UNIVERSITY OF CINCINNATI

Date: 16-Aug-2010

I, Matthew T Alexander, hereby submit this original work as part of the requirements for the degree of:

Master of Science

in Environmental Engineering

It is entitled:

An Integrated Field-Scale Assessment of Chloramine Dynamics, By-Product Formation, and Nitrification Modeling

Student Signature: Matthew T Alexander

This work and its defense approved by:

Committee Chair: Dominic Boccelli, PhD

Dominic Boccelli, PhD
AN INTEGRATED FIELD-SCALE ASSESSMENT
OF CHLORAMINE DYNAMICS, BY-PRODUCT
FORMATION, AND NITRIFICATION MODELING

A thesis submitted to the

Division of Research and Advanced Studies
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in the School of Energy, Environmental,
Biological, and Medical Engineering
of the College of Engineering and Applied Science

2010

by

Matthew T. Alexander

B.S., Civil Engineering, 2008
University of Cincinnati
Abstract

Water distributions systems have generally been operated to provide a steady supply of water at a sufficient pressure. However, stringent water quality regulations, such as the Disinfectants/Disinfection By-Products Rule, have forced water utilities to maintain water quality throughout the distribution system. As a result, chloramine disinfection has gained significant popularity because it provides a longer lasting residual and forms substantially fewer regulated disinfection by-products (DBPs). Unfortunately, chloraminated distribution systems are more complex, relative to chlorinated systems, because they are impacted by a variety of parameters (e.g., pH, alkalinity, chlorine/nitrogen ratios). Thus, the ability to represent these complex dynamics with a distribution system water quality model could assist in making operational and management decisions to maintain adequate water quality.

The objectives of this study were to perform a field-scale assessment associated with chloramine dynamics, DBP formation, and nitrification, and assess the ability of existing bench-scale models to represent complex water quality dynamics utilizing EPANET-MSX – a multi-species distribution system network water quality solver. The results of the field-scale study and modeling assessment were used to identify potential “knowledge gaps” that exist in current advanced water quality models and provide motivation for future improvements associated with distribution system water quality modeling.

A two week field-scale study was performed in conjunction with our partner utility to collect water samples for assessing chloramine dynamics, DBP formation, and nitrification. The samples and analysis included measurements for: total and combined chlorine, ammonia, nitrite, nitrate, pH, alkalinity, and organic carbon (chloramine
dynamics); sulfate (as a pseudo-tracer); N-nitrosodimethylamine (DBP formation); and the absence/presence of ammonia oxidizing bacteria (AOB) and anaerobic ammonia oxidizing bacteria (ANAMMOX) (nitrification). The distribution system network model (provided by the utility) was updated using data obtained from the SCADA system, and the chloramine dynamics and NDMA formation simulated using existing water quality models with EPANET-MSX. The observed and model predicted results were utilized to perform a comprehensive water quality assessment.

With respect to the chloramine dynamics, the model provided mixed results for representing the observed water quality data. During the first week of the study, the model represented the observed results reasonably well with relatively small differences due to inaccurate representation of source water blending and lack of temporal variability in the input data. However, during week two, there were more significant deviations (particularly with respect to monochloramine and ammonia) that may not be entirely explained by the lack of modeling associated with pipe wall interactions or nitrification, but clearly indicated a “missing piece” in the overall modeling framework. With respect to NDMA formation, the model provided reasonable NDMA predictions. However, the assessment was limited due to a small number of samples and analytical uncertainty associated with very low NDMA concentrations.

With respect to the microbial analysis, the absence, or presence, of nitrifying bacteria was evaluated at monitoring locations representative of the source and at locations with relatively long residence times. Large-volume samples were collected and concentrated from the bulk water with the intent to provide supporting evidence that nitrifying bacteria had an impact on water quality. Of the 52 samples collected, there were three AOB-positive samples and six ANAMMOX-positive samples. While there were few other signs associated with excessive nitrification, the finding of ANAMMOX bacteria was unique because this was the first time that ANAMMOX has been
detected within a potable water system. Thus, this discovery introduces another possible mechanism that can contribute to nitrification and loss of disinfectant residual for chloraminated distribution systems.

The results indicate that tools such as EPANET-MSX are capable of representing complex water quality dynamics and network hydraulics throughout the distribution system, but further improvements can likely be made to improve the underlying model accuracy. Inconsistencies between modeled and observed results may be attributed to the following factors that were not considered: temporal variability in the influent water quality concentrations, interaction between biological and chemical species (nitrification), reactions between the bulk fluid and pipe wall, and accurate representation of spatial distribution and stochastic consumer demands. These “knowledge gaps” should be considered in future modeling efforts to improved the performance of multi-species water quality modeling.
Acknowledgments

I would like to thank the Water Research Foundation (WaterRF) for providing financial contributions to complete this study. I would also like to acknowledge Hillsborough County Water Resource Services (HCWRS) for allowing us to use their system and resources in this study. Their staff at the Lake Park Water Treatment Plant played a critical role in making this study a success. I would also like to thank my advisor, Dr. Dominic Boccelli. It has genuinely been a pleasure working with you the past two years. Your guidance, encouragement, and confidence in me has been gratefully appreciated.

I would like to extend my gratitude to Stu Hooper, Ken Nilsson, Joe Wright, and Xueyao Yang for their contributions on the field study. I would also like to acknowledge Dr. Dan Oerther and Mau-Yi Wu for their time and resources related to the biological analysis portion of the study. I would also like to extend my gratitude to Dr. Kartik Chandran, Columbia University, for providing plasmids of targeted bacteria for biological analysis. I would also like to thank my committee members, Dr. Jim Uber and Megan Sekhar, for their valuable time and input. Finally, I would like to thank my loving wife, Paula. I appreciate your patience, encouragement, and full support.
4.3.1 Sample Collection ........................................... 23
4.3.2 NDMA Analysis ............................................. 23
   4.3.2.1 Solid-Phase Extraction Method ....................... 23
   4.3.2.2 Analytical Method ................................... 24
4.4 Biological Analysis .......................................... 27
   4.4.1 Sample Concentration .................................... 27
      4.4.1.1 Ultrafiltration System Configuration ............... 28
      4.4.1.2 Concentration Procedure ........................... 28
      4.4.1.3 Backwash Procedure ................................ 29
      4.4.1.4 Ultrafiltration Disinfection Procedure ............ 29
   4.4.2 DNA Extraction ......................................... 30
   4.4.3 AOB and ANAMMOX Bacteria Identification .......... 30
      4.4.3.1 Primer Sets for PCR ............................... 31
      4.4.3.2 PCR Amplification ................................. 32

5 Pilot Study .................................................... 33
   5.1 Experimental Design ...................................... 33
      5.1.1 Parameter Estimation and Initial Conditions ........ 35
   5.2 Results and Discussion ................................... 36
   5.3 Summary .................................................. 39

6 Primary Study: Chloramine Dynamics ......................... 49
   6.1 Experimental Design ...................................... 49
      6.1.1 Parameter Estimation ................................. 50
      6.1.2 Initial Conditions ................................... 52
      6.1.3 Monitoring Location Selection ....................... 52
      6.1.4 “Flow-Based” vs “Pressure-Based” Models ........... 56
   6.2 Results and Discussion ................................... 58
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>C  “Pressure-Based” Pilot Study Results</td>
<td>181</td>
</tr>
<tr>
<td>D  Total Chlorine Model Results</td>
<td>191</td>
</tr>
<tr>
<td>E  “Pressure-Based” Model Results – Fawn Ridge Week #1</td>
<td>209</td>
</tr>
<tr>
<td>F  “Pressure-Based” Model Results – Fawn Ridge Week #2</td>
<td>221</td>
</tr>
<tr>
<td>G  “Pressure-Based” Model Results – Lake Park Week #1</td>
<td>233</td>
</tr>
<tr>
<td>H  “Pressure-Based” Model Results – Lake Park Week #2</td>
<td>245</td>
</tr>
<tr>
<td>I  “Pressure-Based” NDMA Model Results</td>
<td>257</td>
</tr>
<tr>
<td>J  Gel Electrophoresis Images</td>
<td>267</td>
</tr>
</tbody>
</table>
List of Figures

3.1 Monochloramine decay in the presence of NOM (Duirk et al., 2005). 7
3.2 Proposed mechanism of NDMA formation in chloraminated water containing DMA (Choi and Valentine, 2002a). 9
3.3 Simplified Nitrogen Cycle (Madigan et al., 2009). 10
4.1 HCWRS Northwestern Network Model 15
4.2 Ultrafiltration System Schematic 29
5.1 Pilot Study Monitoring Locations 34
5.2 “Flow-Based” Combined Chlorine and Free Ammonia Results at P-1, P-2, and P-3 41
5.3 “Flow-Based” Combined Chlorine and Free Ammonia Results at P-4, P-5, and P-6 42
5.4 “Flow-Based” Total Chlorine Results at P-1, P-2, and P-3 43
5.5 “Flow-Based” Total Chlorine Results at P-4, P-5, and P-6 44
5.6 “Flow-Based” Nitrite and Nitrate Results at P-1, P-2, and P-3 45
5.7 “Flow-Based” Nitrite and Nitrate Results at P-4, P-5, and P-6 46
5.8 “Flow-Based” pH Results at P-1, P-2, and P-3 47
5.9 “Flow-Based” pH Results at P-4, P-5, and P-6 48
6.1 Network Monitoring Locations 51
6.2 Source Blend Regions 55
6.3 Cumulative Distribution of Water Age .................................................. 57
6.4 Model Predicted and Observed Effluent Flow of “Pressure-Based” and
   “Flow-Based” Approaches ................................................................. 58
6.5 “Flow-Based” Combined Chlorine and Sulfate Results at FR-1, FR-2,
   and FR-3 ....................................................................................... 62
6.6 “Flow-Based” Combined Chlorine and Sulfate Results at FR-4, FR-5,
   and FR-6 ....................................................................................... 63
6.7 “Flow-Based” Free Ammonia Results at FR-1, FR-2, and FR-3 .......... 64
6.8 “Flow-Based” Free Ammonia Results at FR-4, FR-5, and FR-6 .......... 65
6.9 “Flow-Based” Nitrite and Nitrate Results at FR-1, FR-2, and FR-3 ..... 66
6.10 “Flow-Based” Nitrite and Nitrate Results at FR-4, FR-5, and FR-6 ... 67
6.11 “Flow-Based” pH Results at FR-1, FR-2, and FR-3 ......................... 68
6.12 “Flow-Based” pH Results at FR-4, FR-5, and FR-6 ....................... 69
6.13 “Flow-Based” Alkalinity Results at FR-1, FR-2, and FR-3 ............. 70
6.14 “Flow-Based” Alkalinity Results at FR-4, FR-5, and FR-6 ............. 71
6.15 “Flow-Based” Combined Chlorine and Sulfate Results at LP-1, LP-2,
   and LP-3 ....................................................................................... 75
6.16 “Flow-Based” Combined Chlorine and Sulfate Results at LP-4, LP-5,
   and LP-6 ....................................................................................... 76
6.17 “Flow-Based” Free Ammonia Results at LP-1, LP-2, and LP-3 ....... 77
6.18 “Flow-Based” Free Ammonia Results at LP-4, LP-5, and LP-6 ...... 78
6.19 “Flow-Based” Nitrite and Nitrate Results at LP-1, LP-2, and LP-3 ... 79
6.20 “Flow-Based” Nitrite and Nitrate Results at LP-4, LP-5, and LP-6 ... 80
6.21 “Flow-Based” pH Results at LP-1, LP-2, and LP-3 ....................... 81
6.22 “Flow-Based” pH Results at LP-4, LP-5, and LP-6 ....................... 82
6.23 “Flow-Based” Alkalinity Results at LP-1, LP-2, and LP-3 ............. 83
6.24 “Flow-Based” Alkalinity Results at LP-4, LP-5, and LP-6 ............. 84
<table>
<thead>
<tr>
<th>Section Number</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.25</td>
<td>“Flow-Based” Combined Chlorine and Sulfate Results at FR-1, FR-7, and FR-8</td>
<td>88</td>
</tr>
<tr>
<td>6.26</td>
<td>“Flow-Based” Combined Chlorine and Sulfate Results at FR-9, FR-11, and FR-12</td>
<td>89</td>
</tr>
<tr>
<td>6.27</td>
<td>“Flow-Based” Free Ammonia Results at FR-1, FR-7, and FR-8</td>
<td>90</td>
</tr>
<tr>
<td>6.28</td>
<td>“Flow-Based” Free Ammonia Results at FR-9, FR-11, and FR-12</td>
<td>91</td>
</tr>
<tr>
<td>6.29</td>
<td>“Flow-Based” Nitrite and Nitrate Results at FR-1, FR-7, and FR-8</td>
<td>92</td>
</tr>
<tr>
<td>6.30</td>
<td>“Flow-Based” Nitrite and Nitrate Results at FR-9, FR-11, and FR-12</td>
<td>93</td>
</tr>
<tr>
<td>6.31</td>
<td>“Flow-Based” pH Results at FR-1, FR-7, and FR-8</td>
<td>94</td>
</tr>
<tr>
<td>6.32</td>
<td>“Flow-Based” pH Results at FR-9, FR-11, and FR-12</td>
<td>95</td>
</tr>
<tr>
<td>6.33</td>
<td>“Flow-Based” Alkalinity Results at FR-1, FR-7, and FR-8</td>
<td>96</td>
</tr>
<tr>
<td>6.34</td>
<td>“Flow-Based” Alkalinity Results at FR-9, FR-11, and FR-12</td>
<td>97</td>
</tr>
<tr>
<td>6.35</td>
<td>“Flow-Based” Combined Chlorine and Sulfate Results at LP-1, LP-8, and LP-9</td>
<td>101</td>
</tr>
<tr>
<td>6.36</td>
<td>“Flow-Based” Combined Chlorine and Sulfate Results at LP-10, LP-11, and LP-12</td>
<td>102</td>
</tr>
<tr>
<td>6.37</td>
<td>“Flow-Based” Free Ammonia Results at LP-1, LP-8, and LP-9</td>
<td>103</td>
</tr>
<tr>
<td>6.38</td>
<td>“Flow-Based” Free Ammonia Results at LP-10, LP-11, and LP-12</td>
<td>104</td>
</tr>
<tr>
<td>6.39</td>
<td>“Flow-Based” Nitrite and Nitrate Results at LP-1, LP-8, and LP-9</td>
<td>105</td>
</tr>
<tr>
<td>6.40</td>
<td>“Flow-Based” Nitrite and Nitrate Results at LP-10, LP-11, and LP-12</td>
<td>106</td>
</tr>
<tr>
<td>6.41</td>
<td>“Flow-Based” pH Results at LP-1, LP-8, and LP-9</td>
<td>107</td>
</tr>
<tr>
<td>6.42</td>
<td>“Flow-Based” pH Results at LP-10, LP-11, and LP-12</td>
<td>108</td>
</tr>
<tr>
<td>6.43</td>
<td>“Flow-Based” Alkalinity Results at LP-1, LP-8, and LP-9</td>
<td>109</td>
</tr>
<tr>
<td>6.44</td>
<td>“Flow-Based” Alkalinity Results at LP-10, LP-11, and LP-12</td>
<td>110</td>
</tr>
<tr>
<td>7.1</td>
<td>“Flow-Based” NDMA Results at FR-1, FR-2, and FR-3</td>
<td>119</td>
</tr>
<tr>
<td>7.2</td>
<td>“Flow-Based” NDMA Results at FR-4, FR-5, and FR-6</td>
<td>120</td>
</tr>
<tr>
<td>7.3</td>
<td>“Flow-Based” NDMA Results at LP-1, LP-2, and LP-3</td>
<td>122</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>7.4</td>
<td>“Flow-Based” NDMA Results at LP-4, LP-5, and LP-6</td>
<td>123</td>
</tr>
<tr>
<td>7.5</td>
<td>“Flow-Based” NDMA Results at FR-1, FR-7, and FR-8</td>
<td>125</td>
</tr>
<tr>
<td>7.6</td>
<td>“Flow-Based” NDMA Results at FR-9, FR-11, and FR-12</td>
<td>126</td>
</tr>
<tr>
<td>7.7</td>
<td>“Flow-Based” NDMA Results at LP-1, LP-8, and LP-9</td>
<td>128</td>
</tr>
<tr>
<td>7.8</td>
<td>“Flow-Based” NDMA Results at LP-10, LP-11, and LP-12</td>
<td>129</td>
</tr>
<tr>
<td>8.1</td>
<td>Partner Utility Distribution System and Sampling Locations</td>
<td>135</td>
</tr>
<tr>
<td>8.2</td>
<td>Results from amplification of PCR products of extracted nucleic acids.</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>Lane 1, 100 bp ladder; lane 2, negative control; lane 3, <em>Candidatus Brocadia fulgida</em>, 836 bp; lane 4, <em>Candidatus Brocadia</em> sp. 40, 835 bp; lane 5, <em>Candidatus Kuenenia stuttgartiensis</em>, 832 bp; lanes 6-23, selected environmental samples; lane 24, 100 bp ladder.</td>
<td></td>
</tr>
<tr>
<td>8.3</td>
<td>Observed Sulfate Data for A-1 (Both Weeks), A-6 (Week #1), and A-11 (Week #2).</td>
<td>141</td>
</tr>
<tr>
<td>A.1</td>
<td>Parameter estimation curves from hold study results from Fawn Ridge Source Water – Week #1</td>
<td>160</td>
</tr>
<tr>
<td>A.2</td>
<td>Parameter estimation curves from hold study results from Fawn Ridge Source Water – Week #2</td>
<td>161</td>
</tr>
<tr>
<td>A.3</td>
<td>Parameter estimation curves from hold study results from Lake Park Source Water – Week #1</td>
<td>162</td>
</tr>
<tr>
<td>A.4</td>
<td>Parameter estimation curves from hold study results from Lake Park Source Water – Week #2</td>
<td>163</td>
</tr>
<tr>
<td>A.5</td>
<td>Parameter estimation curves from hold study results from THI Source Water – Week #1</td>
<td>164</td>
</tr>
<tr>
<td>A.6</td>
<td>Parameter estimation curves from hold study results from THI Source Water – Week #2</td>
<td>165</td>
</tr>
</tbody>
</table>
A.7 Parameter estimation curve from hold study results from Lake Park
Source Water – Pilot Study .............................................................. 166

B.1 Week #1 EPANET-MSX Input File – Page 1 of 4 .............................. 168
B.2 Week #1 EPANET-MSX Input File – Page 2 of 4 .............................. 169
B.3 Week #1 EPANET-MSX Input File – Page 3 of 4 .............................. 170
B.4 Week #1 EPANET-MSX Input File – Page 4 of 4 .............................. 171
B.5 Week #2 EPANET-MSX Input File – Page 1 of 4 .............................. 172
B.6 Week #2 EPANET-MSX Input File – Page 2 of 4 .............................. 173
B.7 Week #2 EPANET-MSX Input File – Page 3 of 4 .............................. 174
B.8 Week #2 EPANET-MSX Input File – Page 4 of 4 .............................. 175
B.9 Pilot Study EPANET-MSX Input File – Page 1 of 4 ............................ 176
B.10 Pilot Study EPANET-MSX Input File – Page 2 of 4 ............................ 177
B.11 Pilot Study EPANET-MSX Input File – Page 3 of 4 ............................ 178
B.12 Pilot Study EPANET-MSX Input File – Page 4 of 4 ............................ 179

C.1 “Pressure-Based” Combined Chlorine and Free Ammonia Results at
  P-1, P-2, and P-3 ................................................................. 182
C.2 “Pressure-Based” Combined Chlorine and Free Ammonia Results at
  P-4, P-5, and P-6 ................................................................. 183
C.3 “Pressure-Based” Total Chlorine Results at P-1, P-2, and P-3 .......... 184
C.4 “Pressure-Based” Total Chlorine Results at P-4, P-5, and P-6 .......... 185
C.5 “Pressure-Based” Nitrite and Nitrate Results at P-1, P-2, and P-3 .... 186
C.6 “Pressure-Based” Nitrite and Nitrate Results at P-4, P-5, and P-6 .... 187
C.7 “Pressure-Based” pH Results at P-1, P-2, and P-3 ........................ 188
C.8 “Pressure-Based” pH Results at P-4, P-5, and P-6 ........................ 189

D.1 “Flow-Based” Total Chlorine Results at FR-1, FR-2, and FR-3 ......... 192
D.2 “Flow-Based” Total Chlorine Results at FR-4, FR-5, and FR-6 ......... 193
F.1 “Pressure-Based” Combined Chlorine and Sulfate Results at FR-1, FR-7, and FR-8 .......................................................... 222
F.2 “Pressure-Based” Combined Chlorine and Sulfate Results at FR-9, FR-11, and FR-12 .......................................................... 223
F.3 “Pressure-Based” Free Ammonia Results at FR-1, FR-7, and FR-8 .......................................................... 224
F.4 “Pressure-Based” Free Ammonia Results at FR-9, FR-11, and FR-12 .......................................................... 225
F.5 “Pressure-Based” Nitrite and Nitrate Results at FR-1, FR-7, and FR-8 .......................................................... 226
F.6 “Pressure-Based” Nitrite and Nitrate Results at FR-9, FR-11, and FR-12 .......................................................... 227
F.7 “Pressure-Based” pH Results at FR-1, FR-7, and FR-8 .......................................................... 228
F.8 “Pressure-Based” pH Results at FR-9, FR-11, and FR-12 .......................................................... 229
F.9 “Pressure-Based” Alkalinity Results at FR-1, FR-7, and FR-8 .......................................................... 230
F.10 “Pressure-Based” Alkalinity Results at FR-9, FR-11, and FR-12 .......................................................... 231

G.1 “Pressure-Based” Combined Chlorine and Sulfate Results at LP-1, LP-2, and LP-3 .......................................................... 234
G.2 “Pressure-Based” Combined Chlorine and Sulfate Results at LP-4, LP-5, and LP-6 .......................................................... 235
G.3 “Pressure-Based” Free Ammonia Results at LP-1, LP-2, and LP-3 .......................................................... 236
G.4 “Pressure-Based” Free Ammonia Results at LP-4, LP-5, and LP-6 .......................................................... 237
G.5 “Pressure-Based” Nitrite and Nitrate Results at LP-1, LP-2, and LP-3 .......................................................... 238
G.6 “Pressure-Based” Nitrite and Nitrate Results at LP-4, LP-5, and LP-6 .......................................................... 239
G.7 “Pressure-Based” pH Results at LP-1, LP-2, and LP-3 .......................................................... 240
G.8 “Pressure-Based” pH Results at LP-4, LP-5, and LP-6 .......................................................... 241
G.9 “Pressure-Based” Alkalinity Results at LP-1, LP-2, and LP-3 .......................................................... 242
G.10 “Pressure-Based” Alkalinity Results at LP-4, LP-5, and LP-6 .......................................................... 243

H.1 “Pressure-Based” Combined Chlorine and Sulfate Results at LP-1, LP-8, and LP-9 .......................................................... 246
H.2 “Pressure-Based” Combined Chlorine and Sulfate Results at LP-10, LP-11, and LP-12 .......................... 247
H.3 “Pressure-Based” Free Ammonia Results at LP-1, LP-8, and LP-9 .......................... 248
H.4 “Pressure-Based” Free Ammonia Results at LP-10, LP-11, and LP-12 .................. 249
H.5 “Pressure-Based” Nitrite and Nitrate Results at LP-1, LP-8, and LP-9 .......................... 250
H.6 “Pressure-Based” Nitrite and Nitrate Results at LP-10, LP-11, and LP-12 .......................... 251
H.7 “Pressure-Based” pH Results at LP-1, LP-8, and LP-9 .......................... 252
H.8 “Pressure-Based” pH Results at LP-10, LP-11, and LP-12 .......................... 253
H.9 “Pressure-Based” Alkalinity Results at LP-1, LP-8, and LP-9 .......................... 254
H.10 “Pressure-Based” Alkalinity Results at LP-10, LP-11, and LP-12 .......................... 255
I.1 “Pressure-Based” NDMA Results at FR-1, FR-2, and FR-3 .......................... 258
I.2 “Pressure-Based” NDMA Results at FR-4, FR-5, and FR-6 .......................... 259
I.3 “Pressure-Based” NDMA Results at FR-1, FR-7, and FR-8 .......................... 260
I.4 “Pressure-Based” NDMA Results at FR-9, FR-11, and FR-12 .......................... 261
I.5 “Pressure-Based” NDMA Results at LP-1, LP-2, and LP-3 .......................... 262
I.6 “Pressure-Based” NDMA Results at LP-4, LP-5, and LP-6 .......................... 263
I.7 “Pressure-Based” NDMA Results at LP-1, LP-8, and LP-9 .......................... 264
I.8 “Pressure-Based” NDMA Results at LP-10, LP-11, and LP-12 .......................... 265
J.1 Results from amplification of PCR products of extracted nucleic acids using a universal primer set. Lane 1, 100 bp ladder; lane 2, negative control; lane 3, *Escherichia coli*, positive control; lanes 4-23, selected environmental samples; lane 24, 100 bp ladder .......................... 268
J.2 Results from amplification of PCR products of extracted nucleic acids using a universal primer set. Lane 1, 100 bp ladder; lane 2, negative control; lanes 3-23, selected environmental samples; lane 24, 100 bp ladder.

J.3 Results from amplification of PCR products of extracted nucleic acids using a universal primer set. Lane 1, 100 bp ladder; lane 2, negative control; lanes 2-12, selected environmental samples; lane 13, 100 bp ladder.

J.4 Results from amplification of PCR products of extracted nucleic acids using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; lane 2, negative control; lane 3, Candidatus Brocadia fulgida; lane 4, Candidatus Brocadia sp. 40; lane 5, Candidatus Kuenenia stuttgartiensis; lanes 6-23, selected environmental samples; lane 24, 100 bp ladder.

J.5 Results from amplification of PCR products of extracted nucleic acids using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; lane 2-23, selected environmental samples; lane 24, 100 bp ladder.

J.6 Results from amplification of PCR products of extracted nucleic acids using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; lane 2-12, selected environmental samples; lane 13, 100 bp ladder.

J.7 Results from amplification of PCR products of extracted nucleic acids using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; lane 2, negative control; lane 3, Nitrosomonas europaea; lane 4, Nitrospira multiformis; lane 5, Nitrosomonas oligotropha; lanes 6-23, selected environmental samples; lane 24, 100 bp ladder.
J.8 Results from amplification of PCR products of extracted nucleic acids using an AOB-specific universal primer set. Lane 1, 100 bp ladder; lane 2, negative control; lanes 3-23, selected environmental samples; lane 24, 100 bp ladder.

J.9 Results from amplification of PCR products of extracted nucleic acids using an AOB-specific primer set. Lane 1, 100 bp ladder; lanes 2-13, selected environmental samples; lane 14, 100 bp ladder.
# List of Tables

4.1 Chloramine Loss – various pathways of decay (Duirk et al., 2005; Vikesland et al., 2001).

4.2 NDMA Formation – A Nitrogenous Disinfectant By-Product (Chen and Valentine, 2006).

4.3 NDMA Analysis – GC and Injection Parameters

4.4 NDMA Analysis – MSD Parameters

5.1 Initial Concentrations of Multi-Species Model – Pilot Study

5.2 Average “Flow-Based” Model Predicted Source Water and Water Age – Pilot Study

6.1 Estimated Parameters of the Multi-Species Chloramine Model

6.2 Initial Concentrations of Multi-Species Model – Week #1

6.3 Initial Concentrations of Multi-Species Model – Week #2

6.4 Model Predicted Water Age at Monitoring Locations

7.1 Estimated Parameters of the NDMA Formation Model (ng of NDMA Formed/mg of NOM Oxidized)

7.2 Initial NDMA Concentrations (ng/L) for the Formation Model

8.1 Nitrifying Bacteria in the Fawn Ridge Region

8.2 Nitrifying Bacteria in the Lake Park Region
Chapter 1

Introduction

The primary function of a water distribution system is to provide an adequate quantity of treated water from a treatment facility to consumers without compromising the quality of the water. In actuality, water utilities sometimes struggle to provide drinking water without degradation of quality (Kernes et al., 1995). At the time most distribution systems were constructed in the United States, they were often overdesigned in anticipation of satisfying increasing demands (Thompson, 1999). Consequently, excessive water ages are common and maintaining sufficient disinfectant residuals can be challenging. Unfortunately, the use of high concentrations of disinfectant yields the formation of harmful disinfection by-products, yet low concentrations of disinfectant yields the growth of biological contaminants (Hua and Reckhow, 2007; Schoenen, 2002). Thus, operating such a system for disinfectant residual maintenance can be challenging, especially when stringent water quality regulations must be satisfied.

Water quality models have the potential to provide a viable tool for distribution system operators and consultants to utilize in a variety of single- and multi-objective applications. In the past few years, water distribution system network models have emerged as more prominent tools for research and applications in the drinking water
industry. For example, network models may now be used to select regulatory sampling sites (USEPA, 2006), and have been utilized in vulnerability assessments to develop contamination warning systems (Berry et al., 2006; Propato, 2006).

Historically, network models have been focused primarily on simulating hydraulics and limited to modeling a single water quality species. EPANET-MSX, a recently developed extension to EPANET, is capable of modeling complex water quality dynamics as well as network hydraulics. To this point, little research has been conducted to evaluate the results of an integrated hydraulic and multi-species water quality system model associated with an actual distribution system. Verification of network models could facilitate the use of modeling software in troubleshooting and maintaining water quality issues in the future.

This study intends to provide a comprehensive water quality analysis that integrates aspects of chloramine decay, by-product formation, and nitrification into a single model in conjunction with system-wide field-scale measurements. This integrated model will be the first field-scale evaluation of EPANET-MSX, which will focus only on chemical and biological components within the bulk phase, not at the pipe wall surface. Additionally, this comprehensive analysis will assess the accuracy of EPANET-MSX and identify any disparities between advanced water quality simulations and actual distribution system performance. Successful verification of such a comprehensive model would demonstrate that complex water quality models can be used in decision making processes related to distribution system water quality maintenance.
Chapter 2

Research Objectives

The overall objective of this research is to evaluate existing water quality models associated with chloramine dynamics, by-product formation, and nitrification at the distribution system-scale to assess model accuracy and the potential for incorporating these models into water quality maintenance decision support tools.

The specific objectives of the research are to:

1. Generate the first comprehensive, field-scale evaluation of EPANET-MSX.
2. Evaluate existing bench-scale water quality models with field-scale measurements associated with chloramine dynamics, DBP formation, and nitrification.
3. Identify potential “knowledge gaps” between existing advanced water quality models and actual distribution system performance.
4. Provide motivation for future improvements associated with distribution system water quality modeling.
Chapter 3

Literature Review

Bench-scale water quality models have been developed to represent chemical dynamics within an aqueous system. This research will employ previously developed models, and chemical and biological analysis to represent water quality conditions in an actual distribution system. A concise review of chloramine dynamics, disinfectant by-product formation, biological nitrification, and water quality modeling is presented.

3.1 Chloramine Dynamics

The U.S. EPA estimates that more than one out of five water treatment plants in the United States use chloramine disinfectants as a secondary disinfectant (U.S. Environmental Protection Agency. Office of Water, 2009). Chloramines, or combined chlorine, refers to the sum of monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (NCl₃) (Vikesland et al., 1998). Hypochlorous acid (HOCl) will react with free ammonia to form monochloramine,

\[
\text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad (3.1)
\]

which will further react with hypochlorous acid to form dichloramine,
\[ \text{NH}_2\text{Cl} + \text{HOCl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \] (3.2)

which can further react with hypochlorous acid to create trichloramine.

\[ \text{NHCl}_2 + \text{HOCl} \rightarrow \text{NCl}_3 + \text{H}_2\text{O} \] (3.3)

The speciation and fate of chloramines are dependent on factors such as pH, ionic strength, temperature, and alkalinity (Jafvert, 1985). However, monochloramine and dichloramine are predominately found in drinking water treatment, so trichloramine is generally not included in modeling the combined chlorine system (Vikesland et al., 1998). Monochloramine has the same oxidation capacity as free chlorine (on a chlorine atom basis), but is a weaker disinfectant (Wolfe et al., 1984) and oxidizing agent. As a result, chloramines provide a longer lasting disinfectant residual (Vikesland et al., 1998).

Figure 3.1 illustrates that chloramine decay can occur through two primary pathways: auto-decomposition (Vikesland et al., 2001) and the oxidation of natural organic matter (NOM) (Duirk et al., 2005). These pathways share free chlorine (HOCl) as common intermediate, therefore they compete with one another (Vikesland et al., 1998). The following briefly describes the reaction mechanisms with details presented in Section 4.1.3. The auto-decomposition of monochloramine is a complex series of reactions that result in the oxidation of ammonia and the degradation of active chlorine (Jafvert and Valentine, 1992). The rate of this process is dependent on pH and the chlorine to ammonia-nitrogen ratio (\(\text{Cl}/\text{N}\)) of the water (Vikesland et al., 2001). The oxidation of NOM by monochloramine is also a complex series of reactions, which are a function of the total organic carbon concentration and pH of the source water (Duirk et al., 2002). The oxidation of NOM is modeled by a biphasic process that considers the reaction of both monochloramine and free chlorine with assumed
fractions of the NOM, DOC\(_1\) and DOC\(_2\), respectively, where free chlorine is a product of the hydrolysis of monochloramine. The direct reaction of monochloramine with NOM is relatively fast compared to the reaction of free chlorine with NOM (Duirk et al., 2005).

\[
\begin{align*}
\text{NH}_2\text{Cl} & \rightarrow \text{NH}_4^+ + \text{Cl}^- + \text{N}_2(g) \\
2\text{NH}_2\text{Cl} & \rightarrow \text{NH}_4^+ + \text{Cl}^- + \text{N}_2(g)
\end{align*}
\]

Figure 3.1: Monochloramine decay in the presence of NOM (Duirk et al., 2005).

Vikesland et al. (2001) and Duirk et al. (2005) have developed a comprehensive model that describes monochloramine loss in the presence of NOM and due to autodecomposition through extensive bench-scale studies. However, this model only considers chemical reactions within the bulk fluid, not at the pipe surface. The model contains both kinetic rate expressions and non-linear equilibrium equations that predict the concentrations of monochloramine, dichloramine, free ammonia, free chlorine, nitrite, nitrate, pH, carbonate species, and organic carbon. Reaction rate and equilibrium constants are adjusted for temperature and ionic strength.
3.2 Disinfectant By-Product (DBP) Formation

Chloramines are a popular alternative to free chlorine because they reduce the formation of chlorinated disinfection by-products, such as trihalomethanes (THMs), haloacetic acids (HAAs), and total organic halogens (TOX) (Duirk and Valentine, 2006; Hua and Reckhow, 2007). Even though combined chlorine is commonly used to reduce THM, HAA, and TOX formation, both nitrogenous and chlorinated DBPs must still be considered (Hua and Reckhow, 2007; MWH, 2005). In this study, only N-nitrosodimethylamine (NDMA), a carcinogenic nitrosamine, will be investigated.

3.2.1 N-nitrosodimethylamine (NDMA)

Recent research has found that NDMA can be formed from reactions of monochloramine with NOM (Choi and Valentine, 2002b; Gerecke and Sedlak, 2003; Mitch et al., 2003). The USEPA has classified NDMA as a probable human carcinogen, but there are no current federal regulations for NDMA in drinking water (USEPA, 2008). NDMA is found to be highly miscible in water and highly mutagenic at very low concentrations (USEPA, 2008). The exact mechanism of NDMA formation is not known, but Figure 3.2 illustrates a proposed reaction scheme (Choi and Valentine, 2002a) for the formation of NDMA in chloraminated water containing dimethylamine (DMA). Initially, monochloramine reacts with DMA, which can form dimethylchloramine (DMCA) and ammonia (NH₃) through a reversible reaction, or form a reactive intermediate, 1,1-dimethylhydrazine (UDMH), by means of a modification of the Raschig Process¹. Ultimately, monochloramine will then oxidize UDMH to form NDMA. The formation of NDMA is believed to be a relatively slow process, occurring on a time scale of days (Chen and Valentine, 2006).

¹The Raschig Process is the synthesis of hydrazine by the reaction of monochloramine with ammonia (Jones et al., 1955).
Chen and Valentine (2006) have developed a kinetic model to predict NDMA formation in chloraminated water. This model accounts for NDMA formation by assuming the rate of NDMA formed is proportional to the rate of NOM that is oxidized. Therefore, the rate of NDMA formation is simply expressed as the product of the rate of dissolved organic carbon oxidation and a stoichiometric coefficient that correlates NOM oxidation to NDMA formation. This approach is also used to model other DBPs, such as THMs and HAAs (Boccelli et al., 2003; Clark, 1998; Duirk and Valentine, 2006).

### 3.3 Biological Nitrification

The auto-decomposition of monochloramine can be accelerated by the disappearance of ammonia (Fleming et al., 2005). Ammonia loss within a distribution system is typically attributed to assimilation and biological nitrification by aerobic ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB), but anaerobic ammonia oxidizing bacteria (ANAMMOX) may also contribute to ammonia loss. Figure 3.3 illustrates the nitrogen cycle, in which nitrification under aerobic conditions occurs.
when ammonia is oxidized into nitrite followed by further oxidation into nitrate. This nitrification process can be drastically accelerated by the presence of oxidizing bacteria, although the oxidation of ammonia into nitrite is often the rate limiting step of the aerobic nitrification process (Liu et al., 2005). Anaerobically, nitrification occurs through the conversion of nitrite (formed from the aerobic conversion of ammonia from AOB) and ammonia into nitrogen gas. Together these two processes can contribute to the accelerated loss of monochloramine.

Figure 3.3: Simplified Nitrogen Cycle (Madigan et al., 2009).

Fleming et al. (2005) have developed nitrification potential curves based on the growth and inactivation rates of AOB and NOB organisms that can be used to predict the presence of nitrification conditions in a chloraminated system. These curves are rela-
tively straightforward because they are only dependent on the ratio of total chlorine and free ammonia concentrations. Theoretically, these potential curves can be used to assess nitrification conditions in an actual distribution system by only measuring the monochloramine and ammonia concentrations. However, the growth and inactivation rates of the nitrifying bacteria must be estimated for each individual source water.

3.4 Water Quality Modeling

Historically, water quality models have only been capable of modeling the fate and transport of a single water quality species (Males et al., 1988; Rossmann, 2000). The development of EPANET-MSX has enabled complex water quality systems and network hydraulics to be modeled simultaneously (Shang et al., 2008a). EPANET-MSX is able to represent complex water quality systems that consist of algebraic and ordinary differential equations (ODE), also known as a differential algebraic equation (DAE) system, for representing equilibrium and dynamic reactions. This advancement in water quality modeling has provided the industry with a powerful tool for representing complex water quality issues within a distribution system.

Shang et al. (2008b) demonstrated the capability of the multi-species distribution system model through two example applications. The first example implemented a previously developed model that represents the regrowth of bacteria after inactivation by chlorine. This model was represented as an ODE system that consisted of five chemical and biological species as well as interactions between the bulk fluid and pipe wall. The second example used by Shang et al. (2008b) to evaluate EPANET-MSX was a chloramine dynamics model that consisted of both kinetic rate expressions and nonlinear equilibrium equations, or a DAE system, which was based on the dynamics discussed in Section 3.1. While these studies demonstrated the capabilities of EPANET-MSX, the use of these multi-species models in practice has not been
evaluated.
Chapter 4

Materials and Methods

The procedures required to perform this study include distribution system modeling and various methods of water quality analysis. Distribution system modeling consists of both hydraulic and water quality simulations. Water quality analysis includes a variety of both bench-scale and field-scale analysis. A summary of all procedures are given in this chapter.

A one week pilot study was performed April 27th to May 1st of 2009. Additional details and preliminary results regarding the pilot study can be found in Section 5. An extensive two week primary study was performed September 6th to the 18th of 2009. Additional details regarding the primary study are discussed in Section 6.

4.1 Distribution System Modeling

Hydraulic and water quality simulations were performed using EPANET-MSX, an extension of EPANET that provides a general environment for performing multi-species water quality modeling. An existing distribution system network model was provided by our partner utility (see Section 4.1.1). Model hydraulics were updated in anticipation of simulating the hydraulic and water quality conditions associated
with the observed data from the actual system \( \text{(see Section 4.1.2)} \). Existing kinetic models and nonlinear equilibrium relationships associated with chloramine dynamics, by-product formation, nitrification, and other chemical and biological species were incorporated to approximate the interaction of various species within the bulk fluid \( \text{(see Section 4.1.3)} \).

### 4.1.1 Network Characteristics

This study was conducted in collaboration with our partner utility, Hillsborough County Water Resource Services (HCWRS), and focuses on the northwest region of their distribution system. Figure 4.1 shows the model of the distribution system, which serves, on average, 19.2 MGD of chloraminated water to predominately residential customers. The network model is an “all pipes” network with approximately 8500 nodes. The system contains no storage tanks and is supplied by three different water sources. The Fawn Ridge WTP is supplied by ground water, the Lake Park WTP by surface water, and the Tampa-Hillsborough Interconnect (THI) by a combination of surface, ground, and desalinated water. As seen in Figure 4.1, the system can be divided into approximately three regions (dashed lines), where each region is defined by the predominant type of source water predicted by the model. Blended source waters are expected in the areas near these regional boundaries.

### 4.1.2 Hydraulic Simulations

In order to achieve a more accurate representation of water quality parameters, the hydraulics of the network model (i.e., demand pattern multipliers and boundary conditions) were modified to represent the conditions observed from the actual system. With the cooperation of our partner utility, pump operations and flow rates, in-line system flow rates, pressures, and other significant data were provided through their supervisory control and data acquisition (SCADA) system. This data was used to
Figure 4.1: HCWRS Northwestern Network Model

generate global demand pattern multipliers to hydraulically balance the system (i.e., the total volume of water entering the system will balance the water demanded by the system). The hydraulic boundary conditions at the treatment plants were adjusted using two separate approaches with the results from each approach evaluated. The first approach developed pressure patterns for each of the three sources from SCADA data that allowed the flow rates to vary (referred to as the "pressure-based" model). The second approach used system flow rates for each of the three sources
from SCADA data to set the parameters of fictitious flow control valves to match the observed flow rates while using a fixed reservoir level at each source (referred to as the “flow-based” model).

4.1.3 Water Quality Simulations

Chloramine System: Monochloramine (NH₂Cl) and dichloramine (NHCl₂) kinetics were modeled based on an existing model developed by Richard Valentine and coworkers (Duirk et al., 2005; Vikesland et al., 2001). Table 4.1 presents the reactions associated with chloramine autodecomposition and organic matter interactions, which includes hydrolysis reactions involving chlorine with ammonia or chloramines (reactions 1 through 4), disproportionation reactions of the chloramine species (reactions 5 and 6), redox reactions that occur at low levels of free chlorine (reactions 7 through 10), reaction pathways of monochloramine in the presence of natural organic matter (reactions 11 and 12), acid/base equilibrium reactions of chlorine, ammonia, and carbonates (reactions 13 through 16), and the reaction of monochloramine with nitrite (reactions 17 through 22) (Duirk et al., 2005; Vikesland et al., 2001). Rate coefficients and equilibrium constants were adjusted based on temperature (T, kelvin) and ionic strength (Q).

This model requires the estimation of the dissolved organic carbon (DOC) reactive site fractions, represented by DOC₁ and DOC₂, with monochloramine and free chlorine, respectively. Other parameters that were measured for evaluation with the model include pH, temperature, dissolved organic carbon (DOC), conductivity, alkalinity, free chlorine, free ammonia, monochloramine, and dichloramine. Initial water quality conditions of the multi-species model were determined from SCADA data and grab samples.
Table 4.1: Chloramine Loss – various pathways of decay (Duirk et al., 2005; Vikesland et al., 2001).

<table>
<thead>
<tr>
<th>Reaction Stoichiometry</th>
<th>Rate Coefficients &amp; Equilibrium Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 HOCl + NH₃ → NH₂Cl + H₂O</td>
<td>$k_1 = 2.37(10^{12}) \left( \frac{e^{-\frac{1250}{T}}}{M} \right) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>2 NH₂Cl + H₂O → HOCl + NH₃</td>
<td>$k_2 = 6.7(10^{11}) \left( \frac{e^{-\frac{8800}{T}}}{h} \right) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>3 HOCl + NH₂Cl → NHCl₂ + H₂O</td>
<td>$k_3 = 1.08(10^{9}) \left( \frac{e^{-\frac{2010}{T}}}{M} \right) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>4 NHCl₂ + H₂O → HOCl + NH₂Cl</td>
<td>$k_4 = 2.3(10^{-3}) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>5 NH₂Cl + NH₂Cl → NHCl₂ + NH₃</td>
<td>$k_5 = 3.78(10^{10}) \left( \frac{e^{-\frac{2169}{T}}}{M} \right) [H^+] M^{-2} h^{-1}$ + $3.78(10^{35}) \left( \frac{e^{-\frac{22144}{T}}}{M} \right) [H_2CO_3] M^{-2} h^{-1}$ + $2.95(10^{10}) \left( \frac{e^{-\frac{4026}{T}}}{M} \right) [HCO_3^-] M^{-2} h^{-1}$</td>
</tr>
<tr>
<td>6 NHCl₂ + NH₃ → NH₂Cl + NH₂Cl</td>
<td>$k_6 = 2.2(10^{8}) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>7 NHCl₂ + H₂O → I</td>
<td>$k_7 = 4.0(10^{5}) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>8 I + NHCl₂ → HOCl + Products</td>
<td>$k_8 = 1.0(10^{8}) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>9 I + NH₂Cl → Products</td>
<td>$k_9 = 3.0(10^{7}) M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>10 NH₂Cl + NHCl₂ → Products</td>
<td>$k_{10} = 55.0 M^{-1} h^{-1}$</td>
</tr>
<tr>
<td>11 NH₂Cl + DOC₁ → Products</td>
<td>$k_{DOC1}$, Estimated</td>
</tr>
<tr>
<td>12 HOCl + DOC₂ → Products</td>
<td>$k_{DOC2}$, Estimated</td>
</tr>
<tr>
<td>13 HOCl ↔ H⁺ + OCl⁻</td>
<td>$pK_{OCl} = \left( \frac{1.18(10^{-4})T^2 - 7.86(10^{-2})T + 20.5}{(10^{-0.5\sqrt{Q/(1+\sqrt{Q})})^2}} \right)$</td>
</tr>
<tr>
<td>14 NH₄⁺ ↔ NH₃ + H⁺</td>
<td>$pK_{NH3} = \frac{1.03(10^{-4})T^2 - 9.21(10^{-2})T + 27.6}{Q}$</td>
</tr>
</tbody>
</table>
Table 4.1: Chloramine Loss – various pathways of decay (Duirk et al., 2005; Vikesland et al., 2001) (continued).

<table>
<thead>
<tr>
<th>Reaction Stoichiometry</th>
<th>Rate Coefficients &amp; Equilibrium Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 ( \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ )</td>
<td>[ pK_{\text{H}_2\text{CO}_3} = \left( \frac{1.48 \times 10^{-4} T^2 - 9.39 \times 10^{-2} T + 21.2}{10^{-5.5 \sqrt{Q}/(1+\sqrt{Q})^2}} \right) ]</td>
</tr>
<tr>
<td>16 ( \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ )</td>
<td>[ pK_{\text{HCO}_3} = \left( \frac{1.19 \times 10^{-4} T^2 - 7.99 \times 10^{-2} T + 23.6}{10^{-2\sqrt{Q}/(1+\sqrt{Q})}} \right) ]</td>
</tr>
<tr>
<td>17 ( \text{H}^+ + \text{NH}_2\text{Cl} + \text{NO}_2^- \xleftrightarrow[k_A']{k_A} \text{NH}_3 + \text{NO}_2\text{Cl} )</td>
<td>( k_A' = 4.89 \times 10^{10} )</td>
</tr>
<tr>
<td>18 ( \text{HOCl} + \text{NO}_2^- \xleftrightarrow[k_A]{k_A'} \text{NO}_2\text{Cl} + \text{OH}^- )</td>
<td>( k_A = \text{Unknown} )</td>
</tr>
<tr>
<td>19 ( \text{NO}_2\text{Cl} + \text{NO}_2^- \xleftrightarrow[k_B]{k_B'} \text{N}_2\text{O}_4 + \text{Cl}^- )</td>
<td>( k_B/k_D = 217 M^{-1} )</td>
</tr>
<tr>
<td>20 ( \text{N}_2\text{O}_4 + \text{OH}^- \xrightarrow[k_C]{k_C} \text{NO}_3^- + \text{NO}_2^- + \text{H}^+ )</td>
<td>( k_C = \text{Fast} )</td>
</tr>
<tr>
<td>21 ( \text{NO}_2\text{Cl} \xleftrightarrow[k_D]{k_D'} \text{NO}_2^- + \text{Cl}^- )</td>
<td>( k_D = \text{Unknown}, k_A'/k_D = 5.5 \times 10^5 M^{-1} )</td>
</tr>
<tr>
<td>22 ( \text{NO}_2^- + \text{OH}^- \xrightarrow[k_E]{k_E} \text{NO}_3^- + \text{H}^+ )</td>
<td>( k_E = \text{Fast} )</td>
</tr>
</tbody>
</table>

**Disinfectant By-Product Formation:** Formation of the disinfectant by-product \( N \)-nitrosodimethylamine (NDMA) was simulated using an existing kinetic model. Table 4.2 presents the NDMA model developed by Chen and Valentine (2006), which provides a linear relationship between NDMA formation and the reaction pathways of monochloramine and free chlorine with natural organic matter (reaction 23). The rate of chloramine loss and the formation parameter, \( \theta \), is typically estimated through bench-scale kinetic studies (see Section 4.2.1).
Table 4.2: NDMA Formation – A Nitrogenous Disinfectant By-Product (Chen and Valentine, 2006).

<table>
<thead>
<tr>
<th>Reaction Expression</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{dNDMA}{dt} = \theta (k_{DOC1}[NH_2Cl][DOC_1] + k_{DOC2}[HOCl][DOC_2])$</td>
<td>$^a\theta$, Estimated</td>
</tr>
</tbody>
</table>

$^a$Estimated mass ratio of NDMA produced to NOM oxidized

### 4.2 Water Quality Analysis

Water quality data was obtained through both bench-scale and field-scale analysis. Bench-scale studies were performed on water samples collected from the system to estimate the necessary parameters related to the kinetic models (see Section 4.2.1). A comprehensive field study was also performed to assess the performance of the distribution system model and to identify if any potential knowledge gaps exist (see Section 4.2.2).

#### 4.2.1 Bench-Scale Assessment

Parameter estimation studies were performed on finished water samples collected from each network source, during each week of the field study, to estimate parameters related to the kinetic models. These “bottle tests” were performed to assess the kinetics associated with reactions of chloramine ($k_{DOC1}$) and chlorine ($k_{DOC2}$) with natural organic matter and the formation of NDMA ($\theta$). Chlorine demand free bottles (Summers et al., 1996) were filled without head space and stored at distribution system temperature in the dark using a water bath that was continuously flushed with finished water. Sample bottles were removed and the necessary water quality parameters analyzed after 1 hour, 8 hours, and approximately every 12 hours thereafter until the end of the field-study. Water quality measurements taken in the bench-scale assessment include: free chlorine, total chlorine, monochloramine, free ammonia, pH,
temperature, alkalinity, nitrite, and nitrate (see Section 4.2.2.1 for method details). Samples for NDMA analysis were collected in 1-L bottles and the residual monochloramine quenched with sodium thiosulfate. These samples were stored at 4°C and transported to and analyzed at the University of Cincinnati. The kinetic parameters were estimated using a Levenberg-Marquardt approach to minimize the sum-of-the-squared errors between observed and expected values.

4.2.2 Field-Scale Assessment

The field-scale analysis was divided into a pilot study (see Section 5) and a primary study (see Section 6). Due to temporal and spatial challenges, the field-scale assessment only focused on a portion of the overall system. Sampling locations were selected by using the existing network model in an attempt to ensure that the field-scale measurements were spatially distributed and represented the overall distribution of estimated hydraulic residence times and source water blends. In addition to the sampling locations selected by these criteria, additional emphasis was placed on selecting sampling locations in suspected nitrification areas (i.e., areas where the utility has had difficulty maintaining a disinfectant residual).

Water samples were collected throughout the distribution system from the monitoring locations through sampling taps that were connected to fire hydrants. All of the water quality parameters were measured in the field except for alkalinity and NDMA, which were collected for later analysis in the laboratory. In addition to these “grab samples,” continuous conductivity and temperature monitors were installed at all sampling locations. Conductivity measurements were used to determine the ionic strength of water throughout the system.

In addition to water quality sampling, the hydraulic conditions were also monitored throughout the system using utility facilities. As mentioned in Section 4.1.2, pump
operations and flow rates, in-line system flow rates, pressures, and other significant data were provided by our partner utility through their supervisory control and data acquisition (SCADA) system. This data will be used to update the distribution system demand estimates and boundary conditions for the network model.

4.2.2.1 Chloramine System Analysis

Water quality samples related to the “Chloramine System” were taken twice daily from each sampling location. All water quality measurements related to the “Chloramine System” were performed in the field with a Hach DR/850 Colorimeter (Hach, 4845000) and Hach sensION2 Meter with Platinum Series pH and temperature Electrode (Hach, 5172510); excluding sulfate and alkalinity samples that were collected, preserved, and returned to the laboratory for analysis.

Free chlorine and total chlorine were measured using Hach Methods 8021 and 10070 (Hach Company, 2000), both are adaptations of the DPD Colorimetric Method [4500-Cl G] (APHA et al., 2005). These methods use N,N-diethyl-p-phenylenediamine (DPD) reagent packets as an indicator with a colorimeter to measure concentrations of free chlorine and total chlorine (APHA et al., 2005). A Hach DR/800 Series Colorimeter (Hach Company, 2000) was used to make both bench-scale and field-scale measurements.

Monochloramine and free ammonia were measured using Hach Method 10200 (Hach Company, 2000), or indophenol method, which is a proprietary method developed by the Hach Company. In this method, monochloramine reacts with a substituted phenol to form an intermediate monoimine compound in the presence of a cyanoferrate catalyst. The intermediate monoimine further reacts with excess substituted phenol to form indophenol, which is proportional to the amount of monochloramine present in the sample. An excess amount of hypochlorite is added to form additional monochlo-
ramine, the difference in monochloramine with and without the added hypochlorite is proportional to the free ammonia present in the sample (Hach Company, 2000).

Nitrite was quantified by Hach Method 8507 (Hach Company, 2000), or diazotization method; an adaptation of the Colorimetric Method [4500-NO$_2$ B] (APHA et al., 2005). Nitrite was treated with a sulfanilic acid reagent to form an intermediate diazonium salt, which further reacts with added chromotropic acid to form a pink colored complex. The intensity of this complex is directly proportional to the concentration of nitrite in solution. Nitrate was determined by means of Hach Method 8039 (Hach Company, 2000), or cadmium reduction method. This method is similar to the diazotization method; however nitrate is first reduced to nitrate by means of cadmium treated with CuSO$_4$. It should be noted that this method actually measures total nitrite/nitrate (NOX), therefore nitrite was subtracted from total nitrite/nitrate to obtain nitrate.

Alkalinity was analyzed by the Titration Method [2320 B] (APHA et al., 2005) in a laboratory. Samples were collected in 250 mL “chlorine demand-free” (CDF) (Summers et al., 1996) amber glass bottles with polytetrafluoroethylene (PTFE) lined caps. A small amount of sodium thiosulfate ($\approx$ 75 mg/L) was also added to sample containers to eliminate the interference of residual chlorine with the indicators. The containers were filled completely and stored at 4°C for no more than 24 hours. Samples were allowed to warm to room temperature before analysis.

Temperature and pH of various samples was determined by using a Hach Platinum Series glass pH electrode. Sulfate concentration was measured by Hach Method 8051 (Hach Company, 2000), a colorimetric procedure adapted from the Turbidimetric Method [4500-SO$_4^{2-}$ E] (APHA et al., 2005) that utilizes a barium chloride (BaCl$_2$) reagent. Organic carbon analysis was conducted by our partner utility in their laboratory by the Persulfate-Ultraviolet Method [5310 C] (APHA et al., 2005).
4.3 Disinfectant By-Product Analysis

Water samples were collected from all sampling locations throughout the distribution system during the field-scale assessment. These samples were preserved and stored until they were analyzed for N-nitrosodimethylamine (NDMA). A detailed summary of the DBP analysis is given in the following sections.

4.3.1 Sample Collection

One 500-mL amber glass bottle was collected for NDMA analysis once a day at each sampling location. Sampling containers were “chlorine demand free” and sealed with PTFE lined caps. Sodium thiosulfate (60-75 mg/L) was added to all containers prior to sampling to quench chloramine residual and cease NDMA formation. Sample containers were filled “headspace free” and stored at 4°C until analyzed.

4.3.2 NDMA Analysis

NDMA was extracted from the aqueous samples by means of a solid-phase extraction (SPE) method (see Section 4.3.2.1). The extraction method is an adaptation of other SPE methods (Chen and Young, 2009; Jenkins et al., 1995; Luo et al., 2003). Extracted samples were analyzed using an Agilent 7890A gas chromatograph (GC) and an Agilent 5975C mass spectrometer (MS). The analytical method was also a variation of previously developed methods (Chen and Young, 2009; Jenkins et al., 1995; Luo et al., 2003; Prest and Herrmann, 1999; USEPA, 2004)(see Section 4.3.2.2).

4.3.2.1 Solid-Phase Extraction Method

NDMA was isolated from environmental water samples using Carboxen 564 (Sigma, 10264), a granular carbonaceous adsorbent. The 500-mL samples were transferred to clean 1-L amber glass bottles and 200 mg of Carboxen 564 were added directly
to each sample. An internal standard, NDMA-d<sub>6</sub> (Cambridge Isotope Laboratories, Inc., DLM-2130-S), was then injected into each sample (10 ppt) to determine extraction recovery. Samples were then shaken for 1 hour at 100 rpm on a platform shaker (New Brunswick Scientific, Classic C1 Shaker). Samples were then filtered through a paper filter (Millipore, FP10404700) using a vacuum filter apparatus (Millipore, XX1004700). The filtration apparatus was rinsed with high purity water and methanol, and allowed to dry between each sample filtration. The filter paper (with Carboxen 564) was then transferred to a disposable aluminum dish (Fisher, 08-732-101) and allowed to air dry for 30 minutes. The dried Carboxen 564 was then transferred to a 2-mL amber vial with PTFE lined screw-thread caps (Fisher, 03-391-36) and 400-µL of dichloromethane (Fisher, D143-1) were injected into the vial with a syringe. Extracted samples were then stored at −20°C until analyzed by GC/MS.

4.3.2.2 Analytical Method

Standard solutions of various concentrations of N-nitrosodimethylamine (Restek, 31427) and NDMA-d<sub>6</sub> (Cambridge Isotope Laboratories, Inc., DLM-2130-S) were prepared in dichloromethane, as specified by EPA Method 521 (USEPA, 2004), to develop a multipoint calibration curve. The calibration curve was checked twice daily with standard solutions and solvent blanks were analyzed for contamination.

NDMA was chromatographically separated using an Agilent 7890A gas chromatograph (GC) in conjunction with an Agilent 5975C mass selective detector (MSD) operated in the selected-ion-monitoring mode (SIM) using ammonia positive chemical ionization (PCI). An HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness; Agilent Technologies Inc., 19091C-733) was installed in the GC. Samples were manually injected. Operating conditions for the GC and MSD are given in Table 4.3 and Table 4.4 respectively.
Table 4.3: NDMA Analysis – GC and Injection Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Oven Temperature</td>
<td>40°C for 3.00 min</td>
</tr>
<tr>
<td>Oven Temperature Ramp #1</td>
<td>10°C/min to 170°C for 0 min</td>
</tr>
<tr>
<td>Oven Temperature Ramp #2</td>
<td>15°C/min to 240°C for 3.00 min</td>
</tr>
<tr>
<td>Method Run Time</td>
<td>23.667 min</td>
</tr>
<tr>
<td>Injection Type</td>
<td>Splitless</td>
</tr>
<tr>
<td>Injection Temperature</td>
<td>225°C</td>
</tr>
<tr>
<td>Injection Pressure</td>
<td>15.744 psi</td>
</tr>
<tr>
<td>Injection Flow Rate</td>
<td>64.5 mL/min</td>
</tr>
<tr>
<td>Septum Purge Flow</td>
<td>3 mL/min</td>
</tr>
<tr>
<td>Septum Purge Flow Mode</td>
<td>Switched</td>
</tr>
<tr>
<td>Gas Saver</td>
<td>20 mL/min after 2.00 min</td>
</tr>
<tr>
<td>Purge Flow to Split Vent</td>
<td>60 mL/min at 2.00 min</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Column Flow</td>
<td>2.00 mL/min</td>
</tr>
<tr>
<td>Sample Injection Volume</td>
<td>50 µL</td>
</tr>
<tr>
<td>Transfer Line Temperature</td>
<td>220°C</td>
</tr>
</tbody>
</table>

Condensation of ammonia gas must be prevented in the ionization chamber to avoid negative peaks in the chromatographs (Charrois et al., 2004; USEPA, 2004). This condensation was avoided by coiling the reagent transfer line from the floor of the
laboratory to the connection port in the back of the instrument, so that condensed ammonia would reside in the lower portion of the transfer line.

Table 4.4: NDMA Analysis – MSD Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent Gas Flow</td>
<td>1.5 mL/min</td>
</tr>
<tr>
<td>Reagent Gas Pressure</td>
<td>15.744 psi</td>
</tr>
<tr>
<td>EM Voltage</td>
<td>PCI CH₄ AutoTune 1694 V</td>
</tr>
<tr>
<td>Gain Factor</td>
<td>12.00</td>
</tr>
<tr>
<td>Quadrupole Temperature</td>
<td>150°C</td>
</tr>
<tr>
<td>PCI Source Temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Manifold Temperature</td>
<td>150°C</td>
</tr>
<tr>
<td>Ion Trap Temperature</td>
<td>40°C</td>
</tr>
<tr>
<td>Acquisition Mode</td>
<td>SIM</td>
</tr>
<tr>
<td>Scan Time</td>
<td>0.80 sec</td>
</tr>
<tr>
<td>Solvent Delay</td>
<td>3.50 min</td>
</tr>
<tr>
<td>SIM Ion #1</td>
<td>75.1 amu</td>
</tr>
<tr>
<td>SIM Ion #2</td>
<td>92.1 amu</td>
</tr>
</tbody>
</table>

This method assumes that the internal standard recovery is equal to the recovery of the target compound. Therefore, the concentration of NDMA must be calculated based on the recovery rate of the internal standard. According to Munch and Bassett (2006), the method detection limit (MDL) of a similar analytical approach was found
to be as high as 0.33 ng/L and the lowest concentration minimum reporting level (LCMRL) was found to be as high as 1.6 ng/L. Even though the analytical method used in this study was a variation of previously developed methods (Chen and Young, 2009; Jenkins et al., 1995; Luo et al., 2003; Prest and Herrmann, 1999; USEPA, 2004), similar analytical uncertainty is expected.

4.4 Biological Analysis

Large volume samples (100-L) were collected from various locations throughout the system during the field-scale assessment. These samples were taken to a temporary laboratory established at the partner utility’s site to concentrate microorganisms in the water to a smaller volume (500 mL) (*see Section 4.4.1*). DNA was then extracted from the concentrated water samples (*see Section 4.4.2*). Molecular biological methods were then used to selectively detect AOB and ANAMMOX bacteria (*see Section 4.4.3*). A detailed summary of the biological analysis is given in the following sections.

4.4.1 Sample Concentration

Drinking water samples were concentrated in a temporary laboratory in the proximity of the field study. Concentrated samples were temporarily stored in a refrigerator at 4°C until they were returned to the University of Cincinnati for biological analysis. Samples were transported on ice and later stored at −80°C until they were analyzed. The process of concentrating biomass in bulk water by means of ultrafiltration (UF) is an adaptation of the procedures developed and tested by Hill et al. (2005) and Lindquist et al. (2007).
4.4.1.1 Ultrafiltration System Configuration

The UF system setup is shown in Figure 4.2. Large volume drinking water samples were pumped through the UF system using a Cole-Parmer Masterflex I/P peristaltic pump drive (EW-77410-10) equipped with a Masterflex I/P Easy Load pump head (EW-77601-00). Samples were pumped through a tangential flow filter cartridge (Rexeed-25 SX, Asahi Kasei Inc., Memphis, TN). Filtrate was discarded and retentate was recycled through the UF system until the final volume was reduced to approximately 500 mL.

4.4.1.2 Concentration Procedure

Large volume samples (100-L) were collected in multiple plastic holding containers (20-L) that were lined with sterile bags (General Econopak, Inc., Philadelphia, PA). Each 20-L water sample was dechlorinated by adding 6.66 mL of a 30.0 g/L sodium thiosulfate solution. Residual chlorine was measured in each 20-L sample using Hach Method 8021/10070 (Hach Company, Loveland, CO), an adaptation of the DPD Colorimetric Method for total and free chlorine (APHA et al., 2005). The UF membrane was pretreated by cycling 1.0 L of 0.1% w/v sodium polyphosphate (NaPP, Sigma 305553) solution through the system, until the volume of NaPP solution was reduced to 250 mL.

After the membrane was pretreated, the environmental sample was pumped through the UF system. The pump speed was increased until the filtrate flow, leaving the system, was maintained between 1.5 and 1.8 L/min. Flow control clamps and pump speed were used to control flow and pressure throughout the UF system. Pressure of the system was not allowed to exceed 20-25 psi. This process was sustained until all five 20-L samples were reduced to approximately 500 mL.
4.4.1.3 Backwash Procedure

After concentrating the field sample, the filter was backwashed to increase the total recovery of microorganisms. A graduated cylinder containing 150 mL of the backwash solution (0.01% w/v NaPP, Sigma 305553; 0.5% v/v Tween 80, Sigma P1754; and 0.001% v/v Antifoam A, Sigma A5758) was pumped through the system in the opposite direction the field sample was pumped. This was accomplished by closing the filter effluent line and sample influent line hose clamps and placing the filter permeate effluent line in the graduated cylinder containing the backwash solution. Once all the backwash solution has been pumped through the system, the retentate bottle was disconnected, capped, and stored.

4.4.1.4 Ultrafiltration Disinfection Procedure

After concentrating a field sample, the UF system was disinfected by cycling 250 mL of a sodium hypochlorite solution (25 mL of 6.15% w/v, The Clorox Co.; and 225 mL of deionized water) through the UF system for 10 minutes. The sodium hypochlorite
solution was then purged from the system and rinsed twice with 250 mL of deionized water for 1 minute each. After the rinse water was purged from the system, a 250 mL solution of sodium thiosulfate (1.25 mL of 30.0 g/L Na$_2$S$_2$O$_3$; and 248.75 mL of deionized water) was cycled through the UF system for 1 minute. Residual chlorine was measured in the purged solution using Hach Method 8021/10070. If residual chlorine was present, the UF system was rinsed with deionized water followed by the sodium thiosulfate solution until no residual was detected.

### 4.4.2 DNA Extraction

The frozen concentrated environmental water samples were thawed from −80°C in a 50°C water bath. Biomass was further concentrated by vacuum filtering 250 mL of each sample through a 0.22 µm membrane filter (Millipore, GPWP04700). Biomass from each sample was retained on a filter membrane. To prevent cross-contamination, the filter apparatus was rinsed with sodium hypochlorite, sterile water, and ethanol after each filtration run. Since the biomass was attached to the filter, a portion of each membrane was excised using a single-hole punch (found at any office supply store). Extracted segments of the membrane were retained for DNA extraction using a soil DNA extraction kit (MO BIO UltraClean Soil DNA Isolation Kit, #12800-50). For quality control purposes, DNA/RNA-free water was filtered through a membrane and extracted, to confirm that targeted bacteria did not exist in the extraction materials. Nucleic acid concentrations of the extracted environmental samples were quantified by measuring the absorbance at 260 nm with a spectrometer.

### 4.4.3 AOB and ANAMMOX Bacteria Identification

Six species of bacteria were evaluated in this analysis. Three of which were ammonia-oxidizing bacteria (AOB): *Nitrosomonas europaea*, *Nitrosospira multiformis*, and *Nitrosomona oligotropha*. The other three were anaerobic ammonia-oxidizing bacteria
(ANAMMOX): Candidatus Brocadia fulgida, Candidatus Brocadia sp. 40, and Candidatus Kuenenia stuttgartiensis. Plasmids containing the interested regions (AOB: ammonia monooxygenase sub-unit genes; ANAMMOX: partial 16S ribosomal DNA gene) of the targeted bacteria were obtained from Dr. Kartik Chandran, Columbia University, to be used as positive control in the polymerase chain reaction (PCR) analysis. Plasmids were introduced to competent E.coli cells by transduction through electroporation. The E.coli containing plasmid was cultured to duplicate the copies of inserts of interested regions of the targeted bacteria. Subsequently, the target regions were amplified using PCR with specific primer sets for the following positive controls in agarose gel electrophoresis analysis.

4.4.3.1 Primer Sets for PCR

AOBs were detected using a primer set (forward primer, amoA-1F; 5’-GGGGTTTC-TACTGGTGTT-3’ and reverse primer, amoA-2R, 5’-CCCCTCKGSAAAGCCTTCTTTC-3’ [K = G or T; S = G or C]) that specifically targets the amoA gene, which is unique to ammonia-oxidizing bacteria (Rotthauwe et al., 1997). This primer set produces specific PCR products (≈490 bp). Unfortunately, the specific species of the bacteria was not able to be identified.

ANAMMOX bacteria were detected using a primer set (forward primer, Pla46F; 5’-GACTTGCATGCCTAATCC-3’and reverse primer, Amx820R, 5’-AAAACCCCTTC-TACTTAGT-3’, (Schimid et al., 2003)). This primer set produces specific PCR products (≈820 bp). Like the AOB, specific species of ANAMMOX bacteria were not able to be identified.

For quality control purposes, a universal primer set was also used to detect the absence or presence of any bacterium, which can target the selected 16S-rDNA genes of all microorganisms. The forward primer (S-D-Bact-0011-a-S-17, 5’-GTTGATCTCC-17’).
TCAG-3’, (Kane et al., 1993)) and the reverse primer (S-D-Bact-1492-A-A-21, 5’-Aacg gYT ACC TTg TTA CgA CTT-3’5’-TACCTTGTTACGACTT, (Lin and Stahl, 1995)) which generate DNA fragments around 1500 bp.

### 4.4.3.2 PCR Amplification

The presence of AOB and ANAMMOX bacteria was determined by PCR amplification of nucleic acids using an Applied Biosystems Thermal Cycler. Each PCR mixture (50 µL) was prepared using 0.25 µL of Takara Taq (5 units/µL) (Takara Bio Inc., #R001AM), 5 µL of 10X PCR buffer (Mg²⁺ free), 3 µL of MgCl₂ (25 mM), 4 µL of dNTP mixture, 5 µL of forward primer (2 µM), 5 µL of reverse primer (2 µM), 5 µL of template, and 22.75 µL of sterilized distilled water. The PCR conditions were as follows: 5 min. at 94°C, followed by 35 cycles of consisting of 30 sec. at 94°C, 30 sec. at 55°C, and 1 min. at 72°C, followed by a 8 min. final cycle at 72°C. Agarose Gel Electrophoresis was used to confirm the identity of target sequences. Aliquots of the PCR products (8 µL) and loading buffer (2 µL) were electrophoresed and visualized in 1% agarose gel by using standard electrophoresis procedures. Agarose gel was post-stained using SYBR Safe DNA gel stain (Invitrogen, #S33102). A 100 bp ladder (Takara Bio Inc., #3407B) was used to identify the lengths of amplified DNA fragments. Positive control samples (either the ammonia monooxygenase subunit genes of AOBs or partial 16S-rDNA of ANAMMOX bacteria) and negative control samples (RNA/DNA free water) were analyzed for quality control.
Chapter 5

Pilot Study

This chapter discusses the Pilot Study that was performed April 27\textsuperscript{th} to May 1\textsuperscript{st} of 2009. The intent of this study was to provide a preliminary assessment of the distribution system and network model. This was also an opportunity to evaluate the proposed water quality analytical techniques during an actual distribution system field-scale study and to provide preliminary data for improving the primary study to be performed at a later date.

5.1 Experimental Design

The pilot study focused on a region that was primarily supplied by a single network source, the Lake Park WTP, where six sampling locations were visited twice daily. Figure 5.1 shows the sampling sites that were selected to represent the temporal and spatial distribution of the estimated range of water age and source water blends in the region. Water quality analysis primarily focused on species related to the chloramine model (see Section 4.2.2.1).

Network hydraulics were updated as described in Section 4.1.2. Initial water quality conditions and parameter estimation data utilized for distribution system modeling
was performed as described in Sections 6.1.1 and 6.1.2. The MSX input file used in this model may be found in Appendix B.

Figure 5.1: Pilot Study Monitoring Locations
5.1.1 Parameter Estimation and Initial Conditions

A parameter estimation study was performed using source water from the Lake Park network source during the pilot study (see Section 4.2.1). This study determined that the decay constant associated with the oxidation of organic carbon by free chlorine ($k_{DOC2}$) was $2.31 \times 10^7$. The decay constant associated with the oxidation of organic carbon by combined chlorine ($k_{DOC1}$) was not estimated. Previous studies (Duirk et al., 2005) have indicated that the combined chlorine-organic carbon reactions are relatively fast. Since the distribution system evaluation only considers water within the distribution system, not from the point of disinfection, the fast reactions were assumed negligible. The $k_{DOC2}$ parameter were not estimated for the Fawn Ridge and THI source waters because the sampling sites in this study were assumed to be supplied by a single network source. So, the $k_{DOC2}$ parameter was assumed to be $6.5 \times 10^5$. This value was taken from work by Duirk et al. (2005). Appendix A shows the “best-fit” to the kinetic data from the bottle tests from the parameter estimation process.

Species associated with the chloramine model include: combined chlorine (monochloramine), free chlorine, free ammonia, nitrite, nitrate, alkalinity, organic carbon, pH and temperature. Initial concentrations of combined chlorine, free ammonia, and pH were based on the observed concentration at the Lake Park source during the time and date the study began, which was obtained from SCADA data. Nitrite, nitrate, alkalinity, organic carbon, and temperature were based on grab samples that were taken at the Lake Park source by the utility near the beginning of the study. Similar representative samples from the other two network sources were not collected as the current monitoring locations were assumed to be impacted only by one source. Instead, the initial conditions associated with the other two sources were determined by water quality data recorded by the utility during the beginning of the study. Ta-
Table 5.1 shows the initial conditions for the pilot study. A description of each analytical method can be found in Section 4.2.2.1.

Table 5.1: Initial Concentrations of Multi-Species Model – Pilot Study

<table>
<thead>
<tr>
<th>Species</th>
<th>FR Value</th>
<th>LP Value</th>
<th>THI Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochloramine, mg/L as Cl₂</td>
<td>4.53</td>
<td>4.28</td>
<td>4.60</td>
</tr>
<tr>
<td>pH</td>
<td>7.71</td>
<td>7.79</td>
<td>7.73</td>
</tr>
<tr>
<td>Alkalinity, mg/L as CaCO₃</td>
<td>195</td>
<td>195</td>
<td>195</td>
</tr>
<tr>
<td>Total Carbonate, mg/L as CO₃⁻</td>
<td>241.7</td>
<td>241.7</td>
<td>241.7</td>
</tr>
<tr>
<td>Bicarbonate, mg/L as CO₃⁻</td>
<td>232.6</td>
<td>232.6</td>
<td>232.6</td>
</tr>
<tr>
<td>Total Ammonia, mg/L as N</td>
<td>0.27</td>
<td>0.62</td>
<td>0.03</td>
</tr>
<tr>
<td>Ammonia, mg/L as N</td>
<td>0.007</td>
<td>0.019</td>
<td>0.001</td>
</tr>
<tr>
<td>DOC₂, mg/L as C</td>
<td>1.21</td>
<td>1.36</td>
<td>1.28</td>
</tr>
<tr>
<td>Nitrite, mg/L as N</td>
<td>0.008</td>
<td>0.009</td>
<td>0.008</td>
</tr>
<tr>
<td>Nitrate, mg/L as N</td>
<td>0.164</td>
<td>0.001</td>
<td>0.103</td>
</tr>
<tr>
<td>Sulfate, mg/L as SO₄²⁻</td>
<td>2.6</td>
<td>9.8</td>
<td>100.0</td>
</tr>
</tbody>
</table>

5.2 Results and Discussion

As previously described in Section 4.1.2, two separate approaches were used to adjust the hydraulic boundary conditions at each treatment plant. The performance of each approach was evaluated by comparing the model predicted and observed hydraulic and water quality data at the source and monitoring locations. In this section, only results from the “flow-based” model will be presented. The “pressure-based” model
results can be found in Appendix C. Table 5.2 provides the average model predicted source water blend and water age at each monitoring location using the “flow-based” model. All monitoring locations were predominately supplied by the Lake Park source with the average source water supply ranging from 98.96% to 74.92% Lake Park water. The average model predicted water age the monitoring locations ranged from 1.01 to 22.51 hours.

Table 5.2: Average “Flow-Based” Model Predicted Source Water and Water Age – Pilot Study

<table>
<thead>
<tr>
<th>Location</th>
<th>FR (%)</th>
<th>LP (%)</th>
<th>THI (%)</th>
<th>Water Age (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>0.00</td>
<td>98.96</td>
<td>0.00</td>
<td>1.01</td>
</tr>
<tr>
<td>P-2</td>
<td>0.00</td>
<td>90.99</td>
<td>4.81</td>
<td>9.38</td>
</tr>
<tr>
<td>P-3</td>
<td>0.35</td>
<td>82.43</td>
<td>5.07</td>
<td>22.51</td>
</tr>
<tr>
<td>P-4</td>
<td>0.00</td>
<td>84.65</td>
<td>5.04</td>
<td>17.45</td>
</tr>
<tr>
<td>P-5</td>
<td>10.82</td>
<td>74.92</td>
<td>4.65</td>
<td>16.78</td>
</tr>
<tr>
<td>P-6</td>
<td>0.08</td>
<td>82.36</td>
<td>4.88</td>
<td>22.03</td>
</tr>
</tbody>
</table>

Figures 5.2 and 5.3 show that chloramine concentrations were estimated very well throughout the pilot study. Observed chloramine values were typically within 0.5 mg/L from the model predicted concentrations. The free ammonia concentrations were represented reasonably well by the model. Observed ammonia values were variable at sampling locations P-1 and P-6, but less variable at all other locations. Model predicted chloramine and ammonia concentrations were relatively constant at P-1 and P-6, but more variable at all other locations, which may suggest that source water blending influenced model predicted results at these locations.

Figures 5.4 and 5.5 show that total chlorine concentrations were represented reason-
ably well by the model. Model predicted results were qualitatively similar to the modeled chloramine results, which indicates the model did not predict a significant change in the speciation of chlorine species (monochloramine, free chlorine, dichloramine, and trichloramine). Minimal amounts of free ammonia was detected in the system, so combined chlorine results were similar to total chlorine results. Similar observations were found in Section 6. Observed total chlorine results were more variable than observed chloramine results, which may simply be a result of variability in the sampling method. Multiple samples for total chlorine were taken at each monitoring site visit and additional variability was found in the observed, duplicate total chlorine measurements.

As indicated by Figures 5.6 and 5.7, nitrite was typically underestimated by the water quality model. Observed values ranged from 0 to 0.03 mg/L, while modeled values were generally constant at approximately 0.005 mg/L. Discrepancies between modeled and observed values could be a result the biochemical oxidation of ammonia to nitrite by ammonia-oxidizing bacteria, which was not accounted for in the model. However, other observed water quality parameters (chloramine, ammonia, and pH) did not indicate that nitrification was occurring. Also, some of the observed nitrite concentrations were near the detection limit of Hach Method 8507 (Hach Company, 2000), therefore model performance may be more uncertain in those cases.

Nitrate concentrations were inadequately represented by the model during the entire pilot study (see Figures 5.6 and 5.7). As expected, model predicted results at P-1 were constant at 0.002 mg/L, since essentially all of the water was supplied by the Lake Park source. Observed nitrate values at P-1 were variable, ranging from 0 to 0.025 mg/L, which were generally underestimated by the model. Like the results at P-1, observed nitrate results at all locations were variable throughout the study. Model predicted results at all other locations were variable. The water quality model
overestimated the observed nitrate values at P-2, P-3, and P-6, while it both overestimated and underestimated nitrate at P-4. Model performance at P-5 was reasonably accurate, but the model predicted nitrate concentrations spiked dramatically several times throughout the study. These dramatic increases were likely when Lake Park water was predicted to blend with Fawn Ridge water, because the initial modeled concentration of Fawn Ridge water was higher relative to the other network sources.

Figures 5.8 and 5.9 show that pH was underestimated throughout the entire pilot study. Observed pH values were somewhat variable (7.7 to 7.9), but were consistently greater than modeled values. The modeled results were relative constant at 7.7 units. The constant underestimation of the pH was consistent with the Lake Park source, which likely led to underestimation throughout the remainder of the region.

5.3 Summary

In general, the chloramine dynamics model represented the observed water quality parameters reasonably well during the pilot study. Monochloramine was represented very well at all locations, while free ammonia was represented reasonably well at most locations. Nitrite and nitrate were inadequately represented by the model at all sampling locations. The pH model overestimated observed values throughout the entire pilot study. Overall, pilot results were found to be qualitatively similar to the results found in the primary study (see Section 6).

The pilot study provided an opportunity to become familiar with the distribution system and the proposed sampling techniques. It was determined that water quality sampling procedures were time consuming, which would limit the number of sampling sites and samples that could be evaluated in the primary study. Additionally, it was determined that sulfate should be evaluated in the primary study to assist in the analysis of model performance, since each network source provided significantly
different background levels of sulfate.
Figure 5.2: “Flow-Based” Combined Chlorine and Free Ammonia Results at P-1, P-2, and P-3
Figure 5.3: “Flow-Based” Combined Chlorine and Free Ammonia Results at P-4, P-5, and P-6
Figure 5.4: “Flow-Based” Total Chlorine Results at P-1, P-2, and P-3
Figure 5.5: "Flow-Based" Total Chlorine Results at P-4, P-5, and P-6
Figure 5.6: “Flow-Based” Nitrite and Nitrate Results at P-1, P-2, and P-3
Figure 5.7: “Flow-Based” Nitrite and Nitrate Results at P-4, P-5, and P-6
Figure 5.8: “Flow-Based” pH Results at P-1, P-2, and P-3
Figure 5.9: “Flow-Based” pH Results at P-4, P-5, and P-6
Chapter 6

Primary Study: Chloramine Dynamics

This chapter discusses the implementation of the chloramine dynamics model to represent the primary field-study that was performed September 6th through the 18th of 2009. The final assessment included parameter estimation studies, field measurements of species associated with chloramine dynamics, and hydraulic and water quality network simulation and evaluation.

6.1 Experimental Design

The primary study evaluated the chloramine dynamics model throughout the entire distribution system. Figure 6.1 shows the distribution system with the three network sources and twenty monitoring locations shown. The three sources are Fawn Ridge (FR), Lake Park (LP), and the Tampa-Hillsborough Interconnect (THI) and are represented by black symbols on Figure 6.1. The monitoring locations are denoted by two letters (representative of the primary source impacting that location) and a number to serve as an identifier and are presented as white symbols on Figure 6.1. Throughout the two week study, a total of twenty-three sampling sites (3 locations in...
the proximity of network sources and 20 field locations) were visited. During the first week of the study, thirteen sampling sites were monitored twice daily for four days (see Section 4.2.2); 3 network sources and 10 field locations. During the second week of the study, thirteen sites were also monitored twice daily for four days; 3 network sources and 10 field locations (these field locations were different from the first week). It should be noted that the monitoring locations referred to as “network sources” were not directly located at the source effluent. Monitoring locations were spatially and temporally distributed to represent the estimated range of water age and source water blends that exist throughout the distribution system.

Network hydraulics were updated as described in Section 4.1.2. Initial water quality conditions and parameter estimation data utilized for distribution system modeling may be found in Sections 6.1.1 and 6.1.2. Section 6.1.3 describes the monitoring location selection process in detail.

6.1.1 Parameter Estimation

Three separate parameter estimation studies were performed using water from each network source during each week of the study (see Section 4.2.1). These studies were performed to determine the decay constant associated with the oxidation of organic carbon by free chlorine \(k_{DOC2}\) and the NDMA formation constant \(\theta\). The decay constant associated with the oxidation of organic carbon by combined chlorine \(k_{DOC1}\) was not estimated. Previous studies (Duirk et al., 2005) have indicated that the combined chlorine-organic carbon reactions are relatively fast. Since the distribution system evaluation only considers water within the distribution system, not from the point of disinfection, the fast reactions are assumed negligible. This assumption is even more appropriate for LP and THI water as the utility receives previously disinfected water from another utility. Appendix A shows the model fits
to the observed kinetic data after parameter estimation has been performed, and there was no “rapid” reaction observed in the initial few hours of the kinetic studies.

Table 6.1: Estimated Parameters of the Multi-Species Chloramine Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Week #1 Value</th>
<th>Week #2 Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{FR,DOC2}^a$</td>
<td>$3.613(10^{-16})$</td>
<td>$1.000(10^{-5})$</td>
</tr>
<tr>
<td>$k_{LP,DOC2}^b$</td>
<td>$1.866(10^6)$</td>
<td>$1.472(10^{-15})$</td>
</tr>
<tr>
<td>$k_{THI,DOC2}^c$</td>
<td>$6.053(10^{-14})$</td>
<td>$3.475(10^{-2})$</td>
</tr>
</tbody>
</table>

$^a$Fawn Ridge chlorine decay constant  
$^b$Lake Park chlorine decay constant  
$^c$THI chlorine decay constant

The parameter estimation study concluded that, with the exception of the Lake Park
source water during Week #1, the reaction between combined chlorine and organics was negligible. Table 6.1 shows that the magnitude of the Lake Park chlorine decay constant was significantly larger than all other constants (and similar to values observed by Duirk et al. (2005)). These results indicate that autodecomposition was accountable for the majority of chloramine decay at most locations. Plots of the observed data and curve fits of the data can be found in Appendix A.

6.1.2 Initial Conditions

Species associated with the evaluation of the chloramine model include: combined chlorine (monochloramine), free chlorine, free ammonia, nitrite, nitrate, sulfate, alkalinity, organic carbon, pH and temperature. Initial concentrations of combined chlorine, free ammonia, and pH were based on the concentrations observed from the SCADA system during the day the study began. Nitrite, nitrate, alkalinity, organic carbon, and temperature were based on initial grab samples that were taken at the beginning of the study. If the initial observed value was believed to be an “outlier,” an average of the subsequent values was used as an initial value. Tables 6.2 and 6.3 show the initial conditions for Weeks #1 and #2 respectively. A description of each analytical method can be found in Section 4.2.2.1.

6.1.3 Monitoring Location Selection

The objectives of the monitoring location selection process were to determine locations that were spatially diverse that also captured a range of residence times and source water blends. Using the distribution system network model provided by the utility, water age analysis and trace simulations from the three individual sources were performed using EPANET to provide the information for the selection process. The trace analysis associated with the Fawn Ridge, Lake Park, and THI sources allowed the distribution system to be separated into approximate source–blend re-
Table 6.2: Initial Concentrations of Multi-Species Model – Week #1

<table>
<thead>
<tr>
<th>Species</th>
<th>FR Value</th>
<th>LP Value</th>
<th>THI Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochloramine, mg/L as Cl₂</td>
<td>3.56</td>
<td>4.36</td>
<td>4.14</td>
</tr>
<tr>
<td>pH</td>
<td>7.82</td>
<td>7.67</td>
<td>7.75</td>
</tr>
<tr>
<td>Alkalinity, mg/L as CaCO₃</td>
<td>205</td>
<td>183</td>
<td>85</td>
</tr>
<tr>
<td>Total Carbonate, mg/L as CO₃⁻</td>
<td>251.4</td>
<td>227.2</td>
<td>104.8</td>
</tr>
<tr>
<td>Bicarbonate, mg/L as CO₃⁻</td>
<td>243.5</td>
<td>218.0</td>
<td>101.1</td>
</tr>
<tr>
<td>Total Ammonia, mg/L as N</td>
<td>0.34</td>
<td>0.27</td>
<td>0.03</td>
</tr>
<tr>
<td>Ammonia, mg/L as N</td>
<td>0.014</td>
<td>0.008</td>
<td>0.001</td>
</tr>
<tr>
<td>DOC #2, mg/L as C</td>
<td>1.20</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>Nitrite, mg/L as N</td>
<td>0.003</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>Nitrate, mg/L as N</td>
<td>0.007</td>
<td>0.019</td>
<td>0.027</td>
</tr>
<tr>
<td>Sulfate, mg/L as SO₄²⁻</td>
<td>1.6</td>
<td>36.0</td>
<td>99.0</td>
</tr>
</tbody>
</table>

regions. Figure 6.2 presents the seven source blend regions as determined from the trace simulations that include:

- FR-only and LP-only: indicates that greater than 99% of the water came from a single source;
- FR(mostly)/LP and LP(mostly)/THI: represents a blend of source waters where the source listed first comprised 80 – 85% or more of the blend;
- FR/LP and LP/THI: represents a blend of source waters where either component was present between 20 – 80%; and
- blend of all three: the region where FR, LP, and THI waters all blended together.
Table 6.3: Initial Concentrations of Multi-Species Model – Week #2

<table>
<thead>
<tr>
<th>Species</th>
<th>FR Value</th>
<th>LP Value</th>
<th>THI Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochloramine, mg/L as Cl₂</td>
<td>2.42</td>
<td>4.53</td>
<td>4.54</td>
</tr>
<tr>
<td>pH</td>
<td>7.73</td>
<td>7.78</td>
<td>7.79</td>
</tr>
<tr>
<td>Alkalinity, mg/L as CaCO₃</td>
<td>205</td>
<td>155</td>
<td>73</td>
</tr>
<tr>
<td>Total Carbonate, mg/L as CO₃</td>
<td>253.3</td>
<td>190.7</td>
<td>89.8</td>
</tr>
<tr>
<td>Bicarbonate, mg/L as CO₃</td>
<td>244.0</td>
<td>184.3</td>
<td>86.8</td>
</tr>
<tr>
<td>Total Ammonia, mg/L as N</td>
<td>0.30</td>
<td>0.55</td>
<td>0.13</td>
</tr>
<tr>
<td>Ammonia, mg/L as N</td>
<td>0.009</td>
<td>0.019</td>
<td>0.005</td>
</tr>
<tr>
<td>DOC #2, mg/L as C</td>
<td>1.20</td>
<td>1.27</td>
<td>1.29</td>
</tr>
<tr>
<td>Nitrite, mg/L as N</td>
<td>0.004</td>
<td>0.004</td>
<td>0.008</td>
</tr>
<tr>
<td>Nitrate, mg/L as N</td>
<td>0.006</td>
<td>0</td>
<td>0.012</td>
</tr>
<tr>
<td>Sulfate, mg/L as SO₄²⁻</td>
<td>1.0</td>
<td>49.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The line bisecting the system separates the blending regions – above the line the LP water blends with FR water, while below the line all three source waters blend. The regions north and east of the LP and THI regions (truncated from Figure 6.1) were not included in the study. For each study week, the field-scale evaluation focused on two areas of the system to evaluate water from the three sources and at least one blending region. For Week #1, the study focused on the southern region of the system including the LP/THI region, and the FR(mostly)/LP and three-source blending region. For Week #2, the study focused on the northern region of the system including the LP(mostly)/THI and LP-only regions, and the FR/LP and FR-only regions.
Within each of the study areas, five monitoring locations were identified to represent the water age distribution of the overall system. Figure 6.3 shows the empirical cumulative distribution of water age in the system, as well as the approximate water age associated with the quintiles of the distribution. For each study region, the monitoring locations included the three sources and ten other locations (five in each study area). The five additional monitoring locations selected per study area were chosen such that one of the monitoring locations would have an estimated water age within each of the quintile ranges (see Figure 6.3). Table 6.4 shows the average model predicted water age of the selected monitoring locations.
Table 6.4: Model Predicted Water Age at Monitoring Locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Water Age, hours</th>
<th>Location</th>
<th>Water Age, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR-1</td>
<td>6.79</td>
<td>LP-1</td>
<td>1.28</td>
</tr>
<tr>
<td>FR-2</td>
<td>4.87</td>
<td>LP-2</td>
<td>5.17</td>
</tr>
<tr>
<td>FR-3</td>
<td>13.01</td>
<td>LP-3</td>
<td>14.05</td>
</tr>
<tr>
<td>FR-4</td>
<td>17.66</td>
<td>LP-4</td>
<td>17.57</td>
</tr>
<tr>
<td>FR-5</td>
<td>21.54</td>
<td>LP-5</td>
<td>23.57</td>
</tr>
<tr>
<td>FR-6</td>
<td>28.3</td>
<td>LP-6</td>
<td>35.57</td>
</tr>
<tr>
<td>FR-7</td>
<td>4.95</td>
<td>LP-8</td>
<td>8.05</td>
</tr>
<tr>
<td>FR-8</td>
<td>15.34</td>
<td>LP-9</td>
<td>12.48</td>
</tr>
<tr>
<td>FR-9</td>
<td>17.15</td>
<td>LP-10</td>
<td>16.76</td>
</tr>
<tr>
<td>FR-11</td>
<td>22.93</td>
<td>LP-11</td>
<td>22.06</td>
</tr>
<tr>
<td>FR-12</td>
<td>32.72</td>
<td>LP-12</td>
<td>33.36</td>
</tr>
</tbody>
</table>

6.1.4 “Flow-Based” vs “Pressure-Based” Models

As previously described in Section 4.1.2, two separate approaches were used to adjust the hydraulic boundary conditions at each treatment plant. The performance of each approach was evaluated by comparing the model predicted and observed hydraulic and water quality data at the source and monitoring locations. Figure 6.4 shows two scatter plots of observed and estimated hydraulic data. The scatter plot on the left shows the observed and estimated flows at each source from the “pressure-based” model. The scatter plot on the right shows the observed and estimated pressure (relative to the THI pressure) at the LP and FR sources from the “flow-based” model. Pressure was used to illustrate the performance of the “flow-based” model instead
Figure 6.3: Cumulative Distribution of Water Age

of flow because the modeled and observed flows were forced to be exactly the same. Also, since there are no storage tanks that “float” on the system, the relative pressure difference, or pressure gradient, between each source impact the flows delivered by the three sources. For example, if the pressure at each network source in the “flow-based” model was increased by 10 psi, the model predicted flows at each network source would remain the same.

Figure 6.4 shows that the “pressure-based” results tend to bias the flows from the two sources. The Lake Park source is overestimated and the Fawn Ridge source correspondingly underestimated by approximately 2 MGD (from a system with a total system flows of approximately 20 MGD). On the other hand, the “flow-based” model forces the flows from the different sources to be equal to the data from the SCADA system. While both approaches will be impacted by similar uncertainties (such as spatial distribution of demands and pipe roughness coefficients), the use of
the “flow-based” modeling approach reduced at least one uncertainty (source flow rates) that will impact, at a minimum, the flows in the different blending zones (since the demands are the primary driver of transport within the distribution system, the errors associated with uncertain pressure data in the “flow-based” model was assumed less important). Overall, the evaluation of the water quality simulations show little appreciable differences with only modest differences observed in the blending regions between the LP and THI regions, and the FR region. Therefore, this chapter will only discuss the “flow-based” model results. The “pressure-based” model results can be found in Appendices E, F, G, and H.

6.2 Results and Discussion

For discussion purposes, each sampling location was classified into one of four categories, based on location and sampling period. As discussed in Section 6.1.4, only “flow-based” model results will be discussed. Species presented in this section include: combined chlorine, free ammonia, nitrite, nitrate, sulfate, alkalinity, and pH. The to-
tal chlorine results behave very similarly to the combined chlorine results, therefore all of the total chlorine results will be presented in Appendix D. Since sulfate is a non-reactive species that does not directly impact the chloramine dynamics and each network source has significantly different background sulfate concentrations, sulfate was used as a “pseudo-tracer” to characterize the network hydraulics and will be discussed first in each individual study region. The sulfate discussion will be followed by the additional water quality analysis with most of the emphasis placed on the combined chlorine and ammonia results.

6.2.1 Fawn Ridge – Week #1

Six sampling locations (FR-1, FR-2, FR-3, FR-4, FR-5, and FR-6) were evaluated in the Fawn Ridge region during week one. Given that sulfate is a non-reactive species in the chloramine model and each network source has significantly different background concentrations of sulfate, sulfate was used as a “pseudo tracer” to characterize network hydraulics.

Figures 6.5 and 6.6 show that sulfate was satisfactorily modeled at locations that were only supplied by the Fawn Ridge source (FR-1, FR-2, FR-3, and FR-5). The model reasonably depicts the variability of sulfate at FR-4 and FR-6, which are located in a region that is supplied by a blend of Fawn Ridge, Lake Park, and THI source water (see Figure 6.2). The FR-4 monitoring location was represented slightly better than the FR-6 location, the latter of which is located in a branched, dead-end portion of the system.

Monochloramine was adequately approximated throughout the Fawn Ridge region during week one; with the exception of FR-6 which was overestimated by approximately 2 mg/L. Model performance at the FR-6 location may be impacted by stochastic demands associated with this type of branched, dead-end portion of the system.
that could significantly impact water age and transport characteristics.

Figures 6.7 and 6.8 indicate that free ammonia concentrations were generally not adequately represented at all locations. The observed ammonia concentrations were highly variable at the source and that variability was subsequently observed at the other locations throughout this region. These erratic and varied observations resulted in differences from the model predictions up to 0.3 mg/L throughout the Fawn Ridge region during week one. Monitoring location FR-5, also located in a dead-end, looped portion of the system, exhibited a decreasing trend in observed ammonia values that could be attributed to chemical or biological dynamics. However, the good agreement between the observed and model predicted chloramine concentrations does not suggest this decrease was related to the chemical dynamics, and there are no other signs, such as low disinfectant residual or excessive nitrite or nitrate levels, that would suggest nitrification.

Figures 6.9 and 6.10 show the nitrite and nitrate results. The nitrite model consistently underestimated observed nitrite values throughout the Fawn Ridge region during week one, with some of the samples up to 0.02 mg/L greater than model predicted values, which may be a result of microbial oxidation of ammonia. However, the model performance is somewhat inconclusive because several of the observed nitrite values were below the estimated minimum detection limit (0.005 mg/L) of Hach Method 8507 (Hach Company, 2000). Unlike the nitrite model, the nitrate model inconsistently overestimated and underestimated observed nitrate values in this region. The observed nitrate generally differed from the model predicted values from 0.005 to 0.020 mg/L. While some of the locations had observed data that exhibited variability, only the model predicted results from FR-6 had simulated data with similar variability. However, like the nitrite model, performance assessment of the nitrate model is uncertain, because several observed nitrate values were near the estimated
minimum detection limit (0.01 mg/L) of Hach Method 8039 (Hach Company, 2000).

Figures 6.11 and 6.12 illustrate the observed and predicted pH data throughout the Fawn Ridge region during week 1. The variability in the observed pH at FR-1 is not captured in the model predicted values. For the areas receiving mostly FR water (FR-2, FR-3, and FR-5), the model predicted results trend along the average, but did not capture the observed variability, perhaps due to the lack of variability included in the input data. At locations FR-4 and FR-6, near the blending zones, the model predicted variability does not necessarily capture the observed variability.

Figures 6.13 and 6.14 suggest that alkalinity was satisfactorily modeled. The observed variability at FR-4 appears to be adequately modeled, with less accuracy associated with the variability at FR-6. The accuracy in the model predicted alkalinity appears to trend very well with the sulfate data.

In general, water quality in this region of the system was reasonably represented, with the exception of FR-6 and to a lesser extent at FR-4. Inconsistencies between modeled and observed results may be due to a lack of resolution in the data used for representing influent water quality variability. The discrepancies may also be a result of not modeling reactions at the pipe–wall surface and/or associated with biological species. Although, there was no compelling evidence that nitrification was occurring, the influence of biological species should be considered. Furthermore, inadequate representation of the spatial distribution of demands in blending zones and dead-end regions may contribute to some of the inconsistent model performance.
Figure 6.5: “Flow-Based” Combined Chlorine and Sulfate Results at FR-1, FR-2, and FR-3
Figure 6.6: “Flow-Based” Combined Chlorine and Sulfate Results at FR-4, FR-5, and FR-6
Figure 6.7: “Flow-Based” Free Ammonia Results at FR-1, FR-2, and FR-3
Figure 6.8: “Flow-Based” Free Ammonia Results at FR-4, FR-5, and FR-6
Figure 6.9: “Flow-Based” Nitrite and Nitrate Results at FR-1, FR-2, and FR-3
Figure 6.10: “Flow-Based” Nitrite and Nitrate Results at FR-4, FR-5, and FR-6
Figure 6.11: “Flow-Based” pH Results at FR-1, FR-2, and FR-3
Figure 6.12: “Flow-Based” pH Results at FR-4, FR-5, and FR-6
Figure 6.13: “Flow-Based” Alkalinity Results at FR-1, FR-2, and FR-3
Figure 6.14: “Flow-Based” Alkalinity Results at FR-4, FR-5, and FR-6
6.2.2 Lake Park – Week #1

Six sampling locations (LP-1, LP-2, LP-3, LP-4, LP-5, and LP-6) were evaluated in the Lake Park region during week one.

Figures 6.15 and 6.16 show that, during week one of the Lake Park region, the sulfate concentrations at all of the monitoring locations exhibited a decreasing trend in observed sulfate. While these differences could be due to a change in influent concentration or source water blend (LP and THI), the modeled influent data does not adequately represent this decreasing trend. Keeping this limitation in mind, while the model predicted sulfate concentrations are in general agreement with the observed data, the decreasing trend is not captured and the representation of the sulfate concentration earlier in the week are generally underestimated (except for LP-6). In general, the sulfate results suggest that network hydraulics were reasonably represented throughout the Lake Park region during week one of the study.

Figures 6.15 and 6.16 also provide the observed and model predicted chloramine concentrations. For the Lake Park region during week 1, the combined chlorine model satisfactorily fit the observed data at all sampling locations. While there is no specific data associated with the hydraulic residence time for confirmation, the goodness-of-fit in this region suggests that wall decay modeling would likely not improve the modeling efforts.

Figures 6.17 and 6.18 illustrate an increasing trend in observed free ammonia during week one, which suggests, as above, that either the concentration of free ammonia increased at the Lake Park WTP during this week or there was a shift in the source water blend. As with the sulfate model estimates, the model input parameters for ammonia did not account for this increasing trend. As such, the model tended to underestimate the ammonia concentration later in the week. However, the model variability at LP-6 may or may not mask the inability of the model to represent the
observed trend. Again, the model performance implies that the variability of water quality entering the system is inadequately characterized.

Figures 6.19 and 6.20 show that nitrite was consistently underestimated (up to 0.02 mg/L) throughout the Lake Park region during week one. As above, these inaccuracies may be a result of not considering microbial activity in the distribution system, and the model performance assessment may be inconclusive because several of the observed nitrite values were below the estimated minimum detection limit (0.005 mg/L) of Hach Method 8507 (Hach Company, 2000). Unlike the nitrite model, nitrate was consistently overestimated in this region. This is likely due to the overestimation of the nitrate data at the source. The nitrate concentrations at LP-1 overestimate the observed data by approximately 0.01 - 0.02 mg/L, which is generally consistent with the overprediction at the remaining monitoring locations. As with the nitrite data, several observed nitrate values were near the estimated minimum detection limit (0.01 mg/L) of Hach Method 8039 (Hach Company, 2000). However, the model still clearly overestimates the observed data. Discrepancies between the modeled and observed nitrite and nitrate values may be due to biological oxidation of ammonia and nitrite, and inaccuracies associated with the modeled influent concentrations.

Figures 6.21 and 6.22 reveal that pH was generally underestimated throughout the Lake Park region. Like the Fawn Ridge region, modeled pH levels were relatively constant at all locations in this region (between 7.6 and 7.7), while observed pH values had more variability (between 7.6 and 7.9). Given that the pH was underestimated near the network source at LP-1, the remaining pH values were consistently underestimated at the subsequent monitoring locations. This suggests that the initial modeling of the influent pH at the Lake Park source was incorrect.

Figures 6.13 and 6.14 present the alkalinity data for the Lake Park region in week 1. In general, the observed alkalinity data is represented very well. In particular,
the variability at LP-2, LP-3, LP-5, and LP-6 seem to be adequately represented (and consistent with the sulfate data representing the source blending), although the model estimates at LP-6 seem to slightly underestimate the alkalinity.

Overall, water quality in the Lake Park region of the system during week 1 was reasonably represented. The inconsistencies between the modeled and observed data were most likely the result of the insufficient data resolution to represent the influent source water quality variability. While the nitrite and nitrate data suggest a need for improved microbial modeling, there are no other indications that pipe wall reactions or microbial dynamics are necessary.
Figure 6.15: “Flow-Based” Combined Chlorine and Sulfate Results at LP-1, LP-2, and LP-3
Figure 6.16: “Flow-Based” Combined Chlorine and Sulfate Results at LP-4, LP-5, and LP-6
Figure 6.17: "Flow-Based" Free Ammonia Results at LP-1, LP-2, and LP-3
Figure 6.18: “Flow-Based” Free Ammonia Results at LP-4, LP-5, and LP-6
Figure 6.19: “Flow-Based” Nitrite and Nitrate Results at LP-1, LP-2, and LP-3
Figure 6.20: “Flow-Based” Nitrite and Nitrate Results at LP-4, LP-5, and LP-6
Figure 6.21: “Flow-Based” pH Results at LP-1, LP-2, and LP-3
Figure 6.22: "Flow-Based" pH Results at LP-4, LP-5, and LP-6.
Figure 6.23: “Flow-Based” Alkalinity Results at LP-1, LP-2, and LP-3
Figure 6.24: “Flow-Based” Alkalinity Results at LP-4, LP-5, and LP-6
6.2.3 Fawn Ridge – Week #2

Five new sampling locations (FR-7, FR-8, FR-9, FR-11, and FR-12) were evaluated in the Fawn Ridge region during week two. The FR-1 location was also monitored during week two to characterize effluent water quality conditions from the Fawn Ridge WTP.

Figures 6.25 and 6.26 illustrate a range of model performance for representing the observed sulfate concentrations in the Lake Park region during week two. The observed sulfate concentrations at FR-1 clearly indicate that source water blending was occurring, but the modeled sulfate concentrations were not consistent with these observations. The sulfate concentrations were slightly underestimated by the model at FR-7, FR-8, and FR-11, where the modeling results suggest the FR WTP was the primary water source. Sulfate was more accurately represented at FR-9 and FR-12 where the model more accurately represented the observed blend of Fawn Ridge and Lake Park water.

Figures 6.25 and 6.26 illustrate that the combined chlorine concentrations were generally underestimated throughout the entire Fawn Ridge region during week two. For the chloramine concentrations at FR-7, FR-8, and FR-11 (where there appears to be little blending) the model predicted concentrations were generally underestimated by 1 – 2 mg/L. These discrepancies could be due to inaccuracies associated with residence time representation or the lack of wall-decay processes within the modeling framework. The chloramine estimates were better at FR-9 and FR-12 where the source water blends appeared to be more accurately represented.

Similar to week one results, Figures 6.27 and 6.28 show significant variability in the observed ammonia concentrations and poor model representation throughout the region. The model significantly overestimated the observed ammonia concentrations
at FR-8, FR-11, and FR-12, and, to a lesser degree, at FR-7 and FR-9. The observed ammonia variability near the Fawn Ridge WTP (FR-1) may be a result of source water blending. However, observed ammonia concentrations were variable at all sampling locations throughout the region, so the impact of source water blending at FR-1 was unclear. The significant disparity between modeled and observed results could be a result of microbial ammonia oxidation (nitrification). However, there is additional, conflicting information related to potential nitrification including monochloramine concentrations that are consistent with the observed concentrations at FR-1, nitrite concentrations consistent with week one, and the absence of positive microbial data (see Section 8), but increasing nitrate results later in the week (discussed below) that would suggest the final steps of the nitrification process.

Figures 6.29 and 6.30 illustrate that nitrite was generally underestimated in the Fawn Ridge region during the second week of the study even though the observed data were adequately represented at FR-1. There also appears to be slightly elevated nitrite concentrations during this study as some samples from FR-8, FR-9, and FR-11 approach 0.03 mg/L. As mentioned in Section 6.2.1, some of the observed concentrations of nitrite are near the detection limit of Hach Method 8507 (Hach Company, 2000), therefore model performance may be uncertain. The nitrate model performed reasonably well the first three days of week two, but then the observed nitrate concentrations at all locations (including FR-1, which is representative of the source) were observed to increase over the last two days of the study. While the first few days of observed nitrate concentrations were near the method detection limit, the concentrations after the increase are clearly above the detection limit. The discrepancies between the observed and modeled data may be attributed to biological nitrification, which was not accounted for in this model.

Figures 6.31 and 6.32, and 6.33 and 6.34 suggest that the modeled pH and alkalinity
data, respectively, adequately represent the observed data at all locations throughout the Fawn Ridge region during week two. The only exceptions are the alkalinity at FR-1, in which the model overestimated the observed data (interestingly enough, the alkalinity variability at FR-1 was not observed elsewhere), and FR-12, in which the model slightly underestimated the alkalinity.

Overall, the water quality representation of the Fawn Ridge region in week two was questionable. While some discrepancies were observed with respect to source water blending (from the sulfate data), there were significant discrepancies associated with the monochloramine and ammonia representation throughout the region. Inconsistencies between the modeled and observed data was most likely a combination of inadequate representation of water age and transport in blending zones, and the lack of resolution in data to represent the variability of source water quality. Additionally, the inability to adequately assess nitrification in the system is a potential limitation.
Figure 6.25: “Flow-Based” Combined Chlorine and Sulfate Results at FR-1, FR-7, and FR-8
Figure 6.26: “Flow-Based” Combined Chlorine and Sulfate Results at FR-9, FR-11, and FR-12
Figure 6.27: “Flow-Based” Free Ammonia Results at FR-1, FR-7, and FR-8
Figure 6.28: “Flow-Based” Free Ammonia Results at FR-9, FR-11, and FR-12
Figure 6.29: “Flow-Based” Nitrite and Nitrate Results at FR-1, FR-7, and FR-8
Figure 6.30: “Flow-Based” Nitrite and Nitrate Results at FR-9, FR-11, and FR-12
Figure 6.31: “Flow-Based” pH Results at FR-1, FR-7, and FR-8
Figure 6.32: “Flow-Based” pH Results at FR-9, FR-11, and FR-12
Figure 6.33: “Flow-Based” Alkalinity Results at FR-1, FR-7, and FR-8
Figure 6.34: “Flow-Based” Alkalinity Results at FR-9, FR-11, and FR-12
6.2.4 Lake Park – Week #2

Five new sampling locations (LP-8, LP-9, LP-10, LP-11, and LP-12) were evaluated in the Lake Park region during week two. The LP-1 location was also monitored during week two to characterize the effluent water quality conditions from the Lake Park WTP.

Figures 6.35 and 6.36 show that sulfate concentrations were estimated reasonably well throughout the Lake Park region during week two. Observed sulfate values indicate that blending between the Lake Park and THI sources may have occurred at LP-9, LP-11, and LP-12 (due to the increase in sulfate), but only the modeled results of LP-12 indicate a significant blend (the modeled sulfate concentrations from FR-8 and FR-10 estimate small amounts of blending). These results suggest that the underlying hydraulic transport may be slightly misrepresented at FR-9, FR-11, and FR-12.

Figures 6.35 and 6.36 illustrate that combined chlorine was significantly overestimated (up to 2.5 mg/L) throughout the entire Lake Park region during week two, except for LP-1, which was only slightly overestimated. While the discrepancies between the estimated and observed chloramine concentrations could be a result of variations in pH and alkalinity, the observed and modeled pH and alkalinity results were not significantly different to have such a large impact on the monochloramine decay. Another source of model inaccuracy could be the presence of nitrification, but there was no other convincing evidence that nitrification occurred (e.g., elevated nitrite/nitrate concentrations or decreased ammonia levels). Therefore, the only other potential options could be that there is excessive residence time due to a closed valve that is not represented in the model or there are pipe wall interactions that are significant or nitrification is occurring but the appropriate signals are not being observed.

Figures 6.37 and 6.38 illustrate that observed free ammonia concentrations decreased steadily at LP-1, except for an apparent increase in ammonia at LP-10. In the pre-
vious week, any significant trend in the water quality parameters at the source was observed at the other locations. However, this is not observed during this week potentially supporting the idea of a modified travel path. For locations LP-8 through LP-11, the model predictions of ammonia bisected the observed data, while overestimating the concentrations at LP-1. The model predicted results at LP-12 suggest a more distinctive blend of LP and THI water occurs at this location, which is loosely supported by the observed data. These results suggests that the hydraulic transport may not be accurately represented in this region during week two.

Similar to all other monitoring locations in this study, Figures 6.39 and 6.40 indicate that, as with the first week, nitrite was slightly underestimated in the Lake Park region during the second week of the study with the exception of LP-1, which was adequately represented. The disparity between the modeled and observed results is most likely a result of not considering the impact of nitrification in the water quality model. As with the other regions, many of the observed nitrite concentrations were near the detection limit of Hach Method 8507 (Hach Company, 2000), therefore model performance may be uncertain. Unlike the week one results, the nitrate data of week 2 appears to better track, on average, the nitrate concentration. While the influent concentrations at LP-1 were reasonably represented at LP-1 for both weeks, the observed concentrations in the second week appear to be slightly higher, in general, with some concentrations that exceed 0.03 mg/L. Some of these results could be explained by either an altered travel path or nitrification, but neither have conclusive supporting data.

Figures 6.41 and 6.42 show that the pH model slightly overpredicted observed pH levels throughout the Lake Park region, but most of the model predicted values were within approximately 0.1 pH units of the observed data. Figures 6.43 and 6.44 illustrate that the alkalinity is reasonably represented by the model at LP-1 and moderately underestimated at the other locations. As with the ammonia data, the model
predictions at LP-12 are impacted by a more distinctive blend of LP and THI water (as observed by the drops in alkalinity). This discrepancy is likely attributed to inaccurate representation of the source water blends.

As with the second week in the Fawn Ridge region, the model representation of the water quality parameters from the second week of the Lake Park region had more significant deviations than the first week. In particular, there were significant discrepancies between the modeled and observed monochloramine concentrations, which did not have any clear explanation, and ammonia concentrations, which seemed to have inconsistent observed water quality data (i.e., the low concentrations downstream of the source were not observed elsewhere in the region). Unlike the other studies, the inaccuracies between modeled and observed water quality results did not appear to be impacted by the lack of data resolution for representing the influent water quality variability. However, the model hydraulics may have not accurately depicted the transport of source water throughout this region, which could be a result from an unknown operational adjustment, such as a closed valve.
Figure 6.35: “Flow-Based” Combined Chlorine and Sulfate Results at LP-1, LP-8, and LP-9
Figure 6.36: “Flow-Based” Combined Chlorine and Sulfate Results at LP-10, LP-11, and LP-12
Figure 6.37: “Flow-Based” Free Ammonia Results at LP-1, LP-8, and LP-9
Figure 6.38: “Flow-Based” Free Ammonia Results at LP-10, LP-11, and LP-12
Figure 6.39: “Flow-Based” Nitrite and Nitrate Results at LP-1, LP-8, and LP-9
Figure 6.40: “Flow-Based” Nitrite and Nitrate Results at LP-10, LP-11, and LP-12
Figure 6.41: “Flow-Based” pH Results at LP-1, LP-8, and LP-9
Figure 6.42: “Flow-Based” pH Results at LP-10, LP-11, and LP-12
Figure 6.43: “Flow-Based” Alkalinity Results at LP-1, LP-8, and LP-9
Figure 6.44: “Flow-Based” Alkalinity Results at LP-10, LP-11, and LP-12
6.3 Summary

In general, the chloramine dynamics model represented the observed water quality parameters reasonably well during the first week of the field study (the southern portions of the study area), but there were some significant observed deviations during week two (the northern portion of the study area).

During the first week of the field study, the model appeared to represent the source blending (as SO$_4^{2-}$) as well as the monochloramine dynamics reasonably well in both the FR and LP regions with slight deviations at FR-6. This particular location was located within a dead-end, branched portion of the system where typical network model assumptions of constant, 1-hour demands may not be appropriate. One other significant deviation between the observed and modeled results was the lack of temporal representation of the influent variability associated with the NH$_3$ and pH data. Given the relative lack of temporal data, the influent parameters of the model were selected to be constant, which did not adequately represent the observed influent conditions and impacted subsequent model predictions. The model representation of this study area also underestimated the nitrite data and produced some minimal (FR area) to significant (LP area) overestimation of the nitrate data. While these results could be contributed to a lack of nitrification modeling, there was little other supporting evidence to suggest nitrification was significant.

During the second week of the field study, the model again appeared to reasonably represent the source water composition throughout the regions with the exception of FR-1, which clearly was a blend of FR and LP waters. The discrepancy could be a result of, for example, a less than accurate representation of the spatial distribution of network demands. The monochloramine results were more significantly misrepresented than the other water quality parameters. The model generally underestimated the monochloramine concentrations in the FR area, and overestimated the concen-
trations in the LP area. As during the first week, the model did not capture the influent variability associated with NH$_3$ and tended to overpredict the NH$_3$ concentrations in the FR region. While the inaccuracies in monochloramine and ammonia are consistent in the FR region (generally more chloramine decay would result in greater ammonia formation), the same was not observed in the LP region. These differences could be a result of inaccurate residence time representation or, with respect to the LP region, nitrification. However, there was little additional supporting data (for the residence time hypothesis) or corroborating evidence (for the nitrification hypothesis, such as elevated nitrite/nitrate levels) to strongly support these hypotheses.

While the nitrite levels were continually underestimated (as in week 1), the nitrate levels were generally better represented except during the last days of the FR study where there was an observed increase in NO$_3$. While the nitrate results suggest the start of nitrification, the other water quality parameters do not strongly support this possibility (i.e., one would expect a decrease in monochloramine and/or ammonia concentrations corresponding to an increase in nitrate).

Overall, the chloramine dynamics model provided mixed results for representing the observed water quality data. While the week 1 data appeared to be better represented than week 2, one possibility for the observed discrepancy – particularly with regard to the monochloramine data – was that the influent monochloramine concentrations at the FR and LP sources were relatively close during week 1 (differences no more than 1 mg/L) while during week 2 the sources were more disparate (with differences up to 2 mg/L). Thus, during week 1, the discrepancies due to source water blending may not be as apparent as during week 2. One aspect of the model that would improve the water quality representation would be to include an improved representation of the influent water quality dynamics. Other modeling components that could continue to improve the model predicted results include improved spatial representation of the network demands, and representation of the transport to, and chemical and biological
interactions at the pipe wall.
Chapter 7

Primary Study: Disinfectant By-Product Formation

This chapter discusses the implementation of the NDMA formation model during the final study that was performed September 6th through the 18th of 2009. The final assessment included a parameter estimation study, collection of “grab samples” throughout the distribution system, and distribution system network model hydraulic and water quality simulations.

7.1 Experimental Design

The primary study evaluated the NDMA formation model throughout the entire distribution system. Samples were collected at the same sampling locations used to evaluate the chloramine dynamics model (see Figure 6.1). Sampling and analysis were performed as discussed in Section 4.3.
7.1.1 Parameter Estimation

Three separate parameter estimation studies were performed on water from each network source during each week of the study (see Section 4.2.1). These studies were completed to determine the NDMA formation constant \((\theta)\) associated with each network source for both weeks of the study.

The parameter estimation study concluded that, with the exception of the THI source water during Week #1, the formation potential of NDMA was relatively low. Table 7.1 shows that the magnitude of the THI NDMA formation constant was significantly larger than all other constants. Plots of the observed data and curve fits of the data can be found in Appendix A.

Table 7.1: Estimated Parameters of the NDMA Formation Model (ng of NDMA Formed/mg of NOM Oxidized)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Week #1 Value</th>
<th>Week #2 Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\theta_{FR}^a)</td>
<td>3.93(10^1)</td>
<td>3.69(10^{-7})</td>
</tr>
<tr>
<td>(\theta_{LP}^b)</td>
<td>2.18(10^{-6})</td>
<td>3.92(10^2)</td>
</tr>
<tr>
<td>(\theta_{THI}^c)</td>
<td>1.7(10^{20})</td>
<td>7.39(10^{-2})</td>
</tr>
</tbody>
</table>

\(a\)Fawn Ridge NDMA formation constant  
\(b\)Lake Park NDMA formation constant  
\(c\)THI NDMA formation constant

7.1.2 Initial Conditions

Initial NDMA concentrations for each source water for both weeks of the study may be found in Table 7.2. Initial concentrations were determined based on “grab samples” that were collected at the beginning of each study week. While the Initial NDMA concentrations for the Fawn Ridge source was similar for both weeks of the study, the
initial concentrations of NDMA for the Lake Park and THI sources varied significantly from week one to week two.

Table 7.2: Initial NDMA Concentrations (ng/L) for the Formation Model

<table>
<thead>
<tr>
<th>Week</th>
<th>FR Value</th>
<th>LP Value</th>
<th>THI Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1.36</td>
<td>1.40</td>
<td>3.10</td>
</tr>
<tr>
<td>#2</td>
<td>1.48</td>
<td>2.41</td>
<td>1.15</td>
</tr>
</tbody>
</table>

### 7.2 Results and Discussion

For discussion purposes, each sampling location was classified into one of four categories based on location and sampling period. Model performance of the “flow-based” modeling approach are presented and discussed in this chapter. Results from the “pressure-based” hydraulic model may be found in Appendix I.

The interpretation of the NDMA formation model results is significantly dependant on the monochloramine and sulfate concentrations. The formation of NDMA is linearly related to monochloramine decay while the sulfate represents the source blend of the waters, which have different formation parameters. Unfortunately, some samples were not reported due to broken sample bottles or analytical error.

#### 7.2.1 Fawn Ridge – Week #1

NDMA formation was evaluated at six sampling locations (FR-1, FR-2, FR-3, FR-4, FR-5, and FR-6) in the Fawn Ridge region during week one. Figures 7.1 and 7.2 illustrate that NDMA was adequately approximated throughout the Fawn Ridge region during week one by the “flow-based” model. The observed NDMA values were generally within 1 ng/L of the modeled results. Considering that NDMA was quantified
at very low concentrations (less than 4 ppt), model performance was considerably accurate.

As previously discussed in Section 6.2.1, sulfate was used as a “pseudo tracer” to characterize network hydraulics. In this region, sulfate was satisfactorily modeled by the “flow-based” model, including the variability at FR-4, except for some slight differences at FR-6 (see Figure 6.6). The observed variability in source blends at FR-4 and FR-6 (as estimated by the sulfate variability) is also observed in the NDMA results (see Figures 7.1 and 7.2), which reflects the different NDMA formation coefficients associated with the two source waters.

Additionally, the simulated monochloramine concentrations for this region (see Section 6.2.1) matched the observed concentrations very well with the exception of FR-6. The interesting aspect of this result is that even through the simulated monochloramine concentrations are about 2 mg/L greater than the observed concentrations, the simulated NDMA concentrations fall within the range of the model predicted variables – even with the observed variability. These results imply that the additional monochloramine loss in this portion of the system may not be related to the pathway associated with organic reactions. Otherwise, we should have observed larger NDMA concentrations. As discussed before, this area of the system is a dead-end portion of the system and the hydraulics and resulting water quality dynamics may not be adequately described with current modeling approaches.
Figure 7.1: “Flow-Based” NDMA Results at FR-1, FR-2, and FR-3
Figure 7.2: “Flow-Based” NDMA Results at FR-4, FR-5, and FR-6
7.2.2 Lake Park – Week #1

NDMA formation was evaluated at six sampling locations (LP-1, LP-2, LP-3, LP-4, LP-5, and LP-6) in the Lake Park region during week one. Figures 7.3 and 7.4 illustrate that NDMA was adequately approximated throughout the Lake Park region during week one by the “flow-based” model, with the exception of sampling location LP-5. The observed NDMA values were generally within 1 ng/L of the modeled results, excluding LP-5 by the “flow-based” model. Considering NDMA was quantified at very low concentrations (less than 5 ppt), model performance was considerably accurate.

At location LP-1, the model tended to overestimate the NDMA concentration just outside the source. A similar overestimation in the NDMA data was observed at other locations (LP-3, LP-4, and LP-5), but was not consistently observed at all locations. As previously discussed in Section 6.2.2, both the sulfate (as an indication of source water blending) and monochloramine concentrations were satisfactorily simulated by the “flow-based” mode (see Section 6.2.2). As such, there was little supporting information associated with the differences in the observed and simulated NDMA concentrations.
Figure 7.3: “Flow-Based” NDMA Results at LP-1, LP-2, and LP-3
Figure 7.4: “Flow-Based” NDMA Results at LP-4, LP-5, and LP-6
7.2.3 Fawn Ridge – Week #2

NDMA formation was evaluated at five new sampling locations (FR-7, FR-8, FR-9, FR-11, and FR-12) in the Fawn Ridge region during week two. The FR-1 location was also monitored during week two to characterize effluent water quality conditions from the Fawn Ridge WTP. Figures 7.5 and 7.6 illustrate that NDMA was reasonably approximated by the “flow-based” model throughout the Fawn Ridge region during week two. With the exception of location FR-8, the majority of the differences between the observed and simulated NDMA concentrations were within 1 ng/L. Considering NDMA was quantified at very low concentrations (less than 2 ppt), model performance was considerably accurate.

While the NDMA results appeared adequate, the results at FR-8, FR-11, and FR-12 were generally overestimated by the model. For locations FR-9 and FR-11, the overestimation of NDMA was consistent with the overestimation of monochloramine decay at those locations (see Figure 6.26). However, a similar overestimation of NDMA would be expected at FR-7, which had similar monochloramine results, but not at FR-12 where the monochloramine was reasonably estimated at times. Inaccuracies in the source water blends, as indicated by sulfate, could also impact the NDMA formation as the THI water had higher formation potentials than the FR water. While this inaccuracy might benefit the NDMA estimation at FR-12 (as the model is slightly overestimating the sulfate concentration), locations such as FR-7 and FR-11 would be adversely impacted as the model tends to underestimate the percentage of THI water at those locations (which would result in further overestimation of the NDMA concentration).
Figure 7.5: “Flow-Based” NDMA Results at FR-1, FR-7, and FR-8
Figure 7.6: “Flow-Based” NDMA Results at FR-9, FR-11, and FR-12
7.2.4 Lake Park – Week #2

NDMA formation was evaluated at five new sampling locations (LP-8, LP-9, LP-10, LP-11, and LP-12) in the Lake Park region during week two. The LP-1 location was also monitored during week two to characterize effluent water quality conditions from the Lake Park WTP. Unfortunately, “grab samples” at LP-8 were not available due to broken sample bottles or analytical error, although modeled results are still reported.

Figures 7.3 and 7.4 illustrates that NDMA was adequately approximated throughout the Lake Park region during week two by the “flow-based” model, with the exception of sampling location LP-8 because observed NDMA concentrations were not available. The observed NDMA values were generally within 1 ng/L of the modeled results. Considering NDMA was quantified at very low concentrations (less than 4 ppt), model performance was considerably accurate.

As previously discussed in Section 6.2.4, the observed monochloramine concentrations were significantly lower than the estimated monochloramine concentrations (i.e., differences typically between 1 – 3 mg/L). These differences were discussed in relation to the possibility of having excessive residence time, pipe wall reactions, and/or nitrification. Since the observed and estimated NDMA concentrations are generally consistent, the suggestion of increased residence time does not seem likely. However, wall decay (assuming wall reactions do not form NDMA) and nitrification could explain increased monochloramine decay without a significant increase in NDMA concentrations; although, for the latter, other nitrification indicators were not observed (as discussed in Section 6.2.4).
Figure 7.7: “Flow-Based” NDMA Results at LP-1, LP-8, and LP-9
Figure 7.8: "Flow-Based" NDMA Results at LP-10, LP-11, and LP-12
7.3 Summary

In general, the NDMA formation model did a reasonable job estimating the NDMA concentrations, even in locations where source water blending occurred and monochloramine concentrations varied. The NDMA data were typically consistent with the monochloramine data from the associated monitoring locations. However, while the observed NDMA data was reasonably represented by the model during week two of the LP region, the observed NDMA data did not appear to be consistent with the relatively low monochloramine concentrations observed within the same region. Disparities between the observed and model predicted NDMA concentrations could be due to insufficient input data for adequately characterizing the NDMA formation parameters needed to model the data and the temporal variability at each network source. Also, reactions between the bulk fluid and pipe surface were not considered, which would impact how chloramine decay and NDMA formation was represented. Furthermore, inaccuracies in modeling source water blending likely impacted model performance.

Accurate interpretation of the NDMA formation model was challenging because a limited number of samples were collected. Additionally, a full evaluation of the experimental method is essential to adequately assess the analytical uncertainty at such low concentrations. According to Munch and Bassett (2006), the method detection limit (MDL) of EPA Method 521 was found to be as high as 0.33 ng/L and the lowest concentration minimum reporting level (LCMRL) was found to be as high as 1.6 ng/L, which suggests that many of our samples could be near the limits of the instrumentation that could result in measurement uncertainty. Even though the analytical method used in this study was a variation of previously developed methods (Chen and Young, 2009; Jenkins et al., 1995; Luo et al., 2003; Prest and Herrmann, 1999; USEPA, 2004), similar analytical limitations are expected. Furthermore, there
was also a considerable amount of variability associated with the recovery of the solid-phase extraction (SPE) method used in the NDMA analysis procedure (Chen and Young, 2009; Jenkins et al., 1995; Luo et al., 2003), which could possibly cause more uncertainty in the analysis. These uncertainties associated with the detection of NDMA at such low concentrations may have influenced the estimated formation constants.
Chapter 8

Primary Study: Biological Nitrification

This chapter discusses the investigation of biological nitrification during the final study that was performed September 6th through the 18th of 2009. Biological nitrification frequently occurs in chloraminated distribution systems where free ammonia is present (Liu et al., 2005). This microbial consumption of ammonia shifts the chloramine equilibrium (\(\text{HOCl} + \text{NH}_3 \leftrightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}\)) to form more ammonia creating a cycle that results in an accelerated loss of disinfectant residuals and increased populations of microbial communities, which can result in drinking water quality violations and pose a risk to public health (Fleming et al., 2005).

The aerobic oxidation of ammonia (\(\text{NH}_3\)) and nitrite (\(\text{NO}_2^-\)) by ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) in chloraminated water systems has been frequently investigated and are the commonly assumed organisms responsible for nitrification in drinking water distribution systems (Cunliffe, 1991; Fleming et al., 2008; Regan et al., 2003; Skadsen, 1993; Wolfe et al., 1990). To date, the presence of anaerobic ammonia oxidizing bacteria, ANAMMOX, has not been considered.

\(^1\)A modified version of this chapter will be submitted to Applied and Environmental Microbiology (Alexander et al., 2010)
as an ammonia-oxidizer in potable water systems. However, since other anaerobic bacteria have previously been found in water distribution systems (Tuovinen and Hsu, 1982), the presence of ANAMMOX should be considered possible. The detection of ANAMMOX would help to develop a more complete understanding of nitrification in drinking water distribution systems. The objective of this portion of the study was to evaluate the presence of three species of ANAMMOX bacteria in bulk water samples collected from a chloraminated water distribution system during a recent, comprehensive hydraulic and water quality field study.

8.1 Experimental Design

The absence or presence of nitrifying bacteria was evaluated in 52 samples collected from 11 of 23 monitoring locations during the final study. Large volume samples (100-L) were collected and biomass in bulk water samples was concentrated to a volume of 500-mL by means of previously developed ultrafiltration procedures (Hill et al., 2005; Lindquist et al., 2007). Biomass was further concentrated and analyzed by polymerase chain reaction (PCR). Six different species of ammonia-oxidizing bacteria were targeted (3 AOB and 3 ANAMMOX). Plasmids of targeted bacteria were courteously provided by Dr. Kartik Chandran of Columbia University. A detailed description of biomass concentration and PCR analysis may be found in Section 4.4.

8.2 Results and Discussion

A total of 52 microbial samples were collected from 11 locations throughout the distribution system (see the grey symbols of Figure 8.1). Tables 8.1 and 8.2 present the model predicted water age and source water composition along with the positive/negative results for detecting AOB and ANAMMOX for the Fawn Ridge region, and Lake Park and THI regions, respectively. Overall, ANAMMOX bacteria was
Figure 8.1: Partner Utility Distribution System and Sampling Locations
detected in six samples and AOB was detected in three samples. Unfortunately, the specific species of the positive ANAMMOX samples were unable to be determined as Figure 8.2 shows that the difference in base pair length was indistinguishable. Digital images of agarose gels, containing PCR-amplified nucleic acids using a universal, ANAMMOX-specific, or AOB-specific primer set, illuminated with an ultraviolet lamp, may be found in Appendix J. A total of six positive ANAMMOX bacteria samples were detected: three at FR-1 (downstream of the Fawn Ridge source), one at LP-1 (downstream of the Lake Park source), and one each at LP-6 and LP-11. Given that LP-1 (downstream of the source) and two additional locations in the Lake Park region tested positive for ANAMMOX; one hypothesis is that ANAMMOX was entering into the system through the Fawn Ridge source, which is possible since this location receives water purchased by another utility that also chloramines. For the positive sample at FR-1, there could be similar source transmission of ANAMMOX through the source water (although this source water comes straight from a ground water field), or the positive ANAMMOX sample could come from the Lake Park source. Using sulfate as a natural source water trace (Fawn Ridge $\simeq 1 – 2$ mg/L; Lake Park $\simeq 40 – 50$ mg/L, THI $\simeq 100$ mg/L), the observed water quality clearly indicates that there is a blending of Fawn Ridge and Lake Park water throughout the Fawn Ridge region. Figure 8.3 illustrates that the blending of water at FR-1 is intermittent and can be relatively small (week #1) or large (week #2). The blended water at sites FR-6 and FR-12 illustrate that some locations in the Fawn Ridge region continually receive blended water (the sulfate levels of FR-5 and FR-11 are similar to FR-1 – week #1). While the positive ANAMMOX samples occurred when the blended source water was observed, the other sampling sites in the Fawn Ridge region also received blended water, but no positive ANAMMOX samples were observed. In addition to the microbial samples, there was no additional water quality evidence (e.g., reduced NH$_2$Cl or NH$_3$ concentrations, or excessive NO$_2^-$ or NO$_3^-$) typically
associated with excessive nitrification (Fleming et al., 2005, 2008; Odell et al., 1996; Wilczak et al., 1996).

8.3 Summary

While questions remain regarding the microbial community structure at the pipe wall interface, these results are the first to illustrate that ANAMMOX - an anaerobic organism - exist in potable water systems. Other studies have shown that, given an aerobic system, a biofilm community can result in depleted oxygen concentration at the pipe surface resulting in favorable conditions for anaerobic organisms to cohabit in a synergistic relationship (Bishop, 1997; Schramm et al., 1996; Tuovinen and Hsu, 1982). Such results support the observed presence of ANAMMOX in an aerobic system. Ultimately, this discovery introduces another possible mechanism contributing to nitrification and loss of disinfectant residual for chloraminated distribution systems that should be considered in future water quality models and distribution system operations.

In addition to the discovery of anaerobic ammonia-oxidizing bacteria, the detection of AOB and ANAMMOX bacteria in this distribution system suggests that the interaction between biological and chemical species should be included in future chloraminated water quality studies. Even though strong evidence of excessive nitrification was not apparent, the impact of biological species on model performance is unknown. Further investigations may want to quantify the amount of nitrifying bacteria in both the bulk fluid and pipe wall; this study only confirmed the presence or absence of nitrifying bacteria in the bulk fluid, not pipe wall. Quantification of nitrifying bacteria would also allow modeling of bacteria concentrations throughout the distribution system.
Table 8.1: Nitrifying Bacteria in the Fawn Ridge Region

<table>
<thead>
<tr>
<th>Location</th>
<th>Water Age</th>
<th>Model Predicted Source Water</th>
<th>Sampling Date</th>
<th>Primer Set</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR-1</td>
<td>6.77</td>
<td>99.5% FR</td>
<td>9/8/2009</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/9/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/10/2009</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3% LP</td>
<td>9/11/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2% THI</td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/17/2009</td>
<td>+</td>
</tr>
<tr>
<td>FR-5</td>
<td>24.86</td>
<td>96.4% FR</td>
<td>9/8/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/9/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/10/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2% LP</td>
<td>9/11/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4% THI</td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/17/2009</td>
<td>-</td>
</tr>
<tr>
<td>FR-6</td>
<td>31.23</td>
<td>44.4% FR</td>
<td>9/8/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/9/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/10/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/11/2009</td>
<td>-</td>
</tr>
<tr>
<td>FR-11</td>
<td>25.09</td>
<td>99.0% FR</td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/17/2009</td>
<td>-</td>
</tr>
<tr>
<td>FR-12</td>
<td>37.61</td>
<td>64.3% FR</td>
<td>9/14/2009</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/17/2009</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 8.2: Nitrifying Bacteria in the Lake Park Region

<table>
<thead>
<tr>
<th>Location</th>
<th>Water Age</th>
<th>Model Predicted Source Water</th>
<th>Sampling Date</th>
<th>Primer Set</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/8/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0% FR</td>
<td>9/9/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/10/2009</td>
<td>-</td>
</tr>
<tr>
<td>LP-1</td>
<td>1.36</td>
<td>99.8% LP</td>
<td>9/11/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2% THI</td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/17/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9% FR</td>
<td>9/8/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/9/2009</td>
<td>-</td>
</tr>
<tr>
<td>LP-5</td>
<td>27.13</td>
<td>61.3% LP</td>
<td>9/10/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/11/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37.8% THI</td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/17/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8% FR</td>
<td>9/8/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/9/2009</td>
<td>-</td>
</tr>
<tr>
<td>LP-6</td>
<td>40.85</td>
<td>62.5% LP</td>
<td>9/10/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/11/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36.7% THI</td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/17/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0% FR</td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td>LP-11</td>
<td>24.29</td>
<td>100.0% LP</td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0% THI</td>
<td>9/17/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0% FR</td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td>LP-12</td>
<td>36.34</td>
<td>98.3% LP</td>
<td>9/15/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.7% THI</td>
<td>9/17/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0% THI</td>
<td>9/16/2009</td>
<td>-</td>
</tr>
<tr>
<td>THI</td>
<td>1.32</td>
<td>0.0% LP</td>
<td>9/11/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9/14/2009</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.0% THI</td>
<td>9/16/2009</td>
<td>+</td>
</tr>
</tbody>
</table>
Figure 8.2: Results from amplification of PCR products of extracted nucleic acids.

Lane 1, 100 bp ladder; lane 2, negative control; lane 3, Candidatus Brocadia fulgida, 836 bp; lane 4, Candidatus Brocadia sp., 835 bp; lane 5, Candidatus Kuenenia stuttgartiensis, 832 bp; lanes 6-23, selected environmental samples; lane 24, 100 bp ladder.
Figure 8.3: Observed Sulfate Data for A-1 (Both Weeks), A-6 (Week #1), and A-11 (Week #2).
Chapter 9

Summary and Conclusions

A comprehensive field-scale analysis of multiple water quality parameters indicated that EPANET-MSX is capable of satisfactorily representing a complex water quality system within drinking water distribution systems. This study integrated proven bench-scale chloramine decay and disinfectant by-product formation models into a comprehensive model that was validated by system-wide field-scale measurements. In addition to water quality modeling, the absence or presence of nitrifying bacteria was evaluated throughout the distribution system to assess nitrification conditions. Significant “knowledge-gaps” between advanced water quality models and actual distribution system performance were identified. These “knowledge-gaps” will provide motivation and direction for future improvements associated with distribution system water quality modeling.

A unique characteristic of this water system was that background sulfate concentrations of each network source water were significantly different. From a modeling perspective, sulfate is a non-reactive species that was considered to be a “pseudo-tracer.” As a result, network hydraulics were evaluated based on the observed sulfate concentrations at each monitoring location. EPANET-MSX was found to represent the majority of water quality species associated with the chloramine dynamics reason-
ably well at most monitoring locations that were supplied by a blend of network source waters. Likewise, the NDMA formation model was found to adequately represent the NDMA concentrations monitored throughout the network.

Even though the observed water quality was reasonably represented throughout the network, the influence of inaccurate representation of network hydraulics was apparent at some locations. Based on the predictive ability of the model for representing sulfate, network hydraulics were characterized quite well during the both weeks of the study, with the exception of a few monitoring locations. Approximately four monitoring locations were observed to have a meaningful discrepancy with the model predicted concentrations. While these observations provided a qualitative metric of source water blending throughout the network, the information was not sufficient enough to provide significant evaluation of water age due to the lack of temporal resolution in source water quality.

The chloramine dynamics model was found to satisfactorily represent monochloramine concentrations quite well during the first week of the study, with the exception of one monitoring location that was likely influenced by inaccurate representation of stochastic network demands. During the second week of the study, the monochloramine concentrations were underestimated at all locations in the Fawn Ridge region, which would most likely due to inaccurate representation of water age and source water blending. Additionally, the monochloramine concentrations were overestimated at all locations in the Lake Park region. There was no conclusive evidence that could be attributed to represent the observed discrepancy, but some other issues not included in the current model framework could have had an effect such as an inaccurate physical representation of the system (e.g., unknown closed valve) and/or the interactions between chemical and biological species in the bulk fluid and pipe wall.

During the week two study, the multi-species model did not satisfactorily represent
free ammonia at any of the monitoring locations. The observed free ammonia concentrations were highly variable at the sources in both sampling regions during both weeks of the study. The inability of the model to represent the observed concentrations may be a result of inadequately representing the influent water quality variability. Both nitrite and nitrate were also misrepresented by the multi-species model at most locations throughout the system. Nitrite was generally underestimated, while nitrate was typically overestimated. Inconsistencies between these modeled and the observed nitrogenous species (ammonia, nitrite, and nitrate) could possibly be impacted by the microbial oxidation of ammonia and nitrite, but there was little strong evidence that extensive nitrification was occurring.

In addition to the chloramine dynamics model, a NDMA formation model was evaluated to assess disinfectant by-product formation throughout the system. The NDMA formation model was found to reasonably estimate NDMA concentrations, even in locations were source water blending occurred and where monochloramine concentrations varied. Given the low observed NDMA concentrations, the uncertainty associated with the low-level measurements of NDMA and the relatively small number of samples may have also influenced the ability of the model to more accurately represent NDMA formation.

The absence, or presence, of nitrifying bacteria was evaluated at 11 of 23 sampling locations throughout the study. This investigation intended to provide supporting evidence that nitrifying bacteria had some impact on water quality. A total of 52 samples were collected and AOB were detected in three samples and ANAMMOX bacteria were detected in six samples. The finding of ANAMMOX bacteria was unique because this was the first time that ANAMMOX, an anaerobic organism, was observed within a potable water system. This discovery introduces another possible mechanism that can contribute to nitrification and loss of disinfectant residual for
chloraminated distribution systems that should be considered in future water quality models and distribution system operations.

In general, the multi-species chloramine model was found to be capable of satisfactorily representing water quality species at monitoring locations that were supplied by a single network source. However, model performance appeared to deteriorate in regions of the network that were supplied by a blend of source waters. With that said, additional research should be performed to address some of the key “knowledge gaps” that were identified in this study:

• The temporal variability in the influent water quality variability should be considered to remove one source of variability from the model assessments.

• The interaction between biological and chemical species, such as nitrification, should be considered in the model.

• Reactions between the bulk fluid and pipe wall should be included in the model to account for additional chloramine loss that was not accounted for in this model.

• Representation of spatial distribution and stochastic consumer demands should be improved for better evaluation of water age and source blending.
Chapter 10

Future Work

Future research should focus on four primary issues to improve multi-species water quality modeling of a chloraminated distribution system including: 1) improved representation of network model hydraulics; 2) temporal representation of the influent water quality variability; 3) interactions between the biological and chemical species, such as nitrification; and 4) reactions between the bulk fluid and pipe wall to account for additional chloramine loss.

The influence of inaccurate representation of network model hydraulics was apparent throughout this study. This includes inaccurate representation of spatial distribution and stochastic consumer demands, which hinders the models ability to correctly characterize water age and source blending. In this study, sulfate was used as a “pseudo tracer,” which indicated that the hydraulics were inaccurately represented at several sampling locations in this study. As a result, all water quality parameters were mis-represented at these sampling locations. The best way to accurately represent network hydraulics is to perform a tracer study. Tracer studies can be resource intensive, but they provide indispensable information about network hydraulics. If feasible, future studies should perform a tracer study in conjunction with water quality sampling to accurately characterize hydraulics throughout the system.
In this study, influent water quality conditions were assumed to be constant at each source during both weeks of the study. However, results from this study indicated that temporal variability of the influent water quality variability should be considered in future modeling efforts. An example of this would be the free ammonia at the Lake Park source during week one of the study. Figure 6.17 shows that the observed concentration of free ammonia leaving the Lake Park source continually increased throughout the week, but model predicted values remained relatively constant. These results suggest that the initial concentration of free ammonia leaving the Lake Park source should have gradually increased, like the observed results, throughout the week. Future studies should not assume that initial influent water quality conditions are constant throughout a modeling simulation, but should incorporate variable initial water quality conditions.

The interaction between chemical and biological species, such as nitrification, was not considered in this study. Nitrification can drastically accelerate chloramine decay by the consumption of free ammonia in the system. As free ammonia is consumed, the chloramine equilibrium (\(\text{HOCl} + \text{NH}_3 \rightleftharpoons \text{NH}_2\text{Cl} + \text{H}_2\text{O}\)) shifts to form more ammonia creating a cycle that results in an accelerated loss of disinfectant residuals and increased populations of microbial communities, which can result in drinking water quality violations and pose a risk to public health (Fleming et al., 2005). Future research should incorporate a kinetic model, similar to that of Liu et al. (2005) or Sathasivan et al. (2005), to describe microbiologically assisted chloramine decay in a drinking water system.

Reactions between species in the bulk fluid and pipe surface were also not taken into account. Such interactions include biochemical reactions (as described above), chloramine wall decay, and wall decay between chloramine and ferrous iron (Vikesland et al., 1998). Reactions at the pipe wall could cause additional disinfectant decay that
was not accounted for in the model. Incorporating these interactions into the current model, such as Westbrook and DiGiano (2009), may help identify the unaccounted chloramine loss that was found in some areas of this distribution system. Overall, the model implemented in the study clearly exhibited some limitations in adequately representing observed water quality throughout the system, but addressing the limitations described in this section would likely improve future efforts of modeling a chloraminated distribution system.
11 References


and National Homeland Security Research Center, U. S. Environmental Protection Agency.


Appendix A

Model Parameter Estimation

During the final study, a parameter estimation study was performed on source water from each network source each week (see Section 4.2.1). These studies were completed to determine the decay constant associated with the oxidation of organic carbon by free chlorine ($k_{\text{DOC2}}$) and the NDMA formation constant ($\theta$). Parameters were estimated by fitting “best-fit” curves to observed data using a nonlinear curve-fitting algorithm (lsqcurvefit) in Matlab. Figures A.1 and A.2 show “best-fit” curves for monochloramine and NDMA obtained from Fawn Ridge source water during weeks one and two, respectively. Figures A.3 and A.4 show “best-fit” curves for Lake Park water, while Figures A.5 and A.6 show “best-fit” curves for THI water.

During the pilot study, only the decay constant associated with the oxidation of organic carbon by free chlorine ($k_{\text{DOC2}}$) was estimated. Figure A.7 shows a “best-fit” curve for observed monochloramine decay. This data was obtained from a hold study that was performed on Lake Park source water during the pilot study.
Figure A.1: Parameter estimation curves from hold study results from Fawn Ridge Source Water – Week #1
Figure A.2: Parameter estimation curves from hold study results from Fawn Ridge Source Water – Week #2
Figure A.3: Parameter estimation curves from hold study results from Lake Park Source Water – Week #1
Figure A.4: Parameter estimation curves from hold study results from Lake Park Source Water – Week #2
Figure A.5: Parameter estimation curves from hold study results from THI Source Water – Week #1
Figure A.6: Parameter estimation curves from hold study results from THI Source Water – Week #2
Figure A.7: Parameter estimation curve from hold study results from Lake Park Source Water – Pilot Study
Appendix B

MSX Input Files

This appendix contains the three different MSX input files that were used in this study; one from the pilot study and one for both weeks of the final study. Figures B.1, B.2, B.3, and B.4 show the input file used during week #1 of the final study. Figures B.5, B.6, B.7, and B.8 show the input file used during week #2 of the final study. Lastly, Figures B.9, B.10, B.11, and B.12 show the input file used during the pilot study. For further details on EPANET-MSX input files, refer to Shang et al. (2008a).
Multi-Species Analysis - HCWS Network Analysis - 9/3/09 - 9/12/09

[OPTIONS]
RATE_UNITS HR Reaction Rates are Molar Concentration (MOU/L)/Hour
SOLVER ROS2 2nd Order Rosenbrock Integrator
COUPLING FULL 1st Order coupling
COMPIILER VC Visual C++ Compiler
TIMESTEP 300 300 sec (5 min) solution time step
RTOL 1.0e-8 Relative concentration tolerance
ATOL 1.0e-8 Absolute concentration tolerance

[SPECIES]
BULK NH2CL MOL Monochloramine
BULK NH3L2 MOL Dichloramine
BULK I MOL Unknown Intermediate Compound
BULK N2 MOL Nitrogen Gas
BULK CL MOL Chloride ion
BULK TOTDOCDr MOL Fawn Ridge DOC Reacted
BULK TOTDOCLPr MOL Lake Park DOC Reacted
BULK TOTDOCTHi MOL THI DOC Reacted
BULK OCL MOL Hypochlorite ion
BULK HOCL MOL Hypochlorous Acid
BULK NH3 MOL Ammonia
BULK NH4 MOL Ammonium ion
BULK H MOL Hydrogen ion
BULK OH MOL Hydroxide ion
BULK ALK MOL Alkalinity
BULK DOCFR1 MOL Dissolved Organic Carbon Fawn Ridge #1
BULK DOCFR2 MOL Dissolved Organic Carbon Fawn Ridge #2
BULK DOCLP1 MOL Dissolved Organic Carbon Lake Park #1
BULK DOCLP2 MOL Dissolved Organic Carbon Lake Park #2
BULK DOCTHi MOL Dissolved Organic Carbon THI #1
BULK DOCTHi2 MOL Dissolved Organic Carbon THI #2
BULK NO2 MOL Nitrite ion
BULK NO3 MOL Nitrate ion
BULK CO3 MOL Carbonate ion
BULK HC03 MOL Bicarbonate ion
BULK HC023 MOL Carbonic Acid
BULK SO4 MOL Sulphate ion
BULK TOTCO3 MOL Total Carbonate
BULK TOTCL MOL Total Free Chlorine
BULK TOTNH3 MOL Total Free Ammonia
BULK TOTH MOL Total Hydrogen
BULK NDOMA MOL N-Nitrosodimethylamine
BULK CHCL3 MOL Chloroform
BULK CHCL2BR MOL Dichlorobromomethane
BULK CHCLBR2 MOL Dibromo-chloromethane
BULK CHBFR3 MOL Bromoform

[COEFFICIENTS]
; TEMP = 301.7
; ION = 0.007

PARAMETER k1 1.589e10 [2.37e12*exp(-1510/TEMP)] Vikesland et al. 2001
PARAMETER k2 1.441e-1 [6.7e11*exp(-1880/TEMP)] Vikesland et al. 2001
PARAMETER k3 1.381e6 [1.08e6*exp(-2010/TEMP)] Vikesland et al. 2001
PARAMETER k4 2.3e-3 ; Vikesland et al. 2001
PARAMETER kh 2.853e7 [3.78e10*exp(-2168/TEMP)] Vikesland et al. 2001
PARAMETER khCO3 1.995e3 [1.5e35*exp(-22144/TEMP)] Vikesland et al. 2001
PARAMETER kh2CO3 4.725e4 [2.95e10*exp(-4026/TEMP)] Vikesland et al. 2001

Figure B.1: Week #1 EPANET-MSX Input File – Page 1 of 4
PARAMETER k6  2.16e8  ;  Hand and Margerum 1983
PARAMETER k7  5.5e3  ;  Leao 1981
PARAMETER k8  4.0e5  ;  Jalvert and Valentine 1987
PARAMETER k9  1.0e8  ;  Leao 1981
PARAMETER k10  3.0e7  ;  Leao 1981
PARAMETER k11FR  3.04e4  ;  k10 * Fast Rate Constant
PARAMETER k12FR  1.96e-2  ;  k11 * Fast Rate Constant
PARAMETER k11LP  3.04e4  ;  k10 * Slow Rate Constant
PARAMETER k12LP  2.69e6  ;  k11 * Slow Rate Constant
PARAMETER k12THI  3.04e4  ;  k10 * Fast Rate Constant
PARAMETER k12THII  1.70e-20  ;  k11 * Slow Rate Constant
PARAMETER k13  4.81e10  ;  k1 Nitrate Rate #1
PARAMETER k14  2.17e2  ;  k2 Nitrate Rate #2
PARAMETER k15  5.5e3  ;  k3 Nitrate Rate #3
PARAMETER k16  8.2e8  ;  k4 Nitrate Rate #4
PARAMETER k17  1.8e5  ;  k5 Nitrate Rate #5
PARAMETER k18FR  3.93e1  ;  NDMA Formation FR
PARAMETER k18LP  2.18e-6  ;  NDMA Formation LP
PARAMETER k18THI  1.70e20  ;  NDMA Formation THI
PARAMETER k19  1.485e-4  ;  Chloroform Formation
PARAMETER k20  1.0821e-4  ;  Dichlorobromomethane Formation
PARAMETER k21  8.5114e-3  ;  Dibromochloromethane Formation
PARAMETER k22  7.0144e-3  ;  Bromoform Formation

CONSTANT g1  0.1914  ;  10^g2 * [sqrt(ON)] / [g1 + [sqrt(ON)]]
CONSTANT g2  0.7008  ;  10^g2 * [sqrt(ON)] / [g1 + [sqrt(ON)]]
CONSTANT kw  1.577e-14  ;  [exp(-6723.7/TEMP)] * [6.3e-5] / [0.5]
CONSTANT kh2  6.475e-10  ;  [10^3] * (0.103-4 * [TEMP] - 9.21e-2 * [TEMP] + 27.6)
CONSTANT kocl  3.549e-8  ;  [10^3] * (1.184-4 * [TEMP] - 7.86e-2 * [TEMP] + 20.5) / [g1]

[TERMS]
a1  k12h**hocl**kocl**nh3
a2  k2hnh2cl
a3  k3**h**kocl**kocl**nh2cl
a4  k4**nh2cl
a5  k7**h**k3**hocl**k3**hocl**nh2cl**nh2cl
a6  k8**nh2cl**nh2cl
a7  k9**nh2cl**nh2cl
a8  k10**hocl**kocl**nh2cl
a9  k11fr**dofr1**nh2cl
a10  k12fr**dofr2**momocl**kocl
a11p  k11p**dopcl2**hocl
a12p  k12p**dopcl2**momocl**kocl
a11thi  k11thi*docthi**momocl
a12thi  k12thi*docthi**momocl**kocl
a11  a11fr + a11lp + a11thi
a12  a12fr + a12lp + a12thi
a13  (k13**h**k3**hocl**nh2cl**nh2cl**h2o**k14**no2) / (k15**nh3 + k14**no2)

[K Pipes]
RATE  nhocl  a1 - a2 - a3 + a4 - a5 + a6 + a7 - a8 - a9
RATE  nh2cl  a3 + a4 + a5 - a6 - a7 - a8 - a9 - a10
RATE  nh3  a6 - a7 - a8 - a9

Figure B.2: Week #1 EPANET-MSX Input File – Page 2 of 4
RATE    N2    a7 + a9 + a10
RATE    CL    3*a7 + 2*a8 + a9 + a10 + a11 + a12 + a13
RATE    TOTDOCFR  -a11FR - a12FR
RATE    TOTDOCCL  -a11LP - a12LP
RATE    TOTDOCTHI -a11THI - a12THI
EQUIL    OCl  TOTOCl - (H*OCl)/KOC1
EQUIL    NH3  TOTNH3 - NH3 - (H*NH3)/KNH3
EQUIL    NH4  (H*NH3)/KNH3
EQUIL    H    TOTOH - H + KWH + OCl + NH3 + HCO3 + 2*KHCO3*HCO3/H
EQUIL    OH   KWH/H
RATE    ALK   0
RATE    DOCFRI -a11FR
RATE    DOCFPI -a11LP
RATE    DOCTHI1 -a11THI
RATE    DOCFR2 -a12FR
RATE    DOCFPI2 -a12LP
RATE    DOCTHI2 -a12THI
RATE    NO2   -a13
RATE    NO3   a13
FORMULA  CO3  KHCO3*HCO3/H
FORMULA  HCO3  TOTCO3 - KHCO3*HCO3/H - HCO3 - H*HCO3/KH2CO3
FORMULA  H2CO3  H*KHCO3/KH2CO3
RATE    SO4   0
RATE    TOTCO3  0
RATE    TOTOCl -a1 + a2 - a3 + a4 + a9 - a12
RATE    TOTNH3 -a1 + a2 + a5 -a6 + a11 + a13
RATE    TOTOH -3*a7 - 2*a8 - a9 - a10
RATE    NDMA  a14 + a15 + a16;
RATE    CHCL3  a17
RATE    CHCLBR2 a18
RATE    CHBR3  a19
RATE    NH3   a20

[SOURCES]

,NODE    RES9000 FR
,NODE    7384  LP
,NODE    311   THI

CONCEN    RES9000 NH2CL  1.004e-4
CONCEN    RES9000 H   1.514e-8
CONCEN    RES9000 TOTH  4.066e-3
CONCEN    RES9000 TOTCO3 4.190e-3
CONCEN    RES9000 HCO3  4.059e-3
CONCEN    RES9000 NH3  9.958e-7
CONCEN    RES9000 TOTNH3 2.427e-5
CONCEN    RES9000 DOCFR2 1.000e-4
CONCEN    RES9000 NO2  2.142e-7
CONCEN    RES9000 NO3  4.998e-7
CONCEN    RES9000 SO4  1.688e-5
CONCEN    RES9000 NDMA 1.834e-11

CONCEN    7384 NH2CL  1.230e-4
CONCEN    7384 H   2.138e-8
CONCEN    7384 TOTH  3.657e-3
CONCEN    7384 TOTCO3 3.787e-3
CONCEN    7384 HCO3  3.633e-3
CONCEN    7384 NH3  5.666e-7
CONCEN    7384 TOTNH3 1.928e-5
CONCEN    7384 DOCFR2 1.146e-4
CONCEN    7384 NO2  7.139e-8
CONCEN    7384 NO3  1.356e-6
CONCEN    7384 SO4  3.748e-4
CONCEN    7384 NDMA 1.884e-11

Figure B.3: Week #1 EPANET-MSX Input File – Page 3 of 4
CONCEN 311  NH2CL  1.168e-4
CONCEN 311  H      1.778e-8
CONCEN 311  TOTH   1.698e-3
CONCEN 311  TOTCO3 1.746e-3
CONCEN 311  HCO3   1.685e-3
CONCEN 311  NH3    7.524e-8
CONCEN 311  TOTNH3 2.142e-6
CONCEN 311  DOCTH2 1.163e-4
CONCEN 311  NO2    2.142e-7
CONCEN 311  NO3    1.928e-6
CONCEN 311  SO4    1.031e-3
CONCEN 311  NOMA   4.179e-11

[QUALITY]
GLOBAL  NH2CL  1.134e-4
GLOBAL  H      1.810e-8
GLOBAL  TOTH   3.150e-3
GLOBAL  TOTCO3 3.241e-3
GLOBAL  HCO3   3.126e-3
GLOBAL  NH3    5.450e-7
GLOBAL  TOTNH3 1.523e-5
GLOBAL  NO2    1.666e-7
GLOBAL  NO3    1.261e-6
GLOBAL  SO4    4.742e-4
GLOBAL  NOMA  1.834e-11

[REPORT]
NODES  NONE  ,Report results for all nodes
SPECIES  NH2CL  NO  12  ,Monochloramine
SPECIES  NHCL2  NO  12  ,Dichloramine
SPECIES  NO  NO  12  ,Unknown Intermediate Compound
SPECIES  N2    NO  12  ,Nitrogen gas
SPECIES  CL    NO  12  ,Chloride ion
SPECIES  TOTDOCR  NO  12  ,Total DOC Fawn Ridge Reacted
SPECIES  TOTDOCP  NO  12  ,Total DOC Lake Park Reacted
SPECIES  OCL   NO  12  ,Hydrochloric acid
SPECIES  HOC1  NO  12  ,Hydrochloric Acid
SPECIES  NH3   NO  12  ,Ammonia
SPECIES  NH4   NO  12  ,Ammonium ion
SPECIES  H     NO  12  ,Hydrogen ion
SPECIES  OH    NO  12  ,Hydroxide ion
SPECIES  ALK   NO  12  ,Alkalinity
SPECIES  DOCR1  NO  12  ,DOC Fawn Ridge #1
SPECIES  DOCR2  NO  12  ,DOC Fawn Ridge #2
SPECIES  DOCP1  NO  12  ,DOC Lake Park #1
SPECIES  DOCP2  NO  12  ,DOC Lake Park #2
SPECIES  DOCRH1 NO  12  ,DOC TH #1
SPECIES  DOCRHI NO  12  ,DOC TH #2
SPECIES  NO2   NO  12  ,Nitrite ion
SPECIES  NO3   NO  12  ,Nitrate ion
SPECIES  O3    NO  12  ,Ozone ion
SPECIES  HCO3  NO  12  ,Bicarbonate ion
SPECIES  H2CO3 NO  12  ,Carbonic Acid
SPECIES  SO4   NO  12  ,Sulfate ion
SPECIES  TOTCO3 NO  12  ,Total Carbonate
SPECIES  TOTOC1 NO  12  ,Total Free Chlorine
SPECIES  TOTNH3 NO  12  ,Total Ammonia
SPECIES  TOTH   NO  12  ,Total Hydrogen
SPECIES  NOMA  NO  12  ,1-Nitrosodimethylamine
SPECIES  CHL1  NO  12  ,Chloroform
SPECIES  CHL2BR NO  12  ,Dichlorobromoform
SPECIES  CHLBR2 NO  12  ,Dibromochloroform
SPECIES  CHBR3 NO  12  ,Bromoform

Figure B.4: Week #1 EPANET-MSX Input File – Page 4 of 4
Multi-Species Analysis - HCWR5 Network Analysis - 9/10/09 - 9/19/09

OPTIONS
RATE_UNITS HR Reaction Rates are Molar Concentration (MOL/L)/Hour
SOLVER ROS2 2nd Order Rosenbrock Integrator
COUPLING FULL FULL coupling
COMPILER VC Visual C++ Compiler
TIMESTEP 300 300 sec (5 min) solution time step
RTOL 1.0e-8 Relative concentration tolerance
ATOL 1.0e-8 Absolute concentration tolerance

SPECIES
BULK NH2CL MOL Monochloramine
BULK NHCl2 MOL Dichloramine
BULK I MOL Unknown Intermediate Compound
BULK N2 MOL Nitrogen Gas
BULK CL MOL Chloride ion
BULK TOTDOCFr MOL Fawn Ridge DOC Reacted
BULK TOTDOClP MOL Lake Park DOC Reacted
BULK TOTDOCTHr MOL THI DOC Reacted
BULK OCL MOL hypochlorite ion
BULK HOCL MOL Hypochlorous Acid
BULK NH3 MOL Ammonia
BULK NH4 MOL Ammonium ion
BULK H MOL Hydrogen ion
BULK OH MOL Hydroxide ion
BULK AUK MOL Alkalinity
BULK DOCFr1 MOL Dissolved Organic Carbon Fawn Ridge #1
BULK DOCFr2 MOL Dissolved Organic Carbon Fawn Ridge #2
BULK DOClP1 MOL Dissolved Organic Carbon Lake Park #1
BULK DOClP2 MOL Dissolved Organic Carbon Lake Park #2
BULK DOCTH1 MOL Dissolved Organic Carbon THI #1
BULK DOCTH2 MOL Dissolved Organic Carbon THI #2
BULK N02 MOL Nitrite ion
BULK N03 MOL Nitrate ion
BULK C03 MOL Carbonate ion
BULK HCO3 MOL bicarbonate ion
BULK H2CO3 MOL Carbonic Acid
BULK SO4 MOL Sulphate ion
BULK TOTCO3 MOL Total Carbonate
BULK TOTCL MOL Total Free Chlorine
BULK TOTNH3 MOL Total Free Ammonia
BULK TOTH MOL Total Hydrogen
BULK NDMA MOL N-Nitrosodimethylamine
BULK CH3L MOL Chloroform
BULK CHL2BR MOL Dichlorobromomethane
BULK CHLBR2 MOL Tribromochloromethane
BULK CHBRS MOL Bromoform

COEFFICIENTS
;TEMP = 300.6
;ION = 0.007

PARAMETER k1 1.560e10 [2.37e12*exp(-1510/TEMP)] Vikelsland al. 2001
PARAMETER k2 1.295e-1 [6.7e11*exp(-4800/TEMP)] Vikelsland al. 2001
PARAMETER k3 1.347e6 [4.06e9*exp(-2010/TEMP)] Vikelsland al. 2001
PARAMETER k4 3e-3 [3.78e10*exp(-2160/TEMP)] Vikelsland et al. 2001
PARAMETER kH 2.779e7 [9.38e10*exp(-2160/TEMP)] Vikelsland et al. 2001
PARAMETER kHCO3 1.525e3 [1.5e35*exp(-2214/TEMP)] Vikelsland et al. 2001
PARAMETER kH2CO3 4.500e4 [2.95e10*exp(-4026/TEMP)] Vikelsland et al. 2001

Figure B.5: Week #2 EPANET-MSX Input File – Page 1 of 4
Figure B.6: Week #2 EPANET-MSX Input File – Page 2 of 4
RATE N2  a7 + a9 + a10
RATE CL  3*a7 + 2*a8 + a9 + a10 + a11 + a12 + a13
RATE TOTDOCFR  -a11FR - a12FR
RATE TOTDOCJP -a11LP - a12LP
RATE TOTDOCTH1 -a11TH1 - a12TH1
EQUIL OCL TOTOCL - (H*OCL)/HOC1 - OCL
FORMULA HOC1 (H*OCL)/HOC1
EQUIL NH3 TOTNH3 - NH3 - (H*NH3)/HNH3
FORMULA NH4 (H*NH3)/HNH3
EQUIL H + TOTH - H + KW/H + OCL + NH3 + HCO3 + 2*KHCO3*HCO3/H
FORMULA OH KW/H
RATE ALK  0
RATE DOCFR1 -a11FR
RATE DOCJP1 -a11LP
RATE DOCTH1 -a11TH1
RATE DOCFR2 -a12FR
RATE DOCJP2 -a12LP
RATE DOCTH2 -a12TH1
RATE NO2 -a13
RATE NO3 a13
FORMULA CO3 KHCO3*HC03/H
EQUIL HC03 TOTCO3 - KHCO3*HC03/H - HCO3 - H*HC03/KH2CO3
FORMULA H2CO3 H*HC03/KH2CO3
FORMULA SO4  0
FORMULA TOTCO3  0
FORMULA TOTOCL -a1 + a2 - a3 + a4 + a9 - a12
FORMULA TOTNH3 -a1 + a2 + a5 + a6 + a11 + a13
FORMULA TOTH -3*a7 - 2*a8 - a9 - a10;
FORMULA NDMA a14 + a15 + a16;
FORMULA CHL2  a17
FORMULA CHLBR2 a18
FORMULA CHBR3 a19
FORMULA CHBR4 a20

[SOURCES]

J, NODE RES9000 FR
J, NODE 7384 LP
J, NODE 311 TH1

CONCEN RES9000 NH2Cl 6.827e-5
CONCEN RES9000 H 1.862e-8
CONCEN RES9000 TOTH 4.066e-3
CONCEN RES9000 TOTCO3 4.222e-3
CONCEN RES9000 HCO3 4.067e-3
CONCEN RES9000 NH3 6.686e-7
CONCEN RES9000 TOTNH3 2.142e-5
CONCEN RES9000 DOCFR2 1.000e-4
CONCEN RES9000 NO2 2.856e-7
CONCEN RES9000 NO3 4.284e-7
CONCEN RES9000 SO4 1.041e-5
CONCEN RES9000 NDMA 1.999e-11

CONCEN 7384 NH2Cl 1.278e-4
CONCEN 7384 H 1.660e-8
CONCEN 7384 TOTH 3.097e-3
CONCEN 7384 TOTCO3 3.179e-3
CONCEN 7384 HCO3 3.072e-3
CONCEN 7384 NH3 1.170e-6
CONCEN 7384 TOTNH3 3.927e-5
CONCEN 7384 DOCJP2 1.058e-4
CONCEN 7384 NO2 2.856e-7
CONCEN 7384 NO3 0
CONCEN 7384 SO4 5.101e-4
CONCEN 7384 NDMA 3.257e-11

Figure B.7: Week #2 EPANET-MSX Input File – Page 3 of 4
<table>
<thead>
<tr>
<th>SPECIES</th>
<th>CONCEN</th>
<th>QUALITY</th>
<th>REPORT</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH1OCL</td>
<td>1.281e-4</td>
<td>NO</td>
<td>NH1OCL</td>
</tr>
<tr>
<td>H</td>
<td>1.622e-8</td>
<td>NO</td>
<td>H</td>
</tr>
<tr>
<td>TOTH</td>
<td>1.459e-3</td>
<td>NO</td>
<td>TOTH</td>
</tr>
<tr>
<td>TOTCO3</td>
<td>1.496e-3</td>
<td>NO</td>
<td>TOTCO3</td>
</tr>
<tr>
<td>HCO3</td>
<td>1.446e-3</td>
<td>NO</td>
<td>HCO3</td>
</tr>
<tr>
<td>NH3</td>
<td>3.311e-7</td>
<td>NO</td>
<td>NH3</td>
</tr>
<tr>
<td>TOTNH3</td>
<td>9.281e-6</td>
<td>NO</td>
<td>TOTNH3</td>
</tr>
<tr>
<td>DOCTHI2</td>
<td>1.071e-4</td>
<td>NO</td>
<td>DOCTHI2</td>
</tr>
<tr>
<td>NDMA</td>
<td>5.057e-1</td>
<td>NO</td>
<td>NDMA</td>
</tr>
</tbody>
</table>

**GLOBAL**

- NH1OCL: 1.080e-4
- H: 1.714e-8
- TOTH: 2.886e-3
- TOTCO3: 2.966e-3
- HCO3: 2.862e-3
- NH3: 4.457e-7
- TOTNH3: 2.332e-5
- NO2: 3.808e-7
- NO3: 4.284e-7
- SO4: 5.205e-4
- NDMA: 1.557e-11

**REPORT**

- TOTCO3
- HCO3
- NH3
- TOTNH3
- NO2
- NO3
- SO4
- NDMA

**Nodes**

- NONE

**Species**

- NH1OCL: Monochloramine
- NH1CL2: Dichloramine
- NH3: Unknown Intermediate Compound
- N2: Nitrogen Gas
- CL: Chloride Ion
- TOTDOCfr: Total DOC Fawn Ridge
- TOTDOCL: Total DOC Lake Park
- TOTDOCTHI: Total DOC THI
- OCL: Hypochlorite Ion
- HOCL: Hypochlorous Acid
- NH4: Ammonium
- H: Hydrogen Ion
- OH: Hydroxide Ion
- ALK: Alkalinity
- DOCFR1: DOC Fawn Ridge #1
- DOCFR2: DOC Fawn Ridge #2
- DOCLP1: DOC Lake Park #1
- DOCLP2: DOC Lake Park #2
- DOCTHI1: DOC THI #1
- DOCTHI2: DOC THI #2
- NO2: Nitrite Ion
- NO3: Nitrate Ion
- CO3: Carbonate Ion
- HCO3: Bicarbonate Ion
- H2O2: Peroxide
- SO4: Sulfate Ion
- TOTCO3: Total Carbonate
- TOTCL: Total Chlorine
- TOTNH3: Total Ammonia
- TOTH: Total Hydrogen
- NDMA: N-Nitrosodimethylamine
- CHCl3: Chloroform
- CHCL2BR: Dichlorobromomform
- CHCLBR2: Dibromochlorform
- CHBR3: Bromoform

Figure B.8: Week #2 EPANET-MSX Input File – Page 4 of 4
[OPTIONS]
RATE_UNITS HR Reaction Rates are Molar Concentration (MOL/L)/Hour
SOLVER ROS2 2nd Order Rosenbrock Integrator
COUPLING FULL Full coupling
COMPILER VC Visual C++ Compiler
TIMESTEP 300 300 sec (5 min) solution time step
RTOL 1.0e-8 Relative concentration tolerance
ATOL 1.0e-8 Absolute concentration tolerance

[SPARCIES]
BULK NH2CL MOL ;Monochloramine
BULK NHCl2 MOL ;Dichloramine
BULK I MOL ;Unknown Intermediate Compound
BULK N2 MOL ;Nitrogen Gas
BULK CL MOL ;Chloride ion
BULK TTTDOCFCr MOL ;Fawn Ridge DOC Reacted
BULK TTTDOCPLr MOL ;Lake Park DOC Reacted
BULK TTTDOCThr MOL ;THI DOC Reacted
BULK OCl MOL ;Hypochlorous ion
BULK HOCl MOL ;Hypochlorous Acid
BULK NH3 MOL ;Ammonia
BULK NH4 MOL ;Ammonium ion
BULK H MOL ;Hydrogen ion
BULK OH MOL ;Hydroxide ion
BULK ALK MOL ;Alkalinity
BULK DOCFCr1 MOL ;Dissolved Organic Fawn Ridge #1
BULK DOCFCr2 MOL ;Dissolved Organic Fawn Ridge #2
BULK DOCLPr1 MOL ;Dissolved Organic Lake Park #1
BULK DOCLPr2 MOL ;Dissolved Organic Lake Park #2
BULK DOCTHIr MOL ;Dissolved Organic THI #1
BULK DOCTHI2 MOL ;Dissolved Organic THI #2
BULK NO2 MOL ;Nitrite ion
BULK NO3 MOL ;Nitrate ion
BULK CO3 MOL ;Carbonate ion
BULK HC03 MOL ;Bicarbonate ion
BULK H2CO3 MOL ;Carbonic Acid
BULK SO4 MOL ;Sulfate ion
BULK TOTCO2 MOL ;Total Carbonate
BULK TOTOCl MOL ;Total Free Chlorine
BULK TOTNH3 MOL ;Total Free Ammonia
BULK TOTH MOL ;Total Hydrogen
BULK NDMA MOL ;N-Nitrosodimethylamine
BULK CH3Cl MOL ;Chloroform
BULK CHL2BR MOL ;Dichlorobromomethane
BULK CHLBR2 MOL ;Dibromochloromethane
BULK CH8BR3 MOL ;Bromoform

[COEFFICIENTS]
;TEMP = 300.6
;ION = 0.007

PARAMETER k1 1.560e10 [1.27e12*exp(-1510/(TEMP))] Vikesland et al. 2001
PARAMETER k2 1.295e-1 [1.67e-1*exp(-8800/(TEMP))] Vikesland et al. 2001
PARAMETER k3 1.347e-6 [1.08e-6*exp(-2010/(TEMP))] Vikesland et al. 2001
PARAMETER k4 2.3e-3 ; Vikesland et al. 2001
PARAMETER kh 2.773e7 [3.78e10*exp(-2168/(TEMP))] Vikesland et al. 2001
PARAMETER kHC03 1.525e3 [1.15e3*exp(-22144/(TEMPI)] Vikesland et al. 2001
PARAMETER kH2CO3 4.500e4 [2.95e10*exp(-4026/(TEMP)) Vikesland et al. 2001

Figure B.9: Pilot Study EPANET-MSX Input File – Page 1 of 4
PARAMETER k6  2.16e8  ;  Hand and Margerum 1983
PARAMETER k7  5.5e1  ;  Leao 1981
PARAMETER k8  4.0e5  ;  Jaifret and Valentine 1987
PARAMETER k9  1.0e8  ;  Leao 1981
PARAMETER k10  3.0e7  ;  Leao 1981
PARAMETER k11FR  3.04e4  ;  k012s1 Fast Reverse Rate Constant  Durik et al. 2005
PARAMETER k12FR  6.5e5  ;  k012s2 Slow Reverse Rate Constant  Estimated [4/21/10]
PARAMETER k11LP  3.04e4  ;  k012s1 Fast Reverse Rate Constant  Durik et al. 2005
PARAMETER k12LP  2.33BB6e7  ;  k012s2 Slow Reverse Rate Constant  Estimated [4/21/10]
PARAMETER k11THI  3.04e4  ;  k012s1 Fast Reverse Rate Constant  Durik et al. 2005
PARAMETER k12THI  6.5e5  ;  k012s2 Slow Reverse Rate Constant  Estimated [4/21/10]
PARAMETER k13  4.89e10  k1 Nitrate Rate #1  Vikesland et al. 2001
PARAMETER k14  2.17e2  k2 Nitrate Rate #2  Vikesland et al. 2001
PARAMETER k15  5.5e5  k3 Nitrate Rate #3  Vikesland et al. 2001
PARAMETER k16  8.2e3  k4 Nitrate Rate #4  Durik Dissertation 2003
PARAMETER k17  1.8e5  k5 Nitrate Rate #5  Durik Dissertation 2003
PARAMETER k18FR  3.69e-7  NDMA Formation FR  Estimated [4/21/10]
PARAMETER k18LP  3.92e-2  NDMA Formation LP  Estimated [4/21/10]
PARAMETER k18THI  7.3e-2  NDMA Formation THI  Estimated [4/21/10]
PARAMETER k19  1.485e-4  Chloroform Formation
PARAMETER k20  1.0821e-4  Dichlorobromoform Formation
PARAMETER k21  8.5114e-3  Dibromochloroform Formation
PARAMETER k22  7.0144e-3  Bromoform Formation

CONSTANT g1  0.9149  \[10^0.5*\text{sqrt}(\text{ION})/(1 + \text{sqrt}(\text{ION}))\]
CONSTANT g2  0.7008  \[10^0.5*\text{sqrt}(\text{ION})/(1 + \text{sqrt}(\text{ION}))\]
CONSTANT KW  1.454e-14  \[\exp(-6723.7/\text{TEMP})*1.3e-5/(g1^4)\]
CONSTANT KHCOCO3  5.373e-7  \[10^{-6}(1.18e-4*\text{TEMP}^3*\text{TEMP}^2 - 9.39e-2*\text{TEMP} + 2.21)/(g1^4)\]
CONSTANT KHCOCO3  6.599e-11  \[10^{-6}(1.19e-4*\text{TEMP}^3*\text{TEMP}^2 - 7.99e-2*\text{TEMP} + 23.0)/(g1^3)\]
CONSTANT KNH3  6.000e-10  \[10^{-6}(10^{-4}*(\text{TEMP}^3*\text{TEMP}^2 - 9.2e-2*\text{TEMP} + 27.6))\]
CONSTANT KOCL  3.482e-8  \[10^{-6}(1.18e-4*\text{TEMP}^3*\text{TEMP}^2 - 7.86e-2*\text{TEMP} + 20.5)/(g1^4)\]

[TERMS]

a1  k1*HOCLO*KOCO*NH3
a2  k2*HOCL
a3  k3*HOCO*KOCO*NH2CL
a4  k4*NH2CL
a5  k(HOCH2CHO+HOCH2CHO) + k(HOCH2CHO+HOCH2CHO)*KOCO3*KOCO3/KOCO2/KOCO2/KOCO2/KOCO2
a6  k(H2O+HOCH2CHO)

[PIPES]

RATE NH2CL  a1 + a2 + a3 + a4 + 2*a5 + a6 + a7 + a8 + a9 + a10
RATE NH2CL  a3 + a4 + a5 + a6 + a7 + a8 + a9

Figure B.10: Pilot Study EPANET-MSX Input File – Page 2 of 4
RATE N2  a7 + a9 + a10
RATE CL  2*a7 + 2*a8 + a9 + a10 + a11 + a12 + a13
RATE TOTDOCFR - a11FR - a12FR
RATE TOTDOCLp - a11LP - a12LP
RATE TOTDOCTHI - a11THI - a12THI

FORMULA HDCL (H*DOCL)/KOCL
FORMULA NH3 TOTNH3 - NH3 - (H+NH3)/KNH3
FORMULA NH4 (H*NH3)/KNH3
FORMULA H - TOTH - H + KW/H + OCL + NH3 + HCO3 + 2*KHCO3*HCO3/H
FORMULA OH - KW/H

RATE ALK  0
RATE DOCFR1 - a11FR
RATE DOCLP1 - a11LP
RATE DOCTHI1 - a11THI
RATE DOCFR2 - a12FR
RATE DOCLP2 - a12LP
RATE DOCTHI2 - a12THI
RATE NO2 - a13
RATE NO3 - a13

FORMULA CO3 KHCO3*HCO3/H
FORMULA HCO3 TOTCO3 - KHCO3*HCO3/H - HCO3 - H*HCO3/KH2CO3
FORMULA H2CO3 H*HCO3/KH2CO3
FORMULA SO4  0

FORMULA TOTCO3 0
FORMULA TOTDOCL - a1 + a2 - a3 + a4 + a9 - a12
FORMULA TOTNH3 - a1 + a2 + a5 - a6 - a11 + a13
FORMULA TOTH - 3*a7 - 2*a8 - a9 - a10;
FORMULA NDMA a14 + a15 + a16;
FORMULA CHCL3 a17
FORMULA CHCL2BR a18
FORMULA CHLBR2 a19
FORMULA CHBR3 a20

[SOURCES]

1 NODE RES9000 FR
1 NODE 7384 LP
1 NODE 311 THI

CONCEN RES9000 NH2Cl 1.277E-4
CONCEN RES9000 H 1.950E-8
CONCEN RES9000 TOTH 3.904E-3
CONCEN RES9000 TOTCO3 4.036E-3
CONCEN RES9000 HCO3 3.878E-3
CONCEN RES9000 NH3 4.870E-7
CONCEN RES9000 TOTNH3 1.938E-5
CONCEN RES9000 DOCFR2 1.007E-4
CONCEN RES9000 NO2 5.712E-7
CONCEN RES9000 NO3 1.171E-5
CONCEN RES9000 SO4 2.686E-5

CONCEN 7384 NH2Cl 1.207E-4
CONCEN 7384 H 1.822E-8
CONCEN 7384 TOTH 3.904E-3
CONCEN 7384 TOTCO3 4.029E-3
CONCEN 7384 HCO3 3.877E-3
CONCEN 7384 NH3 1.388E-6
CONCEN 7384 TOTNH3 4.436E-5
CONCEN 7384 DOCLP2 1.132E-4
CONCEN 7384 NO2 6.425E-7
CONCEN 7384 NO3 7.199E-8
CONCEN 7384 SO4 1.016E-4

CONCEN 311 NH2Cl 1.298E-4
CONCEN 311 H 1.841E-8

Figure B.11: Pilot Study EPANET-MSX Input File – Page 3 of 4
<table>
<thead>
<tr>
<th>CONCEN</th>
<th>NODES</th>
<th>SPECIES</th>
<th>CONCEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NH2CL</td>
<td>1.134E-4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>1.810E-8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TOTH</td>
<td>3.150E-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TOTCO3</td>
<td>3.241E-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCO3</td>
<td>3.126E-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH3</td>
<td>5.459E-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TOTNH3</td>
<td>1.523E-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N02</td>
<td>1.666E-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N03</td>
<td>1.261E-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO4</td>
<td>4.743E-4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NOMA</td>
<td>1.834E-11</td>
</tr>
</tbody>
</table>

**REPORT**

<table>
<thead>
<tr>
<th>NODES</th>
<th>SPECIES</th>
<th>CONCEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH2CL</td>
<td>3.904E-3</td>
</tr>
<tr>
<td></td>
<td>TOTCO3</td>
<td>4.029E-3</td>
</tr>
<tr>
<td></td>
<td>HCO3</td>
<td>3.877E-3</td>
</tr>
<tr>
<td></td>
<td>NH3</td>
<td>5.659E-8</td>
</tr>
<tr>
<td></td>
<td>TOTNH3</td>
<td>2.142E-6</td>
</tr>
<tr>
<td></td>
<td>DOCTH2</td>
<td>1.070E-4</td>
</tr>
<tr>
<td></td>
<td>N02</td>
<td>5.712E-7</td>
</tr>
<tr>
<td></td>
<td>N03</td>
<td>7.318E-6</td>
</tr>
<tr>
<td></td>
<td>SO4</td>
<td>1.041E-3</td>
</tr>
</tbody>
</table>

**GLOBAL**

- NH2CL
- H
- TOTH
- TOTCO3
- HCO3
- NH3
- TOTNH3
- N02
- N03
- SO4
- NOMA

**RESULTS**

- Report results for all nodes
- Monochloramine
- Dichloramine
- Unknown Intermediate Compound
- Nitrogen Gas
- Chloride Ion
- Total DOC Fawn Ridge Reacted
- Total DOC Lake Park Reacted
- Total DOC THI Reacted
- Hypochlorite Ion
- Hypochlorous Acid
- Ammonia
- Ammonium Ion
- Hydrogen Ion
- Hydroxide Ion
- Alkalinity
- DOC Fawn Ridge #1
- DOC Fawn Ridge #2
- DOC Lake Park #1
- DOC Lake Park #2
- DOC THI #1
- DOC THI #2
- Nitrate Ion
- Nitrite Ion
- Carbonate Ion
- Bicarbonate Ion
- Carbonic Acid
- Sulfate Ion
- Total Carbonate
- Total Free Chlorine
- Total Ammonia
- Total Hydrogen
- Nitrosodimethylamine
- Chloriform
- Dichlorobromoform
- Dibromochloriform
- Bromoform

Figure B.12: Pilot Study EPANET-MSX Input File – Page 4 of 4
Appendix C

“Pressure-Based” Pilot Study Results

This appendix contains figures of the experimental data from the “pressure-based” model results from the pilot study. Figures C.1 and C.2 show the combined chlorine and free ammonia data for the “pressure-based” model. Figures C.3 and C.4 illustrate the total chlorine results. Figures C.5 and C.6 show nitrite and nitrate results. Lastly, Figures C.7 and C.8 depict the alkalinity results from the Fawn Ridge region during week two.
Figure C.1: “Pressure-Based” Combined Chlorine and Free Ammonia Results at P-1, P-2, and P-3
Figure C.2: “Pressure-Based” Combined Chlorine and Free Ammonia Results at P-4, P-5, and P-6
Figure C.3: “Pressure-Based” Total Chlorine Results at P-1, P-2, and P-3
Figure C.4: "Pressure-Based" Total Chlorine Results at P-4, P-5, and P-6
Figure C.5: "Pressure-Based" Nitrite and Nitrate Results at P-1, P-2, and P-3
Figure C.6: “Pressure-Based” Nitrite and Nitrate Results at P-4, P-5, and P-6
Figure C.7: “Pressure-Based” pH Results at P-1, P-2, and P-3
Figure C.8: "Pressure-Based" pH Results at P-4, P-5, and P-6
Appendix D

Total Chlorine Model Results

Results from the chloramine dynamics model indicated that the minimal amounts of free chlorine were present in this system, so total chlorine results were similar to combined chlorine results. This appendix contains figures of the experimental data from both the “flow-based” and “pressure-based” total chlorine results. Figures D.1, D.2, D.5, and D.6 show total chlorine results from the “flow-based” model in the Fawn Ridge region, while Figures D.3, D.4, D.7, and D.8 show results from the “pressure-based” model. Figures D.9, D.10, D.13, and D.14 show total chlorine results from the “flow-based” model in the Lake Park region, while Figures D.11, D.12, D.15, and D.16 show results from the “pressure-based” model.
Figure D.1: “Flow-Based” Total Chlorine Results at FR-1, FR-2, and FR-3
Figure D.2: “Flow-Based” Total Chlorine Results at FR-4, FR-5, and FR-6
Figure D.3: “Pressure-Based” Total Chlorine Results at FR-1, FR-2, and FR-3
Figure D.4: “Pressure-Based” Total Chlorine Results at FR-4, FR-5, and FR-6
Figure D.5: “Flow-Based” Total Chlorine Results at FR-1, FR-7, and FR-8
Figure D.6: “Flow-Based” Total Chlorine Results at FR-9, FR-11, and FR-12
Figure D.7: “Pressure-Based” Total Chlorine Results at FR-1, FR-7, and FR-8
Figure D.8: “Pressure-Based” Total Chlorine Results at FR-9, FR-11, and FR-12
Figure D.9: “Flow-Based” Total Chlorine Results at LP-1, LP-2, and LP-3
Figure D.10: “Flow-Based” Total Chlorine Results at LP-4, LP-5, and LP-6
Figure D.11: “Pressure-Based” Total Chlorine Results at LP-1, LP-2, and LP-3
Figure D.12: “Pressure-Based” Total Chlorine Results at LP-4, LP-5, and LP-6
Figure D.13: “Flow-Based” Total Chlorine Results at LP-1, LP-8, and LP-9
Figure D.14: “Flow-Based” Total Chlorine Results at LP-10, LP-11, and LP-12
Figure D.15: “Pressure-Based” Total Chlorine Results at LP-1, LP-8, and LP-9
Figure D.16: “Pressure-Based” Total Chlorine Results at LP-10, LP-11, and LP-12
Appendix E

“Pressure-Based” Model Results – Fawn Ridge Week #1

This appendix contains figures of the experimental data from the “pressure-based” model results in the Fawn Ridge region during the first week of the study. Figures E.1 and E.2 show the combined chlorine and sulfate data for the “pressure-based” model during the first week in the Fawn Ridge region. Figures E.3 and E.4 illustrates the free ammonia results from the week one model. Figures E.5 and E.6 show nitrite and nitrate results from the “pressure-based” model. Figures E.7 and E.8 show observed and modeled pH results from the Fawn Ridge region. Lastly, Figures E.9 and E.10 depict the alkalinity results from the Fawn Ridge region during week one.
Figure E.1: “Pressure-Based” Combined Chlorine and Sulfate Results at FR-1, FR-2, and FR-3
Figure E.2: “Pressure-Based” Combined Chlorine and Sulfate Results at FR-4, FR-5, and FR-6
Figure E.3: “Pressure-Based” Free Ammonia Results at FR-1, FR-2, and FR-3
Figure E.4: “Pressure-Based” Free Ammonia Results at FR-4, FR-5, and FR-6
Figure E.5: “Pressure-Based” Nitrite and Nitrate Results at FR-1, FR-2, and FR-3
Figure E.6: “Pressure-Based” Nitrite and Nitrate Results at FR-4, FR-5, and FR-6
Figure E.7: “Pressure-Based” pH Results at FR-1, FR-2, and FR-3
Figure E.8: “Pressure-Based” pH Results at FR-4, FR-5, and FR-6
Figure E.9: “Pressure-Based” Alkalinity Results at FR-1, FR-2, and FR-3
Figure E.10: “Pressure-Based” Alkalinity Results at FR-4, FR-5, and FR-6
Appendix F

“Pressure-Based” Model Results – Fawn Ridge Week #2

This appendix contains figures of the experimental data from the “pressure-based” model results in the Fawn Ridge region during the second week of the study. Figures F.1 and F.2 show the combined chlorine and sulfate data for the “pressure-based” model during the second week in the Fawn Ridge region. Figures F.3 and F.4 illustrates the free ammonia results from the week two model. Figures F.5 and F.6 show nitrite and nitrate results from the “pressure-based” model. Figures F.7 and F.8 show observed and modeled pH results from the Fawn Ridge region. Lastly, Figures F.9 and F.10 depict the alkalinity results from the Fawn Ridge region during week two.
Figure F.1: “Pressure-Based” Combined Chlorine and Sulfate Results at FR-1, FR-7, and FR-8
Figure F.2: “Pressure-Based” Combined Chlorine and Sulfate Results at FR-9, FR-11, and FR-12
Figure F.3: “Pressure-Based” Free Ammonia Results at FR-1, FR-7, and FR-8
Figure F.4: “Pressure-Based” Free Ammonia Results at FR-9, FR-11, and FR-12
Figure F.5: “Pressure-Based” Nitrite and Nitrate Results at FR-1, FR-7, and FR-8
Figure F.6: “Pressure-Based” Nitrite and Nitrate Results at FR-9, FR-11, and FR-12
Figure F.7: “Pressure-Based” pH Results at FR-1, FR-7, and FR-8
Figure F.8: “Pressure-Based” pH Results at FR-9, FR-11, and FR-12
Figure F.9: “Pressure-Based” Alkalinity Results at FR-1, FR-7, and FR-8
Figure F.10: “Pressure-Based” Alkalinity Results at FR-9, FR-11, and FR-12
Appendix G

“Pressure-Based” Model Results – Lake Park Week #1

This appendix contains figures of the experimental data from the “pressure-based” model results in the Lake Park region during the first week of the study. Figures G.1 and G.2 show the combined chlorine and sulfate data for the “pressure-based” model during the first week in the Lake Park region. Figures G.3 and G.4 illustrates the free ammonia results from the week one model. Figures G.5 and G.6 show nitrite and nitrate results from the “pressure-based” model. Figures G.7 and G.8 show observed and modeled pH results from the Lake Park region. Lastly, Figures G.9 and G.10 depict the alkalinity results from the Lake Park region during week one.
Figure G.1: “Pressure-Based” Combined Chlorine and Sulfate Results at LP-1, LP-2, and LP-3
Figure G.2: “Pressure-Based” Combined Chlorine and Sulfate Results at LP-4, LP-5, and LP-6
Figure G.3: “Pressure-Based” Free Ammonia Results at LP-1, LP-2, and LP-3
Figure G.4: "Pressure-Based" Free Ammonia Results at LP-4, LP-5, and LP-6
Figure G.5: “Pressure-Based” Nitrite and Nitrate Results at LP-1, LP-2, and LP-3
Figure G.6: “Pressure-Based” Nitrite and Nitrate Results at LP-4, LP-5, and LP-6
Figure G.7: “Pressure-Based” pH Results at LP-1, LP-2, and LP-3
Figure G.8: "Pressure-Based" pH Results at LP-4, LP-5, and LP-6
Figure G.9: “Pressure-Based” Alkalinity Results at LP-1, LP-2, and LP-3
Figure G.10: “Pressure-Based” Alkalinity Results at LP-4, LP-5, and LP-6
Appendix H

“Pressure-Based” Model Results – Lake Park Week #2

This appendix contains figures of the experimental data from the “pressure-based” model results in the Lake Park region during the second week of the study. Figures H.1 and H.2 show the combined chlorine and sulfate data for the “pressure-based” model during the second week in the Lake Park region. Figures H.3 and H.4 illustrate the free ammonia results from the week two model. Figures H.5 and H.6 show nitrite and nitrate results from the “pressure-based” model. Figures H.7 and H.8 show observed and modeled pH results from the Lake Park region. Lastly, Figures H.9 and H.10 depict the alkalinity results from the Lake Park region during week two.
Figure H.1: “Pressure-Based” Combined Chlorine and Sulfate Results at LP-1, LP-8, and LP-9
Figure H.2: “Pressure-Based” Combined Chlorine and Sulfate Results at LP-10, LP-11, and LP-12
Figure H.3: “Pressure-Based” Free Ammonia Results at LP-1, LP-8, and LP-9
Figure H.4: “Pressure-Based” Free Ammonia Results at LP-10, LP-11, and LP-12
Figure H.5: “Pressure-Based” Nitrite and Nitrate Results at LP-1, LP-8, and LP-9
Figure H.6: “Pressure-Based” Nitrite and Nitrate Results at LP-10, LP-11, and LP-12
Figure H.7: “Pressure-Based” pH Results at LP-1, LP-8, and LP-9
Figure H.8: “Pressure-Based” pH Results at LP-10, LP-11, and LP-12
Figure H.9: “Pressure-Based” Alkalinity Results at LP-1, LP-8, and LP-9
Figure H.10: “Pressure-Based” Alkalinity Results at LP-10, LP-11, and LP-12
Appendix I

“Pressure-Based” NDMA Model Results

This appendix contains figures of the modeled and observed NDMA data from the “pressure-based” NDMA results. Figures I.1, I.2, I.3, and I.4 show NDMA results from the Fawn Ridge region from both weeks of the study. Figures I.5, I.6, I.7, and I.8 show NDMA results from the Lake Park region from both weeks of the study.
Figure I.1: “Pressure-Based” NDMA Results at FR-1, FR-2, and FR-3
Figure I.2: “Pressure-Based” NDMA Results at FR-4, FR-5, and FR-6
Figure I.3: “Pressure-Based” NDMA Results at FR-1, FR-7, and FR-8
Figure I.4: “Pressure-Based” NDMA Results at FR-9, FR-11, and FR-12
Figure I.5: “Pressure-Based” NDMA Results at LP-1, LP-2, and LP-3
Figure I.6: “Pressure-Based” NDMA Results at LP-4, LP-5, and LP-6
Figure I.7: “Pressure-Based” NDMA Results at LP-1, LP-8, and LP-9
Figure I.8: “Pressure-Based” NDMA Results at LP-10, LP-11, and LP-12
Appendix J

Gel Electrophoresis Images

This appendix contains digital images taken of 1% agarose gel, containing PCR-amplified nucleic acid, illuminated with an ultraviolet lamp. A 100-bp ladder was used to identify the lengths of amplified DNA fragments. Figures J.1, J.2, and J.3 show digital images of agarose gels containing PCR-amplified nucleic acid using a universal primer set that amplifies any bacterium, by targeting the 16S-rDNA genes of all microorganisms. Figures J.4, J.5, and J.6 show images of gels using an ANAMMOX-specific primer set and Figures J.7, J.8, and J.9 show images of gels using an AOB-specific primer set. Positive samples can be identified by the presence of a solid DNA-band in the respective sample well, negative samples do not produce a DNA-band. These images were used to obtain the results in Section 8.
Figure J.1: Results from amplification of PCR products of extracted nucleic acids using a universal primer set. Lane 1, 100 bp ladder; lane 2, negative control; lane 3, Escherichia coli, positive control; lanes 4-23, selected environmental samples; lane 24, 100 bp ladder.
Figure J.2: Results from amplification of PCR products of extracted nucleic acids using a universal primer set. Lane 1, 100 bp ladder; Lane 2, negative control; Lanes 3-23, selected environmental samples; Lane 24, 100 bp ladder.
Figure J.3: Results from amplification of PCR products of extracted nucleic acids using a universal primer set. Lane 1, 100 bp ladder; lane 2, negative control; lanes 2-12, selected environmental samples; lane 13, 100 bp ladder.
Figure J.4: Results from amplification of PCR products of extracted nucleic acids using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; lane 2, negative control; lane 3, Candidatus Brocadia fulgida; lane 4, Candidatus Brocadia sp. 40; lane 5, Candidatus Kuenenia stuttgartiensis; lanes 6-23, selected environmental samples; lane 24, 100 bp ladder.

100 bp Ladder
Negative Control, DNA/RNA-free Water
Positive Control, Candidatus B. fulgida
Positive Control, Candidatus B. sp. 40
Positive Control, Candidatus K. stuttgartiensis
LP-6, 9/10/2009
LP-6, 9/9/2009
FR-POE, 9/17/2009
LP-11, 9/16/2009
FR-POE, 9/9/2009
LP-POE, 9/10/2009
FR-POE, 9/10/2009
LP-POE, 9/11/2009
LP-5, 9/9/2009
THI-POE, 9/9/2009
FR-6, 9/8/2009
LP-6, 9/8/2009
LP-11, 9/14/2009
LP-6, 9/11/2009
FR-11, 9/17/2009
FR-11, 9/16/2009
LP-POE, 9/15/2009
LP-POE, 9/8/2009
100 bp Ladder
Figure J.5: Results from amplification of PCR products of extracted nucleic acids using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; lane 24, 100 bp ladder.
environmental samples; lane 13, 100 bp ladder. Lane 1, 100 bp ladder; lane 2-12, selected
using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; lane 2-12, selected
products of extracted nucleic acids.

Figure J.6: Results from amplification of PCR products of extracted nucleic acids.
Figure J.7: Results from amplification of PCR products of extracted nucleic acids using an ANAMMOX-specific primer set. Lane 1, 100 bp ladder; Lane 2, negative control; Lane 3, *Nitrosomonas europaea*; Lane 4, *Nitrospira multiformis*; Lane 5, *Nitrosomonas oligotropha*; lanes 6-23, selected environmental samples; lane 24, 100 bp ladder.
Figure J.8: Results from amplification of PCR products of extracted nucleic acids using an AOB-specific primer set. Lane 1, 100 bp ladder; lanes 2-23, selected environmental samples; lane 24, 100 bp ladder.

Figure J.9: Results from amplification of PCR products of extracted nucleic acids using an AOB-specific primer set. Lane 1, 100 bp ladder; lanes 2-13, selected environmental samples; lane 14, 100 bp ladder.