention Tests

An increase in solute concentration occurs during the aerosolization and aerosol transport processes. The Na$_2$SO$_4$ concentration of the original solution was 135 mg/L, whereas the concentration of the liquid effluent from jet aerosols was 152 mg/L, and from ultrasonic aerosols it was 136 mg/L.

6.2.2.2 Soybean Oil Survivability Tests

Inoculation with the culture concentrate delivered in soybean oil induced indications of reductive dechlorination within all test groups (Figure 6.11). There were relatively large initial decreases in TCE concentrations in the oversaturated Soybean Oil Survivability tests (Figure 6.11A,C). Complete reduction of TCE to ethene also occurred in these microcosms, which is atypical in comparison with other soybean oil containing microcosms (Figure 6.9D-F). The manner in which soybean oil and culture were added may play a role in this difference, however, it is most likely related to the fact that only half of the intended TCE was added during microcosm preparation.

A 30 to 50 day lag period occurs between the start of the test and the start of degradation where soybean oil was the lone electron donor (Figure 6.11A,B), similar to the patterns observed in Donor/Saturation test results (Figure 6.9D-F). The lag period was less pronounced or absent when lactate was present in the system (Figure 6.11C,D). Stalling of the bioreduction process after 60 to 70 days was characteristic of both undersaturated treatments, but more TCE was degraded when lactate was included as
compared to soybean oil alone (Figure 6.11B,D). With the exception of AER-SST-1, there was little consistency between replicates during the Soybean Oil Survivability Tests (Appendix D). Little to no reductive dechlorination occurred during Tests 14B, 14C, or 15C, and stalling occurred during Tests 14A, 16B, and 16C (Appendix D).

Figure 6.11- Scaled chlorinated compound concentrations as a function time, e− donor, and inoculum from Soybean Oil Survivability Tests (AER-SST-1 through 4). Activity in alternates: ↑ (greater); = (similar); ↓ (lesser); 0 (none).

6.2.2.3 Aerosol Survivability Tests

A direct addition group variation within Aerosolization Survivability tests was designed to serve as a positive control, representing degradation rates that should be
expected under ideal conditions (Figure 6.12A). The time required to completely reduce TCE to ethene was approximately 100 days (Figure 6.12A), however, rates were slower, and extents of degradation were less in the other replicates (Appendix E). As a whole, performance of AER-AST-1 microcosms (Appendix E) was poor as compared to Donor/Saturation tests that were constructed identically (Figure 6.9A). The culture used for each set of experiments came from the same source, however, samples were collected eight months apart.

Inoculation of microcosms with aqueous inoculum collected from jet aerosols produced little activity in one replicate (AER-AST-2C, Appendix E), however, results from the other replicates were similar to those from direct inoculation (Figure 6.12B). Inoculation of microcosms with aqueous inoculum collected from ultrasonic aerosols produced indications of biodegradation in only one of the three replicates (Figure 6.12C). The extent of bioreduction in this case was relatively small (Figure 6.12C).

6.2.2.4 Aerosol Delivery Tests

6.2.2.4.1 Alternative Aerosol Delivery Containers

Multiple tests were conducted using each alternative aerosol delivery container variation. The results obtained for each container type tended to be similar; therefore, one typical example of each is shown (Figure 6.13). The TCE concentration dropped quickly
Figure 6.12- Scaled chlorinated compound concentrations as a function of time and inoculum used during Aerosolization Survivability Microcosms (AER-AST-1 through 3). Activity in alternatives: ↑ (greater); = (similar); ↓ (lesser); 0 (none).

over the first 10-20 days when using each of the three container types. Concentrations continued to quickly decrease to zero for threaded PVC containers, tended to slow for glued PVC containers, and decreased at a fairly constant rate when using metal containers (Figure 6.13). Large masses of unknown volatile compounds were continuously measured in samples from glued PVC containers (not shown), but no indication of
reductive dechlorination was ever detected (Figure 6.13B). Daughter products were measured intermittently in threaded PVC and metal containers, however, they never accumulated to significant levels (Figure 6.13A,C).

Figure 6.13- Typical results achieved when using A) Threaded PVC, B) Glued PVC, and C) Metal aerosol delivery containers.
6.2.2.4.2 Aerosol Delivery Serum Bottles

Complete reduction of TCE to ethene occurred in every example when delivering components as aqueous aerosols (Figure 6.14A-C). Reductive dechlorination activity followed a similar pattern for all replicates regardless of whether nutrient water and/or inoculum were delivered directly or as aerosol (Figure 6.14A-C). Complete reduction in direct inoculation microcosms tended to require slightly less time than microcosms inoculated using aerosol delivery, with ranges of 40 to 50 days compared to 60 to 80 days respectively. Results from replicates within each aqueous aerosol delivery group were similar, and there was also little observable difference between results of the three component delivery variations (Appendix F).

Indications of bioreduction were observed in only two of the eight soybean oil aerosol inoculation replicates (Appendix F), and the TCE daughter product accumulation that occurred in these two replicates was relatively small (Figure 6.14D). Initial measurements indicating the presence of daughter products were obtained after a long period of non-sampling, and the bioreduction process seems to have stalled by that point, as no further changes were measured (Figure 6.14D). Increases in cDCE, VC, and ethene were measured, but cDCE and VC trends are only observable when plotted over a smaller scale (Figure 6.14D-inset).
Figure 6.14- Scaled chlorinated compound concentrations as a function of time, nutrient water delivery method, and inoculum delivery method for Aerosol Delivery Tests (AER-ADT-1 through 4). Activity in alternates: ↑ (greater); = (similar); ↓ (lesser); 0 (none).
6.3 Discussion

6.3.1 Mass Balance

The Serum Bottle Loss test container was stored upside-down during the first two months, which put liquid in direct contact with the septum and crimp-cap. Over this period TCE and cDCE concentrations decreased while VC concentrations remained constant (Figure 6.6). Storing the bottles right-side-up puts gas in contact with the septum. The result of this change (starting at 2 months) was a significant increase in the rate of TCE and DCE mass decrease, and VC loss at a relatively slow rate (Figure 6.6).

These increases in loss rate did not coincide with increases in mass loss of less chlorinated compounds, which indicates that leakage rates for TCE and cDCE increased. Storing the bottles upside-down effectively utilizes the liquid as a diffusive barrier, therefore, if leakage is occurring then rate increases would be expected when bottles are turned right-side-up. Leakage would take place at the contact between the septum and glass bottle and/or through the holes in the septum created by the syringe during sampling. Loss rates increased with time, an indication that leakage through the holes is the major contributor (more holes with time)(Figure 6.6). Oversaturated variations were stored upside-down, whereas saturated and undersaturated variations were stored right-side-up. Mass balances were not well maintained in microcosms that were stored right-side-up, which resulted from increased leakage rates.

TCE concentrations in microcosms tend to decrease sharply after test initiation when soybean oil is present (Figure 6.8C). This decrease results due to the fact that chlorinated solvents tend to partition into soybean oil (Pfeiffer et al., 2005). The
reduction in initial molar ratio represents the TCE mass that has partitioned into the NAPL phase. The lesser chlorinated compounds exhibit similar behavior, therefore, it must be considered that partitioning into the NAPL phase impacted mass balance at all times during tests that involved soybean oil.

6.3.2 Electron Donor and Saturation Effects

Donor/Saturation microcosms that contained TCE and were not inoculated produced no indications of TCE degradation regardless of liquid saturation (Figure 6.7). This confirms that any significant reduction of chlorinated compounds in other test results was brought about by the microbes present in the inoculation culture. Limited activity that stalled within 5 to 15 days occurred in samples that were inoculated without addition of nutrient water or electron donor (Figure 6.7). These results indicate that some residual nutrient water and electron donor were present in the inoculum. Each category of microcosm tests was created with a different batch of culture collected from the same source, but at different times. Effect of residual electron donor was not characterized for other categories, but must be considered as a possibility in cases where relatively small activity was detected.

Electron donors that were investigated in this work include hydrogen, lactate, soybean oil, and EOS. Complete reduction of TCE to ethene was observed in cases where hydrogen was the only electron donor present (Figure 6.8A), and when lactate was the only electron donor present (Figure 6.9A). Significant biodegradation was commonly observed when soybean oil was the only electron donor present, however, the process only progressed to completion at lower TCE concentrations (Figure 6.11A).
It would be expected that complete reduction of TCE to ethene would occur when hydrogen was present in microcosm headspace, as hydrogen is the only electron donor utilized by *Dehalococcioides*. However, evidence of biodegradation was not produced from microcosms that contained EOS even when hydrogen and/or lactate were also present (Figure 6.8E,F). This suggests that the EOS was actually inhibitory to the biodegradation process, which disagrees with a previous study suggesting that EOS can serve as an electron donor for the SRS culture (Eaddy, 2008). The EOS used for these experiments came from the same containers as that used by Eaddy (2008), which had been stored in a refrigerator for approximately 2 years. It is hypothesized that some type of spoilage took place during that time.

The degree of water saturation had limited effect on reductive dechlorination activity in microcosms (Figure 6.9). Trends observed in soybean oil survivability tests could be interpreted as an exception (Figure 6.11A,B), however, the unintentional addition of less TCE in the oversaturated microcosms is a more likely cause of apparent differences. With the exception of one replicate (NA-DST-3B), TCE was completely reduced to ethene under all saturation conditions in direct addition microcosms when lactate was the sole electron donor (Figure 6.12). Results of previous studies have shown that the culture used for this research is capable of reducing TCE to ethene when using lactate in oversaturated microcosms (Eaddy, 2008), and that reductive dechlorination could occur under partially saturated conditions while using H₂ as an electron donor (Mihopoulos et al., 2000). Results of this work show that the process also occurs for undersaturated conditions while using lactate (Figure 6.9C). These results are significant
because they demonstrate the ability of the culture to degrade TCE under partially saturated conditions while using an indirect (not H₂) electron donor, which is a good indication for successful application in contaminated vadose zones.

Reductive dechlorination of TCE occurred to varying degrees in microcosms utilizing soybean oil as the only electron donor. A 30 to 50 day lag period followed by a significant increase in activity characterizes most of the microcosms using soybean oil (Figure 6.9D-F). The lag period is assumed to represent the time required for soybean oil fermentation to hydrogen, which must occur before *Dehalococcoides* can degrade cDCE and VC, as well as TCE. The degradation activity that occurs prior to this point most likely can be attributed to residual electron donor present in the inoculum, as was observed in experiments where exogenous electron donor was not supplied (Figure 6.7). Hydrogen can be utilized directly if present, and hydrogen production from fermentation of lactate is much faster than fermentation of soybean oil, which is why the presence of hydrogen and/or lactate in soybean oil microcosms tended to eliminate the lag period (Figures 6.8C,D and 6.11D).

Another trend associated with soybean oil microcosms is that dechlorination activity tends to stall. Stalling is likely due to an accumulation of long-chain fatty acids, which are produced when soybean oil undergoes fermentation (Borden and Rodriguez, 2006). Long-chain fatty acids can inhibit anaerobic biodegradation when present beyond a threshold concentration (Li et al., 2005; Borden and Rodriguez, 2006). Fatty acids tend to partition out of solution in the presence of organic matter, therefore, this problem could be reduced under field conditions where organic matter is present in the vadose zone.
The oversaturated examples from Soybean Oil Survivability Tests (Figure 6.11A,C) inadvertently received only half of the TCE concentration used for other microcosms, and the volume of soybean oil delivered for inoculation purposes is greater than the volume delivered for solely electron donor purposes (Table 6.2). The relatively high oil content increased the extent of phase partitioning and is likely responsible for the large initial drop in TCE concentration (Figure 6.11A,C). Addition of less TCE was unintentional, however, results from these tests provide some insight. Complete TCE reduction to ethene occurred in both variations (with and without lactate) (Figure 6.11A,C). The microbes were apparently able to completely degrade the lesser TCE mass before fatty acids could accumulate to toxic levels.

Soybean oil fermentation in undersaturated microcosms caused reductive dechlorination stalling even when lactate was present (Figure 6.11D). These microcosms were spiked with 10% of the TCE used for the oversaturated examples; however, they were also constructed with approximately 95% less water (Table 6.2). Less fatty acid production would be required to create toxic conditions in the undersaturated systems.

There were no discernible differences observed between microcosm tests constructed with liquid lactate or powdered lactate as the electron donor (Figure 6.10). These results would indicate that the powdered lactate used for these tests is just as viable as the lactate obtained in syrup form. The powdered lactate is not laboratory grade, and purity tolerances are assuredly not as stringent during production. However, powdered lactate is much less expensive and would allow for potentially beneficial application techniques during aerosol delivery operation at the field-scale.
6.3.3 Aerosol Production Method

Analysis of liquid collected from jet and ultrasonic aerosols show that solutes are not only retained within aerosol particles, but that the concentration tends to increase (Table 6.3). The increase in solute ($\text{SO}_4^{2-}$) is most likely due to evaporation of water composing the aerosol particles. This mechanism would fit with the observation that effects during jet aerosolization are greater than during ultrasonic aerosolization. Gas jets are used during the jet aerosolization process, which exposes a small volume of liquid to a large volume of high velocity gas. The high velocity through the jet drops the gas pressure, which likely causes adiabatic cooling and condenses water from the gas. The condensation presumably increases the size of existing aerosols, increasing the likelihood that they will settle out of the flow in the aerosolizing chamber. The temperature of the gas jet increases as the jet expands and this causes the relative humidity of the gas to become drier. The dry gas evaporates the water aerosols, and the smaller size fraction evaporates preferentially compared to the larger aerosols. A slow steady gas flow is used as a carrier for aerosol particles in the ultrasonic system. A greater aerosol liquid to gas volume ratio can be maintained, and the humidity of the gas can be high, which explains why there is relatively little evaporation while using ultrasonic technology.

Microcosms were inoculated with liquid collected from ultrasonically aerosolized culture. Indications of bioreduction were observed in only one of three replicates, and they occurred as a relatively small mass of daughter product produced after a 75 to 100 day dormant period (Figure 6.12C). It is possible that the occurrence of daughter product represents activity of a small number of *Dehalococoides* that were able to survive.
delivery. As a whole, these results suggest that microorganisms in the culture tend not to survive ultrasonic aerosolization. Exposing microbes to ultrasonic frequencies is actually a practiced method of cell lysing (Boisits and Klosek, 1974), therefore, low survivability during this process is unsurprising.

A set of Aerosol Survivability microcosms were inoculated with liquid collected from jet aerosolized culture (Figure 6.12B). Complete reduction of TCE to ethene was induced, indicating that the microbes survive jet aerosolization and aerosol transport. The rates and degradation patterns observed in results from these tests were similar to those from the direct inoculation tests (Figure 6.12A). The similarity indicates that jet aerosolization and aerosol transport over short distances have little effect on microbial activity.

One group of microcosms within the Aerosol Survivability Test set was constructed using direct inoculation with the culture (no aerosols) (Figure 6.12A). Complete reduction of TCE to ethene took place in one replicate, however, the rates and overall extent of dechlorination were slower than other microcosms constructed similarly (Figure 6.9A) (Table 6.2). This suggests that the batch of culture used during Aerosol Survivability tests may have been lower quality, possibly due to a lower cell count or other factors.

6.3.4 Aqueous Aerosol Delivery

Each of the three flow-through aerosol container designs performed poorly during experiments (Figure 6.5, 6.13). The design required the ability to inject aerosols through one end and exhaust through the other, while also allowing a complete seal to be created
following injection. This design negated the use of glass, and required some number of joints in the container (either glued or threaded). Decreases in TCE concentration observed during testing with the original threaded PVC containers (Figure 6.13A) indicated that losses were occurring as leakage through the threaded joints and/or diffusion through the PVC (Figure 6.5A).

The characteristic behavior observed in the glued PVC containers was a decrease in TCE concentration of the first few weeks, followed by a relatively constant concentration over the remaining duration (Figure 6.13B). The flow-through containers are large in comparison to the serum bottles, and it is possible that decrease observed over the first few weeks represents a TCE phase equilibration period. However, it is also possible that TCE was diffusing through the PVC, and that the change in loss rate represents the equilibration of a TCE concentration gradient through the PVC (Figure 6.13B). There was zero indication of TCE reduction during experiments in glued PVC containers, which could be attributable to large concentrations of unidentified volatiles trapped within. The unidentified volatiles are assumed to have been released from the PVC cement even after being allowed to dry in a ventilation hood for three days.

The metal containers were designed to eliminate materials from the system through which chlorinated solvents could diffuse (Figure 6.13C). Results from sampling these containers following inoculation by aerosols showed that in some cases TCE concentrations decreased without accumulation of daughter products. This suggests that leakage was taking place, presumably through the threaded fittings, which had Teflon tape applied and were well tightened by use of pipe wrenches and a chain vise (Figure
6.5C). Daughter products were intermittently measured in the metal containers, suggesting that reduction of chlorinated compounds was occurring in some cases. Leakage out of the container would explain why the concentration of these compounds remained low (Figure 6.13C).

Aqueous aerosol delivery variations involved combinations of nutrient water and/or inoculum added directly or as aerosols (Figure 6.14A-C). The results from these tests were similar for each delivery combination (Figure 6.14A-C). This indicates that delivery of nutrient water and/or inoculum as aqueous aerosol is effective. The TCE concentration decreased more rapidly in directly inoculated microcosms than in ones that used aerosol delivery, suggesting that cells per liquid volume may be reduced during the aerosolization and transport processes. However, the slight decrease in efficiency observed during these experiments would likely be insignificant during field application.

6.3.5 Soybean Oil Aerosol Delivery

Soybean Oil Survivability tests involved mixing microbes into soybean oil, and using this mixture to directly inoculate microcosms. Dechlorination activities were observed in results of these microcosms (Appendix D), indicating that the culture is capable of surviving the extraction and mixing processes associated with soybean oil inoculum preparation. Inoculation of microcosms took place within a few minutes of mixing the culture solids into soybean oil. The solids were water wet when mixed into the soybean oil by shaking during soybean oil inoculum preparation. Therefore, the mixture most likely occurs as a water-in-oil emulsion. It is possible that the small water droplets within the oil could house microbes during the period prior to inoculation.
The soybean oil variations of Aerosol Delivery Tests involved delivering the soybean oil inoculum mixture as aerosols. Indications of biodegradation were produced in only two of eight replicates. The biological activity was initiated after a 75 to 100 day lag period and quickly stalled (Figure 6.14D). The relatively small mass of daughter products produced is similar to that produced in ultrasonic Aerosolization Survivability Tests (Figure 6.12C).

Reductive dechlorination was induced in Soybean Oil Survivability Tests (Appendix D) and aqueous Aerosolization Survivability Tests (Figure 6.12B), the combination of which indicated that successful inoculation with aerosolized soybean oil mixture should be possible. The soybean oil variations of Aerosol Delivery Tests were designed to mimic field conditions that would be achievable by utilizing only soybean oil aerosol delivery (undersaturated and no lactate). It stands to reason that constructing soybean oil aerosol delivery microcosms as oversaturated and/or with lactate would have produced a more ideal environment for dechlorination activity. However, these variations were not tested.

There may be microbe survivability problems associated with aerosolization of the soybean oil mixture. One consideration is the time that microbes spend submerged in the soybean oil. Inoculation occurred immediately after the soybean oil mixture was created during construction of direct addition Soybean Oil Survivability Tests. Addition of the oil mixture by aerosolization requires storage in the aerosolization chamber and recirculation while aerosols are produced. Inoculation by aerosolization requires about 20 minutes, whereas direct inoculation occurs 1-2 minutes after soybean oil inoculum
preparation. The difference in submersion time could possibly affect microbe efficiency once inoculation takes place.

The soybean oil mixture is another factor to consider. The method used to create the soybean oil inoculum mixture most likely produces a water-in-oil emulsion. The fate of microorganisms in this case could depend on positioning within an aqueous microbubble instead of surviving direct contact with soybean oil. Aerosols created from an emulsion have not been characterized. The aerosolization process may displace microbes from aqueous microbubbles into the oil, or could result in phase separation that would promote evaporation of the small amount of aqueous phase that is present. These possibilities would be detrimental to microbe survivability, and could serve as explanations for why inoculation with soybean oil by direct addition would work and aerosol delivery would not.

6.4 Conclusions

Microcosm tests allowed characterization of chlorinated ethene degradation activity as a function of electron donor, liquid saturation, and component delivery method. TCE degradation was achieved when delivering nutrients and/or microbes as aerosols, which suggests that field implementation for the purpose of biostimulation and bioaugmentation is a promising possibility. However, inconsistencies when using soybean oil based aerosols for inoculation and a potential for evaporative limitations when using aqueous aerosols indicate that condition-specific injection methodologies will be required for successful implementation.
It had previously been demonstrated by Eaddy (2008) that the culture used for this work was capable of completely dechlorinating TCE while utilizing lactate as electron donor. Results of this work confirmed these observations and also demonstrate that the process could occur under partially saturated conditions (Figure 6.9C) and while using soybean oil as an electron donor (Figure 6.9D). Utilizing soybean oil as an electron donor presents a potential issue in the form of stalling due to long-chain fatty acid accumulation (Figure 6.9D-F). However, this may not be an issue under field conditions when contaminant concentrations are relatively low and/or when soil organic matter is present.

Aerosol delivery technologies are intended to be a method for enhancing remedial methods in the vadose zone, therefore, remedial conditions generated by aerosol delivery must be conducive to application in unsaturated media. This condition is satisfied in the case of enhanced bioremediation when using lactate as the electron donor, as lactate microcosm results indicate that degree of liquid saturation does not significantly affect reductive dechlorination activity (Figure 6.9A-C). Degree of saturation does have some influence on dechlorination activity when using soybean oil as the lone electron donor (Figure 6.9D-F and 6.11A,B), presumably due to greater fatty acid concentrations when liquid saturations are lower. Inducing TCE degradation in un-saturated media is promising with respect to successful enhanced bioremediation in contaminated vadose zones. However, some minimum aqueous saturation must be maintained to sustain survivable conditions for microbes and to dilute fatty acid concentrations when using soybean oil.
Solutes are retained within jet and ultrasonically generated aerosol particles (Table 6.3), therefore, these constituents can be delivered as solution when aerosol particles are transported effectively. Results of microcosms constructed by delivering nutrients and/or culture as jet-generated, aqueous aerosols are very positive (Figure 6.14A-C). Dechlorination activity indicates that addition of components as aqueous, jet aerosols is just as effective as direct addition. The method would be effective when scaled-up, assuming that delivery to microcosms is directly analogous to field-scale implementation. According to findings from column and wedge tests (Chapters 3,4), delivery over the distances used for microcosm construction may significantly underestimate the effect of evaporation that would occur at the field-scale. Column test results indicate that evaporation of aerosol particles can result in solid precipitates that can be effectively transported as solid aerosols, which could provide an effective means for emplacing nutrients. It is possible that the effect of evaporative drying in the formation could compromise microbe survivability.

Utilization of ultrasonic aerosolization could potentially alleviate evaporative effects. However, test results indicate that microbes do not survive the aerosolization process (Figure 6.12C), and the pressure differential across the ultrasonic plate during injection tends to break the device. Delivery of inoculum in soybean oil aerosols also offers the potential for alleviating problems caused by evaporation. Culture survivability during submersion in soybean oil over short time durations has been demonstrated (Appendix D), however, disruption of the water-in-oil emulsion structure of the soybean oil mixture may limit inoculation using an aerosol delivery approach.
Chapter 7 - Conclusions

The feasibility of using aerosols to improve remediation of the vadose zone was evaluated by conducting experiments and theoretical analyses. Aerosolizer characterization experiments focused on determining effects of aerosolizer design, operating parameters, and liquid composition on resulting particle size distribution. Transport experiments using columnar and wedge-shaped chambers characterized aerosol mobility as a function of operating parameters, porous medium properties, gas flow geometry, and liquid composition of the aerosols. A numerical model was developed to simulate aerosol transport in flowing gas, and data collected during transport experiments at the lab-scale were used to calibrate the model before evaluating field-scale scenarios.

7.1 Conceptual Model

This work has resulted in a conceptual model for transport of compounds relevant to remediation of the vadose zone. Soybean oil injected through a jet aerosolizer is dispersed into droplets, a significant fraction of which are less than 10 microns in diameter (Figure 2.19). The distribution of particle sizes in the mobile phase depends on the configuration of the aerosolizer, and directing the aerosol stream to an impact plate appears to decrease average particle size in the stream, thereby increasing mobility (Figure 2.19).

The smaller aerosols are suspended in flowing air where they can be transported through pipes, into the casing, through the well screen, and into a partially saturated formation. The highest concentrations of oil occur in close proximity to the well screen
(Figure 3.26), and significant fractions of oil may be removed from the air flow when using a fine mesh screen (Figure 3.1).

Oil that enters the pore space appears to be deposited at a rate this is roughly proportional to the aerosol concentration, which results in a distribution that resembles a negative exponential with distance (Figure 4.10). Aerosol deposition causes concentration and average particle size to decrease with flow distance during linear flow (Figure 3.21), and concentrations are further diminished with distance during radial flow. The majority (85 to 90%) of oil aerosols deposit within the first 2 m when flowing through Coarse sand (~2.6 mm)(Figure 4.8). The aerosols that are transported 2 m consist of the most mobile particles, and presumably these are the particles in the sub-micron size. As a result, the bulk of the injected oil will deposit within 1 to 2 m of an injection well, but approximately 10% of the injected oil mass may be transported distances of many meters (Figure 5.12).

7.2 Controlling Factors

Results of this research indicate the primary factors controlling the delivery of compounds as aerosols during a field-scale implementation include

A.) Composition of the liquid being aerosolized (Figure 3.3);
B.) Aerosolizer design affecting evaporation (Figure 2.14);
C.) Aerosol particle size (Figure 5.12);
D.) Formation grain size and saturation (Figures 4.8,4.9);
E.) Formation permeability and geometry affecting liquid flow following aerosol deposition (Figure 5.8).
7.2.1 Liquid Aerosolized

Injection of fresh water, salt water, and soybean oil aerosols revealed consistent tendencies based on aerosol particle composition. A greater majority of injected soybean oil (Figure 3.16) and salt water (solids) (Figure 3.12B,C,D) aerosols penetrate 1-inch sand columns as compared to when using water (Figure 3.12A). Evaporation over this distance would not account for these discrepancies; therefore, these results suggest poor mobility of fresh water aerosols as compared to soybean oil or salt water aerosols.

Relative immobility of water aerosols is assumed to be due to a surface interaction phenomenon that does not affect, or affects soybean oil and salt water aerosols to a lesser degree. This interaction represents a water affinity (hydrophilic vs. hydrophobic) and/or electrostatic forces (Elimelech and O’Melia, 1990). The magnitude of these effects could be affected during column injection experiments. These experiments involved coating sand grains with soybean oil, where the treatment significantly increased fresh water aerosol penetration (Figure 3.11). Also, the penetration rate of fresh water aerosols increased during early injection times when using Coarse sand (Figure 3.5A,B), which suggests a transient “wetting” phase (Dyer et al., 2012). Proper characterization of fresh water aerosol transport would require inclusion of a collection efficiency term to characterize the surface interaction (Nielsen and Hill, 1976); however, evaporation was determined to be the primary controlling factor on fresh water aerosol transport over distances more than a few inches.
7.2.2 Evaporation and Water Aerosols

Creating aerosols using a high velocity jet, such as with the devices used in this work, appears to cause evaporation of the liquid used in the process. This occurs because the high gas velocity (many hundreds of m/s) in the aerosolizer causes low pressures, which results in adiabatic cooling and condensation of humidity in the gas. The low pressure is only fleeting, however, and the pressure increases when the gas expands a few cm downstream from the aerosolizer. Presumably the accompanying warming of the gas causes the relative humidity to drop and the air becomes undersaturated in water. This causes the air downstream from the aerosolizer to evaporate water aerosols, even when the air entering the aerosolizer is saturated in water. Water must condense from the cooling air and form droplets that are too large to become transported as aerosols themselves.

A consequence of this process is that it was nearly impossible to increase water contents over more than a few cm in dry sand when injecting water aerosols created from a jet aerosolizer. Considerable effort was put forth to saturate the air upstream of the aerosolizer, but this only had a minor effect. The vapor pressure of water at 25 °C is 3.2 kPa, whereas it ranges from 0.2 kPa to 0.7 kPa for the soybean oils measured by Ndiaye et al. (2005). Apparently the lower vapor pressure of soybean oil limits evaporation through the aerosolizer and accounts for the larger transport distances of oil compared to water.

This process will depend on the performance of the aerosolizer, so water transport as aerosols could be more effective than the results obtained during this work. Shorter
injection durations may limit evaporation of ambient water in the formation (Lourenco et al., 2012), and use of aerosolizers that operate at lower gas flow rates may decrease evaporation of aqueous aerosols (Dyer et al., 2012).

7.2.3 Particle size control

Decreasing aerosol particle size will increase average transport distance during injection into porous media (Equations 1-2 through 1-5). Use of an impact plate has been shown to be an effective mechanism for decreasing average particle size when using soybean oil (Figure 2.17). Impact plates are useful for removing the largest particles, however, removal of these particles could result in significant decreases in total mass delivered as aerosols. This issue could be partially overcome by utilizing operating parameters that reduce average aerosol particle size that is produced from the aerosolizer. Equation 1-1 suggests that decreasing aerosol particle size could be accomplished by decreasing gas and liquid orifice diameters, decreasing liquid flow rate, increasing gas flow velocity, and/or decreasing liquid surface tension. Decreasing liquid orifice diameter was the most effective parameter manipulation for decreasing aerosol particle size during soybean oil tests (Figure 2.19).

7.2.4 Formation Properties

Aerosol transportability is controlled by properties of the aerosol particles (size, density), injection methodologies (gas injection rate, duration), and properties of the formation material (particle size). Aerosol particle properties and injection methodologies can be controlled to a degree, however, formation properties are fixed. Total collection
efficiency is a function of particle to formation grain size ratio (Equation 1-3), and injection test results consistently showed that aerosol transportability was decreased with decreasing sand grain size when using fresh water (Figures 3.8-3.10), salt water (Figure 3.15), and soybean oil (3.16). The fill materials used during experiments were relatively coarse overall and it is expected that successful application of aerosol delivery technologies will be limited in finer-grain formation materials.

7.2.5 Mobilization of Liquid

Liquid aerosol transport and deposition resembles an advective process with a first-order mass transfer controlling deposition, which follows from basic assumptions used for analyzing porous filters (Yao et al., 1971). This implies that the concentration profile along the flow path is

\[ N = N_0 e^{-\alpha \lambda x} \]  

where \( N_0 \) is the concentration at \( x = 0 \), \( \alpha \) is a collision efficiency, and \( \lambda \) is an effective filtration parameter. Many of the concentration distributions from the laboratory tests (Figure 4.10) resemble behaviors suggested by Equation (5-8 through 5-13), which are based on analyses of solid particles flow in air through a filter. In cases where the concentration of particles is small enough so that deposition does not affect the filtration capacity, then it seems feasible for Equation (7-1) to approximate the filtration process. However, significant changes in the transport properties of the sand occurred during experiments conducted for this work. The filtration capacity (\( \lambda \) in Equation 7-1) must change with time to accommodate transient effects. Filtration theory (Equations 5-9...
through 5-13) allows calculation of the collection efficiency (analogous to filtration capacity) at different times based on transport and formation parameters, which appears to be the closest analog to this work. Therefore, we adopted the concept of a collection efficiency (Yao et al., 1971) to describe the deposition process.

Large accumulation of oil in the pore space is a good example of an important contrast with Equation 7-1. Indeed, there was concern that oil deposition would completely fill pores around the well and prevent further injection of aerosol, but this was never observed in the experiments where oil aerosols moved through the sand media (Figure 4.10). What appears to occur is that deposition of aerosols increases the degree of oil saturation, which reduces the effective air filled porosity, decreases the gas phase relative permeability, and increases the oil phase relative permeability. These changes are expected to diminish the deposition rate of aerosols, but perhaps more importantly, it initiates the flow of oil as a liquid phase.

It appears that oil deposited from aerosol droplets flows as a liquid phase away from the gas injection zone. Drainage of the liquid phase allows a gas-filled pore space to persist and allows this aerosol transport process to continue. Relatively large gas flow velocities were sufficient to limit oil saturations in the vicinity of the air inlet while saturations increased at greater distances where the gas velocity diminished (Figure 4.10), an effect that was also observed numerical analyses (Figure 5.8).

7.3 Solid Aerosols

The evaporation of water was a persistent concern with respect to using aqueous aerosols to transport compounds into the subsurface. Although transporting water itself is
difficult, it appears to be feasible to transport aqueous solutes using the aerosolization technique. The solutes apparently precipitate as the water evaporates, leaving small solid particles that are readily transported. Salt was detected 1.5 m from the injection point during column experiments, even though the region remained dry while saline water was used to create aerosols (Figure 3.21). This technique appears to be a viable approach for delivering nutrients or other treatment compounds as micron-scale solid aerosols.

7.4 Application for Enhanced Bioremediation

Biostimulation and bioaugmentation facilitate remediation in many settings, and the possibility of delivering nutrients and/or microbes as aerosols is appealing. TCE degradation was readily induced during lab tests when delivering nutrients and microbes as aqueous aerosols (Figure 6.14A-C), however, aerosol transport distances during these experiments were <1 m. Transport distances during field operation could be many ten’s of meters, which would likely increase evaporative effects when using aqueous aerosols. Evaporation of water aerosols may have little effect on the ability to deliver nutrients, which can precipitate and be transported as a solid and then dissolve in pore water after deposition. However, the evaporation process may affect bioaugmentation because desiccation of the culture may reduce the survivability of microbes.

Delivery of microbes in an oil-based inoculum represents a possible alternative for bioaugmentation. It was demonstrated that microbes could survive in an oil based mixture (Figure 6.11), however, inoculation of microcosms with aerosols created from the same mixture resulted in little to no TCE degradation (Figure 6.14D). Possible explanations are that microbes are killed by the pressure drop or high shear in the
aerosolizer, or that microbes die because encapsulating water droplets in the water-in-oil emulsion are disrupted during aerosolization.

7.4 Field-Scale Applications

Initial field-scale simulations involved parameter values that were selected to represent wedge experiment conditions. The radius of influence (ROI) from these simulations was estimated to be 1.9 m and 1.6 m after 4-weeks of injection into Coarse and Fine sand, respectively (Figure 5.13). Additional simulations suggest that adjustment of a few injection parameters (rate, particle size) could increase ROI to ~4 m, which would increase the volume of influence by up to 800% (Figure 5.13).

These results are promising, but additional analyses are required to fully evaluate parameters affecting transport and to optimize the injection process. This work focused on coarse-grained, well-sorted sediments, and it seems likely that transport in other materials will differ from the results obtained here. The size of the aerosol particles was an important factor affecting the ROI in sand during the experiments conducted for this work, and the ability to create and deliver small aerosols is expected to be even more important in applications involving finer-grained sediments with smaller pore sizes.

Remedial applications that could benefit from soybean oil emplacement include sequestration barriers for prevention of vapor intrusion, and delivery of oil-phase electron donor for enhanced bioremediation. Ability to transport solids also expands the applicability of aerosol delivery. Injecting aerosols created by induction of dry powders or by precipitation of solutes could be used for a variety of in situ oxidation and biostimulation applications.
References


Eaddy, A. 2008. Scale-up and characterization of an enrichment culture for bioaugmentation of the P-Area chlorinated ethene plume at the Savannah River Site. MS Thesis, Clemson University, Clemson, SC.


Appendix A
Nutrient Water Preparation (Modified from Eaddy, 2008)

Stock solutions needed for media:
- Phosphate buffer: 5.25 g K$_2$HPO$_4$
  Fill to 100 mL with DDI water.
- Salt solution: 5.35 g NH$_4$Cl
  0.46976 g CaCl$_2$·2H$_2$O
  0.17787 g FeCl$_2$·H$_2$O
  Fill to 100 mL with DDI water.
- Trace metals solution: 0.03 g H$_3$BO$_3$
  0.0211 g ZnSO$_4$·7H$_2$O
  0.075 g NiCl$_2$·6H$_2$O
  0.1 g MnCl$_2$·4H$_2$O
  0.01 g CuCl$_2$·2H$_2$O
  0.15 g CoCl$_2$·6H$_2$O
  0.002 g Na$_2$SeO$_3$
  0.01 g Al$_2$(SO$_4$)$_3$·16H$_2$O
  1 mL concentrated HCl.
  Fill to 100 mL with DDI water.
- Magnesium sulfate solution: 6.25 g MgSO$_4$·7H$_2$O
  Fill to 100 mL with DDI water.
- Bicarbonate solution: 8.0 g NaHCO$_3$
  Fill to 500 mL with DDI water.
- Yeast extract solution: 0.5 g yeast extract
  Fill to 100 mL with DDI water.

Nutrient Water Preparation:
1) In a 1 L bottle add:
   10 mL phosphate solution
   10 mL salt solution
   2 mL trace metals solution
   2 mL magnesium sulfate solution
   1 mL redox solution
   905 mL DDI water
2) Autoclave the above solution and allow to cool.
3) Add: 50 mL filter sterilized bicarbonate solution
   10 mL filter sterilized yeast extract
Appendix B

Hydrogen Inclusion
Microcosm Test Results
**Appendix B**

*Test NA-HIT-1 (A-C)*
- Oversaturated
- Hydrogen
- Inoculated

*Test NA-HIT-2 (A-C)*
- Oversaturated
- Hydrogen, Lactate
- Inoculated

**Graphs:**
- Y Axis: Mol/Mol TCE Added
- X Axis: Time

Legend:
- TCE
- cDCE
- VC
- Ethene
Appendix B

Test NA-HIT-3 (A-F)
- Oversaturated
- Hydrogen, Veg Oil
- Inoculated

Y Axis: Mol/Mol TCE Added
X Axis: Time

A  B  C
D  E  F
Appendix B

Test NA-HIT-4 (A-C)
- Oversaturated
- Hydrogen, Veg Oil, Lactate
- Inoculated

Test NA-HIT-5 (A-C)
- Oversaturated
- Hydrogen, EOS
- Inoculated

Test NA-HIT-6 (A-C)
- Oversaturated
- Hydrogen, EOS, Lactate
- Inoculated

Y Axis: Mol/Mol TCE Added  X Axis: Time
Appendix C

Donor/Saturation
Microcosm Test Results
Appendix C

Y Axis: Mol/Mol TCE Added  X Axis: Time

Test NA-DST-1 (A-B)
- Oversaturated
- Lactate
- Inoculated

Test NA-DST-2 (A-B)
- Saturated
- Lactate
- Inoculated

Test Test NA-DST-3 (A-B)
- Undersaturated
- Lactate
- Inoculated
Appendix C

Y Axis: Mol/Mol TCE Added  X Axis: Time

Test NA-DST-4 (A-B)
- Oversaturated
- Soybean Oil
- Inoculated

Test NA-DST-5 (A-B)
- Saturated
- Soybean Oil
- Inoculated

Test NA-DST-6 (A-B)
- Undersaturated
- Soybean Oil
- Inoculated
Appendix D

Soybean Oil Survivability
Microcosm Test Results
Appendix D

Test AER-SST-1 (A-C)
- Oversaturated
- Soybean Oil
- Inoculated (Veg Oil Mix)

Test AER-SST-2 (A-C)
- Undersaturated
- Soybean Oil
- Inoculated (Veg Oil Mix)

Y Axis: Mol/Mol TCE Added  X Axis: Time
Appendix D

Test AER-SST-3 (A-C)
- Oversaturated
- Soy Oil, Lactate
- Inoculated (Veg Oil Mix)

Test AER-SST-4 (A-C)
- Undersaturated
- Soy Oil, Lactate
- Inoculated (Veg Oil Mix)

Y Axis: Mol/Mol TCE Added  X Axis: Time
Appendix E

Aerosol Survivability
Microcosm Test Results
Test AER-AST-1 (A-C)
- Oversaturated
- Lactate
- Inoculated (Straight Culture)

Test AER-AST-2 (A-C)
- Oversaturated
- Lactate
- Inoculated (Jet Aerosolized Culture)

Test AER-AST-3 (A-C)
- Oversaturated
- Lactate
- Inoculated (Ultrasonic Aerosolized Culture)
Appendix F

Aerosol Delivery
Microcosm Test Results
Appendix F

Y Axis: Mol/Mol TCE Added  X Axis: Time

(M) = Manual Addition  (A) = Aerosol

Test AER-ADT-1 (A-D)
- Undersaturated
- Lactate (M)
- Inoculated (A)

Test AER-ADT-2 (A-D)
- Undersaturated
- Lactate (A)
- Inoculated (M)
Appendix F

Y Axis: Mol/Mol TCE Added  X Axis: Time
(M)= Manual Addition  (A)= Aerosol

Test AER-ADT-3 (A-D)
- Undersaturated
- Lactate (A)
- Inoculated (A)
Appendix F

Y Axis: Mol/Mol TCE Added   X Axis: Time
(M)= Manual Addition   (A)= Aerosol

Test AER-ADT-4 (A-D)
- Undersaturated
- Soy Oil (A)
- Inoculated (A)
(Soy Oil Mixture)