

**Advancing Potable Water Infrastructure through an Improved Understanding of Polymer  
Pipe Oxidation, Polymer–Contaminant Interactions, and Consumer Perception of Taste**

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# **Advancing Potable Water Infrastructure through an Improved Understanding of Polymer Pipe Oxidation, Polymer–Contaminant Interactions, and Consumer Perception of Taste**

Andrew James Whelton

## **Abstract**

While more than 100 years of research has focused on removing acute and chronic health threats from water, substantially less study has focused on potable water infrastructure and water quality deterioration, monitoring technologies, and relationships between water taste and consumer health. These knowledge–gaps have left infrastructure users, owners, regulators, and public health professionals largely unaware of how premise and buried polymer water pipes deteriorate and sorb/ desorb organic contaminants during normal operations and following water contamination events. These knowledge–gaps also prevent infrastructure managers from producing drinking water that optimizes mineral content for both water taste and health benefits, and employing a monitoring tool capable of immediately detecting water contamination or equipment failures.

Research was conducted to address these challenges using analytical chemistry, environmental engineering, food science, polymer chemistry, public health, and material science principles. This work was enhanced by collaborations with sixteen American water utilities and the National Institute for Standards and Technology. These efforts were funded by the National Science Foundation, American Water Works Association, and the Water Research Foundation.

Research results are unique and provide important scientific contributions to the public health, potable water, and material science industries. Particular achievements include the: (1) Evaluation of linkages between minerals, water palatability, and health useful for water production and public health decisions; (2) Creation of a novel infrastructure and water quality surveillance tool that has begun water utility implementation in the USA; (3) Development of an accelerated chlorinated water aging method with stable water pH, free chlorine, and alkalinity concentration that enables interpretation of polymer pipe surface and bulk characteristic changes; (4) Discovery that polar compounds are 2–193% more soluble in PEX than HDPE water pipes; (5) Finding that several polymer and contaminant properties can be used to predict contaminant diffusivity and solubility during sorption and desorption in new, lab aged, and water utility PE

pipes; and the (6) Discovery that chlorinated water exposure of HDPE and PEX pipes increases polar contaminant diffusivity during sorption by 50–162% and decreases diffusivity during desorption as much as 211%. Outcomes of this work have domestic and global significance, and if engaged, can greatly improve public health protection, potable water infrastructure operations, water quality, sustainability, and regulation.

## **Acknowledgement**

One year ago I started writing this acknowledgement to make certain I thanked everyone. Looking back, there's no doubt I probably have forgotten a few folks so please accept my sincere apologies if you are one of those people reading this document. To state it simply, this dissertation would not have been possible without the support, friendship, and technical guidance of many people. I am truly blessed to have met and crossed paths with so many great people. I wish to personally acknowledge those who made it possible for completion of my dissertation work. Some individuals provided technical advice, allowed me to use their lab equipment or assisted in the conduct of experiments, convinced their organization to support and participate in this research, while others provided a listening ear and advice as to how I could better approach challenges. Thank you. I look forward to crossing paths with you again in the future.

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## Table of Contents

<b>Abstract</b> .....	ii
<b>Acknowledgement</b> .....	iv
<b>List of Tables</b> .....	xii
<b>List of Figures</b> .....	xiv
<b>Author’s Preface &amp; Attribution</b> .....	xvii
<b>Chapter 1 Minerals in Drinking Water: Impacts on Taste and Importance to Consumer Health</b> .....	1
1.1 Abstract .....	1
1.2 Introduction .....	1
1.3 Consumer Sensitivity to the Taste of Drinking Water .....	2
1.4 Exploring the Role of Water Chemistry.....	3
1.4.1 World Variations, Standards, and Non–Mineral Influential Factors.....	3
1.4.2 Mineral Sensitivity .....	4
1.5 Consumer Taste Studies .....	7
1.5.1 Military Drinking Water Acceptability .....	7
1.5.2 Preference Testing for Tap vs. a COTS Filtered Tap Water .....	7
1.5.3 Comparison of Tap and Commercial Bottled Waters .....	8
1.6 Conclusion.....	8
1.7 Acknowledgement.....	9
1.8 References .....	9
<b>Chapter 2 Customer Feedback Tool for Distribution System Monitoring for Improved Drinking Water Surveillance</b> .....	17
2.1 Abstract .....	17
2.2 Introduction .....	18
2.3 Project Purpose and Participants .....	19
2.3 Methods.....	19
2.3.1 Utility Visits .....	19
2.3.2 Regional Survey .....	20
2.4. Results and Discussion.....	20

2.4.1 Significance .....	20
2.4.2 Customer Contact Handling .....	20
2.4.3 General Interview Questions, Department Call–Back, and Urgent Issues .....	21
2.4.4 Feedback Data Characteristics.....	23
2.4.4.1 Utility Comparison.....	23
2.4.4.2 One Utility Example .....	24
2.4.5 Storage, Tracking, and Analyses Methods and Frequencies .....	25
2.4.6 Investigative Response to Customer Feedback .....	26
2.4.6.1 Preparation and Equipment.....	26
2.4.6.2 Investigation Description .....	26
2.4.6.3 Onsite Response Time .....	27
2.4.6.4 Onsite Procedures .....	27
2.4.6.5 Onsite Analyses .....	28
2.4.6.6 Laboratory Analyses .....	29
2.4.6.7 Post Analyses and Follow-up.....	29
2.5 Conclusion.....	30
2.6 Acknowledgement.....	31
2.7 References .....	31
<b>Chapter 3 Integration of Customer Feedback into Utility Operations for Improved Water Quality and Infrastructure Monitoring.....</b>	<b>39</b>
3.1 Abstract .....	39
3.2 Introduction .....	40
3.3 Project Goal and Objectives.....	42
3.4 Methods.....	42
3.5 Results and Discussion.....	43
3.5.1 Literature Review. ....	43
3.5.2 Utility Site Visits. ....	44
3.5.2.1 Points of Customer Contact .....	44
3.5.2.2 Data Recording .....	45
3.5.2.3 Uniform Terminology.....	46
3.5.2.4 Data Storage and Integration .....	47



3.5.2.5 Relationships with Other Agencies.....	48
3.6 Recommendations .....	48
3.6.1 Terminology .....	49
3.6.2 Other Improvements .....	51
3.6.2.1 Customer Education.....	51
3.6.2.2 Training.....	51
3.6.2.3 Local Relationships.....	52
3.7 Summary .....	52
3.8 Acknowledgement.....	53
3.9 References .....	53
<b>Chapter 4 Critical Considerations for the Accelerated Aging of Polyethylene Potable Water Material.....</b>	<b>71</b>
4.1 Abstract .....	71
4.2 Introduction .....	71
4.3 Experimental Methods .....	76
4.3.1 Materials and Polymer Preparation. ....	76
4.3.2 Water Quality Measurements and Accelerated Aging Methods. ....	76
4.3.3 Polymer Characterization .....	78
4.3.3.1 Application of Characterization Techniques .....	78
4.3.3.2 Bulk Properties.....	78
4.3.3.3 Mechanical Properties.....	79
4.3.3.4 Surface Characteristics.....	79
4.3.3.5 Water Sorption.....	79
4.4 Results and Discussion.....	79
4.4.1 New HDPE .....	79
4.4.2 Aging Method with 5,000 ppm as Cl <sub>2</sub> at 70 °C and No Alkalinity .....	80
4.4.2.1 Oxidant Solution Changes during Aging.....	80
4.4.2.2 Polymer Degradation during Aging.....	81
4.4.3 Aging Method with Temperature/Chlorine Matrix and Alkalinity at pH 6.5 .....	82
4.4.3.1 Oxidant Solution Changes during Aging.....	82
4.4.3.2 Polymer Degradation during Aging.....	83

4.4.3.3 Comparison of HDPE Pipe Morphological and Mechanical Characteristics after Aging .....	84
4.4.3.4 Water Desorption .....	84
4.5 Conclusion .....	85
4.6 Acknowledgement .....	87
4.7 References .....	87
<b>Chapter 5 Contaminant Diffusion, Solubility, and Material Property Differences between HDPE and PEX Potable Water Pipes .....</b>	<b>110</b>
5.1 Abstract .....	110
5.2 Introduction .....	110
5.3 Experimental Section .....	114
5.3.1 Materials and Polymer Preparation .....	114
5.3.2 Polymer Characterization .....	114
5.4 Results and Discussion .....	116
5.4.1 Material Bulk and Oxidative Properties .....	116
5.4.2 Equilibrium & Solubility .....	117
5.4.3 Diffusivity .....	119
5.5 Conclusion .....	120
5.6 Acknowledgement .....	122
5.7 References .....	122
<b>Chapter 6 Impact of Chlorinated Water Exposure on Chemical Diffusivity and Solubility, Surface and Bulk Properties of HDPE and PEX Potable Water Pipe .....</b>	<b>140</b>
6.1 Abstract .....	140
6.2 Introduction .....	140
6.3 Methods .....	144
6.3.1 Polymers & Water Utility Conditions .....	144
6.3.2 Aging Condition and Solution Characterization .....	144
6.3.3 Polymer Characterization .....	144
6.3.4 Contaminant Interactions .....	145
6.4 Results and Discussion .....	145
6.4.1 Lab Accelerated Aging Solution Stability .....	145
6.4.2 Lab Aged PE Surface and Bulk Characteristics .....	146

6.4.3 Lab Aged PE Contaminant Interactions .....	147
6.4.3.1 Equilibrium .....	147
6.4.3.2 Solubility .....	147
6.4.3.3 Diffusivity .....	149
6.4.4 Water Utility PE (wu-PE) Pipe Comparison to Lab Aged PEs .....	150
6.5 Conclusion .....	151
6.6 Acknowledgement .....	153
6.7 References .....	153
<b>Chapter 7 Organic Contaminant Desorption from New and Aged Polyethylene and Poly(1-butene) Potable Water Pipes .....</b>	<b>174</b>
7.1 Abstract .....	174
7.2 Introduction .....	174
7.2.1 Existing Knowledge–Gaps and Need for Research .....	174
7.2.2 Previously Reported Polymer Characteristics for New and Lab Aged Polyethylene Examined in this Work .....	178
7.3 Materials and Methods .....	179
7.3.1 Materials and Preparation .....	179
7.3.2 Accelerated Aging in Chlorinated Water .....	179
7.3.3 Polymer Characterization, Contaminant Sorption and Desorption .....	180
7.3.4 Assessment of Immersion and Air Drying Equilibrium for Each Polymer–Contaminant Pair .....	181
7.4 Results and Discussion .....	182
7.4.1 Sorption and Desorption Equilibrium for New and Lab Aged PEs .....	182
7.4.2 Time Required to Desorb 50% of the Contaminant for New and Lab Aged PEs .....	182
7.4.3 Contaminant Diffusivity during Sorption and Desorption and their Relationships ...	183
7.4.3.1 Contaminant Sorption into New and Lab Aged PEs .....	183
7.4.3.2 Contaminant Desorption from New and Lab Aged PEs .....	184
7.4.3.3 Comparing Contaminant Diffusion during Sorption and Desorption in New and Lab Aged PEs .....	185
7.4.4 Pipes Removed from a Buried Water Distribution Network .....	186
7.5 Conclusion .....	188
7.6 Acknowledgement .....	189

7.7 References .....	190
<b>Limitations and Future Work</b> .....	206
<b>Appendix A Copyright Permissions</b> .....	210

## List of Tables

### Chapter 1

Table 1–1 Comparison of Canadian, European Economic Community (EEC), US, and World Health Organization (WHO) Drinking Water Regulations, Concentration, mg/L .....	13
Table 1–2 TDS, TOC, IOC, Cation, and Free Chlorine Levels of Tap and Filtered Tap Waters .....	14
Table 1–3 Anion Contents of Tap and Filtered Tap Waters .....	14
Table 1–4 Water pH, Hardness, and TDS Analyses Results of Four of Seven Bottled Waters ...	14
Table 1–5 Anion and Cation Analyses Results of All Seven Bottled Waters .....	15
Table 1–6 Summary of Mineral Affects on the Taste of Drinking Water .....	16

### Chapter 2

Table 2–1 Characteristics of Thirteen Utilities Visited .....	33
Table 2–2 Common Methods for Customer Initial Telephone Call Receiving and Routing .....	33
Table 2–3 Methods for Storing Customer Feedback at Utilities Visited.....	34
Table 2–4 Method for Tracking and Analyzing Customer Complaints at Surveyed Utilities.....	34

### Chapter 3

Table 3–1 Characteristics of Thirteen Participating Utilities .....	59
Table 3–2 Common Methods for Receiving and Routing the Customers' Initial Telephone Call	59
Table 3–3 Most Commonly Asked Questions by Utility Personnel to Determine the Cause of the Customers Concern .....	60
Table 3–4 Descriptors Used at Four Utilities to Describe Customer Reported .....	61
Table 3–5 Descriptors Used for Coding Black and Chlorine Water Quality Issues.....	62
Table 3–6 Methods for Storing Customer Feedback Data.....	62
Table 3–7 Current and Desired Methods for Integrating Customer Feedback Data with Utility Operation and Monitoring Systems .....	63
Table 3–8 Examples of Three Tiered Approach to Customer Feedback Data Coding .....	64

### Chapter 4

Table 4–1 American Society for Testing and Materials (ASTM) and National Sanitation Foundation (NSF) Accelerated Aging Methods for Polyethylene and Elastomeric Potable Water Materials.....	104
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Table 4–2 Literature Reported Accelerated Aging Conditions for Polymeric Potable Water Materials .....	105
Table 4–3 Physical and Bulk Characteristics of New HDPE Resin and HDPE Water Pipe Examined .....	106
Table 4–4 Initial and Change in Aging Solution Characteristics Every 72 Hours .....	107
Table 4–5 Mechanical Properties of Convection Oven Dried for New and Temperature/Chlorine Aged HDPE Pipe .....	108
Table 4–6 New and Aged HDPE Pipe Drying Results .....	108
Table 4–7 Recommended Conditions for the Accelerated Aging of Polyethylene Materials Using Chlorinated Water, a 72 Hr Water Change Frequency, and the Immersion Method	109

## **Chapter 5**

Table 5–1 Effect on Contaminant Diffusivity and Solubility in Polymers when Environmental, Polymer, or Contaminant Property is Increased .....	128
Table 5–2 Contaminant Characteristics at 25 °C .....	129
Table 5–3 Bulk Characteristics of Polyethylene Materials .....	130
Table 5–4 Time to Half Contaminant Saturation of Polyethylene Specimens .....	131
Table 5–5 Contaminant Solubility of Polyethylene Materials .....	132
Table 5–6 Contaminant Diffusivity of Polyethylene Materials .....	133

## **Chapter 6**

Table 6–1 Contaminant Properties .....	158
Table 6–2 Stability of Accelerated Aging Solution during Test Periods .....	159
Table 6–3 Bulk and Mechanical Properties for New and Lab Aged Polyethylene .....	160
Table 6–4 Change in Time to Half–Equilibrium for New and Lab Aged Polyethylene .....	161
Table 6–5 Contaminant Solubility in New and Lab Aged Polyethylene .....	162
Table 6–6 Contaminant Diffusivity in New and Lab Aged Polyethylene .....	163
Table 6–7 Attributes of Water Utility Polyethylene Pipes .....	164

## **Chapter 7**

Table 7–1 Contaminant Characteristics at 25 °C .....	196
Table 7–2 Bulk Characteristics of New and Lab Aged Polyethylene .....	197
Table 7–3 Weight Gain as Percent of New and Lab Aged Polyethylene due to Contaminant Sorption .....	198
Table 7–4 Time to Desorb 50% of the Contaminant from New and Lab Aged Polyethylene ...	199
Table 7–5 Contaminant Diffusivity during Desorption for New and Lab Aged Polyethylene ..	200
Table 7–6 Water Utility Pipe Bulk Properties .....	201
Table 7–7 Toluene and Trichloromethane Sorption and Desorption Results for Water Utility Pipes .....	201

## List of Figures

### Chapter 1

None

### Chapter 2

Figure 2–1 General Flow Path of Customer Concerns Through a Utility .....	35
Figure 2–2 Total Number of Customer Water Quality Concerns Per Year, 2002–2005 .....	35
Figure 2–3 Percent of Customer Water Quality Concerns Separated by Utility Categories, 2002–2005 .....	36
Figure 2–4 Frequency of Customer Water Quality Concerns Per Month, 2002–2005 .....	36
Figure 2–5 Frequency of Customer Water Quality Concerns Per Day of Week, 2002–2005 .....	37
Figure 2–6 Frequency of Customer Water Quality Concerns Per Day, 2002–2005 .....	37
Figure 2–7 Review Frequency for Historical Complaint Data for Surveyed Utilities .....	38

### Chapter 3

Figure 3–1 Causes of Twenty Two Drinking Water Incidents Detected by Customer Feedback Warnings, 1977–2003 .....	65
Figure 3–2 Comparison of Outcome Trends among Water Quality, Customer Complaint, and Diarrhea Illness Data at the Time of the 1993 Milwaukee Cryptosporidium Outbreak Investigation .....	66
Figure 3–3 Customer Feedback Descriptors used by Utilities to Detect 21 Contamination and Infrastructure Access Incidents, 1990–2005 .....	67
Figure 3–4 The Recommended Filter, Funnel, and Focus Approach to Customer Feedback Data Optimization .....	68
Figure 3–5 Three Tier Approach to Customer Feedback Data Coding .....	69
Figure 3–6 Proposed Drinking Water Industry Check Sheet .....	70

### Chapter 4

Figure 4–1 Techniques Used to Analyze HDPE Samples from the 5,000 mg/L Cl <sub>2</sub> Aging Method .....	96
Figure 4–2 Techniques Used to Analyze HDPE Samples from the Temperature/Chlorine Matrix Aging Method .....	97
Figure 4–3 HDPE pipe sample surface images obtained using optical microscopy .....	98
Figure 4–4 Some HDPE resin (left) and HDPE pipe (right) samples can be seen resting on the bottom of a 1L bottle containing reagent water on Day 28 (672 hr) .....	99
Figure 4–5 Change in sample mass during 23 °C desiccation for or (a) HDPE resin and (b) HDPE pipe samples exposed to chlorinated water (5,000 mg/L as Cl <sub>2</sub> , pH 6.5, 70 °C, no calcium carbonate added) for 9 (216 hr), 14 (336 hr), and 28 days (336 hr). .....	100

Figure 4–6 Comparison of Oxidation Induction Time Results for New HDPE Pipe and HDPE Pipe Aged in 45 mg/L as $\text{Cl}_2$ , 37 °C Solution.....	101
Figure 4–7 HDPE Pipe Oxidation Induction Time Changes for the Accelerated Aging Treatments .....	102
Figure 4–8 Infrared Spectrum for New HDPE Pipe and HDPE Pipe Aged in 45 mg/L as $\text{Cl}_2$ , 37 °C Aging Solution as Wave Number vs. Transmittance (%) .....	103

## Chapter 5

Figure 5–1 Two–Dimensional Molecular Structure of (a) HDPE, (b) Peroxide Crosslinked PE, and (c) Silane Crosslinked PE Materials .....	134
Figure 5–2 Sorption Data and Curves for (a) Toluene, (b) Benzaldehyde, (c) MTBE, and (d) 1–Butanol in PEX–A Pipe .....	135
Figure 5–3 Relationships between Material Bulk Density and Contaminant Solubility for (a) Nonpolar and (b) Polar Contaminants .....	136
Figure 5–4 HDPE Pipe Contaminant Solubility Relationships for (a) Dipole Moment, (b) Log $K_{ow}$ , and (c) Molar Volume .....	137
Figure 5–5 Relationships between Material Bulk Density and Contaminant Diffusivity for (a) Nonpolar Contaminants and (b) Polar Contaminants.....	138
Figure 5–6 HDPE Pipe Contaminant Diffusivity Relationships for (a) Dipole Moment and (b) Molar Volume. ....	139

## Chapter 6

Figure 6–1 Representation of Polyethylene Degradation due to Chlorinated Potable Water Exposure .....	165
Figure 6–2 Infrared Spectra for (a) HDPE Pipe and (b) PEX–B Pipe Surfaces during Accelerated Aging in 45 mg/L as $\text{Cl}_2$ , 50 mg/L as $\text{CaCO}_3$ at 37 °C.....	166
Figure 6–3 Change in Oxidation Induction Time for HDPE Resin, HDPE Pipe, PEX–A Pipe, and PEX–B Pipe during Accelerated Aging in 45 mg/L as $\text{Cl}_2$ , 50 mg/L as $\text{CaCO}_3$ at 37 °C .....	167
Figure 6–4 Sorption Data and Curves for (a) Toluene, (b) Benzaldehyde, (c) Benzyl Alcohol, and (d) 1–Butanol in New PEX–A Pipe .....	168
Figure 6–5 Relationship between Contaminant (a) Solubility and (b) Diffusivity in New and Lab Aged PEs for Nonpolar and Polar Contaminants.....	169
Figure 6–6 Relationship between Lab Aged PEX–B Pipe Contaminant Solubility and Contaminant (a) Molar Volume, (b) Log $K_{ow}$ , and (c) Dipole Moment .....	170
Figure 6–7 Comparison of New and Lab Aged Polyethylene Diffusivity for (a) Benzaldehyde, (b) 2–Butanone, (c) 2–Propanone, and (d) 1–Butanol .....	171
Figure 6–8 Statistically Significant Relationships between Lab Aged Polymer Bulk Density and Contaminant Diffusivity .....	172

Figure 6–9 Infrared Spectrum for (a) New HDPE Pipe from a Plumbing Supply Store and Water Utility PE (wu–PE) Pipe Samples Removed from a Buried Water Distribution System after Chlorinated Water Exposure, (b) wu–PE 1 (7 year exposure), (c) wu–PE 2 (20 year exposure), (d) wu–PE 3 (25 year exposure) .....	173
---	-----

## Chapter 7

Figure 7–1 Sorption and Desorption Data and Curves for (a) Toluene, (b) Benzaldehyde, (c) MTBE, and (d) 1–Butanol in New and Lab Aged PEX–A Pipe .....	202
Figure 7–2 Statistically Significant Relationships between Material Bulk Density and Contaminant Diffusivity for (a) New and (b) Lab Aged Polyethylene .....	203
Figure 7–3 Relationship for Contaminant Diffusivity during Desorption with New and Lab Aged Polyethylene .....	204
Figure 7–4 Relationship between Contaminant Diffusivity during Sorption and Desorption for (a) New and (b) Lab Aged Polyethylene .....	205



## Author's Preface & Attribution

This dissertation is a compilation of seven manuscripts as Chapters spanning three major industries: public health, potable water, and material science. Each manuscript is meant to stand individually and within each manuscript is a review of the scientific literature as it applies to the manuscript topic. Contributing authors and an abstract summarizing the results are provided at the beginning of each manuscript. Research explained in this dissertation contains significant scientific contributions spanning multiple disciplines.

Although each chapter is a separate manuscript, this dissertation is organized to explain results from four major projects. Chapter 1 was partially funded by National Science Foundation (NSF) *Project CMMI-0329474 BE-MUSES: Towards Sustainable Materials Use for Drinking Water Infrastructure*. Chapters 2 and 3 stem from research conducted under a jointly funded American Water Works Association Water Industry Technology Action Fund and American Water Works Association Research Foundation (AwwaRF) Project 3140, *Pilot Study on the Integration of Customer Complaint Data With Online Water Quality Data As an Early Warning System, 3140*. Chapters 5–7 were partially funded under two different grants: AwwaRF Unsolicited Research Program Project 4138, *Evaluating Critical Relationships Between New and Aged Polyethylene Water Pipe and Drinking Water Contaminants Using Advanced Material Characterization Techniques*, and the NSF, Chemical, Bioengineering, Environmental, and Transport Systems Environmental Sustainability Program Project CBET-0755342, *Engineering and Chemistry of Sustainable Polyethylene Water Infrastructure*. Additional funding for this work was received from the Macromolecular Interfaces at Life Science Integrated Graduate Education and Traineeship (IGERT) Program at Virginia Tech funded by the National Science Foundation, and Virginia Tech Graduate Student Research Development Program.

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Daniel L. Gallagher, Ph.D., P.E. (Dept. Civil & Environmental Engineering, Virginia Tech) is an Associate Professor and contributed to this research in terms of discussing research ideas, designing and developing a computational program for compiling data, and conducting some statistical analysis, and document revisions.

Brian J. Love, Ph.D. (Dept. Materials Science & Engineering, University of Michigan, formerly at Virginia Tech) is a Professor and contributed to the discussion and appropriateness of polymer characterization and aging techniques.

James Tanko, Ph.D. (Dept. Chemistry, Virginia Tech) is a Professor and contributed to the discussion of the polymer oxidation principles in aqueous environment and polymer aging experimental plan, as well as interpretation of polymer surface oxidation results.

Marc A. Edwards, Ph.D. (Dept. Civil & Environmental Engineering, Virginia Tech) is Charles Lunsford Professor of Civil Engineering in the College of Engineering and 2007 John D. and Catherine MacArthur Fellow. Dr. Edwards contributed to this study in terms of discussing aquatic chemistry aspects of polymer accelerated aging methods.

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**Chapter 5, 6, and 7:** As explained previously, Dr. Gallagher contributed to designing and developing a computational program for compiling data used in these chapters, conducted some statistical analysis, and revised these chapters.

## **Chapter 1 Minerals in Drinking Water: Impacts on Taste and Importance to Consumer Health**

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### **1.1 Abstract**

More than 100 years of research has focused on removing acute and chronic health threats to produce safe drinking water, but limited research has focused the consequences of removing minerals that affect drinking water taste and health. This manuscript covers the human sense of taste, typical variations in drinking water taste, comparisons of global taste standards, the role of water chemistry, and future research needs for understanding consumer preference. Results of several consumer tap and bottled water acceptability investigations conducted by the authors are presented.

**Keywords:** Bottled water; hardness; health; minerals; odour; taste

### **1.2 Introduction**

Safe drinking water standards are heavily enforced in nations around the world to reduce consumer risk to acute and chronic health threats. While much research in the past 100 years has centered upon reducing contaminant health risk, the importance of taste and effects of removing vital nutrients during treatment has received little attention. In the absence of this research, “many consumers believe that natural mineral waters have medicinal properties or offer other health benefits” (WHO, 2005). Research has not shown this linkage, but has revealed that the taste of drinking water can significantly impact consumer health.

Water is vital to life and taste has a profound effect on a person’s willingness to drink water. When consumers encounter an unacceptable tasting drinking water they typically seek out alternate water sources (Levallois et al., 1999). The explosive growth of the bottled water

industry can be attributed to this notion (Kolodziej, 2004). In addition, the emergence of point-of-use/point-of-entry water treatment devices and their installation in buildings and at consumer taps also signals that consumers are searching for ways to improve drinking water taste (Mackey et al., 2003).

Drinking water consumers are also searching for ways to improve their health. Researchers have proven that taste and a consumer's level of hydration and disease state are related. Under strenuous conditions, water intake volume can vary as a function of drinking water taste (Szlyk et al., 1989; Szlyk et al., 1990; Szlyk et al., 1998). Bad tasting water can prompt consumers to increase their risk of disease by seeking out a nonpotable, but more palatable water source. This scenario is a significant concern to people around the world who must forage and treat their own drinking water.

On a global level, nutrient intake from drinking water is an emerging health concern. As advanced water treatment/membrane processes remove more and more minerals, the nutritional value of the product drinking water is questioned. In many cases minerals are added back into treated water to prevent distribution system infrastructure corrosion. Questions though remain of which vital nutrients and how much of each are needed for taste and health benefits. While researchers have proven that minerals are vital to nutrition and defense against disease, no one has determined the optimal drinking water mineral content necessary to maintain or improve health.

Limited research has focused the consequences of removing minerals that affect drinking water taste and health. The objectives of this manuscript were to (1) review the human sense of taste and typical variations, (2) compare global taste standards, (3) evaluate the role of water chemistry, and (4) identify future research needs for understanding consumer preference. Results of several consumer tap and bottled water acceptability investigations conducted by the authors are presented.

### **1.3 Consumer Sensitivity to the Taste of Drinking Water**

Consumers smell, taste, and visually assess drinking water to form preferences. They feel it in their mouths, and sometimes listen to it as it pours into their glass. Water quality judgments are then made before, during, and after tasting. Sweet, sour, bitter, salty, and umami are the five

basic tastes consumers attribute to foods. Other descriptors are also used for water such as metallic, musty, and chlorinous, but these are not widely accepted tastes (Mallevialle and Suffet, 1987; Dietrich, 2006).

Psychological and physiological factors also influence drinking water preferences. Psychological factors include personal experience, memory, and external stimuli. Physiological factors include biochemistry, physical body factors, age, health, and external factors such as humidity and temperature. Flavorants can also enhance tastes such as sweetness and bitterness (Frank et al., 1993).

Consistency is one of the most important factors in consumer product satisfaction. Consumers do not want variations in their drinking waters. Individuals can notice changes to their local water quality—whether it is tap or bottled water (McGuire, 1995; Lawless and Heymann, 1998). Based on the consumers' ability to detect changes in product consistency and their location in distribution systems, Whelton (2003) proposed that utilities monitor consumer feedback.

In US and Canadian surveys, the taste of water was found to be an important factor for consumers. A US survey of more than 1,700 bottled water users found that 39% chose bottled water because it tasted better, while only 18% said it was because of safety (Kolodziej, 2004). In another US survey concerning home plumbing and drinking water, 76% said aesthetics (taste, odor, and color) were important factors and one of the reasons why they used in-home treatment devices (Kleczyk et al., 2005). A Canadian survey also revealed that about 50% of 2,009 people surveyed consumed tap water, and of those, 30% were dissatisfied with taste or flavor (Levallois et al., 1999).

## **1.4 Exploring the Role of Water Chemistry**

### **1.4.1 World Variations, Standards, and Non-Mineral Influential Factors**

Waters are found in many “natural” flavors. Surface waters usually have higher dissolved oxygen, microbial, organic matter, and particulate content as well as experience temperature variations from near freezing to warm. Ground waters typically maintain a constant cool temperature but contain a higher mineral content, with fewer microorganisms and particulates. Water can be an important source of nutrients and micronutrients, such as calcium and copper

and their concentration can be higher in hard waters. Other minerals can add salty, sweet, or bitter tastes to water and are responsible for much of a waters' "mouth feel".

Consumers typically taste common chemicals before they reach levels that affect health. The taste threshold concentration (TTC) is the concentration at which consumers can detect a taste, whereby below this level a taste is not detected. TTCs are highly dependant on the ions, associated ions, pH, and water temperature (WHO, 2004). TTCs are also dependant on a person's prior flavor evaluation experience, local water treatment practices, and background tastes (Piriou et al., 2004).

Many drinking water taste standards worldwide are based on mineral content. Claes et al. (1997) reported significant differences in maximum admissible mineral concentrations in drinking water for 13 Eastern and Western European countries. Some mineral standards reported include copper (0.1–3.0 mg/L), iron (0.1–0.5 mg/L), manganese (0.05–2.0 mg/L), and zinc (1.0–5.0 mg/L). **Table 1–1** compares standards from Canada, Europe, and the US (van der Leeden et al., 1990; WHO, 2004).

Water temperature is one of the most important factors influencing taste intensity and an individual's degree of liking for a water (Pangborn and Bertolero, 1972; Zellner et al., 1988). Ideal drinking water temperature is 15–25°C (cooler than body temperature). Tap water varies between 4–60°C.

Water pH also strongly influences drinking water taste. A pH range of 6.5–8.5 is desirable to avoid a bitter taste. Outside this range, a metallic taste can occur at <pH 6.5, and a slippery feel or soda taste at >pH 8.5. Tap water pH is typically 7–8, but can vary from 5–11. Water pH can also influence bicarbonate and carbonate levels.  $\text{HCO}_3^-/\text{CO}_3^{2-}$  influence taste by combining with cations (e.g.,  $\text{NaHCO}_3$ ,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Na}_2\text{CO}_3$ ).

#### **1.4.2 Mineral Sensitivity**

Total dissolved solids (TDS) is used to assess mineral content and is dependent on water source, local geology, and treatment scheme. TDS is a measure of the cations including  $\text{Al}^{+3}$ ,  $\text{Fe}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and anions such as  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ . According to Daniels (1988), when TDS is 1,000 mg/L, approximately 2% of the adult

population may refuse to drink water, while at  $\text{TDS} \geq 2,800 \text{ mg/L}$ , 50% of the same population might refuse this water. Daniels (1988) conclusions were based on work conducted by Bruvold and Ongerth (1969). Typical tap water ranges for low, moderate, and high TDS waters are  $<100$ ,  $101\text{--}250$ , and  $251\text{--}500 \text{ mg/L}$  concentrations, respectively. Water close to zero TDS has a flat taste. US drinking water palatability assessments have revealed the following TDS ratings:  $80 \text{ mg/L}$  excellent,  $81\text{--}450 \text{ mg/L}$  good,  $451\text{--}800 \text{ mg/L}$  fair,  $801\text{--}1,000 \text{ mg/L}$  poor, and  $>1,000 \text{ mg/L}$  unacceptable (Bruvold and Daniels, 1990).

Hardness also impacts taste and is a measure of multivalent metallic cations. Hardness primarily includes  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ , while  $\text{Sr}^{+2}$ ,  $\text{Fe}^{+2}$ , and  $\text{Mn}^{+2}$  also contribute usually to an insignificant degree. Soft, moderately hard, hard, and very hard tap water contains  $0\text{--}75$ ,  $76\text{--}150$ ,  $151\text{--}300$ , and  $>300 \text{ mg/L}$  as  $\text{CaCO}_3$  concentrations, respectively. Because all previously mentioned hardness constituents but  $\text{Sr}^{+2}$  contribute to TDS, hard waters are associated with high TDS concentrations. However, due to the differences between hardness and TDS, hardness can remain unchanged as TDS increases (e.g., increased  $\text{K}^+$  and  $\text{Na}^+$  concentrations do not affect hardness). In the US, the Food and Drug Administration defines bottled “mineral water” as having a TDS value of  $\geq 250 \text{ mg/L}$  though this water may or may not be considered as hard (van der Aa, 2003).

Cations such as calcium, sodium, and potassium impact drinking water taste. Calcium is common in water at levels found in saliva, and is also important in cellular metabolism and human health. Tastants such as  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{CaSO}_4$ ,  $\text{CaCl}_2$  are likely to be dissolved in tap water. Calcium’s TTC is  $100\text{--}300 \text{ mg/L}$  (WHO, 2004). A neutral taste is encountered where  $\text{CaCl}_2 < 120 \text{ mg/L}$  and  $\text{Ca}(\text{HCO}_3)_2 > 610 \text{ mg/L}$ , though when  $\text{CaCl}_2$  is at levels  $> 350 \text{ mg/L}$ , water is disliked. Sodium is also commonly found in water (TTC =  $200 \text{ mg/L}$ ). The optimum sodium concentration is  $125 \text{ mg/L}$  for distilled water and is typically found as  $\text{NaHCO}_3$  and  $\text{Na}_2\text{SO}_4$ . Water is disliked when  $\text{NaHCO}_3$  exceeds  $630 \text{ mg/L}$  and  $> 75 \text{ mg/L}$   $\text{Na}_2\text{CO}_3$ . Potassium is typically present at low levels as  $\text{KHCO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{KCl}$ , and is important at the cellular level of the taste buds. A low potassium concentration has positive effects on water acceptance.  $\text{KCl}$  acts similar to  $\text{NaCl}$  in taste effects.

Metals such as magnesium, iron, copper, zinc and manganese influence taste. The level of magnesium that people report as having an objectionable taste is affected by the anion with

which it is associated. Magnesium is typically present in water as  $\text{MgCO}_3$ ,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{MgSO}_4$ , and  $\text{MgCl}_2$ , can impart an astringent taste, and can be tasted at 100–500 mg/L (Lockhart et al., 1955). Water containing magnesium salts at 1,000 mg/L has been considered acceptable (Bruvold and Pangborn, 1966). Consumers dislike water containing  $\text{MgCl}_2 > 47$  mg/L and  $\text{Mg}(\text{HCO}_3)_2 > 58$  mg/L. Iron is typically present in soluble, suspended, or hydroxide forms, and can be tasted at 0.1–1.0 mg/L. Most iron drinking water standards are 0.3 mg/L because of laundry staining, turbidity, and color formation, but iron can also impart a bitter or metallic taste. Copper can be detected at  $< 1$  mg/L; although, when the copper concentration exceeds about 4 mg/L, gastrointestinal upset, a bitter taste, and toxicity can occur (Cohen et al., 1960; Pizzaro et al., 1999; Dietrich et al., 2004). Zinc can be detected as  $\text{ZnSO}_4$  at 4 mg/L. Manganese has been found to impart an astringent taste ( $\text{TTC} = 0.05$  mg/L). Manganese levels should be low in tap water, near levels found in saliva.

Anions such as bicarbonate, chloride, and sulfate also impact taste. At neutral pH the bicarbonate is more common than carbonate and helps keep cations in solution. Much lower levels of bicarbonate occur in tap water than would be found in saliva. In contrast, carbonate increases at higher pH and at lower dissolved  $\text{CO}_2$  levels. Aeration also adds  $\text{O}_2$  and removes  $\text{CO}_2$ , promoting carbonate precipitation. The TTC for chloride is 200–300 mg/L (Richter and MacLean, 1939; Lockhart et al., 1955). Increased chloride levels in water, in the presence of sodium, calcium, potassium, and magnesium can cause water to become objectionable. Preference testing has revealed that water containing  $\text{NaCl} < 290$  mg/L is acceptable and  $\text{NaCl} > 465$  mg/L is disliked. Saliva contains  $\text{NaCl} > 500$  mg/L. Testing also indicates that  $\text{CaCl}_2 < 120$  mg/L is neutral, while  $\text{CaCl}_2 > 350$  mg/L is disliked. Tap water chloride concentrations should be well below concentrations that cause salty taste problems and levels found in saliva. Sulfate has minimal taste impact at low levels ( $\text{TTC} = 200\text{--}400$  mg/L). Sulfate though can act as a laxative at high levels and impart a salty taste. Common aqueous sulfate compounds include  $\text{CaSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ , and  $\text{K}_2\text{SO}_4$ . Consumers dislike water containing  $\text{Na}_2\text{SO}_4 > 1,000$  mg/L,  $\text{MgSO}_4 > 840$  mg/L, and  $\text{CaSO}_4 > 1,020$  mg/L. The taste of distilled water is improved when  $\text{CaSO}_4 > 270$  mg/L. Sulfate also suppresses magnesium and reduces effects of calcium. Tap water should contain low levels of sulfate.



## **1.5 Consumer Taste Studies**

### **1.5.1 Military Drinking Water Acceptability**

A US Army study determined the acceptability of chlorinated field drinking water (Whelton et al., 2004). This investigation was conducted in response to taste and odor complaints from field soldiers. A five point scale was used to rate water acceptability: unacceptable, somewhat unacceptable, neither acceptable or unacceptable, somewhat acceptable, and acceptable. Bottled water Brand A samples were presented to panelists and contained 0, 1, 2.5, and 5 mg/L free chlorine concentrations, pH 7.1–7.4, and were chilled (0 °C), room temperature (21 °C), and warm (35 °C).

The two most acceptable waters based on the participants selecting them were served chilled and at room temperature. The two most unacceptable waters were those that were warm. Preferences were significant based on water temperature and not chlorine concentration. In all cases, the participants felt that the colder water sample was more acceptable than the warmer one. Pangborn and Bertolero (1972) and Whelton and Dietrich (2004) have proven that water temperature and free chlorine concentration affect a person's perception. Based on previous research, field equipment is being outfitted with water chillers to improve drinking water taste (Ryzack, 2004).

### **1.5.2 Preference Testing for Tap vs. a COTS Filtered Tap Water**

Consumer preference and difference testing was performed on tap water from a conventional surface water treatment plant that used free chlorine. The same tap water was filtered by a commercial-off-the-shelf (COTS) filter that was comprised of granular activated carbon and ion exchange resin (Cuppett, 2004). Water samples were evaluated using discrimination and preference tests.

The ionic and carbon content of the waters are presented in **Tables 1–2 and 1–3**. Results indicate that the filter removed about 80% of the free chlorine, 30% of the inorganic and organic carbon, and about 15% of the TDS. The COTS filter specifically removed 85% of the calcium, 80% of the magnesium, and increased the sodium and potassium by 11% and 900%, respectively. Discrimination testing (which determines whether a difference can be detected) revealed a significant difference between the tap and filtered water samples. In a separate 56

person paired-comparison test (which determines if one water is preferred over another water), no significant preference for the tap or filtered water samples was found. While panelists could detect a difference between the two waters they did not prefer one water over another. Results also indicated that individuals detected differences in the chlorine and mineral content of water, but their ability to detect a difference did not influence a preference based on chlorine and/or mineral content.

### **1.5.3 Comparison of Tap and Commercial Bottled Waters**

One tap water source and seven commercial bottled waters were analyzed to determine how water quality parameters might be associated with taste perception at room temperature (**Tables 1–4 and 1–5**). Results indicate that Brand A bottled water samples were found different than Brand B bottled water due to a plastic taste. Also, neither Brand A nor Brand B could be differentiated from distilled water. Additional findings were that Brand B could be differentiated from Philadelphia tap water (mean pH 7.2) due to a plastic taste and lack of chlorinous, musty, and metallic tastes. Brand A bottled water could not be differentiated from Philadelphia tap water. Mean Philadelphia tap water levels are (mg/L): total hardness (88), TDS (175), alkalinity (41),  $\text{Ca}^{+2}$  (26),  $\text{Mg}^{+2}$  (6),  $\text{Na}^{+}$  (18),  $\text{K}^{+}$  (1.9),  $\text{Cl}^{-}$  (50),  $\text{SO}_4^{-2}$  (16),  $\text{NO}_3^{-}$  (1.1).

### **1.6 Conclusion**

The optimum mineral content for excellent drinking water taste and improved health has not been thoroughly investigated. Literature reports have identified a strong link between taste and consumer health. Several studies in our laboratories indicate that consumers can taste the differences between some but not all brands of bottled water and their local tap water. Many individuals can also perceive differences in water quality or detect off-tastes at values well below those indicated by drinking water taste standards of nations worldwide. Our results identify that different individuals have different preferences and these preferences can directly relate to mineral content. Research is needed to identify specific drinking water characteristics and concentrations that cause consumers to choose to seek another water source, purchase a household treatment device, or purchase bottled water. Existing drinking water standards are based on individual constituent taste tolerances. **Table 1–6** provides a summary of information concerning drinking water minerals and their effect on taste.

## 1.7 Acknowledgement

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**Table 1–1 Comparison of Canadian, European Economic Community (EEC), US, and World Health Organization (WHO) Drinking Water Regulations, Concentration, mg/L**

<b>Contaminant</b>	<b>WHO Guideline</b>	<b>EEC Guide Level</b>	<b>EEC MAC<sup>1</sup></b>	<b>US SMCL<sup>2</sup></b>	<b>Canadian MAL<sup>3</sup></b>
Chloride	250	250	NS <sup>4</sup>	250	250
Sulfate	400	250	NS	250	500
Copper	1.0	0.100 at WTP <sup>5</sup> ; 3.0 after 12 hr. in pipe	NS	1.0	1.0
Iron	0.3	0.050	0.300	0.3	0.3
Manganese	0.1	0.020	0.050	0.05	0.05
Zinc	5.0	0.100 at WTP; 5.0 after 12 hr. in pipe	NS	5	5
pH	6.5–8.5	6.5–8.5	NS	6.5–8.5	6.5–8.5
TDS	1000	NS	NS	500	500

1. Maximum admissible concentration; 2. Secondary maximum contaminant level; 3. Maximum allowable level; 4. No standard; 5. Water treatment plant.

**Table 1–2 TDS, TOC, IOC, Cation, and Free Chlorine Levels of Tap and Filtered Tap Waters**

Water Type	Concentration, mg/L			Concentration of Cations, mg/L					Free Chlorine, mg/L as Cl <sub>2</sub>
	TDS	TOC	IOC	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>+2</sup>	Ca <sup>+2</sup>	
Tap	61.72	0.752	9.94	8.92	<0.5	1.05	4.89	13.00	1.10
Filtered	53.13	0.501	6.69	10.20	<0.5	10.04	1.09	1.96	0.20

1. TDS = Total dissolved solids; TOC = Total organic carbon; IOC = Inorganic carbon

**Table 1–3 Anion Contents of Tap and Filtered Tap Waters**

Water Type	Concentration of Anions, mg/L						
	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup> as N	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup> as N	PO <sub>4</sub> <sup>-2</sup> as P	SO <sub>4</sub> <sup>-2</sup>
Tap	0.73	13.72	<0.5	NT <sup>1</sup>	0.63	<0.5	7.00
Filtered	0.72	15.54	<0.5	NT	<0.5	<0.5	6.19

1. Not tested

**Table 1–4 Water pH, Hardness, and TDS Analyses Results of Four of Seven Bottled Waters**

Water Brand <sup>1</sup>	pH (pH unit)	Total Hardness (mg/L as CaCO <sub>3</sub> )	Hardness Rating	TDS (mg/L)	TDS Rating
A	6.0	<1	Soft	4	Low
B	6.5	<12	Soft	21	Low
C	7.4	>255	Very Hard	319 (309 <sup>2</sup> )	High
D	7.5 (7.5 <sup>1</sup> )	90.5	Moderately Hard	214 (210 <sup>2</sup> )	Moderate

1. Samples E, F, and G were not tested for pH, hardness, and TDS levels; 2. Water quality results listed on product label



**Table 1–5 Anion and Cation Analyses Results of All Seven Bottled Waters**

Water		Water Quality Parameter, mg/L								
Brand	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>+2</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Mg <sup>+2</sup>	Alk. <sup>3</sup>	NO <sub>3</sub> <sup>-</sup>	SiO <sub>2</sub>
A	0.8	0.08	<0.1	NT <sup>2</sup>	<5	<5	<0.1	3	<.25	NT
B	3.5	3.0	<0.1	NT	5.3	11	2.9	6	<.25	NT
C	5.9, 7.2, 7.9	0.9, 0.99, 1.3	78, 83, >60, (78 <sup>1</sup> )	NT, (357 <sup>1</sup> )	4.6,4.7, 6.5, (4 <sup>1</sup> )	11, 11, 12, (10 <sup>1</sup> )	27, 35, 26, (24 <sup>1</sup> )	288	0.75	NT, (14 <sup>1</sup> )
D	19	4.4	16.2, (17 <sup>1</sup> )	140, (140 <sup>1</sup> )	9.7	<5	12.1, (13 <sup>1</sup> )	125	0.26	NT, (85 <sup>1</sup> )
E	2.2	2.7	74, 97	NT	2.5, 2.6	15, 15	20, 25	NT	NT	NT
F	0	0	0	NT	0.5	0	0	NT	NT	NT
G	NT	0.5, 0.6	162, 170	NT	NT	38, 41	4.1, 4.3	NT	NT	NT

1. Water quality results taken from product label; 2. Not tested; 3. Alkalinity

**Table 1–6 Summary of Mineral Affects on the Taste of Drinking Water**

Constituent	Influence on Taste	Taste Implications
Cl <sup>-</sup>	Neutral or Negative	Acceptance decreases when Na <sup>+</sup> and K <sup>+</sup> present.
SO <sub>4</sub> <sup>-2</sup>	Negative	Avoid usage; Ca <sup>+2</sup> and Mg <sup>+2</sup> preferred over sodium forms.
HCO <sub>3</sub> <sup>-</sup>	Positive or Neutral	Bicarbonate preferred to carbonate and carbonic acid.
Ca <sup>+2</sup>	Positive or Neutral	Acceptance dependant on Cl <sup>-</sup> .
Na <sup>+</sup>	Positive or Neutral	Acceptance decreases when Cl <sup>-</sup> present.
K <sup>+</sup>	Positive	Acceptance decreases when Cl <sup>-</sup> present.
Mg <sup>+2</sup>	Neutral or Negative	Acceptance decreases at high levels.
Cu <sup>+2</sup> , Fe <sup>+2</sup>	Negative	Use low levels; Do not exceed 0.1–1.0 mg/L.
Mn <sup>+2</sup> , Zn <sup>+2</sup>	Negative	Use low levels; Do not exceed 0.1–1.0 mg/L.
Hardness	Neutral or Negative	Acceptance decreased for hard waters/ high pH.
pH	Neutral or Negative	Near neutral pH preferred; High/Low pH could promote carbonate and carbonic acid.
TDS <sup>1</sup>	Variable	High levels can approach mineral water.

1. Different populations have different preferences for mineral content.

## **Chapter 2 Customer Feedback Tool for Distribution System Monitoring for Improved Drinking Water Surveillance**

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### **2.1 Abstract**

A US pilot study revealed that regular analysis of customer feedback data has the potential to be an effective drinking water contamination event monitoring technique. The pilot study involved onsite interviews and data analyses at 13 water utilities that served 30,000 to >8,000,000 customers. A literature review and regional survey of 16 utilities that served 1,400 to >1,000,000 were also conducted. Project results revealed that customer feedback has been used to uncover >56 incidents (e.g., water main breaks, treatment failures, contamination events, and intrusion attempts). Utilities visited used between 10–197 different feedback categories, with appearance, illness, organoleptic, suspicious activity, and flow being the most useful. No uniform water industry standard exists for coding and handling drinking water customer feedback. Of the utilities visited, 83% used customer call centers, 50% of the call centers directly transferred the customer to another utility department without entering data, and 50% of utilities stored customer feedback data in a database. Employee experience (100%) determined whether or not a customer concern required immediate attention (n=13). Analyses of utility consumer feedback data tended to be monthly which could not detect an immediate problem. Few utilities visited (6/13) and surveyed (1/16) used charts or graphs. Analyses of one utility's records revealed that the number of customer calls varied based on time of year, month, and day of week. The amount of historical customer feedback data stored at each utility varied from 1–4 years. Operations and Maintenance (O&M) and Water Quality (WQ) departments were the most likely to be forwarded customers who had water system operation, drinking water quality, and health concerns. Onsite actions conducted by O&M personnel would include flushing of nearby hydrants, while WQ representatives would typically interview the customer, enter the customer's

building, and collect and test water samples. 92% of the utilities visited dispatched only one representative to the customer's building. The onsite response time depended on the type of concern, time it was received, day of week, personnel workload, and resources. 60% of the utilities permitted employee entry into the customer building. Disinfectant residual (free and combined chlorine) was the most common onsite analyses parameter and significant changes in it were considered to indicate a problem and/or the presence of a contaminant. Drinking water illness complaints were considered to be unfounded if disinfectant residual and pH results were within acceptable limits and bacteria test results were negative. Before customer feedback monitoring can be effectively implemented, utilities must optimize information flow, communication, storage, investigative procedures, and consistent terminology.

**Keywords:** Customer feedback, surveillance, drinking water, complaint, monitoring

## **2.2 Introduction**

The detection of water quality problems, such as low disinfectant residual or cross-connections as well as accidentally or intentionally caused problems in water distribution system networks is critical to protecting consumer health and infrastructure. Water utility staff must quickly identify when and where drinking water exists that has reduced quality, poses a consumer health threat, or an operational risk to distribution infrastructure. Swift discovery and response can limit the population and infrastructure exposed as well as prevent loss of customer confidence or negative economic impacts.

To better protect public health and infrastructure, water utilities need better detection techniques to identify contamination and access incidents in their distribution system (GAO, 2003). Current thinking is that water utilities need a comprehensive and integrated early warning system (EWS) (Roberson and Morley, 2005; EPA, 2005). An EWS is a system that monitors, analyzes, interprets, and communicates data used to make protective public health decisions. Ideally EWSs should consist of a series of water quality monitoring platforms that alerts utility staff when an anomaly has occurred in the distribution network. Unfortunately, “viable integrated drinking water EWSs ... are several years away” (EPA, 2005). In absence of this all-inclusive online monitoring system, water utilities must develop and optimize other surveillance strategies.

Monitoring of customer input for improved surveillance is one proposed strategy that has the potential to work well into an EWS (Whelton, 2003; Whelton et al., 2004; Dietrich, 2006). In the past, customer complaints have been scrutinized by drinking water providers due to their unique nature of providing insight into the water quality reaching consumer taps. Burlingame (2006) found that "consumers can provide useful, real-time data on drinking water-related concerns." Specifically, several utilities have used customer complaints to identify the occurrence of algal blooms in source waters that have resulted in malodorous byproducts in finished drinking water. Other utilities have used customer input to also identify changes in source water quality as well as the effectiveness of treatment operations, and the occurrence and extent of distribution operational and water quality problems (McGuire and Burlingame, 2004).

Customers are everywhere in the distribution system and they evaluate their water for safety, aesthetics, and quantity. If the water does not meet their expectations or they suspect their drinking water is making them sick, they contact their utility and complain. However, customers also report observations of activities at water utility assets (tanks, hydrants, fences) and concerns. By this analysis, customer "feedback" is the more appropriate term. Water utilities provide service to their customers, who in turn provide feedback to the utility that can be used to help improve product quality and operations.

## **2.3 Project Purpose and Participants**

This project examined the ability of American water utilities to harness consumer feedback to detect contaminated drinking water and protect consumer health and infrastructure. The project included historical reviews of literature reported contamination events, thirteen onsite utility visits, and a regional survey of sixteen water utilities.

## **2.3 Methods**

### **2.3.1 Utility Visits**

Interviews with utility as well as several local health department personnel were conducted at 13 water utilities around the USA. These utilities served a median of 500,000 customers and varied in size treatment, disinfectant, and geographical location (**Table 2–1**). One utility was a wholesaler, did not have a direct service population, but provided water to five other utilities. Several utilities operated more than one water system. Because of this, multiple

disinfectants were used at each utility. Forty–six percent of the utilities visited used free available chlorine as a residual disinfectant, while 67 percent used combined chlorine.

### **2.3.2 Regional Survey**

Survey data were also obtained from sixteen different drinking water utilities. Utility respondents represented Virginia utilities and one from Tennessee that serve between 1,400 to more than 1,000,000 consumers. The median utility service population was estimated to be approximately 62,500. Utilities included in this survey served small towns as well as major urban centers and some provide water to more than 8 communities. Respondents who filled out the questionnaire held mainly utility laboratory positions.

## **2.4. Results and Discussion**

### **2.4.1 Significance**

Evaluation of historical literature and onsite staff interviews revealed that consumer complaints were frequently the first indication of a problem for more than 56 incidents. Customer reported problems involved drinking water appearance, illness reports, organoleptic quality, and water flow problems, as well as suspicious activity around water system assets. By investigating these customer reports utilities uncovered not only water main breaks, but treatment failures, contaminated water events and intrusion attempts.

### **2.4.2 Customer Contact Handling**

No uniform standard exists within the water industry for coding and handling drinking water customer feedback. All utilities reported receiving customer feedback regarding billing, service issues, as well as facilities, water quality, and overall perception of drinking water safety. **Figure 2–1** shows the general flow path of customer concerns through a utility.

Most utilities visited relied upon County, City, or Utility call center staff (83%) to field drinking customer calls. For the two utilities that did not, all customer calls went directly to the water treatment plant operations desk. **Table 2–2** shows that the most common method for receiving customer calls was to transfer that customer to a utility department subject matter expert (SME) (e.g., billing, water quality, operations). Entry of customer concern data into a database during the initial contact occurred at less than half of the utilities visited. Attempting to answer the customer’s concern on the initial telephone call occurred at one–third of the utilities.

At utilities where customer service representatives (CSR) attempted to but could not answer customer calls regarding water quality and operations, the CSR would either transfer the customer to the department they deemed appropriate or instruct the customer that someone from the utility would call them back to discuss the problem.

To help Customer Service Center, Water Quality, or Operations staff handle customer inquiries, 50% of the utilities visited (n=12) used scripts or standard drinking water customer troubleshooting manuals. Scripts contained guidance on how to troubleshoot and solve several common customer concerns over the telephone (e.g., air in water, clogged aerator). Most utilities that used scripts provided them in paper form (4/6), while the remaining utilities made scripts available in electronic/ web-based form (2/6). Utility representatives using electronic/ web-based scripts strongly promoted their usefulness in troubleshooting customer concerns.

Data recording practices varied between and within utilities. Results of customer concerns addressed during the initial contact were not always recorded in a utility paper or electronic file. Recording practices were a function of utility-wide policy (if present), utility representative experience, and the position of the utility representative. Variable data recording practices resulted in incomplete customer feedback data sets. Incomplete data sets made historical analyses difficult.

#### **2.4.3 General Interview Questions, Department Call-Back, and Urgent Issues**

Several interview questions that were frequently asked for each customer concern are listed below. Initial questions focused on the customer's location (e.g., building) and subsequent questions revolved around describing the problem and environment. At the end of most initial customer interactions, utility representatives thanked the customer for their input. If customer concerns were resolved over the telephone (e.g., bubbles rose to the glass surface due to air in water), the utility representative advised the customer to call again if the problem persisted and situation did not improve. If the initial customer concern could not be resolved over the telephone, the CSR passed on the complaint to a SME investigator.

### **List of Common Questions Asked During Initial Customer Calls by Customer Service Representatives (CSR) and Utility Subject Matter Experts (SME)**

- Can you describe the problem?
- Is the problem at one faucet or throughout the building?
- When did you first notice the problem?
- Is the problem in both the hot and cold water?
- Has there been any recent plumbing work done on the premises? Has the water heater been turned off?
- Are you new to the premises?
- Have you noticed any unusual tastes or odors in the water?
- What is the phone number where a utility representative can reach you today?

If customer concerns were not answered during the initial contact, the CSR would pass the customer's information along to the appropriate department and a SME department representative would be assigned to follow-up. Operations and Maintenance and Water Quality departments were the most likely to be asked to follow-up with customers regarding water system operation and drinking water quality and health issues.

At most of the utilities visited (64%), a SME representative would first call the customer back to find out more about the reported problem. During this conversation, the SME would attempt to determine what caused the problem. If determined, the customer concern would be considered closed and depending on the data storage process used, this conversation and results may or may not be documented on a paper form or (least likely) in an electronic database. Instead of calling the customer to find out more about the customer's problem, other utilities instead directly dispatched a representative to the site to investigate (36%).

Determination of whether or not a customer concern required immediate attention was 100% based on employee experience. At all utilities the person receiving the call or communicating with the customer was the person solely responsible for making this determination. "Life-issues" such as no water or water outages warranted an immediate response



at all utilities. Other issues such as taste and odor or low pressure did not. The time before a utility representative would be dispatched onsite varied and is discussed later.

#### **2.4.4 Feedback Data Characteristics**

**2.4.4.1 Utility Comparison.** All utilities visited indicated that customer billing issues were the most common reason for a customer contacting the utility. The percentage of customer calls related to drinking water system operations and quality was reportedly far less than the number of calls the utility received from customers per day.

Of the utility representatives interviewed in Water Quality, Operations and Maintenance, Engineering, Security Departments, the most common explanation for the customer's problem regarding water quality or quantity was a building issue, not a utility caused problem. Building issues included odors in hot water heaters due to improper operation and dip tube disintegration, dirty sink drain odors, and pressure/water quality problems caused by clogged or deteriorated point-of-use devices. Problems caused by utility activities included suspended sediment, color, and pressure problems caused by main breaks and flushing activities as well as the presence of odor causing compounds (e.g., geosmin) due to ineffective treatment. The number one and two causes for utility related customer concerns were:

1. Discolored water / dirty water / particles in the water, and
2. Taste and odor

Aging infrastructure and system expansion that caused “dirty water” typically generated more customer drinking water concerns than water quality issues such as taste and odor.

Customer concerns were generally classified into one of many categories during the initial customer-utility contact. Utilities visited used between 10–197 different categories for coding customer feedback that related to several general categories: appearance, illness, organoleptic quality, suspicious activity, and water flow. Two utilities used a two tiered approach for logging customer feedback, whereby tier 1 was listed as the primary descriptor/problem (e.g., brown color) and tier 2 was the secondary problem (e.g., rotten-egg odor). The number of categories used did not correlate with system size or complexity. Also, duplication of similar descriptors was common within different categories. Several utilities indicated that categories

were added as Customer Service, Water Quality, and Operations representatives deemed appropriate.

Direct calculation and comparison of the number of customer concerns filed per month at each utility could not be conducted due to dissimilar data sets. During site visits, utility personnel were asked about the number of customer concerns they received per month. Depending on the representative being questioned (e.g., operations representative vs. lab supervisor vs. CSR), different numbers of complaints per month were provided within the same utility. Further investigation revealed that these numbers varied because the representative did not see all complaints, only those assigned to them, and those that were recorded in their database. For example, the laboratory supervisor only received taste and odor complaints and not pressure. Therefore, the laboratory supervisor provided data to the project team based on his/her taste and odor experience, not that of pressure. Also, customer service centers did not always record customer concerns into a database. Because of this, no comprehensive database existed where all customer concerns were stored. Until utilities develop a standard and consistent terminology and recording practices, quantitative customer concern frequency comparisons between utilities are limited.

**2.4.4.2 One Utility Example.** Customer concern data for one utility located in the Eastern US is provided. **Figure 2–2** shows that the number of water quality concerns for a 4 year period were consistent. Water quality concern data provided by the utility and presented in the next several paragraphs and charts includes Appearance, Taste, Odor, and Other drinking water categories. The total number of concerns counted over this 4 year period was 1,776. An additional 812 concerns regarding pressure are not shown. **Figure 2–3** shows the distribution of these concerns based on category.

In contrast to the frequency of calls per year, customer reports also varied based on time of year, where the maximum number of calls was received in June (**Figure 2–4**). The frequency of calls received per day also varied significantly (**Figure 2–5**). Most customer reports were filed Monday through Friday, while Saturday and Sunday received the least number of reports. Monday had the highest number of water quality reports and the number of calls decreased throughout the week.

Finally, the frequency of water quality concerns per day were examined (**Figure 2–6**) and results indicate as the total number of concerns per day increased from 0 to 9, the frequency of the events became less frequent. All of these findings are important because they reveal that the number of customer concerns per day will vary temporally. Specifically, receiving a high number of customer water quality calls on Monday may not be indicative of a problem, while receiving that same number of calls on a Saturday may warn of an underlying system problem.

#### **2.4.5 Storage, Tracking, and Analyses Methods and Frequencies**

Utility site visits and survey results indicated that customer feedback data is primarily tracked and stored with paper files, 75% and 69%, respectively. In both investigations, fewer utilities used an electronic file to track and store consumer complaints (**Tables 2–3 and 2–4**). Interestingly, a small percentage of utilities visited integrate customer feedback data into a central database on a networked computer. This finding identifies the fact that utility wide integration of customer feedback data will be difficult and will require substantial upgrades to make data accessible to multiple users.

Results of utility site visits indicated that one utility reviewed customer complaints weekly, while all others had less frequent review cycles (11 monthly, 1 never). Primarily, customer feedback was reviewed during monthly department meetings and presented in a list or tabular format where categories of complaints received and completed were summarized. Regional survey results showed that one third of the utilities review data each time, monthly, and yearly and about 1 out of 3 utilities do not review historical complaint data (**Figure 2–7**). Another 1 out of 3 utilities have other review patterns which included “no review presently but planned review in the future”, “random” review, reviewed “when several complaints received in the same area”, and “reviewed historical complaints from memory”. The utility that responded to a review process based on memory served drinking water to 25,000 consumers.

While monthly summaries and discussions about the status of customer concerns were common at utilities visited, the creation of charts and graphs to analyze complaints was not. Only one utility visited created charts and graphs weekly and served more than 1,000,000 people. These graphs showed customer feedback data received over a monthly basis with four different water quality categories. The wholesaler utility also required its five purchasing utilities to submit monthly complaint totals. The wholesaler utility analyzed this information monthly using

charts and graphs. Only one of the 13 utilities surveyed indicated that their utility creates graphs or charts to analyze complaints. The utility that reported creating charts and graphs served approximately 100,000 people.

#### **2.4.6 Investigative Response to Customer Feedback**

**2.4.6.1 Preparation and Equipment.** Customer concerns that were not resolved during the initial interaction and questioning triggered an internal and sometimes an external utility response. This response varied from data mining within the utility, mail out of informational flyers, or dispatch of utility employees to the customer's premises. Prior to leaving the office, the investigators typically determined if there were multiple customer calls from the same area or if system shutdown or flushing actions were or had occurred in the customer's area. Several basic field investigation practices were used at many of the utilities and were developed based on years of practical on the job training and experience.

Equipment that field investigators frequently carried during onsite visits are listed below. Other equipment used included a hydrophone for leak detection and a white 5 gallon bucket to measure flow rate.

##### **List of Equipment Used During Customer Onsite Building Visits**

- Disinfectant residual meter
- pH meter
- Thermometer
- Turbidimeter
- Clean white Styrofoam cup
- Magnifying glass
- Neoprene gloves
- Clean glass and plastic bottles and caps
- Mobile telephone

**2.4.6.2 Investigator Description.** The technical expertise of the onsite investigator primarily depended on the utility department that received the customer concern and dispatched the

investigator and employee experience. Investigators were mainly water quality/laboratory or distribution operations and maintenance personnel. Customer service, construction department, and water treatment plant operators were also sent out to customer buildings by a few utilities.

Actions conducted by the investigators varied based on their technical expertise. For example, many times distribution system personnel dispatched to the site opened hydrants and flushed without contacting the customer directly. In contrast, water quality/laboratory staff would approach the customer. Similarly these differences influenced which onsite tests were conducted, what questions were asked, and if any samples were collected and delivered to the lab for analyses.

All but one utility visited placed responding to customer concern as an added duty to water quality/laboratory and operations and maintenance personnel. If the customer concern was determined to be very serious (e.g., mercury in toilet, cut locks at the drinking water intake fence gate), the utility would dispatch a team of staff to investigate. For routine responses, almost all utilities dispatched only one utility representative to the customer's residence (92%). One utility sent two employees to every site visit. While the assignment of two employees was logistically taxing, their approach was adopted after a customer accused a former utility employee of stealing their personal belongings and other employees felt threatened by customers during several investigations.

**2.4.6.3 Onsite Response Time.** Before utility dispatched a representative, the time for an onsite response to a customer concern varied considerably. The common position was that the response time was a function of the type of concern, time of day it was received (8am–5pm vs. 6pm–7am), day of week (work week vs. weekend), personnel workload, and resources. With the exception of water outage concerns which were considered to be “life–issues” and physical security threats/breaches, all responses to customer concerns occurred during normal business hours. A customer complaint that was received Friday night would at the earliest be responded to on Monday if there was no holiday. Only one utility took the position that if any drinking water illness complaint was filed, an immediate response was conducted day or night.

**2.4.6.4 Onsite Procedures.** At all utilities, the safety of the investigator was the most important component of the investigation. All utility managers and staff interviewed stressed that at no

point should investigators put themselves at risk. If at any point the investigator felt that their safety was in jeopardy, the onsite investigation stopped and this concern was raised to utility supervisors. At one utility, onsite investigators requested police escorts to follow-up on customer taste and odor complaints for certain residences and economically depressed areas of the community.

Another strongly debated point was whether or not the utility employee should or had the authority to enter a customers' residence (e.g., apartment, condo, and house). Most utilities permitted employee entry into the customer's residence (60%). Several utility representatives mentioned that utility responsibility ended at the service connection, though some of the same representatives indicated that they wanted to help customers solve their problem and would enter their residence. In the same discussions, the topic also arose that the Health Department was the only agency with the authority to enter customers' residence. For this reason, one utility chose to forward all drinking water related illness complaints to the local health department.

Utility staff that entered customer buildings followed common investigation techniques. First, field investigators verified that the problem still existed with the customer. Water quality/laboratory staff entered customer buildings more often than distribution operations and maintenance staff. This difference was found to be largely based on the difference between field investigation practices. Investigators that did not enter customer buildings observed the site and sometimes collected water samples from hose bibbs and hydrants. Hose bibb and hydrant analyses results helped determine if the problem was localized or more widespread. Many investigators provided the customers sampling bottles and asked the customer to collect a water sample themselves. Samples collected onsite were transported back to the laboratory for analyses. Operations and maintenance representatives did not collect laboratory samples.

**2.4.6.5 Onsite Analyses.** The most common water analysis technique performed during the onsite visit was disinfectant residual followed by visual inspection, and pH analyses. At utilities that used more than one type of source (e.g., surface, ground, or desalinated), conductivity was used as a means to determine which source or treatment plant the water originated from. Sensory analyses techniques such as direct tasting and smelling were reported. Turbidity and ammonia testing was also reported, but ammonia testing was only reported at those utilities who used

chloramines as a residual disinfectant. Color, iron, hardness, fluoride, pressure, radiological analyses were also provided as less typical field analyses techniques.

**2.4.6.6 Laboratory Analyses.** Less than 33% of the water utilities visited had a set suite of laboratory tests that were conducted on every customer building water sample. Only two water utilities were using rapid test kits such as Microtox<sup>®</sup> and Eclox<sup>®</sup>. No utility visited would analyze customer delivered drinking water samples except by visual observation. Utility responses were typically prefaced with the statement that the types of laboratory tests conducted will vary based on customer descriptions and site investigation results. At both utilities visited and those surveyed, bacteriological testing was the most common analyses performed while metals, water pH, and turbidity were the second most conducted analyses. Positions on bacteriological testing of customer building water varied widely. Two of twelve utilities collected samples for bacteriological testing every time a customer site was visited, while the other utilities refused to collect samples for bacteriological analyses unless the investigator found compelling evidence and deemed it necessary. The latter position was selected because of prior false-positive testing results. Taste and odor analyses were conducted on customer water samples after they had been determined free of chemical and biological contaminants. Threshold odor number test, flavor profile analyses, and direct tasting and sniffing evaluations were conducted.

**2.4.6.7 Post-Analyses and Follow-up.** After laboratory results were obtained, the site investigators typically reviewed the data. Data review consisted of comparing water quality measurements against Federal and State standards as well as any internal goals. If measurements were outside the limits of internal or regulatory limits, the investigator would notify the utility staff immediately and a broader investigation would follow. Most often though, data review revealed that there was no difference between customer drinking water and that routinely distributed by the utility. Few utilities formally determined and noted if the customer issue was a utility caused or customer caused. Drinking water illness complaints were concluded to be unfounded if chlorine and pH results were within acceptable limits and bacteria tests come up negative.

Closure was mainly achieved with the customer by a telephone call from the investigator or department supervisor (62%). Other closure actions used included mailing a letter with a copy

of the water quality test results, a follow-up onsite visit, or delivery of a door hanger that explained the cause of the problem. If the customer demanded that the problem the investigator did not find during the inspection or water quality results was still present, the investigator typically explained that the safety of water was measured on these measurements, contact their doctor, a plumber, or the local department of health.

Investigation records were primarily stored in paper form. Almost half of the utilities entered records a utility database. Of these utilities, one entered investigation records into a local database, while five entered data into a utility wide database. The water quality and laboratory group maintained the majority of the field investigation records.

## **2.5 Conclusion**

Customer feedback has helped alert utilities to water contamination and system access events and should be considered for real-time analyses. Existing data coding, storage, and analyses practices between and within utilities are not consistent. Comparison of customer feedback data between utilities is difficult due these differences. The quality of data stored at utilities strongly depended on the experience of the person handling the customer concern. Determination of whether or not a customer concern required immediate attention was 100% based on employee experience. An overall assessment of utility consumer feedback data tended to be monthly which could not detect an immediate problem. The amount of historical applicable customer feedback data stored at the utility varied from 1 to 4 years.

Real-time analyses for the integration of customer feedback have the potential to improve distribution network monitoring. Before this tool can be implemented though, utilities must conduct a self-evaluation to optimize information flow, communication, storage, investigative procedures, and consistent terminology. Subsequent publications will provide greater insight into recommended actions regarding the: development of a standardized “checksheet” for coding customer concerns; optimization of information flow and communications within the utility; and statistical analyses modules for detection of water intrusion and contamination events.



## 2.6 Acknowledgement

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**Table 2–1 Characteristics of Thirteen Utilities Visited**

<b>Characteristic</b>	<b>Units</b>	<b>Value or Range</b>
Service Population	Persons	30,000–8,000,000
Average Daily Production	Million gallons per day	10–1,600
Types of Source Water	Description	Surface, ground, desalinated
Length of distribution mains	Miles	180–6,000
Water storage tanks and reservoirs	Number of Units	3–180

**Table 2–2 Common Methods for Customer Initial Telephone Call Receiving and Routing**

<b>Method</b>	<b>Percent Responding, %</b>
Direct transfer	50
Data entry, transfer	42
Data entry, answer attempt, transfer	33

1. Percentages do not add up to 100. Many utilities had more than one call receiving and routing method for the same data.; twelve utilities participated in this survey.

**Table 2–3 Methods for Storing Customer Feedback at Utilities Visited**

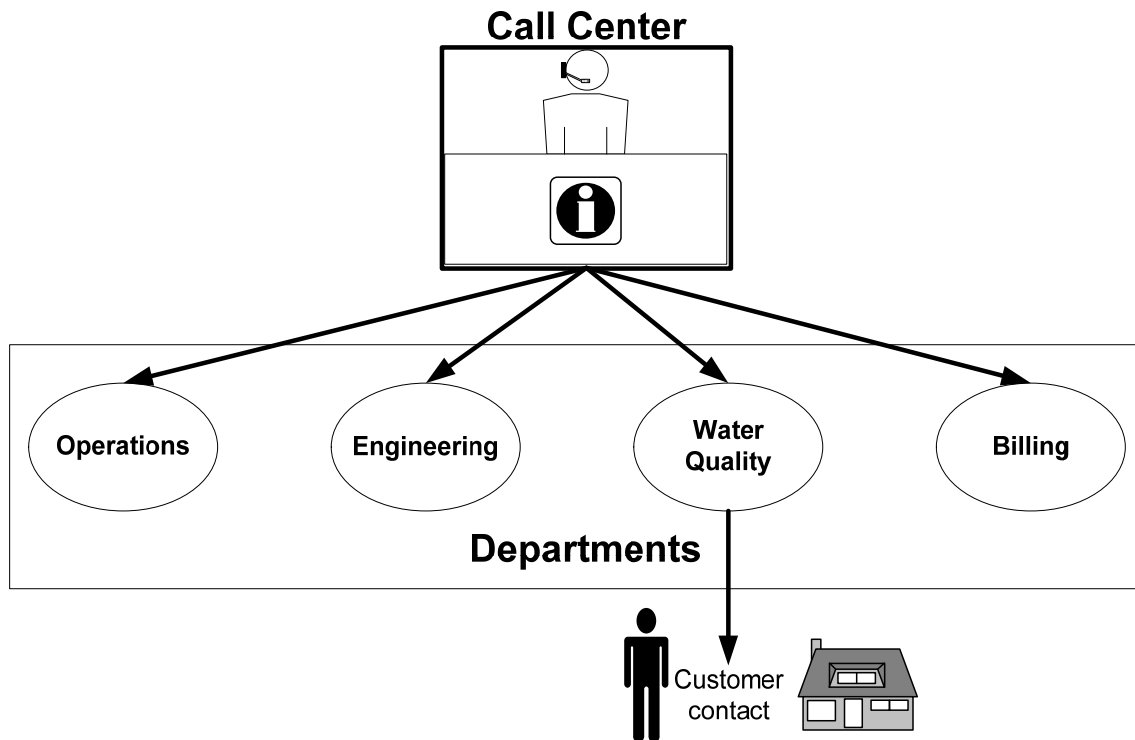
<b>Method</b>	<b>Percent Responding, %</b>
Paper files	75
Spreadsheets	42
Database on one computer, not networked	33
Central database on networked computer	17

I. Percentages do not add up to 100. Many utilities had more than one call receiving and routing method for the same data; Twelve utilities participated in this survey.

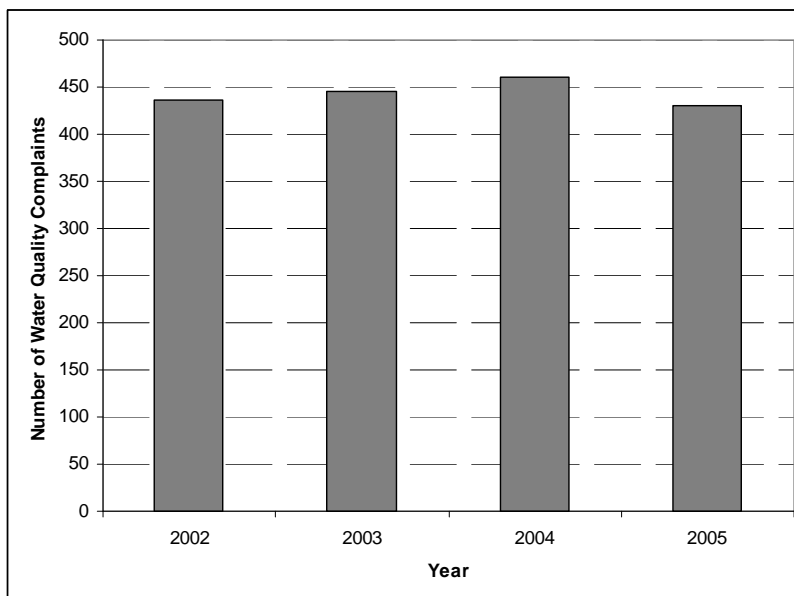
**Table 2–4 Method for Tracking and Analyzing Customer Complaints at Surveyed Utilities**

<b>Method</b>	<b>Percent Responding, %</b>		
	<b>Yes</b>	<b>No</b>	<b>Do Not Know</b>
Paper Form	69	31	0
Electronic File	44	50	6

I. Percentages do not add up to 100. Many utilities had more than one call receiving and routing method for the same data; Sixteen utilities participated in this survey.

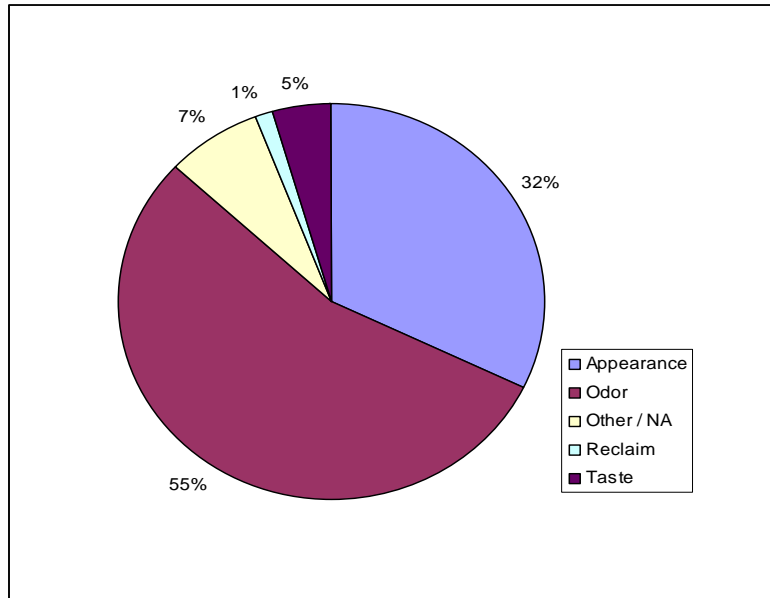


**Figure 2–1 General Flow Path of Customer Concerns Through a Utility**



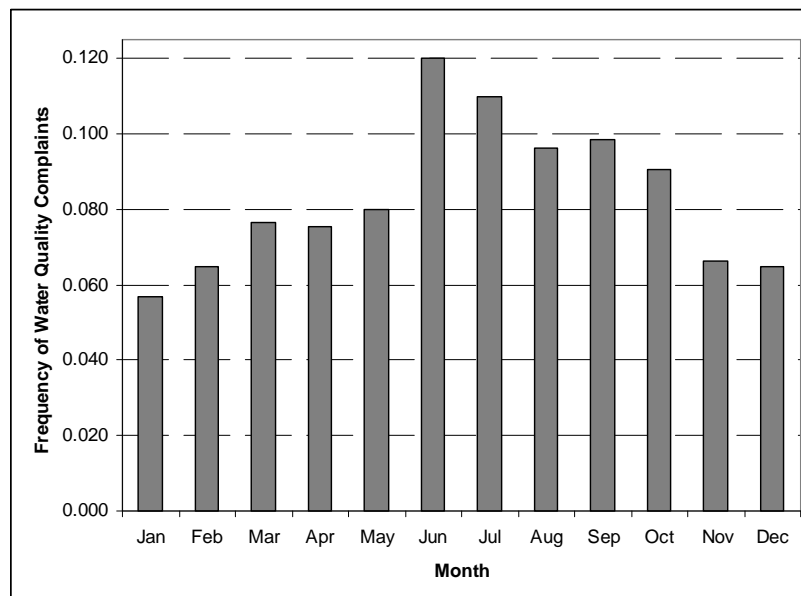
**Figure 2–2 Total Number of Customer Water Quality Concerns Per Year, 2002–2005**

(n=1776)



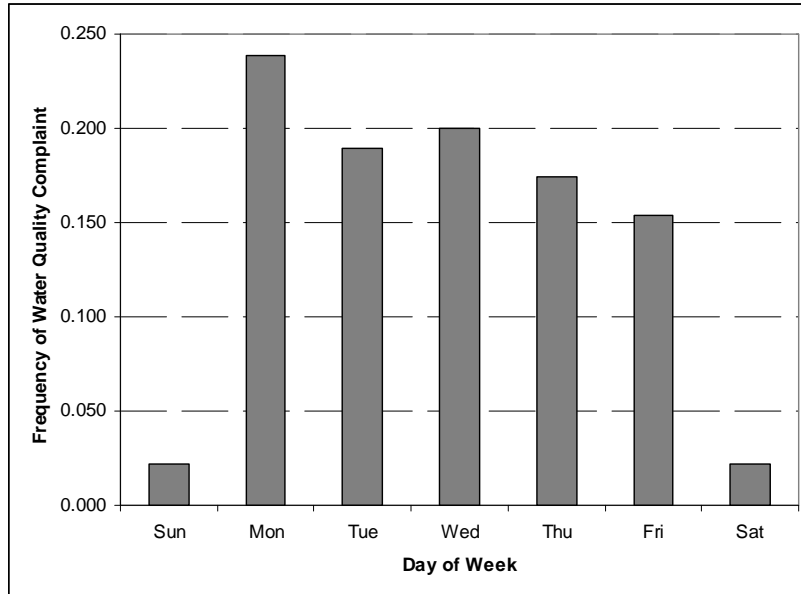
**Figure 2–3 Percent of Customer Water Quality Concerns Separated by Utility Categories, 2002–2005**

(n=1776)

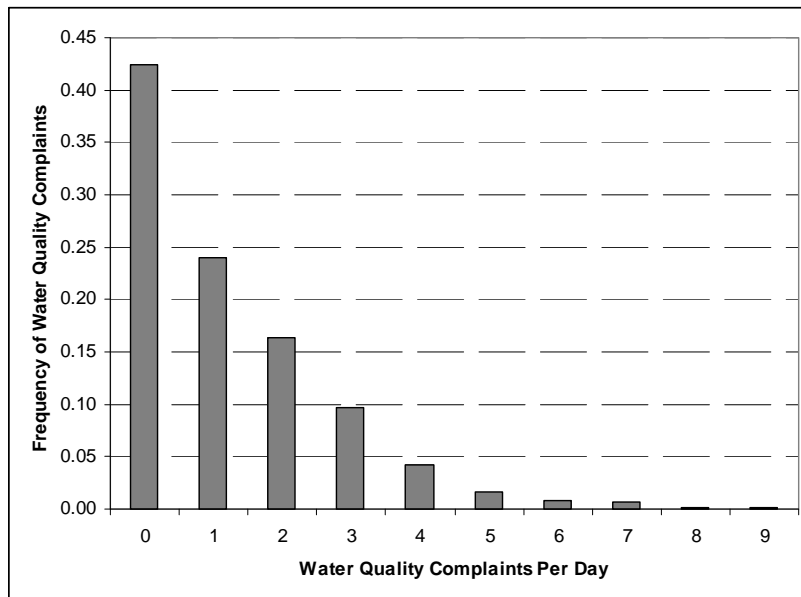


**Figure 2–4 Frequency of Customer Water Quality Concerns Per Month, 2002–2005**

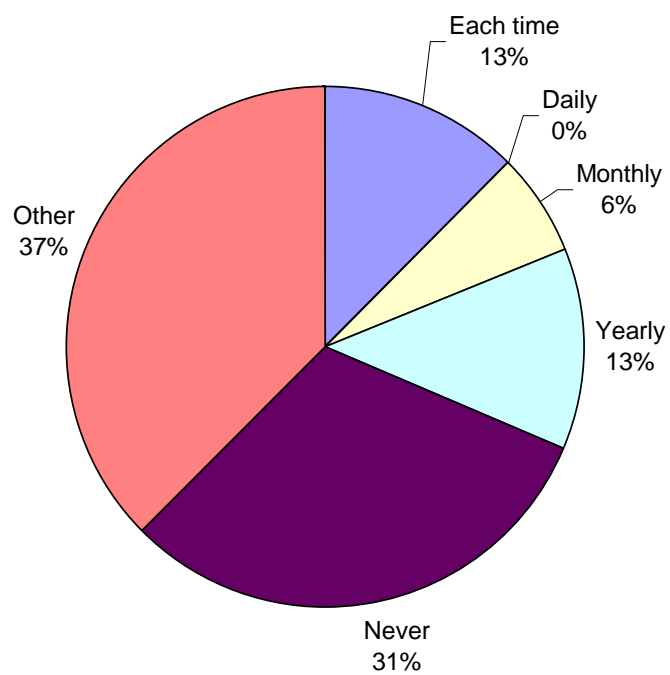
(n=1776)



**Figure 2–5 Frequency of Customer Water Quality Concerns Per Day of Week, 2002–2005**  
(n=1776)



**Figure 2–6 Frequency of Customer Water Quality Concerns Per Day, 2002–2005**  
(n=1776)



**Figure 2–7 Review Frequency for Historical Complaint Data for Surveyed Utilities**  
(n=16)



## **Chapter 3 Integration of Customer Feedback into Utility Operations for Improved Water Quality and Infrastructure Monitoring**

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### **3.1 Abstract**

Capture and analysis of customer feedback (e.g., concerns, complaints, and inquiries) was investigated as an effective early warning system for monitoring water quality, process control, and infrastructure access. Based on detailed, on-site interviews and facility tours at thirteen water utilities, and also a thorough review of the published literature, the investigation revealed that drinking water customer reports of unusual taste, odor, color, clarity, pressure, water outage, suspicious activity, and facility access events helped uncover more than 82 incidents related to previously undetected water treatment process failures, system intrusions, accidental and intentional contamination, and other problems. These data indicate that real-time analysis of customer feedback can be an effective early warning monitoring tool, but utilities must implement uniform terminology and practices to improve data flow, investigation techniques, and data storage and analyses. A recommendation is that utilities adopt a “Funnel, Filter, Focus” approach to effectively harness customer feedback data. Utilities should funnel all customer feedback by designating a single telephone number and e-mail address for contact. Utility staffs who receive customer feedback should initially filter it by resolving issues, for which they are trained, then categorize and forward those remaining to appropriate personnel. These personnel can then focus on gathering in-depth information—from the customer, from possible field samples, and from on-line monitoring—in order to resolve the problem or activate further investigation or possibly issue a warning. To improve infrastructure and water quality surveillance, customer feedback data should also be integrated into geographic information systems and hydraulic and water quality models.

**Keywords:** Water, infrastructure, surveillance, monitoring, customer, feedback

### 3.2 Introduction

As early as 500 B.C.E., drinking water appearance, taste, and odor characteristics were used to assess drinking water quality and safety. More than 2,300 years later, John Snow assessed customer illness reports to determine that a Broad Street Pump was contaminated with cholera and caused illness and fatalities in London (Hall and Dietrich, 2000). Over the next 150 years, scientific exploration uncovered water treatment and distribution techniques that would eventually provide safe drinking water to millions of people worldwide. In addition to these discoveries, researchers also established relationships among drinking water infrastructure, treatment operations, water quality, waterborne disease, and population health. Many of the waterborne disease incidents chronicled during the last 30 years in affluent countries were first detected when customers complained about odd tastes, odors, and illnesses (Payment et al, 1997; Craun and Calderon, 2001; Hrudey and Hrudey, 2004). While tremendous water treatment and distribution technological advances have been achieved, customers, who are located throughout the distribution system, still can act as monitors for water quality and public health.

Outside the drinking water industry, customer input is also used as a valuable indicator of product safety and quality. Today, small to large distribution, manufacturing, and retail companies rely upon customer feedback to identify products and services that are defective or of decreased quality. Many of these companies take customer feedback seriously by advertising how concerned customers can contact them and these companies subsequently catalog, investigate, and resolve the product issues to make certain their products do not, decrease customer satisfaction, pose health risks or affect product sales. Other benefits of proactive customer monitoring programs include “opportunities for product improvement, protecting market share, and boosting consumer loyalty levels” (Reichheld and Sasser 1990; Halstead and Page 1992; Mitchell 1993; Estelami, 2000).

Similar to the commercial sector, many water utilities rely upon customer feedback for improving knowledge of their product and services. Water quality and pressure complaints have been used to detect changes in source water quality, measure the effectiveness of hydrant flushing programs, and determine where main breaks have occurred (Mallevalle and Suffet, 1987; Rashash et al, 1996; Kirmeyer et al, 2000; Taylor et al, 2006). Water quality complaints have also been used to monitor treatment operations and quantify the extent of distribution and

water quality problems (Burlingame and Anselme, 1995; Khiari et al, 2002; McGuire et al, 2005; Dietrich, 2006). Several utilities have even found that customers warn them when water facility intrusion attempts occur (Whelton and Cooney, 2004; Whelton et al, 2004). Because customers provide useful descriptive information from a water quality and infrastructure surveillance perspective, research around the world has centered upon identifying distribution system material caused off-flavors (Burlingame et al, 1994; Rigal, 1992; Rigal and Danjou, 1999; Rogers et al, 2004), particulate matter in distribution and tap waters (Booth and Brazos, 2004), and taste and odor monitoring at the treatment plant and the tap (Bartels et al, 1986; Burlingame et al, 1992; Dietrich et al, 2004; McGuire et al, 2005; Dietrich, 2006).

Within the last 5 years, drinking water customer feedback surveillance has taken another step forward to become a critical water system monitoring tool (Whelton, 2003; Roberson and Morley, 2005; USEPA, 2005). Whelton and colleagues and the U.S. Environmental Protection Agency (USEPA) defined critical components of a customer feedback surveillance system to include a single point-of-contact, effective data reception, established investigation and analyses procedures and protocols, effective electronic data management, automated and integrated analyses, educated consumers, trained and committed personnel, continuous assessment and improvement/training (Whelton, 2003; Whelton and Cooney, 2004; Whelton et al, 2004; USEPA, 2005). A competent customer feedback surveillance system should stress the need for standardized data reception, handling, data analysis, and utility response.

Because of its historical usefulness and perceived value, customer feedback deserves increased scrutiny as a utility monitoring tool. Over the last 2,500 years, drinking water customer feedback has demonstrated its value. From a practical standpoint, customer feedback data are under the control of the utility and have the potential to speed up the detection of water contamination events or process failures. Customers are also on-site monitors that occur throughout the distribution system, and their number and dispersion are prime advantages for a monitoring tool. During emergency situations, utility management, public health officials, and emergency responders may use this information to determine the extent of population exposed to contaminated drinking water as well as identify valve closures for isolation and containment.

USEPA has incorporated customer complaints as part of a multifaceted contaminant warning system that also includes water quality monitoring and notification by public health or

law enforcement agencies. For certain classes of compounds, customer complaints have the advantage of a relatively early time of detection compared to laboratory analyses or clinical diagnoses, and thus allow for a more rapid response. For compounds with tastes and odors, customers are often more sensitive than standard laboratory tests and instrumentation. Examples of USEPA programs incorporating customer complaints include the Response Protocol Toolbox (USEPA, 2003) and Water Sentinel (USEPA, 2005).

### **3.3 Project Goal and Objectives**

The goal of this project was to develop an effective framework for managing customer feedback to monitor water quality, process control, and security. The objectives of this project were to: (1) conduct a literature review to identify prior types and uses of customer feedback for utility monitoring, (2) evaluate existing utility practices for handling customer feedback information, and (3) identify actions needed to integrate customer feedback into utility monitoring.

### **3.4 Methods**

Thirteen utility site visits were conducted across the US. Utilities were selected based on their willingness to participate and their prior experience with receiving and recording feedback from drinking water customers. While these thirteen medium-to large-size utilities are a small percentage of the entire utility population, they do have a wide range of operating, treatment, production, administration, financial, and service population characteristics. In addition, a literature review dating back nearly 30 years was conducted using peer-reviewed journals, government, trade industry, and research foundation publications.

During each site visit, interviews and facility tours were conducted. The project team interviewed personnel responsible for all facets of utility administration, customer service, engineering, information technology, laboratory, operations and maintenance, security, water quality, and water treatment. Each utility was asked a set of 30 standardized questions that were developed based on customer feedback handling guidance in the literature and the experience of the authors. Project team members inventoried each utility's procedures for receiving, analyzing, investigating, and tracking customer feedback. Tours included visiting the call center or entry point for consumer calls, then following the inquiry handling process through analyses, response, and resolution.

Paper and electronic customer feedback historical records were reviewed. Field data sheets, internal data analyses charts, and customer concern/complaint handling standard procedures and manuals were also examined. As site visits were completed, additional questions were identified by the project team. Follow-up telephone interviews were conducted with utilities previously visited to answer these new questions.

Several public health department engineers and epidemiologists were also consulted for their input. These experts were asked to provide insight on the capture, analysis, and filing of drinking water quality, pressure, and illness complaints to health departments, describe how health departments handle/investigate them, and comment on the state of health department/utility relationships. Personnel from two additional water utilities were also interviewed to gain additional insight into customer feedback handling practices.

### **3.5 Results and Discussion**

**3.5.1 Literature Review.** A literature review identified 61 examples where customer feedback was the first indicator to a utility that something was wrong with their infrastructure, operations, or drinking water. Forty of these were compiled by Thompson and Jenkins (1987) and dealt with tastes and odors caused by permeation of petroleum through plastic drinking water pipe. The remaining 21 incidents were individually described in published literature and included reports of drinking water with off-tastes, odors, appearance, and perceived customer illness (**Figure 3–1**). An analysis of these incidents revealed that customer feedback helped utility staff (1) identify the problem cause and source, (2) isolate the contaminated water, (3) estimate the population affected, (4) take action to protect the population unexposed, and (5) help estimate the amount of infrastructure that needed cleaning. These feedback warnings uncovered water contamination at elementary schools, public water fountains, customer residences, commercial buildings, county fairs, mines, health clinics, and in towns, cities, and counties across the globe.

Two of these incidents were particularly noteworthy. Retrospectively, investigators discovered that the 1993 Milwaukee *Cryptosporidium* outbreak was preceded by increased number of customer calls to the water utility immediately after the water treatment system failed (background mean of 0–5 calls per day increasing to a maximum of 45 calls per day) as shown in **Figure 3–2** (Proctor et al, 1998). The increased call volume signified that customers received water of decreased quality, but this feedback warning was not discovered until after the outbreak

had been confirmed. The exact types of customer concerns filed in Milwaukee were never reported, but based on past biological water contamination events that were first detected by receiving customer feedback the Milwaukee complaints were likely discoloration in nature (Jones and Roworth, 1996; Short, 1998).

Customer feedback also helped uncover another well-known intentional drinking water contamination incident on US soil (Moser, 2005). In 1980, reports of kerosene–insecticide odor and milky water appearance lead Pennsylvanian utility and emergency response investigators to find that someone had intentionally injected a pesticide into the water distribution system. Customer feedback data not only helped detect the contaminated water, but also helped (1) pinpoint the location of the contaminated water and population affected, (2) identify valves to be closed for containment, and (3) characterize the unknown contaminants based on descriptions provided by the customers.

**3.5.2 Utility Site Visits.** Table 3–1 shows characteristics of utilities visited. All thirteen utilities treated customer feedback seriously and almost always took field samples for water quality complaints if the cause of the problem was unknown. The belief that customer feedback could be an indicator of an actual system problem was not shared by all utility personnel interviewed. While 50% (6/12) of the utilities visited had conducted a water security exercise, no exercise had incorporated customer feedback as a contamination warning.

Onsite interviews with utility personnel revealed that 21 water system access and contamination events were first detected by customer notifications (**Figure 3–3**). Customer concerns that prompted investigations included customer reports of unusual taste, odor, color, clarity, pressure, and suspicious activity. These incidents were uncovered commercial, public and residential buildings, hydrants, and plant intakes. Utilities used customer feedback to alert them of unauthorized system access, malfunctioning, damaged, and improperly installed equipment, and process failure.

**3.5.2.1 Points of Customer Contact.** Utility literature and policies determined which utility department was most contacted by the customer. Telephone was the most common method customers used to communicate drinking water concerns. Most utilities (83 %, 10/12) relied upon a city, county, multiple agencies, or their own customer call center staffed by

customer service representatives (CSR). Two of thirteen utilities had a single city-wide telephone number where customers would call if they had any community concerns (e.g., water, noise, traffic, etc.). The remaining call centers were utility based. Utilities that did not have a call center, typically the smaller ones, directed all calls to the water treatment plant.

Occasionally, customers bypassed call centers and contacted water quality, operations, director, GIS/Mapping, information technology, public affairs, laboratory, and construction departments directly. Telephone numbers used by customers were obtained from the website, telephone book, and water bill or the customer was provided an employee telephone number on a previous call. At one utility, more than 13 different utility telephone numbers were available for customers to call for drinking water related issues. This overabundance of choices resulted in customers calling the wrong department and also forced the utility personnel receiving these calls to transfer the customer to the department he/she deemed appropriate. Frequent transfers between departments sometimes resulted in customers hanging up (lost data) and/or becoming irate. Typically the caller's information was not entered into the utility's official database by the utility call taker if the call was transferred from another agency.

Customers also filed drinking water concerns by electronic mail (e-mail) messages, on-line question submission forms, U.S. mail letters, and in person to utility offices. Utilities typically responded to telephone calls more quickly than electronic mail (e-mail) messages, but many utilities reported increasing use of e-mail by customers.

Customers also reported drinking water quality and system concerns to the fire, health, and police departments, as well as the County Commissioner's, Sheriff's, Mayor's, City Hall Offices and 9-1-1. With the exception of customer drinking water concerns reported to the health department, these external agency calls were typically forwarded to the water utility's Director's Office or call center.

**3.5.2.2 Data Recording.** Data recording practices were a function of utility representative experience, the position of the utility representative, and utility-wide policies (if present). Customer concern information was not always recorded into a utility electronic or paper file during the initial contact (**Table 2-2**). This informal approach to customer concern reception and

handling resulted in lost data. Decisions of which unit to forward calls were primarily based on the call receivers' experience and knowledge of the utility.

Utility staff typically requested additional information concerning the nature of the complaint. Typical questions are shown in **Table 3–3**. Sometimes initial call receivers would attempt to answer customer concerns during the initial contact based on their experience or utility scripts. Almost 50% (6/13) of the utility call centers used scripts or customer troubleshooting manuals to help staff handle customer inquiries. Scripts contained guidance on how to troubleshoot and solve several common customer concerns over the telephone (e.g., air in water, clogged aerators). Sixty-seven percent (8/12) of the utilities that used scripts provided them in paper form, while 33% (4/12) used electronic/ web-based scripts. Electronic/ web-based scripts were strongly praised for their usefulness in troubleshooting customer concerns.

**3.5.2.3 Uniform Terminology.** There are no standards for coding or handling customer feedback data. **Table 3–4** shows the breakdown of water quality related customer feedback categories used at four utilities. Different utilities chose to record different customer feedback details. In **Table 3–4**, Utility D used only very broad categories such as taste, odor, other. Utilities A and B included specific aesthetic descriptors such as chlorinous, tastes and odors. Utility C tracked four possible colors of water. Overall, between 10 and 197 different categories were used at the utilities visited. While this information is undoubtedly valuable from operations and investigation perspectives, their broad variability made the data difficult to analyze and manage, and severely limited integration of customer feedback into a utility-wide monitoring system. The types and number of categories used did not correlate with system size or complexity and were based on utility experience and the personal preferences of their creators. Several utilities indicated that categories were added as staff deemed appropriate. When interviewed, several call center representatives indicated that they chose categories they were most familiar with.

There are two distinct issues involved with terminology used to record consumer feedback. The first is consistent descriptors within a utility. For example, one utility used 13 descriptors to describe water that was or contained something “black” (**Table 3–5**). Another utility used nine descriptors to describe water containing a chlorine characteristic. Many of these included misspellings, and occurred because the data entry procedure allowed staff to enter



descriptors directly rather than select from a limited predefined list. The overabundance of categories resulted in staff coding customer concerns differently at the same utility and therefore made the data unmanageable. Descriptive information as a comment in text form is useful from a troubleshooting perspective, but cumbersome from a data coding and analyses perspective. The number of codes must be limited and easy to manage.

A second issue relates to a lack of industry-wide standard terminology for customer feedback categories and descriptors that would facilitate data sharing with other utilities and public health agencies. The increased use of water wholesaling, consecutive systems, and interconnected systems argues for consistent terminology across utilities. The public health field has faced this challenge and developed a set of categories that allow data to be transferred and shared. An example is Health Level 7—seven basic health problems e.g., gastrointestinal, rash, respiratory (RODS Laboratory, 2006). The taste-and-odor wheel is an example of an accepted water industry set of descriptors (Burlingame et al, 1991; Suffet et al, 1999; Khairi et al, 2002) and was based on a concept from the food and beverage industry. Development and use of uniform terminology for consumer complaints would greatly aid the water industry in effectively managing consumer feedback.

**3.5.2.4 Data Storage and Integration.** Utilities indicated that customer feedback data is primarily tracked and stored with paper files (75%, 9/12) at some time during customer contact, most commonly when the call is first received. Data are often later transferred to electronic storage. Utilities frequently discarded customer feedback data between six months to four years after reception. This lack of historical data made it difficult to analyze and detect trends and determine what variations were routine at the utilities. Discarding customer complaint data is not acceptable in Pennsylvania and Tennessee that require water utilities to store public utility service complaints in upwards of 5 years (PA, 1999; TN, 1999).

Most utilities used both an electronic and paper file to track and store consumer complaints (**Table 3–6**) but one utility reported using a central database on a networked computer. This finding implies that utility wide integration of customer feedback data will be difficult and will require substantial upgrades to make data accessible to multiple users.

Of those utilities using database storage, nearly half had customer feedback linked into their work order management system. Linkages into asset management systems (33%, 4/12) and geographic information systems (17%, 2/12) were less common. Planned and desired integration of customer feedback data with other systems is shown in **Table 3–7**. Linkage with GIS was the most commonly desired upgrade.

**3.5.2.5 Relationships with other Agencies.** There is a need to improve communications between health departments and water utilities for customer drinking water illness concerns. While no utility recorded a water system malfunction that caused customer health problems, illness complaints were 2% and 8% of total water quality concerns reported at two large size utilities. Surprisingly, 83% (10/12) of the utilities did not have procedures for contacting the health department when a drinking water illness complaint was filed. Also surprising, several health departments received drinking water quality (e.g., appearance, illness, taste, and odor) complaints and investigated them without contacting the utility.

Relationships between law enforcement and utility personnel were also variable. After one utility experienced an intrusion attempt at their intake facility, law enforcement was unable to increase surveillance because they lacked resources. Many other utilities found that police officers indicated that they were too busy with their core duties to assume responsibility for suspicious hydrant access activities. In some cases, the perpetrator had left the scene by the time police arrived onsite. One utility had their own police force which focused on utility issues and greatly improved response time. Public awareness of formal utility hydrant permit and access programs greatly reduced unauthorized access. At one utility two persons attempting to steal water were apprehended by law enforcement due to customer tip offs.

### **3.6 Recommendations**

Utilities that desire to improve drinking water system surveillance should focus on improving their customer feedback handling systems. Customer feedback is under the control of the water utility and improved data handling can aid in the detection and response to problems.

A “**Funnel, Filter, Focus**” approach should be implemented to effectively harness customer feedback data (**Figure 3–4**). Utilities should **funnel** all customer feedback by designating one telephone number and e-mail address for customers to contact with drinking

water concerns. Call receivers should initially **filter** the customer contacts by resolving concerns for which they are trained and categorizing the remaining calls and forwarding them to appropriate personnel. These personnel can then **focus** on gathering in-depth information—from the customer, from possible field samples, and from on-line monitoring—in order to resolve the problem.

A standard utility-wide policy should set forth systematic procedures for call logging, investigating, resolving, and closing out each type of customer drinking water concern. All call and e-mail receivers should be trained according to the customer feedback handling policy.

To optimize the power of customer feedback analyses, a historical record of customer feedback data is needed. Current data can then be compared to the patterns and variability of the historical record to determine if a problem likely exists. Utilities should store customer feedback data in an easily analyzable form indefinitely. This can be accomplished by recording customer feedback in electronic spreadsheets or databases.

Improvements to existing customer feedback data collection include creating a template for data entry, developing consistent terminology, and networking with other databases. The ease and associated cost may depend upon whether or not the utility uses proprietary data management software. Linkages to other information systems such as GIS and work orders can also improve analyses power and can help display customer concerns spatially as recently demonstrated by Mikol (2006).

### **3.6.1 Terminology**

A standard terminology must be adopted to integrate customer feedback into utility monitoring. Based on the literature review results, utility data, and utility staff recommendations, a three tiered data coding approach is proposed (**Figure 3–5**). The three tiered approach takes into consideration 1) a first level tier of four classifications: water quality, engineering, suspicious activity issues, and other; 2) a second level tier of 6 different categories: Facility, Pressure, Appearance, Taste and Odor, Illness, Miscellaneous; and 3) a final tier of category-specific descriptors. Although the three-tiered approach proposed in **Figure 3–5** can be adapted to fit the needs of an individual utility, modifications should try to preserve consistent terminology. For this article, Tier 2 and below only deal with engineering and water quality, but

the concept could be expanded to include the other classifications. **Table 3–8** demonstrates how this approach can be stepwise implemented using actual customer feedback data. Many utilities can simply modify their existing electronic or paper coding approaches to improve their data quality.

Several of the proposed classifications and categories have existing standards to include taste and odor, illness, and facility issues. Taste and odor has a widely used Taste-and-Odor Wheel (Suffet et al, 1999; Khiari et al, 2002). Accepted illness descriptions have been well-defined by Health Level Seven (HL7) and International Classification of Diseases, 9th Revision, Clinical Modification (ICD–9–CM) codes that are used by healthcare experts and information scientists (DHHS, 2005; RODS Laboratory, 2006). Facility descriptions are also provided in the USEPA Response Protocol Toolbox (USEPA, 2003). Description standards are generally lacking for pressure, appearance, and other miscellaneous issues (e.g., spots, noisy pipes).

Coupled with the three tiered data coding framework is a proposed water industry “check sheet” to standardize descriptions of customer reported drinking water issues (**Figure 3–6**). This check sheet would begin the recording and data capture process, and provide a data stream for early warning of possible water contamination or infrastructure access events. Such a check sheet would be useful for utilities that use paper forms to initially capture caller information, or as a design template for those using electronic capture. A consistent set of descriptors in check sheet formats allow for easy data entry, automated analysis, report creation, and early warning detection. Once adopted, this check sheet could be converted into an on-line tracking portal and sample versions could also be sent and explained to customers to illustrate what types of descriptive information the utility is looking for when they notice a problem. These actions will not only demonstrate that the utility take customer feedback seriously but may also improve data quality.

When multiple descriptors are used for the same underlying problem, as shown in the “black” and “chlorinous” examples in **Table 3–5**, utility staff must sort through the complaints by hand in order to perform any detailed analysis or classification. If a limited and consistent set of descriptors is used instead then graphs, statistical analyses, and reports can be created automatically by software. Utility resources can focus on improving service rather than cleaning

and organizing data. As the data analysis becomes more routine and less time consuming, it also becomes more valuable.

In the health field, syndromic surveillance programs act as early warning systems for disease outbreaks by monitoring activities such as emergency rooms visits, over-the-counter drug sales, and school and work absenteeism (Fleming et al, 2003; Henning, 2003; Berger et al, 2006; RODS Laboratory, 2006). Examples of syndromic surveillance programs include Electronic Surveillance System for the Early Notification of Community-based Epidemics (ESSENCE) (DOD GEIS, 2006) and Real-Time Outbreak and Disease Surveillance (RODS Laboratory, 2006). One key requirement is the use of standardized categories and descriptors so that the data can be analyzed and shared, and in the water utility a check sheet for customer concerns could provide the start of the early warning system.

### **3.6.2 Other Improvements**

**3.6.2.1 Customer Education.** Customer education is critical to improving data quality and its usefulness. Utilities should make certain that a single utility telephone number and e-mail address are available for drinking water customer questions or concerns. Customer education regarding upcoming water quality changes, planned or ongoing infrastructure related activities, and guidance on how to spot suspicious activities and water stealing can be accomplished through consumer confidence reports, door hangers, bill inserts, formal hydrant access policy, targeted customer mailings, mailings of informational brochures such as AWWA “Your Hot Water Stinks”, websites, and through the media. Other education programs can include educating consumers about authorized vs. unauthorized users, dashboard and magnetic permits, and security mailings to select locations.

**3.6.2.2 Training.** Integration of customer feedback into utility training is essential. On the job training and routine refresher sessions are helpful. Call Center, Operations, Water Quality, and Security employee cross-training may also help employees understand customer feedback warnings and how customer feedback is handled between and within departments. If a customer feedback inquiry enters one department, that department must know where to direct the customer and/or concern. Emergency response and water security exercises are other vehicles for improving a utility’s ability to handle customer feedback warnings (Whelton, 2005; Whelton et al 2006). These events provided employees the opportunity to acquire, analyze, and investigate

role–played incidents. The AWWA and Awwa Research Foundation also offer guidebooks, such as Lauer (2005), on customer feedback related issues.

**3.6.2.3 Local Relationships.** Relationships with health, police, and fire departments should be developed and maintained. Utilities should identify what agency is responsible for receiving and investigating customer drinking water illness concerns. Utilities should also determine what department will investigate all specific concerns (e.g., taste/odor, appearance, facility, pressure/flow, suspicious activity). An organizational policy on how each of these customer concerns is handled is needed. Improved relationships with law enforcement may also improve system security.

### **3.7 Summary**

- All utilities that participated in this project responded to customer concerns and feedback. Not all utilities perceived broader data analysis as a valuable tool for improving water quality and infrastructure monitoring.
- Customer feedback has helped water utilities worldwide uncover water quality, operations, and infrastructure access problems. An integrated customer feedback analysis tool would allow utilities to improve water quality and infrastructure monitoring.
- Utilities desire and are working to integrate customer feedback data with geographic information systems and hydraulic and water quality models.
- Improved communications and planning between utilities, health agencies, and law enforcement would benefit the customer and the water industry.
- Utilities should evaluate and organize their customer feedback data acquisition and work practices to optimize their drinking water surveillance systems.
- A three tiered approach to customer feedback data coding and a water industry check sheet has been proposed. Agreement for uniform descriptors is needed, especially for between utility communication.
- Utility training is needed on how to receive, investigate, and solve customer feedback issues as they pertain to water quality, operations, and security problems.
- Research is needed to develop and test statistical approaches for customer feedback analyses. Efforts are also needed to develop “trigger” levels at utilities for initiation of a broader investigation in response to a high number of customer concerns.

### 3.8 Acknowledgement

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**Table 3–1 Characteristics of Thirteen Participating Utilities**

<b>Characteristic</b>	<b>Value or Range</b>
Population served	30,000–8,000,000
Geographic location (U.S.)	West (1), Southwest (1), Mid–Atlantic (4), Southeast (7)
Finished water production (million gallons per day)	10–1,600
Length of distribution mains (miles)	180–6,000
No. of finished water storage tanks and reservoirs	3–180
Types of source water	Surface, ground, desalinated

**Table 3–2 Common Methods for Receiving and Routing the Customers’ Initial Telephone Call**

<b>Method</b>	<b>Percent Responding, %</b>
Direct transfer	50 (6/12)
Data entry, transfer	42 (5/12)
Data entry, answer attempt, transfer	33 (4/12)

1. n=12; Percentages exceed 100. Many utilities had more than one call receiving and routing method for the same data. Results show percent of utilities that used each method.

**Table 3–3 Most Commonly Asked Questions by Utility Personnel to Determine the Cause of the Customers Concern**

<b>No.</b>	<b>Question</b>
1	Can you describe the problem?
2	Is the problem at one faucet or throughout the building?
3	When did you first notice the problem?
4	Is the problem in both the hot and cold water?
5	Has there been any recent plumbing work done on the premises?
6	Has the water heater been turned off?
7	Are you new to the premises?
8	Have you noticed any unusual tastes or odors in the water?
9	What is the phone number where a utility representative can reach you today?

**Table 3–4 Descriptors Used at Four Utilities to Describe Customer Reported**

<b>Problem Descriptor</b>	<b>Utility A</b>	<b>Utility B</b>	<b>Utility C</b>	<b>Utility D</b>
Chlorine	6%	9%	—	—
Sulfur/sewage	7%	42%	—	—
Metallic	4%	1%	—	—
Earthy/musty	6%	—	—	—
Solvent/Gasoline	2%	—	—	—
Cloudy	10%	3%	2%	—
Rusty	11%	—	55%	—
Sediments	—	4%	6%	—
Particles	11%	—	—	—
Black	—	8%	2%	—
Green	—	—	1%	—
Blue	—	—	0%	—
Yellow	—	—	1%	—
Health	—	—	8%	—
Odor	—	—	19%	55%
Taste	—	—	4%	5%
Appearance	—	—	—	32%
General WQ	24%	—	—	—
Other T&O	19%	—	—	—
Other/NA	1%	33%	—	7%
X–Connect	—	—	1%	—
Reclaim	—	—	—	1%
Totals	100%	100%	100%	100%

**Table 3–5 Descriptors Used for Coding Black and Chlorine Water Quality Issues**

<i>Water that was or contained something “black”</i>
bl, black, black flakes, black particles, black pc, black plastic pc, black slime, black soot, black specks, black stains, black substance, black oily stuff, black/brown
<i>Water with a “chlorine” characteristic</i>
chlorine, chlorinous, chlorine/sulphur, Cl2, “Cl2”, Cl2 (bad), Cl2 high, strong bleach, strong Cl2.

**Table 3–6 Methods for Storing Customer Feedback Data**

<b>Method</b>	<b>Percent Responding, %</b>
Paper files	75 (9/12)
Spreadsheets	42 (5/12)
Database on one computer, not networked	33 (4/12)
Central database on networked computer	17 (2/12)

1. n=12; Percentages exceed 100. Many utilities use more than one method. Results show percent of utilities that used each method.



**Table 3–7 Current and Desired Methods for Integrating Customer Feedback Data with Utility Operation and Monitoring Systems**

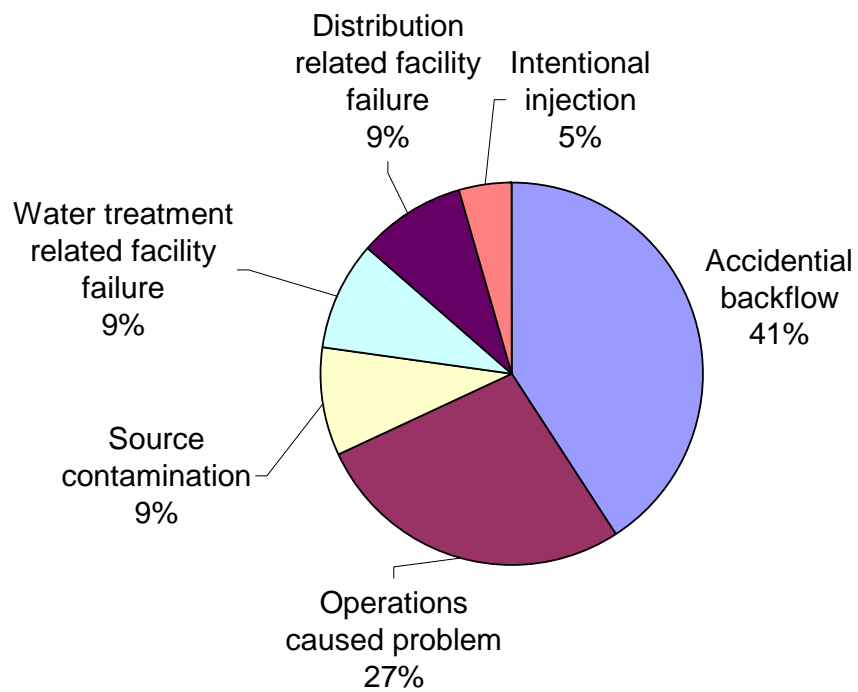
<b>Customer Feedback Data Linkages</b>	<b>Percent Responding, %</b>		
	<b>Current</b>	<b>Desired</b>	<b>TOTAL</b>
Work order or asset management system	77 (10/13)	23 (3/13)	100
Geographic information system / facility drawings	15 (2/13)	62 (8/13)	77
Water quality data on maps	0	46 (6/13)	46
Operations activities on maps	0	38 (5/13)	38
PipelineNet <sup>2</sup>	0	23 (3/13)	23
Medical syndromic surveillance data	0	8 (1/13)	8

1. n=13. Results indicate percent of utilities that have or plan to o desire to implement a specific customer feedback integration action.
2. PipelineNet is a hydraulic and water quality network modeling software package.

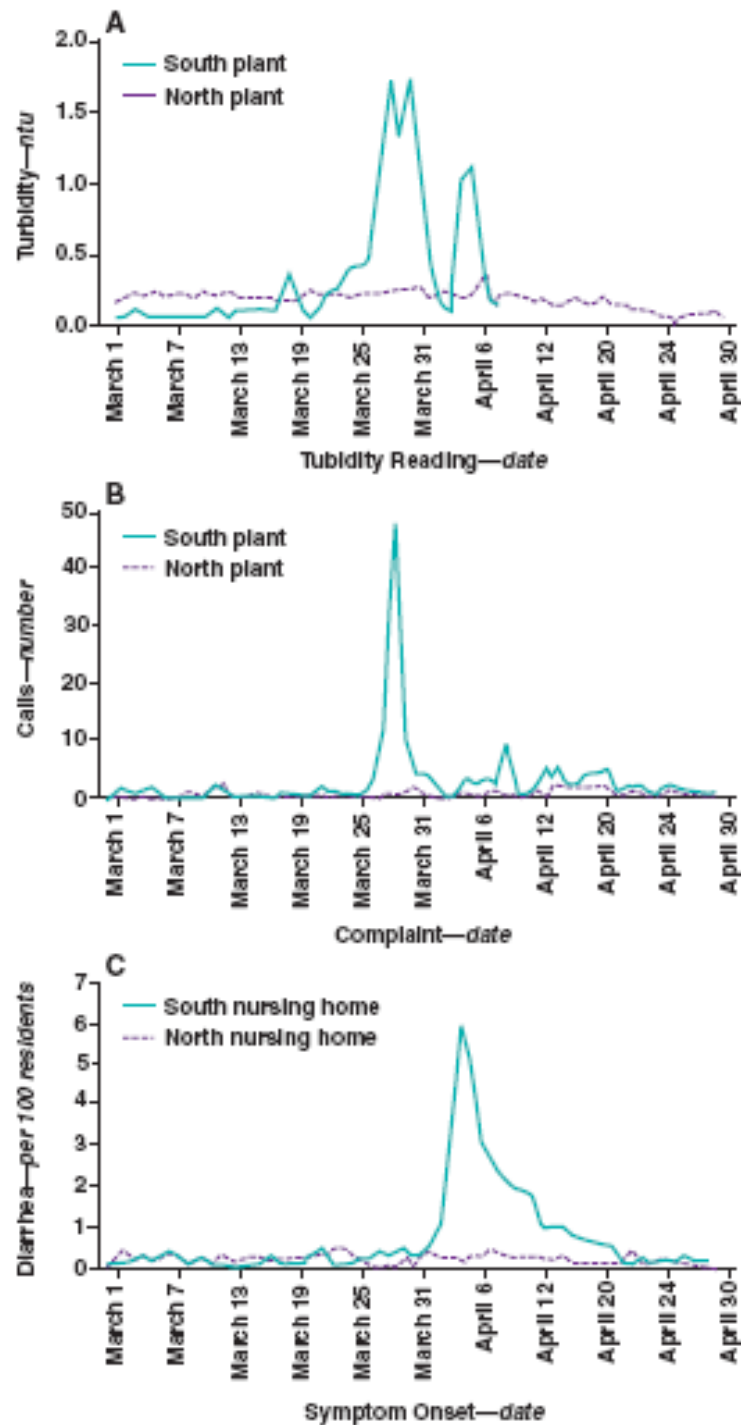
**Table 3–8 Examples of Three Tiered Approach to Customer Feedback Data Coding**

<b>Customer Problem Reported</b>	<b>Tier 1 Classification Selected</b>	<b>Tier 2 Category Selected</b>	<b>Tier 3 Descriptors Selected</b>
Neighborhood watch concerned about and existing hydrant connection	Engineering/Distribution	Facility	Vehicles/Equipment
Water dribbling, sputtering out of faucet	Engineering/Distribution	Pressure/Flow	Other
No water	Engineering/Distribution	Pressure/Flow	No Water
Rocks in urinal drain, toilets running continuously, and no water in urinals	Engineering/Distribution	Pressure/Flow	No Water; Other
Low pressure	Engineering/Distribution	Pressure/Flow	Low Pressure
Clogged water filters	Engineering/Distribution	Pressure/Flow	Other
Grease on skin after showering; black particles; brown water	Water Quality	Appearance	Black; Red / Brown; Other
Discolored water	Water Quality	Appearance	Cloudy / Milky
Oil seen in water	Water Quality	Appearance	Floating Particles
Water caused burning eyes and skin	Water Quality	Illness	Skin / Rash; Vision/Speech
Funny odor in water	Water Quality	Taste/Odor	Chemical / Medicinal

1. The basis of the three tiered customer feedback data coding approach is also shown in **Figures 3–5 and 3–6**.

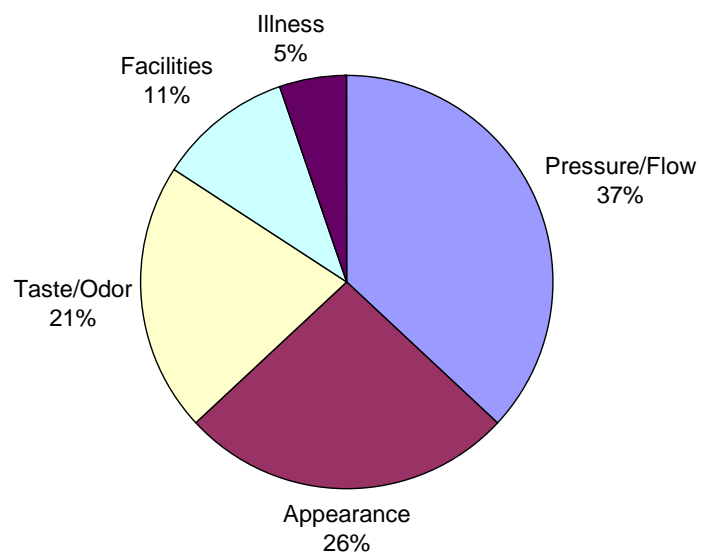


**Figure 3–1 Causes of Twenty Two Drinking Water Incidents Detected by Customer Feedback Warnings, 1977–2003**



**Figure 3–2 Comparison of Outcome Trends among Water Quality, Customer Complaint, and Diarrhea Illness Data at the Time of the 1993 Milwaukee Cryptosporidium Outbreak Investigation**

(a) Daily maximum water treatment plant effluent turbidity value, (b) daily number of water utility customer complaints received by the treatment plant, (c) daily prevalence of nursing home (NH) diarrhea rates per 100 residents.

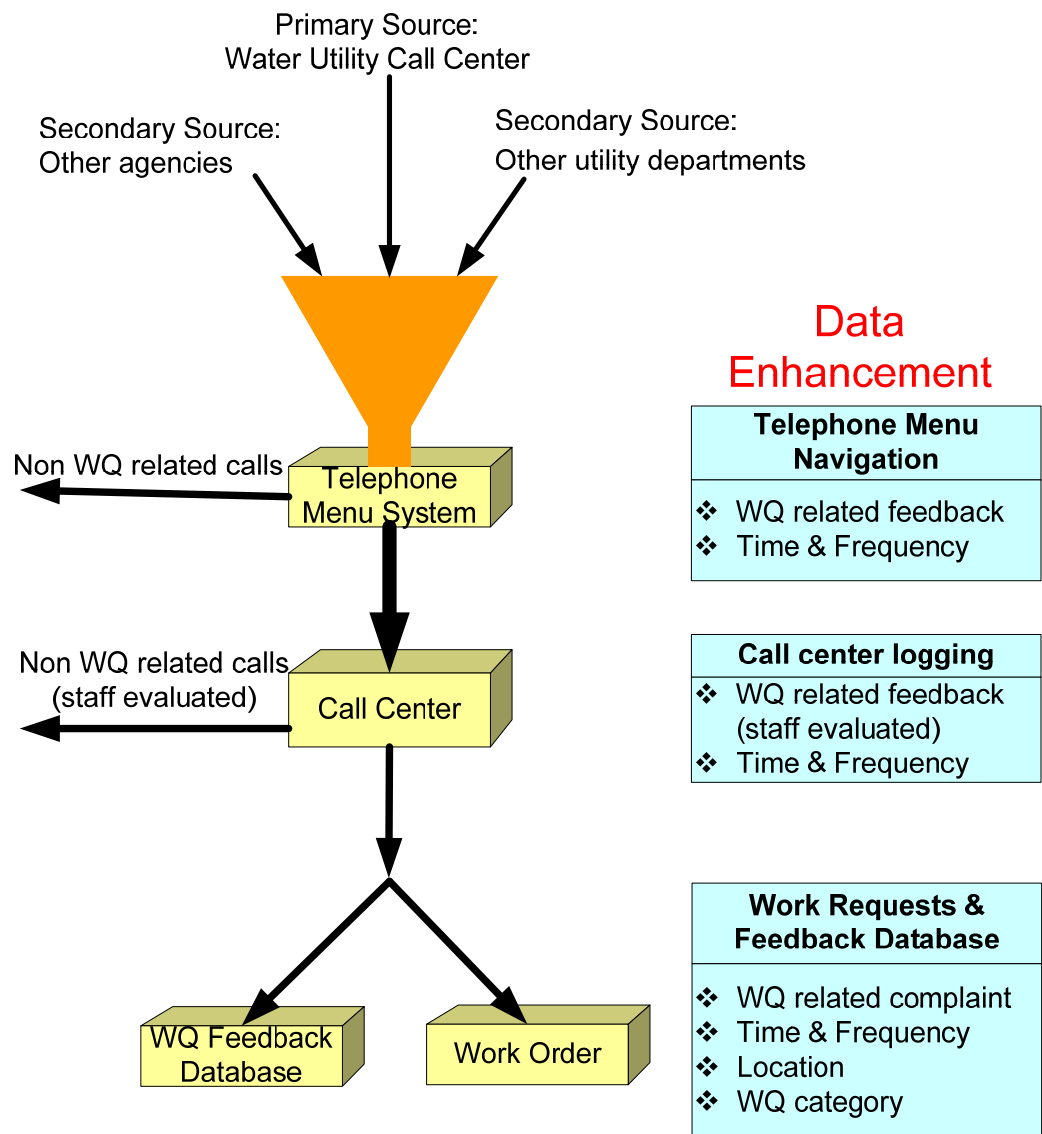


**Figure 3–3 Customer Feedback Descriptors used by Utilities to Detect 21 Contamination and Infrastructure Access Incidents, 1990–2005**

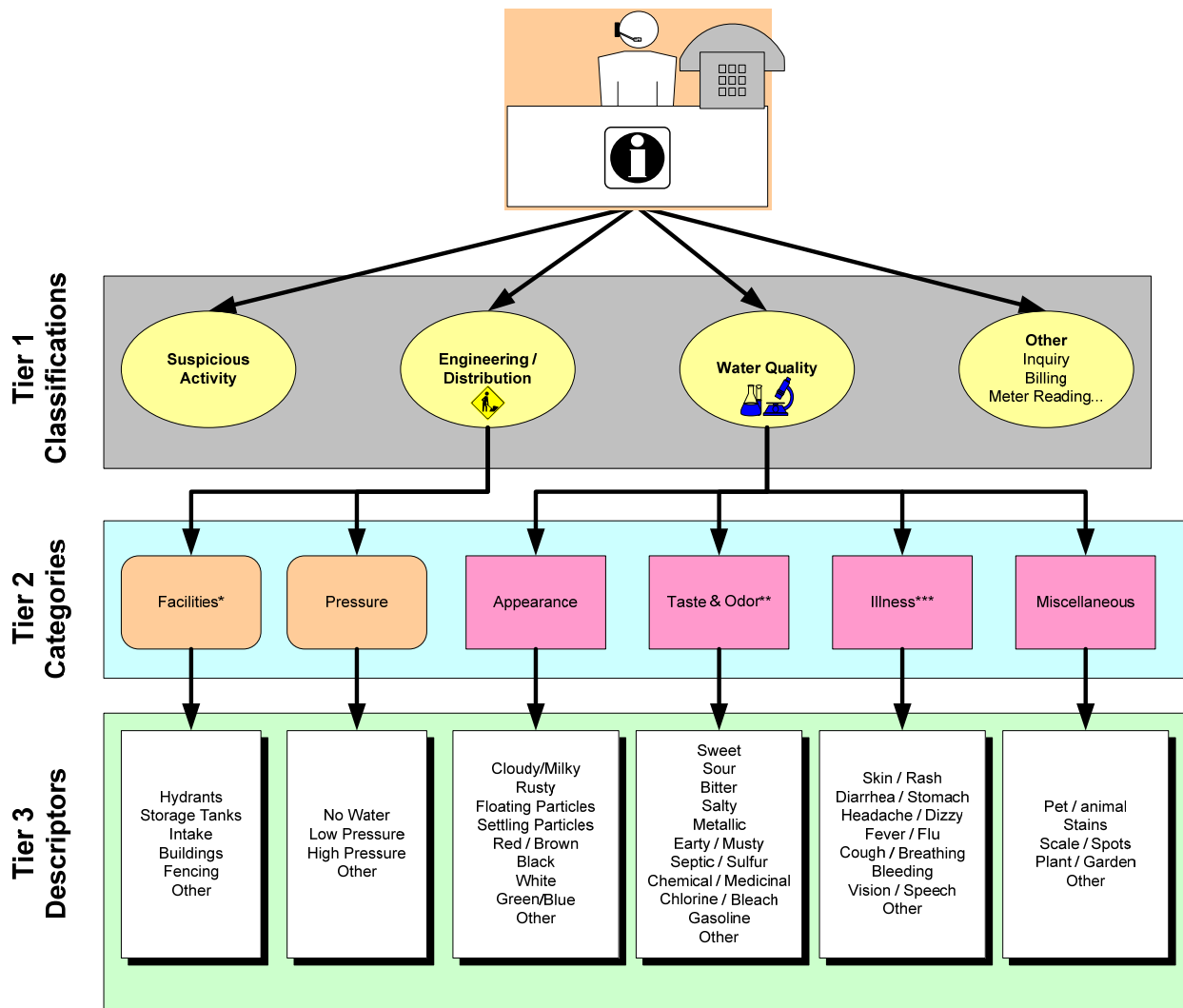
FUNNEL

FILTER

FOCUS



**Figure 3–4 The Recommended Filter, Funnel, and Focus Approach to Customer Feedback Data Optimization**



**Figure 3–5 Three Tier Approach to Customer Feedback Data Coding**

The basis of this approach is also shown in **Table 3–6** and **Figure 3–6**. There are 3 major classifications and 6 major categories. Within each category is a list of descriptors. \*Facility descriptors are based on USEPA (2003); \*\*Taste and Odor descriptors are based on the Taste and Odor Wheel \*\*\*Illness descriptors are adapted from accepted categories of Health Level 7 (RODS Laboratory, 2006); All other descriptors were compiled from utility site visits and literature data.

## Proposed Customer Feedback Check Sheet

PWSID No. 000000000

Water Plant #: (000) 000 -0000

Customer Service #: (000) 000 -0000

RECEIVING INFORMATION		
Customer Name:	Date:	Follow-Up Needed? Yes / No
Address:		Department Notified? Yes / No
Telephone:	Time:	
CODING		
ENGINEERING/DISTRIBUTION	WATER QUALITY	WATER QUALITY
<b>FACILITY ISSUES</b> <input checked="" type="checkbox"/> Descriptor <input type="checkbox"/> Hydrant <input type="checkbox"/> Storage Tank <input type="checkbox"/> Intake <input type="checkbox"/> Building <input type="checkbox"/> Fencing <input type="checkbox"/> Other  <b>PRESSURE ISSUES</b> <input checked="" type="checkbox"/> Descriptor <input type="checkbox"/> No Water <input type="checkbox"/> Low Pressure <input type="checkbox"/> High Pressure <input type="checkbox"/> Other	<b>TASTE AND ODOR ISSUES</b> <input checked="" type="checkbox"/> Descriptor <input type="checkbox"/> Sweet <input type="checkbox"/> Sour <input type="checkbox"/> Bitter <input type="checkbox"/> Salty <input type="checkbox"/> Metallic <input type="checkbox"/> Earthy/Musty <input type="checkbox"/> Septic / Sulfur <input type="checkbox"/> Chemical / Medicinal <input type="checkbox"/> Chlorine / Bleach <input type="checkbox"/> Gasoline <input type="checkbox"/> Other  <b>ILLNESS ISSUES</b> <input checked="" type="checkbox"/> Descriptor <input type="checkbox"/> Skin / Rash <input type="checkbox"/> Diarrhea/ Stomachache <input type="checkbox"/> Headache / Dizzy <input type="checkbox"/> Fever / Flu <input type="checkbox"/> Cough / Breathing <input type="checkbox"/> Bleeding <input type="checkbox"/> Vision / Speech <input type="checkbox"/> Other	<b>MISCELLANEOUS ISSUES</b> <input checked="" type="checkbox"/> Descriptor <input type="checkbox"/> Pet / animal <input type="checkbox"/> Stains <input type="checkbox"/> Scale / spots <input type="checkbox"/> Plant /Garden <input type="checkbox"/> Other  <b>COMMENTS</b>
WATER QUALITY	WATER QUALITY	WATER QUALITY
<b>APPEARANCE ISSUES</b> <input checked="" type="checkbox"/> Descriptor <input type="checkbox"/> Cloudy / Milky <input type="checkbox"/> Rusty <input type="checkbox"/> Floating particles <input type="checkbox"/> Settling particles <input type="checkbox"/> Red / Brown <input type="checkbox"/> Black <input type="checkbox"/> White <input type="checkbox"/> Green / Blue <input type="checkbox"/> Other		

Water Investigation ID No. 000000000

**Figure 3–6 Proposed Drinking Water Industry Check Sheet**

The basis of this approach is also shown in **Table 3–6** and **Figure 3–5**. Facility, pressure, appearance, taste and odor, illness, and miscellaneous are the six major categories. Descriptors (e.g., No Water; Chlorine / Bleach, Skin / Rash) are also provided.



## **Chapter 4 Critical Considerations for the Accelerated Aging of Polyethylene Potable Water Material**

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### **4.1 Abstract**

Accelerated aging conditions with chlorinated water were identified that minimize variations in solution chemistry and water sorption, and that also enable the interpretation HDPE physical and chemical changes during 20 week (3884 h) immersion periods. Of the ten conditions tested, three conditions with an alkalinity concentration of 50 ppm as  $\text{CaCO}_3$  at pH 6.5 and at 23 and 37 °C performed best. These three conditions exhibited stable pH, free available chlorine, and alkalinity concentration during 20 weeks of HDPE immersion with 72 h changes of aging solution. HDPE was periodically characterized using differential scanning calorimetry, thermogravimetric analysis, tensile analysis, a density gradient column, moisture analysis, and optical and infrared spectroscopy. Formation of surface carbonyl bonds and gradual reductions in oxidation induction time were detected, as well as water sorption into HDPE. Aging solution and water sorption monitoring recommendations from this work should be incorporated into accelerated aging protocols and considered when characterizing aged PE drinking water pipe.

**Keywords:** Aging, chlorine, oxidation, polyethylene, sorption, water

### **4.2 Introduction**

Polyethylene (PE) is a popular material for pressurized, cold and/or hot water, buried and premise potable water pipes due to its ease of installation, absence of corrosion related problems, low cost, and projected 50 to 100 year service life. In 2004, PE water pipe accounted for 33.5% of the worlds' plastic pipe demand [1]. In the UK and USA, PE represents 70% of some water utilities total pipe inventory, most commonly installed for pipes with diameters of 300 mm or less [2,3]. Global population growth and failure of drinking water infrastructure may continue to fuel PE water pipe usage worldwide.

Currently, medium-density (MDPE) and high-density polyethylene (HDPE) resins are commonly used and approved for cold water applications at about 25 °C or less. These thermoplastics operate well above their glass-transition temperature ( $T_g$ ) (exact value is under debate ranging from -20 to -140 °C as described by Boyd [4]) and have a melting temperatures ( $T_m$ ) ranging from 120 to 130 °C. When combined with additives such as phosphite and hindered phenol antioxidants, carbon black, and UV stabilizers, they are mechanically strong, elastic, and have great oxidative resistance. Even with the recent advent of bimodal PE resins, the mechanical strength of thermoplastic pipes deteriorate quickly under elevated temperatures so they cannot be used for hot water applications. As a result, crosslinked polyethylene (PEX) water pipes are being produced with higher molecular weights that improve their mechanical degradation resistance. PEX water pipe is extensively used across Europe and Asia and is increasingly being used in the USA for buried and plumbing applications [5].

Long-term exposure to water containing free available chlorine is known to have a deleterious effect on PE pipe mechanical, surface, and morphological characteristics. Mechanical PE pipe failure depends on material properties, pressure, temperature, water pH, free available chlorine concentration, and exposure time. Specifically, chlorinated water aged PE is signified by a reduction in antioxidant levels, increased crystalline content/amorphous region reduction, chain scission, tie molecule layering, broadening of the molecular weight distribution, increased hydroxyl, carbonyl, and/or vinyl group content, and visible striations and cracking on the surface [6–27]. Several researchers report that PE pipe degradation occurs after antioxidants are depleted. This depletion can occur nonuniformly due to natural antioxidant migration from the polymer into water and simultaneous penetration and consumption of chlorine [14,19,21,25]. The three major stages of PE pressure pipe degradation are: (1) chlorinated water attacks the pipe surface leaving a characteristic signature of oxygen, chlorine, hydroxyl, and vinyl components, (2) breakage of interlamellar tie molecules in the degradation region that allow increased chain layering and crystalline content, broader molar mass distribution as large polymer chains are fractured, and (3) microcrack formation which become visible, combine, and propagate through the pipe wall until the water pressure exceeds the pipe's mechanical strength and a leak or catastrophic mechanical burst/failure occur. Differences of opinion exist about the broadening of the molar mass distribution; some researchers propose that a statistical cleavage leads in most cases to narrowing of the distribution.

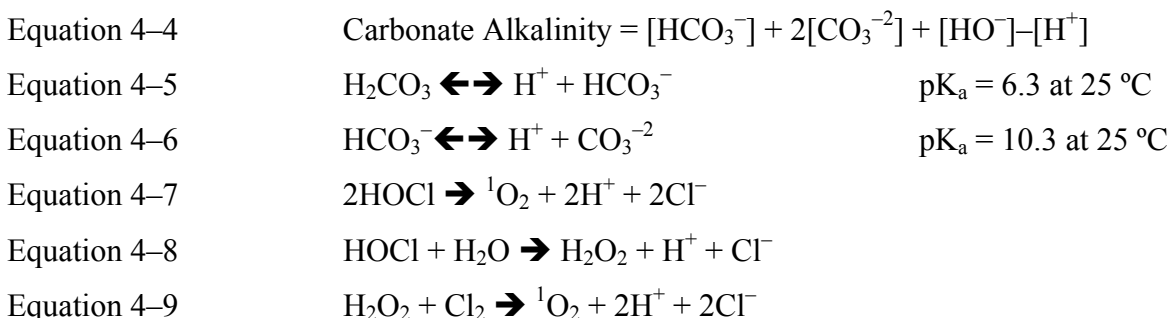
Knowledge gaps exist for aqueous chlorine accelerated aging of PE. First, there is an inconsistency in reporting of aging solution characteristics (e.g., chlorine concentration, pH, temperature, pressure, water change frequency). While there are several standard polymeric potable water material accelerated aging techniques (**Table 4–1**), many studies apply considerably different aging solution, environmental, and temporal conditions for testing PE and other polymers (**Table 4–2**). In particular, pH and water disinfectant levels (e.g., free available chlorine) are not always reported. Free available chlorine is the sum of aqueous HOCl, OCl<sup>–</sup>, and Cl<sub>2(aq)</sub> concentrations and is a measure of the amount of chlorine species that can oxidize organic or inorganic compounds. It is reported in units of “ppm as Cl<sub>2</sub> (w/v),” and concentrations up to 4 ppm as Cl<sub>2</sub> are permissible in USA drinking waters [44]. Water pH is another critical parameter of aquatic chemistry and since 1919 has been known to strongly influence biocidal effectiveness and chlorine equilibrium (**Equations 4–1 to 4–3**). Chlorine speciation depends on the pH thereby influencing the degree of polymer oxidation. Potable water in the USA commonly has a pH between 6.5 and 8.5 in accordance with Federal Regulation [44] and this pH range is common for most drinking waters worldwide. Drinking water pH values from 5 to 10 can occur but are not as common. Maximum rates of polymer degradation are reported to occur at pH values less than 7.5 [34,36,39,40] which indicated that the HOCl species would dominate in the drinking water pH between 6.5–7.5.

$$\text{Equation 4–1} \quad \text{Free Available Chlorine} = [\text{HOCl}] + [\text{OCl}^-] + [\text{Cl}_2]$$



No studies were found in the literature that reported measuring aging solution alkalinity before or after polymer treatment. Alkalinity is the acid–neutralizing capacity of water responsible for preventing water pH changes, is primarily accredited to HCO<sub>3</sub><sup>–</sup>, and CO<sub>3</sub><sup>–2</sup> from dissolved carbonate minerals, and is reported in terms of “ppm as CaCO<sub>3</sub>” [48]. Typical alkalinity values are 20–200 ppm as CaCO<sub>3</sub> for potable waters in the USA and levels >500 ppm as CaCO<sub>3</sub> occur depending on the source water (e.g., river, groundwater, lake, etc.) and the water treatment processes applied [2,45–47]. Several researchers have proposed that free radicals are present in chlorinated water [18,41,49–52] and alkalinity would play a key role in neutralizing

these compounds and preventing PE oxidation. As seen in **Equations 4–4 to 4–6**, alkalinity is influenced by water pH. Other weak acids and strong bases can contribute to alkalinity if their concentrations are in the same range as the carbonate species. Since free available chlorine decomposes to produce hydrogen ions and this decomposition is greatly accelerated at increased concentration and temperatures (**Equations 4–7 to 4–9**) [53], a reduction in alkalinity concentration would change aging solution quality. Another problem with reported aging studies is the magnitude of free available chlorine concentrations examined and the omission of initial and/or final free available chlorine concentration. For example, Dear and Mason [7,11] found drastic differences between polyethylene pipe failure and antioxidant profiles when aging was conducted at 80 °C with 0 to 5000 ppm versus 15000 to 125000 ppm chlorine solutions, whereby uniform antioxidant reduction and slow crack growth through the pipe wall was observed at lower chlorine levels only. Unfortunately, data were not provided to describe solution chemistry during or at the completion of the aging process. This makes interpretation of their PE physical and chemical analysis results difficult. Additionally, equilibrium constants like  $K_a$ 's are temperature dependent, typically reported at 25 °C, but must be adjusted by the van't Hoff equation when working at other temperatures. Water pH, water temperature, and alkalinity, are fundamentally related and because they influence chlorine speciation they need to be monitored and reported for PE aging studies.



A second knowledge gap exists in spite of the fact that water sorption and desorption from PE has been reported as far back as the 1960s. Water penetration into PE water pipe during accelerated aging studies has not been thoroughly examined. The presence of water in aged PE water pipe could impact material properties such as mechanical strength by influencing chain rotation and/or by plasticization. The three accepted water–polymer interactions are: (1) polymer/polymer whereby water penetrates and is located within layered chain cavities, (2) polymer/polymer whereby water penetrates and is located within layered chain cavities, (2) polymer/water where water is hydrogen bonded to additives such as carbon black, antioxidants,

and oxygenated backbone or branches, and (3) water/water where water molecules within cavities hydrogen bond with one another forming “clusters” [54–63]. Historically, water penetration has been reported in LDPE and MDPE films at temperatures greater than 50 °C and oxidized PE sorbed more water than unoxidized PE [55,65,66]. Marshall [67] reported one of the few investigations designed to examine water sorption in PE and concluded that 0.6–0.8 g of water sorbed per gram of PE (when immersed in 168–2000 h at 90 °C). The type of PE and the extent of oxidation were not specified. More recently, Gedde and Ifwarson [26] aged PEX water pipe with a hoop stress of 2.62 MPa, 110 °C, 17136 h exposure (chlorine free water but pH not reported) and concluded that infrared spectroscopy bands detected between 1680 and 1500  $\text{cm}^{-1}$  were not related to double bonding, but were due to water sorbed into the oxidized PEX pipe wall because water absorbs near 1600  $\text{cm}^{-1}$ . Smith et al. [25] “speculated” and Viebke and Gedde [21] proposed that water molecules were sorbed into the wall of MDPE pipe during accelerated aging because results of their antioxidant diffusion model for the internal pipe wall and external pipe wall were two orders of magnitude different (aging conditions: 80, 95, 110 °C, 0.84–2.51 MPa hoop stress, chlorine free water, pH not reported). In summary, the literature shows a precedent for water sorption in LDPE and MDPE at temperatures > 50 °C. No quantitative data were found for water penetration into PE during accelerated aging experiments for HDPE resin or potable water pipe at temperatures equal to or less than 37 °C. To truly understand aging solution effects on PE water pipe aging, aging solution characteristics and effect on PE water pipe oxidation should be evaluated.

A third knowledge gap of existing accelerated aging techniques is producing a polymer that can easily undergo chemical fate and transport investigations. Chemical interaction is very important to potable water pipe stakeholders because it can impact water safety, aesthetics, and structural integrity. Chemical interaction can be examined by immersing polymer samples in neat contaminant solution [68–70] or by exposing them to dilute aqueous solutions [71–74]. Most accelerated aging techniques (**Tables 4–1 and 4–2**) were developed to observe changes in polymer morphology, identify mechanical failure mechanisms, and estimate pipe service life using a pressurized pipe loop. These methods have helped elucidate the three distinct PE pipe failure modes: (1) ductile failure, (2) brittle failure, and (3) chemical degradation caused failure. However, aged pipe interior walls have a limited oxidized surface area for chemical interactions and the exterior un-aged pipe wall presents experimental challenged for immersion studies. The

absence of an accelerated aging method that produces uniformly aged polymer samples “on all sides” limits the study of how aged/oxidized polymeric materials interact with chemicals.

The research goal was to identify batch accelerated aging conditions that minimize variations in solution chemistry, water sorption by HDPE, and enable the interpretation of changes in HDPE physical and chemical properties. Our specific objectives were to: (1) quantify changes in pH, free available chlorine, and alkalinity concentrations during accelerated aging of HDPE resin and pipe (a) under initial pH and free available chlorine conditions representative of the literature which do not add alkalinity, and (b) using a systematic experimental matrix with nine temperature and chlorine combinations and alkalinity added in all solutions at 50 ppm as  $\text{CaCO}_3$ ; (2) ascertain if water is sorbed by HDPE resin or HDPE pipe; (3) provide recommendations for suitable batch accelerated aging conditions for polyethylene potable water materials.

## **4.3 Experimental Methods**

**4.3.1 Materials and Polymer Preparation.** Prepressed HDPE sheets (30.5 cm x 30.5 cm) of resin were obtained from McMaster–Carr, Inc. (Atlanta, GA) with a reported density of  $0.955 \text{ g/cm}^3$ . HDPE potable water pipe 19 mm in diameter, standard inner diameter dimension ratio of 9, made from PE 3408 resin, and reported density of  $0.954 \text{ g/cm}^3$  was obtained from a local plumbing supply company. Dog–bone shaped samples were cut from all polymers using a microtensile die Dewes Gumbs Die Company, Inc. (Long Island City, NY). Samples from HDPE water pipe (0.3 g) were removed from the axial direction (down the length of the pipe) and HDPE resin samples from the prepressed sheets (0.2 g). All samples were then thrice rinsed in distilled water and underwent desiccation at room temperature for 48 hours. Sample dimensions were obtained to the nearest 0.01 mm using a Mitutoyo™ digital micrometer. To attain the appropriate sample mass for thermal analyses (5–10 mg), cylindrical samples were punched from the dog–bone samples using a 1.58 mm diameter metal punch and were then split in half with an Exacto knife. Weight measurements were carried out (0.0001 g) using a Mettler–Toledo (Columbus, OH) balance with a Vernier Scale.

**4.3.2 Water Quality Measurements and Accelerated Aging Methods.** Aging solutions were prepared with reagent water from a Barnstead (Dubuque, IA) Nanopure® ultrapure water system, 6.5% sodium hypochlorite, and  $\text{NaHCO}_3$ . Water pH was adjusted using NaOH and HCl and pH was measured using a bench–top Accumet™ pH Meter 910 with probe. Alkalinity

concentration was measured by titration with 0.025N sulfuric acid to an end-point pH of 4.5 in accordance with Standard Method 2320(B) [75]. Free chlorine concentration was measured by titrating test solutions with added potassium iodide and glacial acetic acid using 0.025N sodium thiosulfate according to Standard Method 4500-Cl(B) [75].

The first aging method (referred to as the 5,000 ppm method) involved adding 6.5% NaOCl directly to reagent water to achieve 5,000 ppm as  $\text{Cl}_2$  free available chlorine concentration. pH was adjusted to 6.5 and no alkalinity was added. These conditions are representative of the literature (**Tables 4-1 and 4-2**). Twenty-five die-cut dog-bone shaped HDPE resin and HDPE pipe samples were placed in separate 1 L glass bottles with polypropylene caps. Chlorine solution was added and sealed bottles were stored vertically in a  $70 \pm 1^\circ\text{C}$  oven in the dark. Daily, solution pH was raised to 6.5 using NaOH. Every 7 days (168 h), HDPE samples were removed from the aging solution, rinsed thrice with reagent water, and placed in freshly prepared aging solution; the used aging solution and rinsate were collected for analyses. On Day 28 (628 h), the resin and pipe samples were removed from chlorinated solution and placed in reagent water and stored in the dark at room temperature. After 24 hours of soaking in reagent water, all remaining HDPE samples were removed and dried in a desiccator for 1 week. Three HDPE resin and HDPE pipe samples were removed from the solutions at Day 9, 14, and 28. These samples were dried in a desiccator. Sample thickness and weight measurements were conducted during the dry out period.

During the second aging method (referred hereafter as the temperature/chlorine matrix method), 150 dog-bone shaped HDPE pipe samples were immersed in one of nine aging solutions with varying chlorine levels (0, 45, and 250 ppm as  $\text{Cl}_2$ ) and water temperatures (23, 37, and  $70 \pm 1^\circ\text{C}$ ) and stored in the dark. In addition, the 250 ppm as  $\text{Cl}_2$  aging solution at  $37^\circ\text{C}$  was duplicated. Free available chlorine levels of 45 and 250 ppm as  $\text{Cl}_2$  were chosen because they are commonly used in shock chlorination of new and repaired water mains and building pipes worldwide [76–79], while 0 ppm as  $\text{Cl}_2$  solutions served as controls. All solutions initially contained 50 ppm alkalinity as  $\text{CaCO}_3$  (added as sodium bicarbonate) at pH 6.5 and water change-out occurred every 3 days. The alkalinity represents a moderately buffered tap water [2,48] and pH 6.5 has been reported to be aggressive for polymeric materials in contact with chlorinated water and within the USEPA regulated pH range [44]. Every three days water pH, free available chlorine, and alkalinity were measured in all solutions and HDPE pipe samples in

each bottle were rinsed thrice with reagent water and then placed in new aging solution in their constant temperature environments. Throughout the experiment, three samples were removed from each bottle for Fourier Transform–Infrared (IR) spectroscopy, OIT and visual observation analyses in an effort to detect signs of oxidation/aging. Aging conditions were stopped when either: (1) antioxidant levels (represented by OIT) decreased by at least 70%, (2) bond indices increased close to or more than 100%, (3) unusual surface changes were noticed, or (4) 20 weeks (3884 h) had passed.

### 4.3.3 Polymer Characterization

**4.3.3.1 Application of Characterization Techniques.** All polymer characterization techniques were carried out on new HDPE samples. In contrast, each set of aged HDPE samples were analyzed using a select set of techniques. **Figure 4–1** shows the polymer analysis techniques used for the 5,000 ppm method, while **Figure 4–2** shows the approach used for the temperature/chlorine matrix aging method.

**4.3.3.2 Bulk Properties.** Polymer composition was examined using a TA Instrument Q<sub>500</sub> thermogravimetric analyzer (TGA) (New Castle, DE), open platinum sample pan, and gas flow rate of 50 mL/min. Samples of 8–10 mg were evaluated and underwent heating from ambient temperature using a ramp of 10 °C /min. to 600 °C under nitrogen gas, purge time of 2 min., then were exposed under air from 600 °C to 800 °C. TGA data were interpreted according to ASTM [80]. A TA Instrument Q<sub>100</sub> differential scanning calorimeter (DSC) (New Castle, DE) was used for all calorimetric measurements. Melting temperature was determined using 5–10 mg samples, a covered aluminum sample pan, and nitrogen. Temperature was ramped at 10 °C/min. from 30 °C to 200 °C, then 200 °C to 30 °C, and then 30 °C to 200 °C. Crystalline content ( $w_c = \Delta H_{m[\text{Experimental}]} / \Delta H_{m[100\% \text{ Theroetical HDPE}]}$ ) was calculated by (1) using the area under the melting trace ( $\Delta H_m$ ) on the first heating where  $\Delta H_{m[100\% \text{ Theroetical HDPE}]}$  is 293 J/g [81], and by (2) using the experimentally measured sample density ( $1/\rho_s$ ), completely crystalline sample ( $\rho_c = 1.00 \text{ g/cm}^3$ ) and completely amorphous ( $\rho_a = 0.852 \text{ g/cm}^3$ ) bulk density [82]: Crystallinity =  $100 \times (1/\rho_s - 1/\rho_a) / (1/\rho_c - 1/\rho_a)$ . Oxidation induction time (OIT) was determined using 5–9 mg samples with an open aluminum sample pan. Under nitrogen with a flowrate of 50 mL/min., cell temperature was ramped from 50 °C to 200 °C at 10 °C/min. and this final temperature was held constant for 5 min. before the switch to pure oxygen. The onset of sample oxidation was determined by



drawing a line tangent to the isothermal baseline and the steepest slope of the exothermic peak. The bulk density of each polymer was determined with a density gradient column using a mixture of 2-propanol (>99% purity) and distilled water to generate a density range of 0.88 to 1.00 g/cm<sup>3</sup> at 23 ± 0.1 °C as outlined in ASTM [83].

**4.3.3.3 Mechanical Properties.** Tensile strength and percent elongation at break were determined using a Stable Microsystems, Ltd. (Surrey, UK) TA–XT2i texture analyzer at 23 °C. Sample width, thickness, and gauge length were measured prior to testing. The crosshead speed (1 mm/s) resulted in sample fracture in about 1 min. Stress ( $\sigma$ ) and percent elongation were calculated using the applied force, sample dimensions, initial ( $L_0$ ), and final sample length ( $L$ ):  $\sigma = \text{Force} / \text{Area}$ ;  $\text{Area} = \text{Sample width} * \text{Sample thickness}$ ;  $\text{Percent elongation} = 100 * (L - L_0) / L_0$ .

**4.3.3.4 Surface Characteristics.** Surface chemistry was characterized using a Perkin Elmer Spectrum One Fourier Transform Infrared spectrometer (Waltham, MA) in Attenuated Transform Reflectance (ATR) mode with a ZnSe crystal at 4 cm<sup>-1</sup> resolution. Background was determined using 100 scans from 4000 to 600 cm<sup>-1</sup>, and 25 scans were conducted for each sample also over this range. Select bond indices were calculated based on IR data [36,84]. These include: carbonyl ( $\sigma_{1715} / \sigma_{2912}$ ), vinyl ( $\sigma_{908} / \sigma_{2912}$ ), hydroxyl ( $\sigma_{1725} / \sigma_{2912}$ ), and chlorine ( $\sigma_{660} / \sigma_{2912}$ ). Optical microscopy images were obtained using a HIROX (River Edge, NJ) KH–7700 3D digital video microscope.

**4.3.3.5 Water Sorption.** A convection oven, moisture analyzer, desiccator, and DSC were used to determine HDPE moisture content. Aged samples were placed in a convection oven for 8 hours at 70 ± 1°C. Samples were also dried using a moisture analyzer at 105 °C and drying was halted once a 0.005% change in sample mass over 1 min. was not achieved. DSC was used to cool samples from 23 °C to –120 °C and heat them from –120 °C to 20 °C with ramps of 10 and 20 °C/min similar to Bair et al. [59].

## 4.4 Results and Discussion

**4.4.1 New HDPE.** Bulk property results for HDPE specimens are shown in **Table 4–3**. The oxidative resistance (OIT and  $T_{deg}$ ) of commercial HDPE pipe was greater than HDPE resin, which can be attributed to the presence of additives in the commercial product and limited

amount of these in the resin. As expected, HDPE pipe contained 2% carbon black which is a common pipe additive, while the HDPE resin did not. The OIT of large ( $9.5 \pm 0.6$  mg,  $n=3$ ) and small ( $6.2 \pm 0.5$  mg,  $n=3$ ) HDPE pipe samples were not different ( $p<0.05$ ). Experimentally measured density for the new HDPE resin ( $0.9572 \pm 0.0000$  g/cm<sup>3</sup>,  $n=3$ ) was 0.3% greater than the manufacturer's reported value (0.955 g/cm<sup>3</sup>) while the measured commercial HDPE pipe density ( $0.9494 \pm 0.0000$  g/cm<sup>3</sup>,  $n=3$ ) was lower than the reported density (0.954 g/cm<sup>3</sup>). Crystalline content comparisons verify that HDPE resin was denser than HDPE pipe and within typical HDPE density and crystallinity range [82]. However, variability between these two estimation techniques is quite great which cannot be easily explained.

#### **4.4.2 Aging Method with 5,000 ppm as Cl<sub>2</sub> at 70 °C and No Alkalinity**

**4.4.2.1 Oxidant Solution Changes during Aging.** During the 28 day exposure period with water changes every 168 h (7 days), free available chlorine levels consistently decreased from approximately 5,000 ppm to  $260 \pm 98$  ppm as Cl<sub>2</sub> solutions containing HDPE resin and to  $245 \pm 118$  ppm as Cl<sub>2</sub> in solutions containing HDPE pipe during each 7 day (168 h) exposure period. A lower free available chlorine concentration reduction ( $680 \pm 495$  ppm as Cl<sub>2</sub>) was detected in control solutions without HDPE. In all chlorine solutions, water pH decreased daily from pH 6.5 to about pH 3.0 from Day 1 to Day 5 (120 h) due to daily acid production from chlorine decomposition (**Equations 4–7 to 4–9**). A less significant reduction in water pH occurred between Day 5 (120 h) and Day 7 (168 h) and can be attributed to a less hydrogen ions production due to degradation of remaining free available chlorine. For days 21 to 28, a total of 0.0749, 0.0796, and 0.0805 eq NaOH/L were added to raise the pH to 6.5 in resin, pipe, and control solutions, respectively. Roughly the same amount of acid was produced in each bottle during Day 21 (504 h) through 28 (672 h).

After three days of chlorinated water exposure, particles were present at the bottom of bottles containing resin and pipe samples and were consistently present throughout the experiment. Aging solutions visually increased in cloudiness from the 3<sup>rd</sup> to 7<sup>th</sup> day of exposure during each seven day aging period. No particles were found in control solutions during any exposure period. Particle composition was investigated by collecting a 10 mL filtered (0.45 µm) and unfiltered water sample from the resin, pipe, and control aging solutions. No residue was detected on the control sample filter surface; however, yellowish–white residue and pinkish–

white residue remained on the filters from resin water and pipe water, respectively. Residue from unfiltered samples was digested using 2% by volume of 15N nitric acid at 70 °C for 48 h. After 48 h the particles were still present in unfiltered resin and pipe solutions containing nitric acid which indicates they were organic particles and likely originated from PE.

**4.2.2.2 Polymer Degradation during Aging.** Visual changes in polymer color for both HDPE resin and pipe were noticeable after 9 days of exposure. The opaque HDPE resin turned a bright white and black HDPE pipe turned a grayish–white and these color differences were more noticeable after desiccation. **Figure 4–3** indicates a progression of small surface pits (Day 9 / 216 h), which increased in size and abundance (Day 14 / 336 h), and ultimately led to complete surface coverage (Day 28 / 672 h).

On Day 28 (672 h), resin and pipe samples were removed from chlorinated water and placed in reagent water. Interestingly, after placing the resin and pipe samples in reagent water, 7.9 % and 26.9% of resin and pipe samples, respectively rested at the bottom of the 1L bottles (**Figure 4–4**). This was surprising because all resin and pipe samples rose to the water surface in chlorinated water. No reports of similar HDPE sinking phenomena in chlorinated water immersion aging solutions were found in the literature.

No changes in sample thickness were detected on dried samples removed on Days 9 (216 h) and day 14 (336 h). This was determined by comparing the mean thickness of 25 die-cut samples of resin ( $1.65 \pm 0.02$  mm) and pipe ( $2.63 \pm 0.07$  mm) against the mean of 3 samples removed on Days 9 (216 h) and day 14 (336 h). The aged polymers samples lost weight during 23 °C desiccation (**Figure 4–5**).

Differences, however, were detected when 28 day (336 h) aged HDPE pipe samples were analyzed by DSC using an open sample pan. A cylinder was punched from a 28 day (336 h) aged HDPE pipe sample and split into 3 subsections (2 exterior and 1 interior). The interior pipe region OIT was 13 min. and was 46% crystalline, while exterior regions had OIT values of about 3 min. and were 50 and 43% crystalline. A reduction in exterior subsection melting temperature was also observed ( $121 \rightarrow 117$  °C). In comparison, another cylinder was punched from the 28 day (336 h) aged HDPE resin, but was sliced through–and–through (sample contained all regions). Analysis results for this composite sample revealed an OIT of 3 min. and 51%

crystallinity (10% less than the new HDPE resin). There was no difference between the melting temperature of new and 28 day aged HDPE resin. These data imply that crystalline content was reduced in both PE types over the 28 day (336 h) period, the antioxidant level was drastically reduced in the exterior HDPE pipe region, and antioxidants remained at a low level inside the HDPE pipe even though the HDPE pipe surface showed extensive visual degradation. This variation could be due to sorbed water being released during heating under OIT analyses as well as chain scission caused by chlorinated water induced oxidation.

Weight loss during desiccation is likely due to desorption of water molecules which sorbed into the polymer during aging. This observation is supported by HDPE samples resting at the bottom of the reagent water solutions which happens when their density is greater than water. Also, a 0.015–0.020 g of loss occurred during desiccation for samples aged for 28 days (672 h). The differences in the melting thermogram could also be due to water desorption during sample heating in an open sample pan, which was not detected in new HDPE. It is also possible that chlorine attacked the amorphous component of the polymer causing some porosity. This is the first study to evaluate water sorption into HDPE, and while the exact quantity of water was not determined, the results imply water sorption occurred.

#### **4.4.3 Aging Method with Temperature/Chlorine Matrix and Alkalinity at pH 6.5**

**4.4.3.1 Oxidant Solution Changes during Aging.** Table 4–4 provides the measured initial characteristics of the aging solutions and reveals that significant water quality changes were observed in some but not all aging solution characteristics during each three day exposure period. The 250 ppm as  $\text{Cl}_2$  solution at 70 °C was halted after one 3 day exposure period because water pH dropped from 6.5 to 4.1 and this does not represent typical drinking water conditions. On Day 30, both the 0 and 45 ppm as  $\text{Cl}_2$  aging solutions at 70 °C were halted because visual physical degradation/graying of the polymer was observed and OIT was almost zero for HDPE in the 45 ppm as  $\text{Cl}_2$  solution. The 250 ppm as  $\text{Cl}_2$  solution at 37 °C was halted on Day 60 because surface pits were observed while a replicate aging condition was continued until Day 90 even though pits were observed at Day 60. All other treatments were conducted for 141 days.

In summary, the following water quality changes were detected in control and chlorine aging solutions. For 0 ppm as  $\text{Cl}_2$  37 and 70 °C control solutions, consistent statistically significant increases were detected in water pH, and the magnitude of the pH change generally

increased with increased temperature. A pH increase can be explained by the leaching of pipe antioxidants [12]. Alkalinity remained constant in all control solutions at all temperatures ( $p > 0.05$ ); therefore, under these temperature conditions, the temperature and exposure time used did not change alkalinity. In contrast, changes in pH, chlorine, and alkalinity were detected in solutions that contained 250 ppm as  $\text{Cl}_2$  at 37 °C. Specifically, chlorine decomposition consumed alkalinity and less chlorine decomposition occurred at lower temperatures as shown by results in **Table 4–4**. Aside from the control, the 50 ppm as  $\text{Cl}_2$  aging conditions were the most stable. Statistically significant changes in pH, chlorine, and alkalinity were detected at the 70 °C conditions, while no changes in these parameters were detected at either 23 or 37 °C. For the 45 ppm as  $\text{Cl}_2$  and 70 °C solutions, the free available chlorine level consistently decreased from 45 to 4 ppm as  $\text{Cl}_2$  and alkalinity decreased from 50 to 30 ppm as  $\text{CaCO}_3$ .

**4.4.3.2 Polymer Degradation during Aging.** OIT values for chlorinated water aged HDPE were difficult to determine because heat was gradually evolved and the tangent to the onset of oxidation varied considerably. This variation likely represents stabilizer package consumption and migration into water. Heat was not evolved from new HDPE until a sharp increase was detected (**Figure 4–6**). These leading edges indicate that the oxidation reaction is slow [85]. Slow oxidation observed in aged HDPE samples could be due to the change in molar mass distribution because of chain fracture due to chlorinated water attack. OIT reduction trends shown in **Figure 4–7** are consistent with the literature and show a gradual reduction of OIT over time. A greater OIT reduction was observed at higher chlorine concentrations and water temperatures. Rapid OIT reductions occurred for HDPE pipe aged in all 70 °C solution. This rapid reduction could be attributed to simultaneous water penetration into the HDPE, accelerated antioxidant migration out of the polymer, and possibly thermal destruction of the antioxidant within the polymer. The OIT of pipe samples aged in 23 and 37 °C control solutions (no chlorine present) were unchanged.

HDPE surface oxidation occurred under some aging conditions and indicated by IR spectroscopy data from 0, 720, 2160, and 3884 h; this oxidation occurred *before* sample OIT levels were zero. Absorbance intensities were unchanged for control samples at all temperatures over the entire 3884 h exposure period. In contrast, detectable changes in absorbance were found for chlorine aging solutions at different exposure times. Primarily, a broad carbonyl band, likely representing a compilation of several carbonyl species as described by Silverstein and Webster

[86] was detected near 1710 and 1730  $\text{cm}^{-1}$  and gradually increased in intensity for a number of the chlorinated water treatments (**Figure 4–8**). The broad carbonyl band was detected after 720 hr on HDPE samples exposed to the following solutions: 250 ppm as  $\text{Cl}_2$  at 23 and 37 °C, 45 ppm as  $\text{Cl}_2$  at 23 and 37 °C. No other IR band differences for the exposure periods examined were detected. Previous research examined PEX and attributed the presence of water to bands detected between 1660 and 1500  $\text{cm}^{-1}$  [26], but results from our study do not show any spectral differences for new HDPE and aged HDPE bands in this region.

**4.4.3.3 Comparison of HDPE Pipe Morphological and Mechanical Characteristics after Aging.** The bulk density of new ( $0.9494 \pm 0.0002 \text{ g/cm}^3$ ) HDPE pipe and samples aged at 250 ppm as  $\text{Cl}_2$  at 37 °C for 2880 h ( $0.9495 \pm 0.0027 \text{ g/cm}^3$ ) and 250 ppm as  $\text{Cl}_2$  at 23 °C for 3884 h ( $0.9508 \pm 0.0004 \text{ g/cm}^3$ ) were not significantly different from new HDPE pipe (ANOVA,  $p > 0.05$ ). Even though HDPE was oxidized as shown by the loss of antioxidant and surface oxidation, the extent of oxidation did not significantly alter crystallinity. A density of  $0.9494 \text{ g/cm}^3$  was obtained for HDPE pipe aged using 45 ppm as  $\text{Cl}_2$  at 37 °C for 3884 h. This single measurement was similar to the densities of new and HDPE pipe aged at 250 ppm as  $\text{Cl}_2$  23 and 37 °C. HDPE pipe aged at 250 ppm as  $\text{Cl}_2$  at 37 °C for 2880 h was expected to have the greatest degree of oxidation and thus we expect no difference in crystallinity for HDPE pipe aged using lower chlorine levels at the same temperature and exposure time. Paired comparison testing of mechanical strength data demonstrated that a statistically significant difference existed only for tensile strength at break for HDPE pipe aged in 250 ppm as  $\text{Cl}_2$  at 37 °C in comparison to new and all other aged HDPE ( $p < 0.05$ ). Surprisingly, differences for elongation at break and tensile strength at yield were insignificant between new and all aged HDPE pipe samples (**Table 4–5**). There was, however, great variability in elongation at break results and a clear brittle failure mode for 250 ppm as  $\text{Cl}_2$  37 °C samples in comparison to ductile fracture for new and all other aged HDPE pipe samples. Ductile failure can be attributed to chain fracture as well as chain disentanglement [87] which were caused by chlorinated water induced oxidation.

**4.4.3.4 Water Desorption.** HDPE samples from 0, 45, and 250 ppm solutions at 37 °C were dried using three approaches. In contrast to Bair et al. [59], who detected water in polycarbonate, no endothermic or exothermic peaks were detected in thermograms for HDPE pipe aged for 2880 h in 250 ppm as  $\text{Cl}_2$  solution at 37 °C during cooling under liquid nitrogen

from 23 °C to -120 °C and reheating to 23 °C. These analyses include two and three replicates for 20 °C/min and 10 °C/min ramps, respectively. Convection oven and bench-top desiccation resulted in only a statistically significant reduction in the mass of HDPE pipe samples aged in 250 ppm as  $\text{Cl}_2$  37 °C solution (**Table 4–6**). The moisture analyzer technique did not prove effective as shown by the highly variable moisture levels detected in the 3.2 g samples. The 3.2 g samples represent the combined mass of 10 dog-bone samples dried simultaneously in an effort to increase the likelihood of detecting a mass reduction. Great variability in the moisture analyzer method could be due to the inability of the moisture analyzer to detect small changes of sample mass (0.001 g) and/or the water molecules trapped inside HDPE required greater time to desorb than was provided. Another complicating factor could be that samples containing a greater amount of oxygen sorb a greater amount of water [55]. In addition, an oxidized region/front may penetrate polyethylene due to chlorinated water exposure. In our study, water molecules may have had a greater affinity for oxygenated HDPE surfaces and thus the most oxidized HDPE was the most susceptible to water penetration. While we did not specifically measure the depth of an oxidized region/front, such an oxidized front may have contributed to water sorption for HDPE pipe samples immersed in 250 ppm as  $\text{Cl}_2$  at 37 °C. Finally, the volatilization of fractured chains due to chlorinated water attack and/or material components could have also contributed to mass reduction in 250 ppm as  $\text{Cl}_2$  37 °C HDPE pipe samples, but contrary to that presumption reductions in HDPE pipe mass for new and samples in 0 ppm as  $\text{Cl}_2$  at 37 °C aging solution were negligible. Because relatively mild treatments were applied in the temperature/chlorine matrix aging approach, results from the 5,000 ppm as  $\text{Cl}_2$  aging condition and similar literature reports, we believe that a limited amount of water sorbed into HDPE exposed to the 250 ppm 37 °C solution only and was quickly desorbed by 8 h of convection oven drying.

#### 4.5 Conclusion

This research demonstrates that chlorinated water aging solution pH, free available chlorine, alkalinity, and temperature must be carefully monitored during sample exposure. Without monitoring and reporting the initial and final aging solution characteristics, interpretation of polymer physical and chemical results is difficult as is study replication. Drastic pH reductions can occur within 24 h for an aging solution that contains 5000 ppm as  $\text{Cl}_2$  at 70 °C due to chlorine decomposition and the absence of an acid-neutralizing component. This drastic

pH shift is not typical of drinking water in water distribution system and changes the solution's chlorine equilibrium chemistry. HDPE resin and pipe aged at 5000 ppm as  $\text{Cl}_2$  and 70 °C physically deteriorated within 72 h to the extent that HDPE sinks when placed in reagent water.

Solution chemistry changes can occur even when aging solution characteristics are less drastic and more typical of potable water. A 50 ppm as  $\text{CaCO}_3$  alkalinity concentration will prevent pH shifts for 45 and 250 ppm as  $\text{Cl}_2$  aging solutions at 23 and 37 °C over 72 h. Drastic and moderate pH reductions will occur in 70 °C aging solutions with 250 ppm and 45 ppm as  $\text{Cl}_2$ , respectively. The pH reduction is caused by an increased chlorine decomposition rate to form a strong acid and subsequent alkalinity consumption. While lesser changes in aging solution quality occur when alkalinity is present, pH, free available chlorine, and alkalinity concentrations should still be monitored so that these data can be used to interpret polymer property changes.

This is the first study to demonstrate water sorption and desorption by HDPE resin and HDPE potable water pipe. The exact quantity of water sorbed could not be measured by DSC freezing, convection oven, and desiccation drying methods. Based on the 5000 ppm as  $\text{Cl}_2$  results, it is concluded that water sorption by HDPE resin and pipe occurred at 70 °C. Water sorption was not detected in most of the 23 and 37 °C HDPE pipe aging conditions with the exception of the 250 ppm as  $\text{Cl}_2$  at 37 °C. HDPE pipe aged in 250 ppm as  $\text{Cl}_2$  at 37 °C sorbed water and then desorbed all of that water during 8 h of 70 °C convection oven drying and most of the water during 2 weeks 23 °C desiccation. The difference between desiccation and oven drying could be due to clustered and/or hydrogen bonded water that will not desorb at room temperature. Future work should be conducted to elucidate the PE water sorption phenomena.

**Table 4–7** describes recommended water quality conditions for the accelerated aging of polyethylene materials. Conditions listed in **Table 4–7**, or similar conditions such as aging at 25 or 40 °C, represent those that minimize pH, free available chlorine, and alkalinity changes during a 72 h immersion period (in absence of flow and pressure). The conditions in **Table 4–7** emphasize aging in chlorinated drinking water and minimize thermal degradation. This is appropriate for HDPE when used for most cold–water distribution applications, although it would not be appropriate for drinking water or industrial applications which use warm or hot water. Accelerated chlorine aging of HDPE pipe at 70 °C represents both reaction with chlorine and thermal oxidation. Due to the potential of water sorption in HDPE, accelerated aging should



not be conducted at 70 °C for pipes that are to be used for buried water mains or for those buried water pipes that will be used for subsequent chemical interaction experiments. Aging at, or near, 23 and 37 °C could be conducted on any HDPE pipe as long as the researchers acknowledge that 37 °C aged HDPE sorbed water. Because all American Society for Testing and Materials (ASTM) and National Sanitation Foundation (NSF) accelerated aging protocols omit the importance of alkalinity, and ASTM D6284 does not require monitoring and reporting pH and free available chlorine changes during the experiment, it is recommended that these standards be revised to incorporate monitoring of the aging solution as well as pH control and conditions more representative of potable water.

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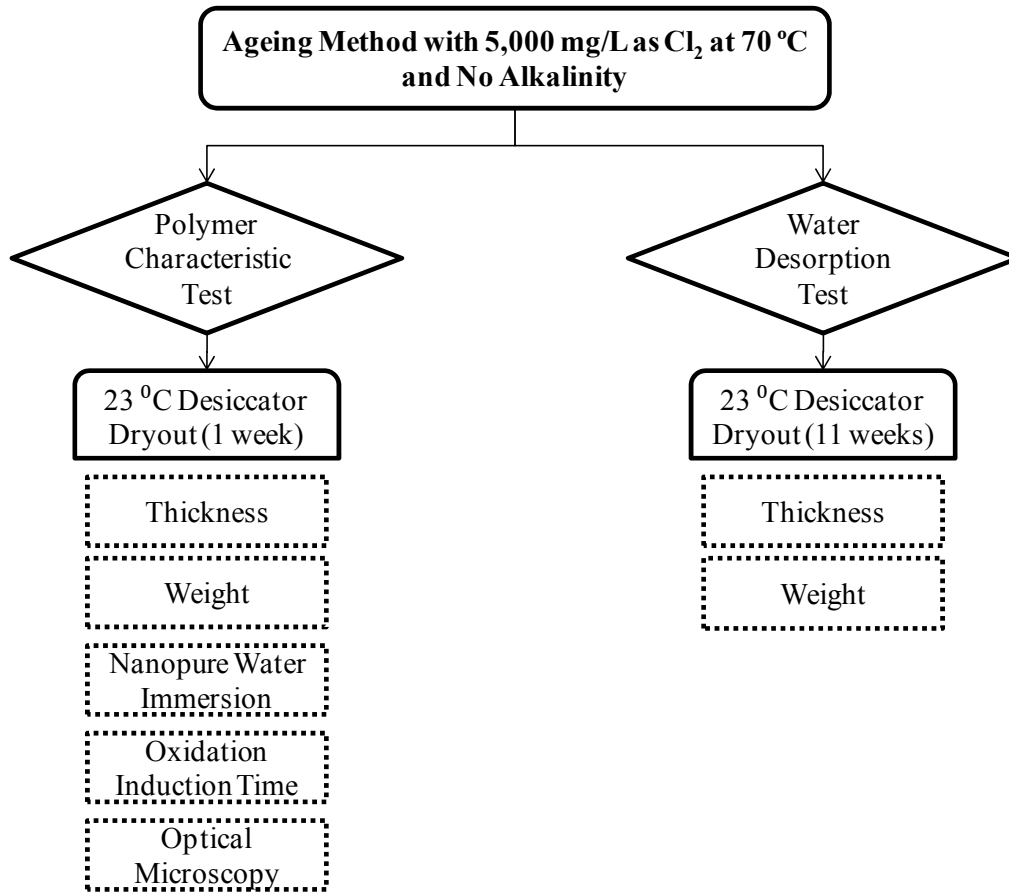
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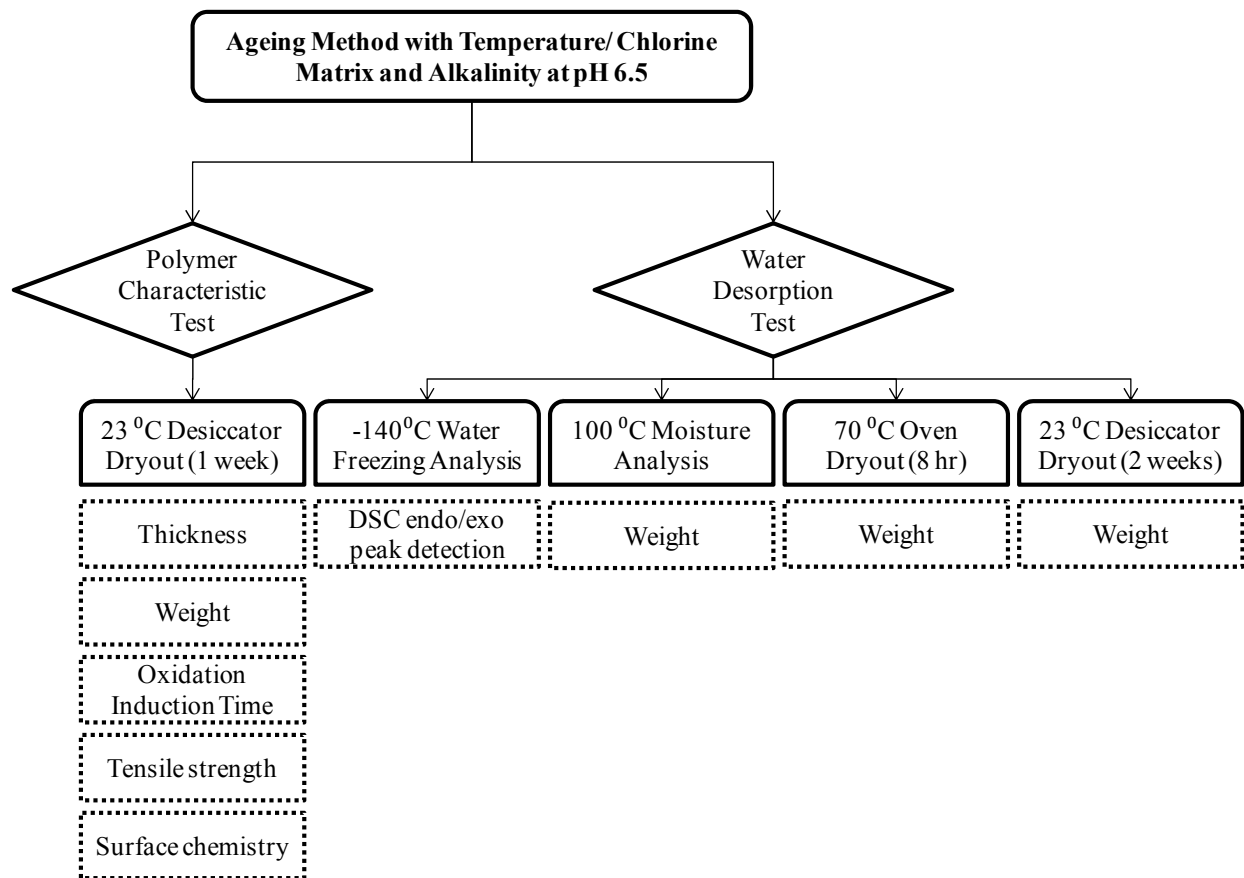
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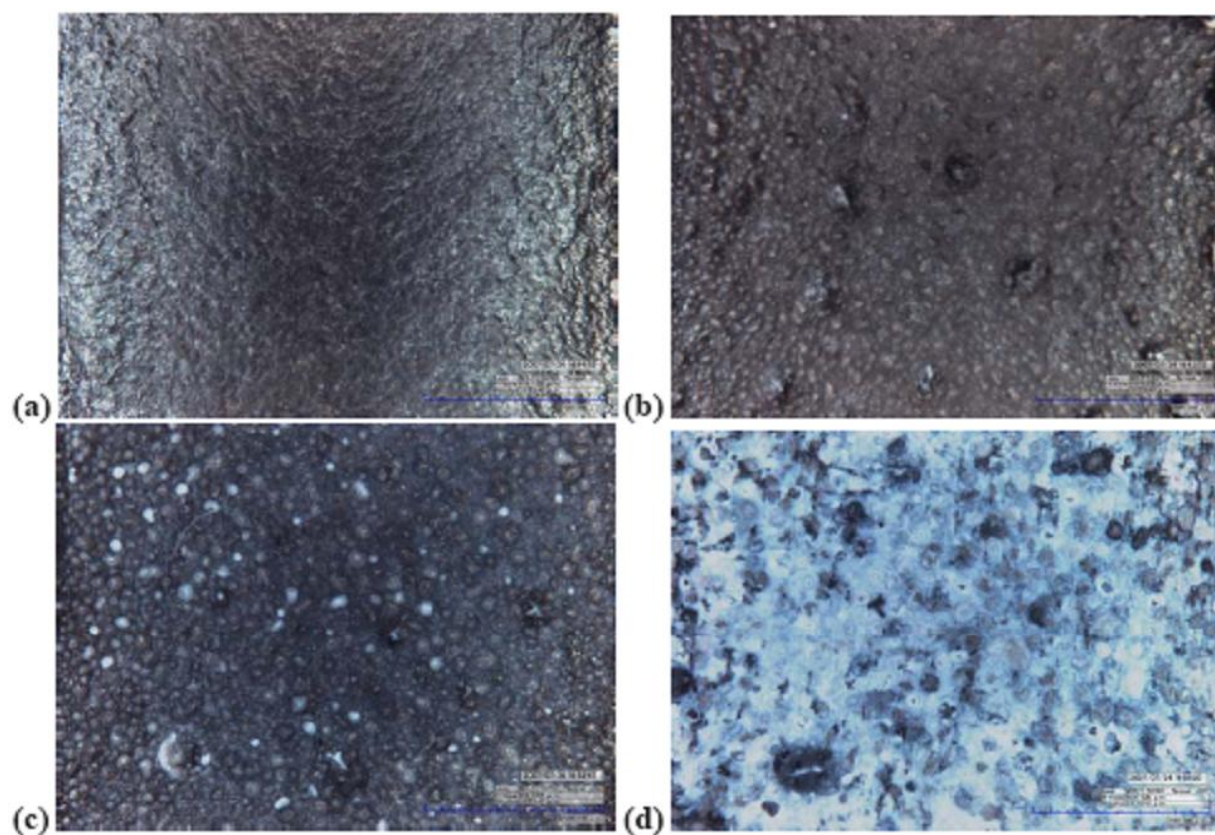
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**Figure 4–1 Techniques Used to Analyze HDPE Samples from the 5,000 mg/L Cl<sub>2</sub> Aging Method**



**Figure 4–2 Techniques Used to Analyze HDPE Samples from the Temperature/Chlorine Matrix Aging Method**



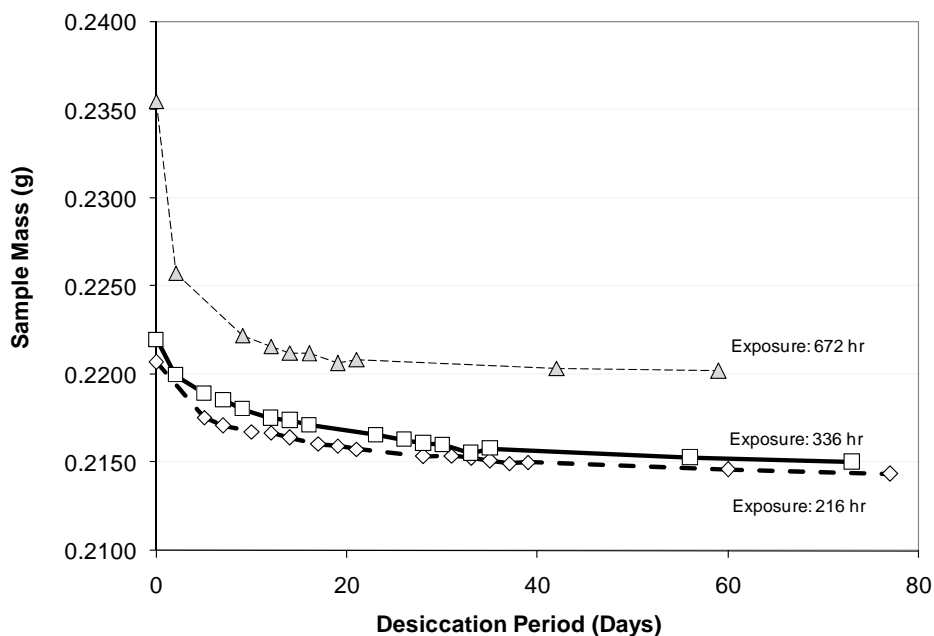
**Figure 4–3 HDPE pipe sample surface images obtained using optical microscopy**

HDPE pipes underwent aging using 5000 mg/L as  $\text{Cl}_2$  at 70 °C: (a) New, (b) 9 day (216 hr), (c) 14 day (336 hr), and (d) 28 day (672 hr) aged samples. Scale bar on each image is 2000  $\mu\text{m}$  in length.

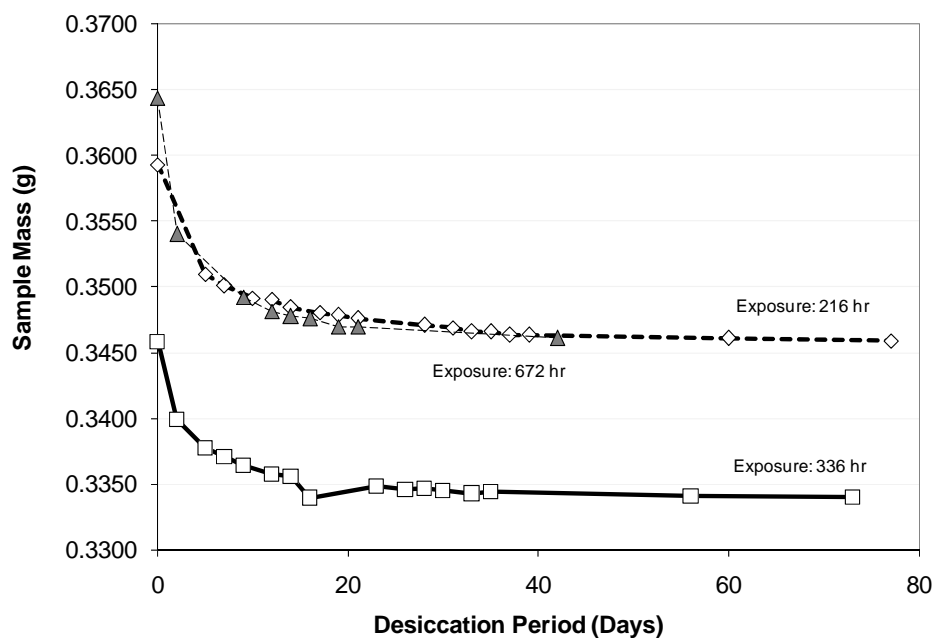


**Figure 4–4 Some HDPE resin (left) and HDPE pipe (right) samples can be seen resting on the bottom of a 1L bottle containing reagent water on Day 28 (672 hr)**

At start of the experiment, all samples floated on surface of the chlorinated water solution.



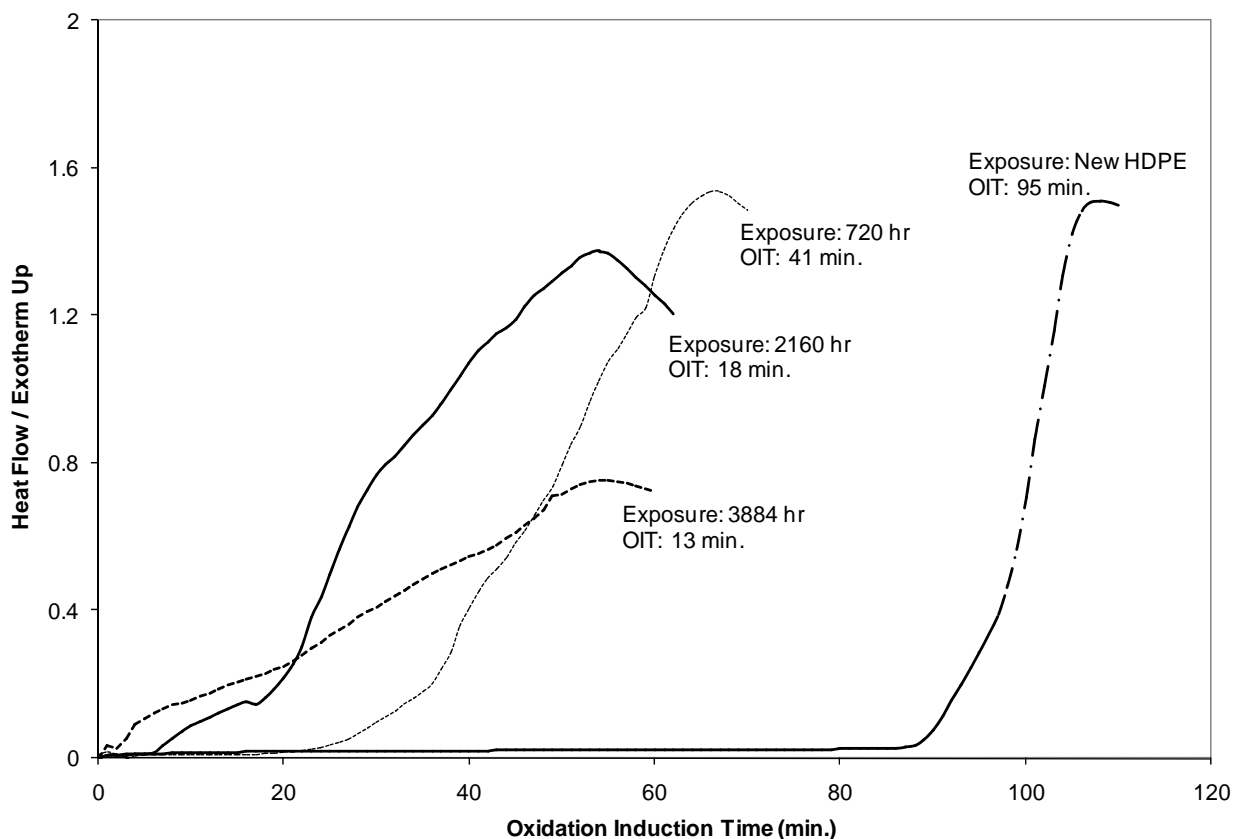
(a)



(b)

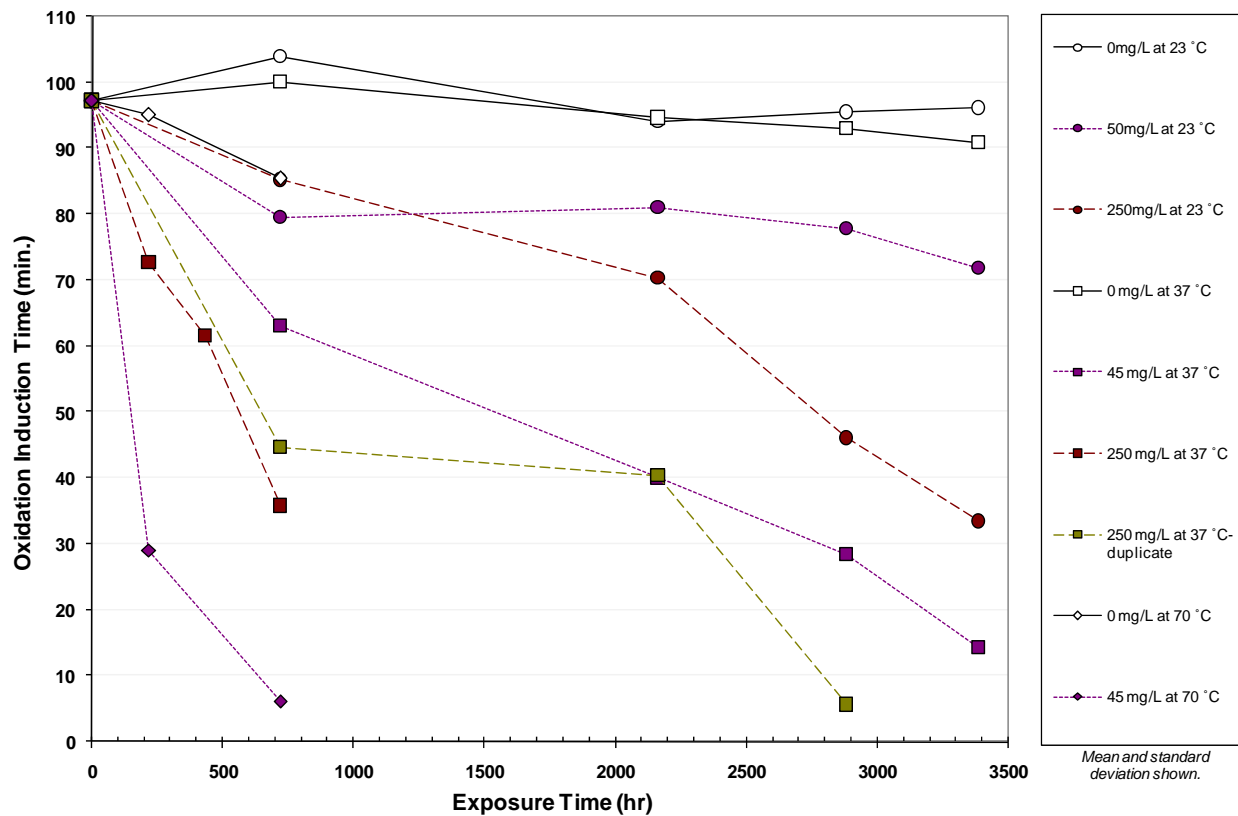
**Figure 4–5 Change in sample mass during 23 °C desiccation for or (a) HDPE resin and (b) HDPE pipe samples exposed to chlorinated water (5,000 mg/L as Cl<sub>2</sub>, pH 6.5, 70 °C, no calcium carbonate added) for 9 (216 hr), 14 (336 hr), and 28 days (336 hr).**

Data represent mean for 3 replicates from Day 0 to 17, and two replicates from Day 18 on. Daily mass standard deviation was  $\pm 0.0003$  to  $0.0014$  g for resin and  $\pm 0.0047$  to  $0.0103$  g for HDPE pipe.



**Figure 4–6 Comparison of Oxidation Induction Time Results for New HDPE Pipe and HDPE Pipe Aged in 45 mg/L as  $\text{Cl}_2$ , 37 °C Solution**

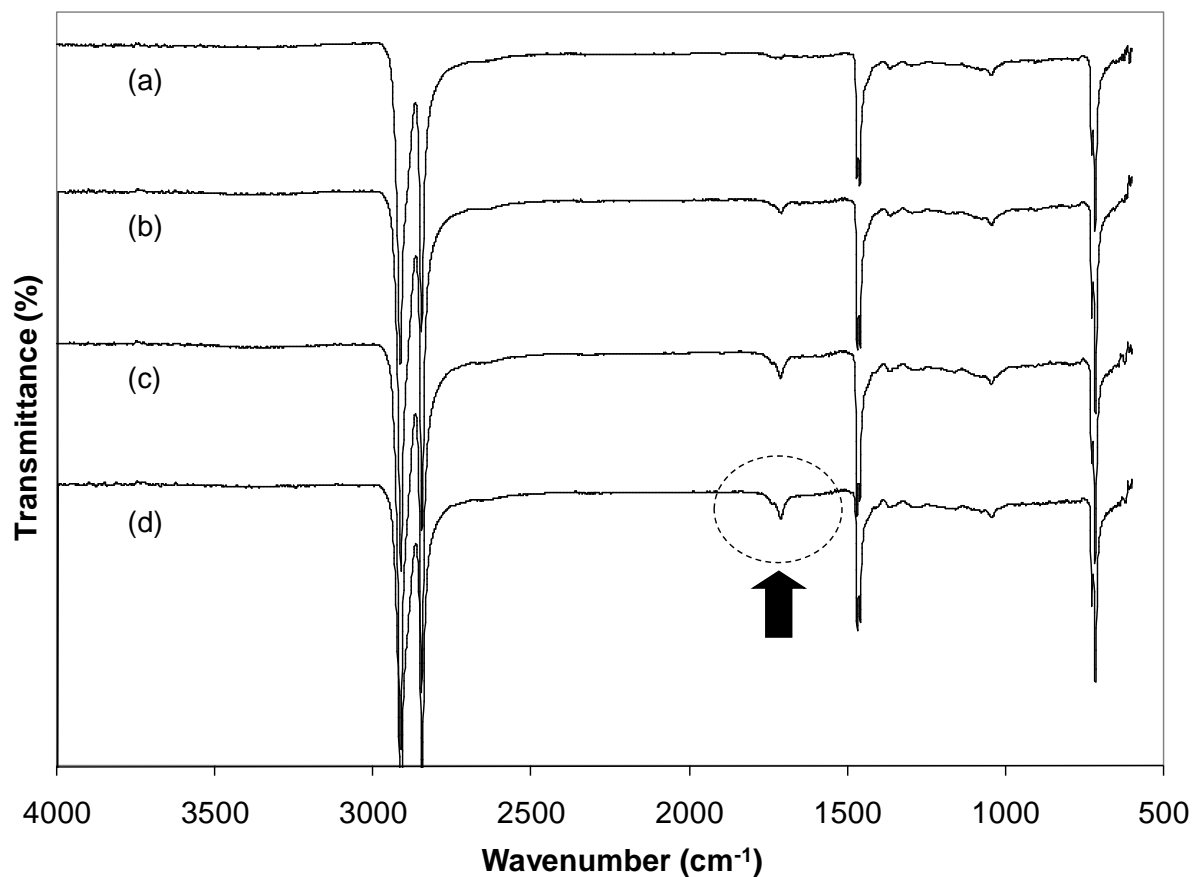
Leading edge frequently observed for aged samples which made determining the OIT of aged samples by the tangent method difficult, while a distinct increase in heat evolution is noticeable for new HDPE.



**Figure 4–7 HDPE Pipe Oxidation Induction Time Changes for the Accelerated Aging Treatments**

Data represent mean of three replicates for each time period shown, except 0 mg/L as  $\text{Cl}_2$  solutions at 23 and 37 °C where only 1 sample shown for 720 hr.





**Figure 4–8 Infrared Spectrum for New HDPE Pipe and HDPE Pipe Aged in 45 mg/L as Cl<sub>2</sub>, 37 °C Aging Solution as Wave Number vs. Transmittance (%)**

The circle and arrow designate carbonyl peaks not found on (a) New HDPE but were detected on HDPE samples aged at (b) 720, (c) 2160, and (d) 3884 hours.

**Table 4–1 American Society for Testing and Materials (ASTM) and National Sanitation Foundation (NSF) Accelerated Aging Methods for Polyethylene and Elastomeric Potable Water Materials**

Method Designation	Description	Reported Initial Conditions				Other Notes	Ref
		Chlorine, mg/L as Cl <sub>2</sub>	Water pH	Water or Air Temp., ° C	Internal Water Pressure, MPa		
ASTM F 2263 & ASTM F 2023	PE (2263) and PEX (2023) pipe exposed to pressurized test–fluid until failure.	2.5–5.0	6.5–8.0	Rec. 70, 80, 90, or 95	Examiner <sup>b</sup>	Air is the external environment. Min. pipe length is 12–18 in. Test solution oxidation reduction potential (ORP) should be 825mV. Flow velocity ≥ 0.04 m/s. Conduct at 3 temperature and 2 pressure/temperature Record time–to–failure for each specimen.	28,29
ASTM D 1599	Loading a pipe specimen to failure in a short–time interval by continuously increasing internal hydraulic–pressure.	Examiner	Examiner	23	Examiner	Air or water is the external environment. Increase the pressure uniformly until the specimen fails. The specimen should burst between 60 and 70 seconds.	30
ASTM D 6284	Rubber–like materials are immersed in bottles that contain a chlorinated water solution.	50	7.0	70	NA <sup>c</sup>	Air is the external environment. Immersion periods range from 22–4366 hrs. Solutions must be changed every 48 hrs or more frequent.	31
NSF Protocol 171	Aging solution is continuously pumped around a closed–pressurized pipe circulation loop or once through and not recirculated.	4.3 ± 0.3	6.8 ± 0.2	Examiner	Examiner	Air is the external environment. Initial TDS ≤ 20 mg/L. Flow rate of 0.227 m <sup>3</sup> /hr. Conduct at 3 temperature and 2 pressure / temperature Condition pipe using 66 ° C test water for 2 hrs. Hourly record temperature, pressure, chlorine level, pH, ORP, and flow rate.	32

a. Alkalinity concentration was not reported in any of the standards found; b. Examiner = Condition is chosen by the test administrator; c. NA = Not applicable because the system is not pressurized; Ref = References.

**Table 4–2 Literature Reported Accelerated Aging Conditions for Polymeric Potable Water Materials**

Name of Method	Description	Reported Initial Conditions				Internal Water Pressure / Pipe Hoop Stress, MPa <sup>c</sup>	References
		Chlorine <sup>b</sup> mg/L as Cl <sub>2</sub>	Water pH	Water or Air Temp., ° C	Change Frequency, Hrs		
Immersion Aging	Polymer samples immersed in containers with a chlorinated solution that is drained and refilled.	NR <sup>d</sup> , 0, 1, 2.5, 3.5, 5, 10, 60, 100, 150, 310, 500, 1000, 2000, 5600, 10000, 40000, 140000	NR, 2, 2.5, 3, 3.5, 4, 5, 5.7, 6, 6.5, 7, 7.2, 7.65, 8, 8.5, 9, 10	NR, 23, 50, 60, 70, 80	NR, 12, 72	NA <sup>e</sup>	7,34–42
Intermittent Pipe Flow Through	Pipe section is filled with chlorinated water and periodically drained and refilled.	0, 3, 5	8.0–8.4	105, 115	NR	0.27 / 1.1	15
Pressurized Pipe Coupon <sup>f</sup>	Pipe section is filled with chlorinated water, pressurized, and periodically drained and refilled.	NR, 0, 100, 500, 1000, 3000, 5000, 10000, 15000, 30000, 45000, 120000	NR	60, 70, 80, 95, 100, 105	NR, 672	NR / NR, 2.47, 2.51, 2.67, 2.7, 3.1, 3.42, 4.6	7,11,23,27
Pressurized Pipe Loop	Aging solution is continuously pumped around a pressurized pipe circulation loop, solution quality is periodically adjusted.	NR, 0, 0.1, 0.5, 1, 3, 4, 5	NR, 6.45, 6.5, 6.6, 6.8 8.0, 8.1, 8.4, 8.5	70, 80, 90, 95, 105, 110, 115, 120	NR	NR, 0.276, 0.48, 0.55, 1.0 / NR, 0.6, 0.7, 1.1, 1.4, 2.62	8,10,12,15,17, 18,23,26,43

a. Alkalinity concentration was not reported in any of the studies found and data shown mostly represent measured conditions at the start of the experiment, not at its conclusion. b. Cl<sub>2</sub> = Free available chlorine. c. Hoop stress is directly related to internal water pressure by:  $2 * \text{Hoop Stress (MPa)} / \text{internal pressure (kPa)} = [\text{pipe average outside diameter (mm)} / \text{minimum wall thickness (mm)}] - 1$ . However, numerous investigators reported internal water pressure or pipe hoop stress, but not both and some did not report enough information to calculate the internal water pressure. d. NR = Not reported and unclear since the ASTM and/or NSF standard referred to does not clear specify, e. NA = Not applicable because water not removed from pipe loop until experiment terminated. e. One investigator reported oxidation reduction potential (ORP) instead of the free available chlorine level. f. Some investigators submerged pressurized pipe sections in a water bath while undergoing aging.

**Table 4–3 Physical and Bulk Characteristics of New HDPE Resin and HDPE Water Pipe Examined**

<b>Characteristic</b>	<b>Resin</b>	<b>Pipe</b>
Thickness, mm.	1.65 $\pm$ 0.00	2.60 $\pm$ 0.01
Volatile Loss at 150 °C, %	0.12	0.08
Polymer, %	99.88	97.82
Char & Carbon Black, %	0	2.06
Ash, %	0	0.03
Degradation Temperature (T <sub>deg</sub> ), °C	431	459
Melting Temperature (T <sub>m</sub> ), °C	135.1 $\pm$ 0.5	128.7 $\pm$ 0.5
Bulk Density ( $\rho$ ), g/cm <sup>3</sup>	0.9572 $\pm$ 0.0000	0.9494 $\pm$ 0.0000
Crystallinity ( $w_c$ ) by T <sub>m</sub> , %	62.7 $\pm$ 0.6	50.9 $\pm$ 1.9
Crystallinity ( $w_c$ ) by Density, %	74.3 $\pm$ 0.1	69.3 $\pm$ 0.1
Oxidation Induction Time (OIT), min.	22.4 $\pm$ 2.4	92.5 $\pm$ 1.3

a. Mean and standard deviation for 3 replicates where shown

**Table 4–4 Initial and Change in Aging Solution Characteristics Every 72 Hours**

Solution	Temp., °C	Free Available Chlorine as Cl <sub>2</sub> , mg/L		Water pH		Alkalinity as CaCO <sub>3</sub> , mg/L	
		Initial	Change After 72 Hrs	Initial	Change After 72 Hrs	Initial	Change After 72 Hrs
<b>Control Solution</b>	23	0	–	6.53 ± 0.02 (45)	+0.24 ± 0.13	52.86 ± 6.82 (42)	+0.70 ± 3.90
	37	0	–	6.53 ± 0.02 (45)	+0.33 ± 0.18 <sup>¥</sup>	52.49 ± 6.88 (44)	+1.49 ± 4.02
	70	0	–	6.54 ± 0.02 (10)	+0.60 ± 0.16 <sup>¥</sup>	51.83 ± 5.36 (9)	+2.43 ± 5.05
<b>45 mg/L Chlorine</b>	23	45.87 ± 9.16 (44)	–3.59 ± 10.08	6.53 ± 0.02 (45)	+0.17 ± 0.12	49.59 ± 5.78 (41)	–0.72 ± 2.46
	37	45.81 ± 9.36 (43)	–5.74 ± 9.14	6.53 ± 0.02 (45)	+0.19 ± 0.16	49.58 ± 5.71 (42)	–1.65 ± 3.08
	70	45.42 ± 5.45 (10)	–37.00 ± 8.62 <sup>¥</sup>	6.54 ± 0.03 (10)	–0.29 ± 0.14 <sup>¥</sup>	53.73 ± 2.56 (9)	–20.69 ± 3.64 <sup>¥</sup>
<b>250 mg/L Chlorine</b>	23	257.5 ± 48.0 (45)	–14.28 ± 35.71	6.53 ± 0.02 (45)	+0.06 ± 0.08 <sup>¥</sup>	51.37 ± 6.56 (41)	–1.81 ± 3.69
	37	255.8 ± 63.7 (11)	–54.38 ± 68.19 <sup>¥</sup>	6.54 ± 0.02 (11)	+0.04 ± 0.06 <sup>¥</sup>	54.36 ± 3.45 (9)	–5.49 ± 4.58 <sup>¥</sup>
	70	310.0 (1)	–177.3 <sup>†</sup>	6.55 (1)	–3.91 <sup>†</sup>	49.40 (1)	–49.41 <sup>†</sup>

a. Number of water quality measurements shown in parentheses; Some aging treatments were stopped at different times resulting in different numbers of sampling periods; ¥ = Indicates a statistically significant difference from the initial aging solution at  $\alpha = 0.05$ ; † = Aging condition halted after the first 72 hr exposure period due to a drastic pH change.

**Table 4–5 Mechanical Properties of Convection Oven Dried for New and Temperature/Chlorine Aged HDPE Pipe**

HDPE Pipe Group Descriptions	Tensile Strength at Yield, MPa	Tensile Strength at Break, MPa	Elongation at Break, %
New HDPE Pipe	33.6 ± 1.7	32.9 ± 5.2	380 ± 220
0 mg/L as Cl <sub>2</sub> , 23 °C <sup>d</sup>	35.3 ± 1.7	37.0 ± 7.4	424 ± 279
45 mg/L as Cl <sub>2</sub> , 23 °C <sup>d</sup>	35.2 ± 1.1	31.0 ± 2.0	243 ± 133
250 mg/L as Cl <sub>2</sub> , 23 °C <sup>d</sup>	32.7 ± 0.9	30.0 ± 2.1	360 ± 127
0 mg/L as Cl <sub>2</sub> , 37 °C <sup>d</sup>	33.7 ± 0.8	32.6 ± 5.4	382 ± 218
45 mg/L as Cl <sub>2</sub> , 37 °C <sup>d</sup>	32.5 ± 1.1	32.5 ± 6.6	416 ± 251
250 mg/L as Cl <sub>2</sub> , 37 °C <sup>c</sup>	33.6 ± 1.6	16.5 ± 2.6 <sup>¥</sup>	189 ± 26 <sup>†</sup>

a. Values shown represent 5 replicates; c. 2880 hr exposure; d. 3884 hr exposure; ¥ represents a statistically significant difference between groups using the Tukey–Kramer paired comparison test at  $\alpha = 0.05$ ; † indicates ductile failure mode observed

**Table 4–6 New and Aged HDPE Pipe Drying Results**

Name of Sample/ Treatment Condition	Percent Reduction in Sample Mass due to Drying, %		
	8 hours in a Convection Oven at a 70 °C <sup>a,b</sup>	Moisture Analysis at 100 °C <sup>d</sup>	1 and 2 Weeks in a Bench-top Desiccator at 23 °C (wk 1 / wk 2) <sup>a</sup>
New HDPE	0	0	0 / 0
0 mg/L as Cl <sub>2</sub> , 23 °C <sup>c</sup>	0	0.09	0 / 0
0 mg/L as Cl <sub>2</sub> , 37 °C <sup>c</sup>	0	0.06	0 / 0
45 mg/L as Cl <sub>2</sub> , 23 °C <sup>c</sup>	0.020 ± 0.018	0.03	0 / 0
45 mg/L as Cl <sub>2</sub> , 37 °C <sup>c</sup>	0.040 ± 0.017	0.06	0 / 0
250 mg/L as Cl <sub>2</sub> , 23 °C <sup>c</sup>	0.041 ± 0.019	0	0 / 0
250 mg/L as Cl <sub>2</sub> , 37 °C <sup>e</sup>	0.219 ± 0.052 <sup>¥</sup>	0.09	0.040 ± 0.018 <sup>¥</sup> / 0.060 ± 0.000 <sup>¥</sup>

a. All values represent measurements for 3 replicates; b. No change in sample weights 1 week after removal from the convection oven; c. 3884 hr exposure; d. Values represent the difference between initial and final weight for 10 samples analyzed; e. 2880 hr exposure; ¥ indicates statistically significant difference between all other groups using the Tukey–Kramer Paired comparison test at  $\alpha = 0.05$ .

**Table 4–7 Recommended Conditions for the Accelerated Aging of Polyethylene Materials Using Chlorinated Water, a 72 Hr Water Change Frequency, and the Immersion Method**

Conditions	Changes in Aging Solution Characteristics						Approx. Time for 50% Reduction in OIT, hr
	pH		Alkalinity, mg/L as CaCO <sub>3</sub>		Free Available Chlorine, mg/L as Cl <sub>2</sub>		
	Unit	Percent	Unit	Percent	Unit	Percent	
45 mg/L as Cl <sub>2</sub> , 23 °C	+0.17	+2.6	−0.72	−1.5	−3.59	−7.8	>3884
45 mg/L as Cl <sub>2</sub> , 37 °C	+0.19	+2.9	−1.65	−3.3	−5.74	−12.5	1550
250 mg/L as Cl <sub>2</sub> , 23 °C	+0.06	+0.9	−1.81	−3.5	−14.28	−5.6	2787

a. Initial pH 6.5 and an alkalinity concentration of 50 mg/L as CaCO<sub>3</sub> added as sodium bicarbonate

## Chapter 5 Contaminant Diffusion, Solubility, and Material Property Differences between HDPE and PEX Potable Water Pipes

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### 5.1 Abstract

The objectives of this work were to identify differences between the composition, bulk properties, and contaminant diffusivity and solubility for new HDPE pipe and PEX pipe, as well as determine which contaminant and polymer properties are useful for predicting contaminant fate in water pipe. Great variations in PE pipe density (0.9371–0.9547 g/ cm<sup>3</sup>), crystallinity (69–72%), crosslinking (60 and 76%), and oxidative induction time (33 to >295 min.) were detected. While numerically these differences seem minor, results show that slight material differences have a profound effect on contaminant diffusivity and solubility. Nonpolar contaminant diffusivity and solubility were best predicted by bulk density. Polar contaminants were more soluble and diffused faster through PEX than HDPE pipes because PEX pipes contained a greater amount of oxygen. For all materials, dipole moment and Log K<sub>ow</sub> were good predictors of contaminant fate and molecular volume was only useful for predicting diffusivity and solubility values for haloalkane and nonpolar aromatic contaminants.

**Keywords:** Polyethylene, permeation, diffusion, MTBE, pipe, crosslink, HDPE, PEX

### 5.2 Introduction

Polyethylene (PE) is the most widely used polymer in the world and PE water pipes are increasingly being installed in buried and building plumbing applications globally (Rabaud and Rozental–Evesque 2008; AWWA 2003; AWWA 1996; UKWIR 1995; Arima and Hasegawa, 1991). These materials are flexible, inexpensive, resist corrosion, and have expected service lives greater than 100 years (Davis et al. 2006). High-density polyethylene (HDPE) water pipes have been used for buried water service in the USA since the 1940s (AWWSC, 2002), while crosslinked polyethylene (PEX) pipes were approved in 2007 for buried water service (AWWA, 2007). Because PEX pipes will be installed for buried service applications, potable water system managers, designers, public health officials, and regulators should understand how PEX pipes differ from their HDPE counterparts with regards to drinking water contaminant interactions and variability in resistance to oxidation. To date, little work has focused on PEX pipe water quality



impacts and no data enable direct comparison of commercially available HDPE and PEX pipe oxidative resistance.

Little data are available regarding the bulk characteristics of commercially available HDPE pipes and PEX pipe. The chemical structure of HDPE and PEX pipes fundamentally differ even though they are manufactured from the same PE resins. HDPE pipe is manufactured with HDPE resin while PEX pipes are manufactured with either HDPE or medium-density polyethylene (MDPE) resins. Resins of different densities have different degrees of crystallinity which are regions of dense polymer chain packing. Crystallinity is important because it has a profound effect on material strength, flexibility, contaminant diffusivity and solubility. Historically, one resin (of one density) has been used to manufacture PE pipes (called monomodal pipe), while today newer PE pipes are being manufactured by blending two different resins (bimodal pipe) to improve the pipe's mechanical failure resistance. The major structural difference between HDPE and PEX materials is that PEX pipes undergo crosslinking, an additional manufacturing step (Peacock 2001). PEX pipes either undergo (a) peroxide crosslinking (PEX-A pipe, 80% crosslinked), (b) silane crosslinking (PEX-B pipe,  $\leq 70\%$  crosslinked), or (c) electron beam irradiation crosslinking (PEX-C pipe,  $\leq 75\%$  crosslinked), and crosslinking causes polymer chains to bond with one another creating oxygen atom bridges (**Figure 5-1**). Crosslinks improve the ability of PEX pipes to resist mechanical failure at elevated temperatures (e.g., hot-water conveyance) (PexConn 2004) compared to HDPE pipes. PE pipe oxidative resistance (reported as oxidation induction time [OIT, minutes]) is a qualitative assessment of material stabilization and is increased by the presence of antioxidants, stabilizers, and carbon black. OIT is important because PE pipes with OIT values near zero indicate that 5–10% of the PE water pipes' lifetime remains (Gedde et al. 1994). Unfortunately, no OIT data were found for new HDPE or PEX pipes and there are no ASTM, AWWA, or NSF International standards requiring disclosure or minimum PE pipe OIT values. In contrast, the landfill liner industry recommends that all HDPE liners have an OIT of at least 100 min. (GSI 2009). Understanding variations in HDPE and PEX pipe crystallinity, crosslink density, and oxidative resistance data would enable water industry stakeholders to compare materials, could help establish minimum property standards like the landfill industry, and data could be used to develop contaminant fate and transport models.

Unlike HDPE pipes, PEX pipes contain oxygen that is intentionally integrated into the polymeric structure during manufacture (**Figure 5–1**). Based on a literature review, the authors hypothesize that polar drinking water contaminants are more soluble in PEX pipes than HDPE pipes because of the increased oxygen presence. It has been proven that water sorbs to a greater extent into oxygen-containing polymers such as poly(vinyl alcohols), poly(acetals), poly(ethylene glycol) in comparison to relatively hydrophobic LDPE (Comyn 1985). McCall et al. (1981) and Jelinski et al. (1984) also discovered that water was more soluble in LDPE telephone cable conduits as the PE oxygen content increased. Unfortunately, prior investigators have mainly studied PE water pipe interactions with nonpolar compounds such as petroleum and degreasing/cleaning solvent permeation of MDPE and HDPE pipes and not PEX pipe interactions with polar contaminants (Ong et al. 2008; Hopman and Hoven 1992; Rigal et al. 1992; Thompson et al. 1992; Holsen et al. 1991; Selleck and Marinas 1991; Park et al. 1989; Thompson and Jenkins 1989; Vonk and Veenendaal 1983).

To examine contaminant transport in PE pipes diffusivity ( $D$ ) and solubility ( $S$ ) must be quantified. Generally, a contaminant partitions into the pipe wall, diffuses through the wall, and diffusion stops once the polymer and contaminant reach equilibrium. Diffusion coefficients in polymeric materials are determined using weight gain–immersion, time lag, and diffusion/permeation methods (Aminabhavi and Naik 1999; Crank 1975). **Equation 5–1** was used to estimate diffusivity in polyethylene (Crank 1975) by fitting data to a regression where the ratio of the polymer weight gain at time  $t$  ( $M_t$ ) and total weight gain ( $M_\infty$ ) versus square root of time ( $\sqrt{t}$ ) knowing sample thickness. Contaminant diffusion coefficients have largely been determined for nonpolar aromatic and chlorinated contaminants in polymeric potable water pipes and gaskets (Ong et al. 2008; Glaza and Park 1992; Hopman and van de Hoven 1992; Rigal et al. 1992; Thompson et al. 1992; Holsen et al. 1991; Selleck and Marinas 1991; Park et al. 1989; Vonk and Veenendaal 1983) and HDPE landfill liners (Chao et al. 2007; Chao et al. 2006; Joo et al. 2005; Sangam and Rowe 2005; Joo et al. 2004; Rowe et al. 2003; Sangam and Rowe 2001; Park and Nibras 1993).

**Equation 5–1**  $M_t / M_\infty = 1 - \sum_{n=0}^{\infty} [8/(2n+1)^2 \pi^2] \exp \{-D[(2n+1)^2 \pi^2 t]/4\ell^2\}$

where

$t$  = Elapsed time (T)

$M_t$  = Mass of contaminant in polymer at time  $t$  (m)

$M_\infty$  = Mass of contaminant in polymer at equilibrium (m)

$D$  = Diffusion coefficient ( $\text{m}^2/\text{T}$ )

$\ell$  = Half sample thickness (L)

Like diffusivity, contaminant solubility is important in describing contaminant–polymer interactions. Solubility is defined as the ability of a solute to dissolve in a polymer and is determined by calculating the mass of contaminant dissolved in a polymer once the system reaches equilibrium [ $S = (M_\infty - M_0) / (M_{t=0} / \rho_{\text{Polymer}})$ ].  $M_\infty$  is the mass of contaminant in the saturated polymer,  $M_{t=0}$  is the mass of the polymer,  $M_0$  is the initial mass of contaminant in the polymer which is equal to zero, and  $\rho$  is the polymer’s bulk density. Thermodynamically, two compounds will mix based on the interaction of each compound’s contacting atoms. Polar compounds typically mix with other polar contaminants, while polar compounds typically do not dissolve in nonpolar compounds. In the polymer synthesis and manufacturing industries, solubility parameter ( $\delta$ ) values are used to predict how well two polymers, polymers–chemicals, or chemicals mix (Hansen, 2000) and may be useful for predicting fate in PE water pipe systems. Barrett and Stessel (1999) used these values to study the fate of gasoline components in HDPE landfill liners.

**Table 5–1** describes how environmental conditions, contaminant, and polymer properties affect diffusivity and solubility (Crank and Park 1968; Comyn 1985). Generally, increased temperature results in faster diffusion through a polymer and can also enable polymer chain mobility which increases diffusivity and solubility. Contaminant diffusion and contaminant dissolution in polymers is restricted to polymer free volume or amorphous regions, and contaminants do not diffuse through (or reside in) highly crystalline/dense regions. Crosslinks generally inhibit contaminant transport and swelling (Guillot et al. 2004; Desai et al. 1998; Sheu et al. 1989; Haxo et al. 1988) and contaminants can interact with polymer additives (e.g., carbon black) (Comyn 2004). Contaminant size, shape, symmetry, and polarity can also influence

polymer interactions and polar contaminants are sparingly soluble in hydrophobic polymers like MDPE and HDPE (Comyn 1985).

The goal of this work was to elucidate contaminant diffusion and solubility for HDPE resin and five commercially available new HDPE and PEX water pipes. The specific objectives were to: (1) ascertain polymer composition and bulk properties for the polyethylene materials, (2) determine contaminant diffusion and solubility behaviors for HDPE and PEX materials at 23 °C, and (3) identify which contaminant and polymer properties are useful for interpreting diffusion and solubility. Absence of this information prevents water utility managers, pipe manufacturers, public health officials, and regulators from understanding how PEX and HDPE pipes impact water quality, being able to predict contaminant fate based on contaminant and material properties, or comparing the initial oxidative resistance of pipes.

## **5.3 Experimental Section**

### **5.3.1 Materials and Polymer Preparation**

Prepressed 30.5 cm x 30.5 cm sheets of HDPE resin were obtained from McMaster–Carr, Inc. (Atlanta, GA). HDPE and PEX pipes were approved for use with potable water, obtained from plumbing supply stores, and were resin classification 3408 except for bimodal HDPE which was 3408 and 4710. Dog–bone shaped samples were cut using a Dewes Gumbs Die Company, Inc. (Long Island City, NY) microtensile die. Water pipe samples (0.3 g) were removed from the axial direction and HDPE resin samples from the prepressed sheets (0.2 g). All specimens were then thrice rinsed in distilled water and underwent desiccation at room temperature for 48 hr. Dimensions were obtained using a Mitutoyo™ digital micrometer to the nearest 0.01 mm. To attain the appropriate sample for thermal analyses (5–10 mg), cylindrical samples were punched from the dog–bone samples (23.0 mm x 8.0 mm) using a 1.58 mm diameter metal punch and were then split in half with an Exacto knife. Weight measurements were carried out (0.0001 g) using a Mettler–Toledo (Columbus, OH) balance with a Vernier Scale.

### **5.3.2 Polymer Characterization**

Composition was determined using a TA Instrument Q<sub>500</sub> thermogravimetric analyzer (TGA) (New Castle, DE), open platinum sample pan, and gas flow rate of 50 mL/min. Samples of 8–10 mg were evaluated and underwent heating from ambient using a ramp of 10 °C /min. to

600 °C under nitrogen gas, purge time of 2 min., and then were exposed under air from 600 °C to 800 °C (ASTM 2003). A TA Instrument Q<sub>100</sub> differential scanning calorimeter (DSC) (New Castle, DE) was used for calorimetric measurements. Melting temperature (T<sub>m</sub>) was determined using 5–10 mg samples, a covered aluminum sample pan, and nitrogen. Temperature was ramped at 10 °C/min. from 30 °C to 200 °C, then 200 °C to 30 °C, and then 30 °C to 200 °C. Crystallinity was calculated using two different methods: using the area under the melting trace ( $\Delta H_m$ ) on the first heating where  $\Delta H_{m[100\% \text{ Theoretical HDPE}]}$  is 293 J/g (Wunderlich 1980) ( $\text{Crystallinity} = \Delta H_{m[\text{Experimental}]} / \Delta H_{m[100\% \text{ Theoretical HDPE}]}$ ), and by using the experimentally measured sample density ( $\rho_s$ ), completely crystalline sample ( $\rho_c = 1.00 \text{ g/cm}^3$ ) and completely amorphous sample ( $\rho_a = 0.852 \text{ g/cm}^3$ ) (Bensason et al. 1996):  $\text{Crystallinity} = 100 \times (1/\rho_s - 1/\rho_a) / (1/\rho_c - 1/\rho_a)$ . Oxidation induction time (OIT) was determined (5–9 mg samples, open aluminum sample pan) under nitrogen with a flowrate of 50 mL/min., cell temperature was ramped from 50 °C to 200 °C at 10 °C/min., and this final temperature was held constant for 5 min. before switching to pure oxygen (ASTM 2007). The onset of sample oxidation was determined by drawing a line tangent to the isothermal baseline and the steepest slope of the exothermic peak. Polymer bulk density was determined using a density gradient column of 2–propanol (>99% purity) and distilled water of a range 0.88 to 1.00 g/cm<sup>3</sup> at  $20 \pm 0.1$  °C (ASTM 2003). Crosslink density was measured by freezing PEX pipe in liquid nitrogen, grinding frozen PEX in a food grinder, sieving the conglomerated particles using an ultrasonic sieve at  $4 \pm 0.1$  °C into < 250, 250–500, 500–1  $\mu\text{m}$ , > 1  $\mu\text{m}$  (ASTM, 2003). Next, 0.3000 g of sample (250–500  $\mu\text{m}$  size) was placed in a stainless steel cage which then underwent xylene 14 hr soxhlet extraction at 140 °C. Following the extraction, cages were dried in a vacuum oven under 710 mmHg at 150 °C until weigh loss halted. Change in cage weight was measured to the nearest 0.0001 g and was used to calculate gel content (=100–percent extract).

Contaminant solubility and diffusion coefficients were determined by immersing PE samples in neat contaminant (**Table 5–2**). Thirteen compounds were selected to represent chemicals regulated under the Safe Drinking Water Act, common plastic pipe permeation agents, and contain functional groups of much larger drinking water contaminants. Compounds examined have moderate variations in molecular weight and density, but major differences in water solubility and polarity. Contaminant molar weight ( $M_v$ ) was determined using *Spartan* (Wavefunction 1997) and other properties were obtained from CHEMFATE (Syracuse Research

Corporation 2009). The varied physiochemical properties allow for the assessment of chemical structure on fate and transport in PE.

Immersion testing was conducted by placing PE samples inside screw-tight amber vials with polytetrafluoroethylene septa containing 15–20 mL of neat contaminant at  $22 \pm 1$  °C. Periodically, samples were removed for < 30 seconds, quickly blotted with KimWIPEST<sup>™</sup> to remove any surface contaminant, weighed on a Vernier scale, and reimmersed in solution until samples attained a constant mass. Immersion was halted after 2500 hr unless equilibrium was achieved before 2500 hr. Sample weight gain and contaminant mass in the polymer were calculated and plots of square root of time versus weight gain were created. Solubility and diffusivity coefficients were fit to the regression using **Equation 5–1**. Asymptotic 95% confidence interval was also calculated from the standard error using R Project version 2.7.1 (RFound, 2008). Type I error of 0.05 was applied in all statistical tests.

## **5.4 Results and Discussion**

### **5.4.1 Material Bulk and Oxidative Properties**

Compositional analysis revealed several material similarities and differences. HDPE resin and PEX pipes were approximately 99% polymer and HDPE pipes contained 2.1% carbon black similar to reports in the literature (Karlsson et al. 1992; Thompson et al. 1992). HDPE and PEX pipe volatile matter weight loss (0.2–0.5%) could be due to the loss of plasticizers, residual solvent, and antioxidants during heating (ASTM 2003) and is similar to 0.5% HDPE pipe volatile loss results reported by Thompson et al. (1992). Bimodal HDPE pipe contained 0.1 % ash indicative of reinforcements and other incombustible materials at 850 °C (ASTM 2003).

Density gradient column and thermal analysis were useful in estimating crystallinity. HDPE resin and bimodal HDPE pipe were statistically the densest and most crystalline materials and PEX–A pipe was the least dense and least crystalline material according to manufacturer and our laboratory testing. While both crystallinity estimation methods were highly correlated ( $r^2 > 0.70$ ), the crystalline content of monomodal and bimodal HDPE as well as PEX–B1 and PEX–B2 pipes were not statistically different by melting temperature method, but were different according to the bulk density method. The crystallinity discrepancy between methods could be due to the presence of additives that may slightly increase pipe density, slight differences in

crystallinity went undetected due to the DSC heating rate, and/or difficulty selecting onset points in thermograms. Results from the two crystallinity estimation techniques are within typical PE density and crystallinity ranges (Bensason et al. 1996) and reported bulk density (0.940–0.965 g/cm<sup>3</sup>) (Thompson et al. 1992) and crystallinity 46–66% (Lundback, 2005; Karlsson et al. 1992). The experimentally determined crosslink density of PEX–A pipe was statistically greater than that of PEX–B1 pipe. PEX–B2 pipe crosslink density was not quantified in this work. PEX pipe crosslink density ranges were only found in an ASTM standard F876 (2008).

Thermal analysis revealed small differences in degradation temperature and its onset, but great differences in material oxidative resistance. With the exception of PEX–A pipe, OIT values were significantly greater than those reported in the literature (Dear and Mason 2000; Karlsson et al. 1992; Thompson et al. 1992). Material stability from greatest to least is  $OIT_{\text{PEX-B2 pipe}} > OIT_{\text{PEX-B1 pipe}} > OIT_{\text{BiHDPE pipe}} > OIT_{\text{MonoHDPE pipe}} > OIT_{\text{PEX-A pipe}} > OIT_{\text{HDPE resin}}$ . OIT values greater than HDPE resin can be attributed to a greater amount of additives in commercial products not present in the resin. Except for PEX–A pipe, all PE pipe OITs were greater than values reported in the literature. The finding that  $OIT_{\text{PEX-A pipe}}$  was significantly less than the  $OIT_{\text{PEX-B pipes}}$  and  $OIT_{\text{HDPE pipes}}$  indicate that the PEX–A pipe is the least resistant to oxidation compared to the other PE pipes (**Table 5–3**).

#### 5.4.2 Equilibrium & Solubility

**Figure 5–2** shows that the model fit the data well, replicates were consistent, and polar contaminants had more variable solubility and longer times to equilibrium than nonpolar contaminants. Plots of  $\sqrt{t}$  versus  $M_t/M_\infty$  were generated because these are traditionally used to identify linear regions of increasing mass over time and are frequently reported by others (Crank, 1976). Time to half saturation results also support the faster achievement of equilibrium for nonpolar contaminants and variability in nonpolar contaminant variability (**Table 5–4**). A definitive equilibrium was achieved for haloalkanes, toluene, xylenes, MTBE, 2–butanone, and 2–propanone by 2500 hr of immersion. Equilibrium for all other contaminants was predicted based on fitting data to a regression.

Solubility results can be segregated into two distinct groups (1) polar contaminants and (2) nonpolar contaminants. Contaminants that are nonpolar were generally most soluble in the least dense material PEX–A pipe and least soluble in the densest material HDPE Resin (**Table**

5–5). There is strong statistical evidence that regression lines for bulk density and nonpolar contaminant solubility were not equal to zero ( $p < 0.05$ ) (**Figure 5–3**). Solubility levels measured for haloalkanes, toluene, and xylenes were similar to the literature (Chao et al. 2006; Aminabhavi and Naik 1999; Park and Nibras 1993; Britton et al. 1989; Park et al. 1989; Haxo and Lahey 1988). For all PEs, haloalkane solubility increased with chlorine content ( $S_{\text{Trichloromethane}} > S_{\text{Dichloromethane}}$ ) and xylenes were the most soluble aromatic compounds, but  $S_{m\text{-Xylene}}$  and  $S_{p\text{-Xylene}}$  were not statistically different ( $p > 0.05$ ).  $S_{\text{MTBE}}$  was greatest in PEX–A pipe while 8–10% less soluble in PEX–B pipes. No published data for MTBE solubility in PE materials were found in the literature. MTBE has been found to permeate buried polymeric drinking water pipes, contaminate drinking water, and is increasingly being discussed for regulation at the US Federal level (IADNR 2007; Suffett 2007). Less polar aliphatic contaminants were *generally* more soluble in each PE ( $S_{\text{MTBE}} > S_{2\text{-Butanone}} > S_{2\text{-Propanone}} > S_{1\text{-Butanol}} > S_{2\text{-Propanol}} > S_{\text{Acetonitrile}} > S_{\text{Water}}$ ).

Results for polar compounds were much more complex than nonpolar compounds. Unlike nonpolar contaminants, regressions indicate that polar contaminant solubility is not influenced by bulk density ( $p < 0.05$ ). However, PEX pipes exerted a statistically significantly greater solubility for benzaldehyde, 2–butanone, 2–propanone, and acetonitrile. A possible explanation for the oxygen–containing contaminants increased PEX pipe solubility is that PEX contains more oxygen in its chemical structure than HDPE pipes (**Figure 5–1**) and polar compounds are generally more soluble in polymers that contain more oxygen (McCall et al., 1981; Jelinski et al. 1984). Water sorption was not detected in any PE.  $S_{\text{Benzyl Alcohol}}$  results were inconclusive because of weight gain variability, except that benzyl alcohol was statistically less soluble in bimodal HDPE than all other PEs.  $S_{\text{Benzaldehyde}}$  and  $S_{\text{Benzyl Alcohol}}$  were significantly less than the solubility of other aromatic contaminants.

Several contaminant and polymer properties were good predictors of solubility. As contaminant dipole moment increased or  $\text{Log } K_{\text{ow}}$  decreased, contaminant solubility decreased (**Figure 5–4**). Results agree with Comyn (1985) where increased molecular diameter or volume increased contaminant solubility. The difference between contaminant and PE solubility parameters was not a good solubility predictor. Regressions revealed a moderate relationship between polymer bulk density and solubility for nonpolar contaminants. As bulk density



increased from 0.937 to 0.957 g/cm<sup>3</sup> contaminant solubility decreased (**Figure 5–3**); however no distinct solubility trend was detected with densities ranging from 0.949 to 0.954 g/cm<sup>3</sup>. S<sub>2</sub>-Butanone > S<sub>2</sub>-Propanone and these ketones were one-fourth that of haloalkanes, toluene, and xylenes and similar to the literature (Aminabhavi and Naik 1999). This preferential solubility finding also coincides with a reduction in alkane chain length generally resulting in decreased PE solubility (Comyn, 1985).

The solubility of oxygen-containing aromatic and aliphatic contaminants did not correlate well with polymer bulk density. Instead, oxygen-containing contaminants were significantly more soluble in three PEX pipes of different bulk densities (0.937, 0.951, 0.952 g/cm<sup>3</sup>) than the three HDPE materials (0.949, 0.954, 0.957 g/cm<sup>3</sup>). All contaminants were more soluble in PEX-A pipe (76% crosslinked MDPE) in comparison to PEX-B1 Pipe (60% crosslinked HDPE). These results are in direct contrast with Crank and Park (1968) and Comyn (1985) who reported greater crosslink density results in decreased solubility. Results of this work clearly show that bulk density controls solubility even when the less dense material is more crosslinked.

#### 5.4.3 Diffusivity

Diffusivity and bulk density comparisons revealed that all contaminants diffused fastest through the least dense material (PEX-A pipe) and slowest through the densest material (HDPE Resin) (**Figure 5–5** and **Table 5–6**). Regressions revealed that bulk density influenced diffusivity for all nonpolar contaminants and 2-butanone, 2-propanone, benzaldehyde, and acetonitrile ( $p < 0.05$ ). For these contaminants, diffusivity decreased as bulk density increased and this was also reported by Crank and Park (1968) and Comyn (1985) because chain packing and chain stiffness limit diffusion. Changes in bulk density however did not affect diffusivity of benzyl alcohol, 1-butanol, and 2-propanol ( $p < 0.05$ ). Variability in experimental results and/or influence of hydrogen-bonding during diffusion could be contributing to this finding.

Contaminant diffusivity in HDPE based pipes is similar (monoHDPE, PEX-B2, PEX-B1, and BiHDPE) and theoretically crosslinking should increase path tortuosity and reduce contaminant diffusivity. All contaminants showed increased diffusion in the 76% crosslinked MDPE PEX-A than the 60% crosslinked HDPE PEX-B pipe. These results imply that PE water pipe bulk density (crystallinity) is the most important driver of contaminant diffusivity. A more

targeted comparison of PEs of equal density with varying degrees of crosslinking would better elucidate the impact of crosslinking on diffusivity.

Trends for diffusivity values based on some contaminant properties were identified. Molar volume decreased diffusivity for all nonpolar contaminants diffusivity increased as aliphatic contaminant molar volume increased (**Figure 5–6**). Crank and Park (1968) also reported that an increase in diffusivity has been observed when molar volume of “small” compounds increases. As a molecule becomes more polar  $D$  should decrease and this trend was detected for haloalkanes and aromatic contaminants.  $D_{\text{Benzaldehyde}}$  and  $D_{\text{Benzyl alcohol}}$  were a factor of 16 less than alkyl-substituted aromatic contaminants and this difference can be attributed to the aldehyde and alcohol functional groups inhibiting transport through the polymer and also impacting the affinity of the contaminant for the polymer. Dipole moment data do not reveal a trend for small compounds.

The preferential diffusivity for  $D_{p\text{-Xylene}} > D_{m\text{-Xylene}}$  can be explained by comparing steric differences between these two isomers. Specifically, methyl group position on the  $p$ -xylene molecule makes the para isomer more linear and more able to penetrate PE, while methyl group position on  $m$ -xylene causes the meta contaminant to be bulky which inhibits PE penetration. A similar explanation can also be provided for  $D_{\text{Dichloromethane}} > D_{\text{Trichloromethane}}$  whereby additional chlorine atoms increase trichloromethane’s molar volume making it bulkier than dichloromethane.

Within PEs, preferential aliphatic contaminant diffusivity was inconsistent:  $D_{2\text{-Propanone}} = D_{2\text{-Butanone}} > D_{\text{MTBE}}$  and  $D_{2\text{-Propanol}} > D_{1\text{-Butanol}}$ ; however,  $D_{2\text{-Propanol}} = D_{1\text{-Butanol}}$  for some materials. No differences were detected across PEs for  $D_{\text{Acetonitrile}}$  or  $D_{\text{Benzyl Alcohol}}$  due to measurement variability.  $D_{1\text{-Butanol}}$  values were also variable, though several observations can be stated: diffusion through PEX–A was greater than PEX–B1, diffusion through PEX–A, bimodal HDPE, and PEX–B2 were equal and  $D_{1\text{-Butanol}}$  for all these materials was statistically greater than  $D_{1\text{-Butanol}}$  for Resin.

## 5.5 Conclusion

Results imply that HDPE and PEX pipe bulk and chemical characteristics influence contaminant diffusivity and solubility. HDPE pipe was primarily 97.8% polymer and 2.1%

carbon black, with moderate oxidative resistance (92–121 min.), and slight crystallinity variation (69–72%). PEX pipe was  $\geq 99.3\%$  polymer, with great variability in oxidative resistance (33 to 295 min.), crystallinity (61–71%), and crosslink density (60–76%). While numerically these differences seem minor, several material characteristics strongly impacted contaminant diffusivity and solubility.

PE pipe bulk density and chemical structure had a profound impact on contaminant fate, while crosslink density did not. Nonpolar and polar contaminants interacted with the PEs very differently. Diffusivity and solubility of nonpolar contaminants in all pipes showed similar trends. Increased bulk density resulted in decreased nonpolar contaminant diffusivity and solubility similar to results reported by others. Nonpolar contaminants were most soluble and diffused fastest through PEX–A pipe which was comprised of the least dense resin MDPE unlike all other pipes that were comprised of HDPE resin.

Polar contaminant (with aldehyde, ketone, and alcohol functional groups) solubility did not follow bulk density, but were more soluble in PEX pipes than HDPE pipes. This is because PEX pipes contain a greater amount of oxygen than HDPE materials promoting conditions where “like dissolves like.” In the literature, this conclusion is supported because polar compounds are more soluble in polymers (including PE) that contain more oxygen (McCall et al., 1981; Jelinski et al. 1984). This finding has gone previously unnoticed in the potable water and polymer pipe industries because prior research has primarily focused on nonpolar contaminants. Crosslinking did not significantly impact diffusivity or solubility even when two PEX pipes of different densities were compared (0.9371 vs. 0.9524 g/cm<sup>3</sup>).

As expected, contaminant size, water partitioning with octanol ( $K_{ow}$ ), and polarity were good predictors of contaminant fate. For all contaminants, solubility was reduced by increasing dipole moment and reducing Log  $K_{ow}$  and diffusivity was reduced by increasing molecular size. The solubility of aromatic and haloalkane contaminants was reduced by increasing molecular size, while small aliphatic contaminants showed a reverse trend and this reverse trend has also been found by Comyn (1985). Solubility parameter values were not helpful in predicting contaminant fate.

Results show that contaminant diffusivity and solubility in PE pipes is complex and impacted by the characteristics of the bulk polymer and contaminant properties. Using relationships uncovered in this work, engineers and scientists can integrate polymer composition and contaminant interaction data into models to more accurately assess contaminant fate in PE potable water pipe networks. Utility managers and pipe manufacturers can also better understand how material–contaminant relationships may impact water quality and use this information for better material selection and manufacturing practices.

## 5.6 Acknowledgement

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**Table 5–1 Effect on Contaminant Diffusivity and Solubility in Polymers when Environmental, Polymer, or Contaminant Property is Increased**

Parameter	Property <sup>1</sup>	
	Diffusivity	Solubility
Temperature	Increase	Increase
Bulk density/crystalline content	Decrease	Decrease
Crosslink density	Decrease	Decrease
Molecular diameter and Molar volume	Decrease	Increase
Carbon black content	Decrease	—

1. References used to create the table include Crank and Park (1968) and Comyn (1985).

**Table 5–2 Contaminant Characteristics at 25 °C**

Contaminant Name	Contaminant Class	$\mu$ , Debye	Contaminant Property <sup>1</sup>						Hydrogen Bonding Power
			$M_m$ , g/mol	$\rho$ , g/cm <sup>3</sup>	$\delta$ , MPa <sup>1/2</sup>	$M_v$ , cm <sup>3</sup>	$S_w$ , mg/L	Log $K_{ow}$	
<i>Polar Contaminants</i>									
Acetonitrile	Aliphatic nitrile	3.92	41.05	0.786	24.3	53.3	Miscible	−0.34	Poor
2–Propanone	Aliphatic ketone	2.88	58.08	0.789	20.2	73.1	Miscible	−0.24	Moderate
Benzaldehyde	Aromatic aldehyde	2.80	106.12	1.041	19.2	120.5	3000	1.48	Moderate
2–Butanone	Aliphatic ketone	2.76	72.11	0.805	19.0	91.4	223000	0.29	Moderate
Water	–	1.85	18.01	1.000	47.9	19.1	Miscible	–	Strong
Benzyl Alcohol	Aromatic alcohol	1.71	108.14	1.041	24.7	125.1	40000	1.10	Strong
1–Butanol	Aliphatic alcohol	1.66	74.12	0.809	23.3	96.2	74000	−0.30	Strong
2–Propanol	Aliphatic alcohol	1.56	60.10	0.789	23.5	77.8	Miscible	0.05	Strong
<i>Nonpolar Contaminants</i>									
Dichloromethane	Chlorinated alkane	1.60	84.93	1.326	19.8	60.6	13030	1.25	Poor
MTBE	Aliphatic ether	1.36	88.15	0.740	15.9	119.1	51000	1.24	Poor
Trichloromethane	Chlorinated alkane	1.01	119.37	1.492	19.0	74.4	7290	1.97	Poor
Toluene	Methylated aromatic	0.36	92.14	0.867	18.2	117.7	526	2.73	Poor
<i>m</i> –Xylene	Methylated aromatic	0.30	106.16	0.864	18.0	135.9	161	3.20	Poor
<i>p</i> –Xylene	Methylated aromatic	0.00	106.16	0.867	18.0	135.8	162	3.15	Poor

1. MTBE = Methyl *t*-butyl ether; ACS = American Chemical Society; GC = Gas Chromatography; HPLC = High Performance Liquid Chromatography; NP = Nanopure water;  $\mu$  = Dipole moment;  $\delta$  = Solubility parameter;  $M_v$  = Molar volume;  $M_m$  = Molar mass;  $S_w$  = Water solubility;  $\rho$  = Density;  $K_{ow}$  = Octanol–water partition coefficient; A  $\delta$  was only found for polyethylene (nonspecific) 23.3 MPa<sup>1/2</sup> (Barton, 1975);  $M_m$ ,  $S_w$ , Log  $K_{ow}$ , and  $\rho$  values obtained from *CHEMFATE* (Syracuse Research Corporation 2009);  $M_v$  calculated molar volume using *Spartan* (Wavefunction 1997)

**Table 5–3 Bulk Characteristics of Polyethylene Materials**

Property	Type of Polyethylene <sup>1</sup>					
	HDPE Resin	Monomodal HDPE Pipe	Bimodal HDPE Pipe	PEX–A Pipe (MDPE)	PEX–B1 Pipe (HDPE)	PEX–B2 Pipe (HDPE)
Thickness, mm.	1.65 ± 0.02 <sup>a</sup>	2.61 ± 0.05 <sup>b</sup>	2.59 ± 0.08 <sup>b</sup>	2.60 ± 0.02 <sup>c</sup>	2.64 ± 0.03 <sup>d</sup>	2.63 ± 0.03 <sup>d</sup>
<i>Composition, % of 100</i>						
Polymer	99.9	97.8	97.7	99.8	99.4	99.4
Char & Carbon Black	0	2.1	2.0	0	0.1	0.1
Volatile Loss at 150 °C	0.1	0.1	0.2	0.2	0.5	0.5
Ash	0	0	0.1	0	0	0
<i>Oxidative Resistance and Morphology</i>						
Tdeg <sub>onset</sub> , °C	431	459	465	460	462	461
Tdeg, °C	465	479	485	482	484	484
Tm <sub>onset</sub> , °C	127.0 ± 0.6 <sup>a</sup>	121.7 ± 0.2 <sup>b</sup>	123.4 ± 0.5 <sup>b</sup>	120.3 ± 1.2 <sup>c</sup>	119.8 ± 1.1 <sup>c</sup>	119.5 ± 0.6 <sup>c</sup>
Tm, °C	135.1 ± 0.5 <sup>a</sup>	128.7 ± 0.5 <sup>b</sup>	130.2 ± 0.1 <sup>c</sup>	130.1 ± 0.4 <sup>d</sup>	130.0 ± 0.3 <sup>d</sup>	129.7 ± 0.2 <sup>d</sup>
OIT (min.)	22.4 ± 2.4 <sup>a</sup>	92.5 ± 1.3 <sup>b</sup>	119.6 ± 1.1 <sup>c</sup>	33.6 ± 3.9 <sup>d</sup>	119.6 ± 12.3 <sup>c</sup>	> 295 <sup>e</sup> *
Bulk Density, g/cm <sup>3</sup>	0.9572 ± 0.0001 <sup>a</sup>	0.9494 ± 0.0002 <sup>b</sup>	0.9547 ± 0.0001 <sup>c</sup>	0.9371 ± 0.0005 <sup>d</sup>	0.9524 ± 0.0001 <sup>e</sup>	0.9510 ± 0.0001 <sup>f</sup>
Crystallinity						
by T <sub>m</sub> , %	62.7 ± 0.6 <sup>a</sup>	50.9 ± 1.9 <sup>b</sup>	51.7 ± 2.4 <sup>b</sup>	45.4 ± 2.1 <sup>c</sup>	54.4 ± 2.7 <sup>b</sup>	54.9 ± 1.1 <sup>b</sup>
by Density, %	74.3 ± 0.1 <sup>a</sup>	69.3 ± 0.1 <sup>c</sup>	72.7 ± 0.1 <sup>c</sup>	61.3 ± 0.3 <sup>d</sup>	71.2 ± 0.0 <sup>e</sup>	70.4 ± 0.1 <sup>f</sup>
Crosslink Density, % of 100	–	–	–	76.1 ± 5.5	60.4 ± 2.2	–

1. Tdeg<sub>onset</sub> = Onset Temperature of Degradation; Tdeg = Degradation Temperature; Tm<sub>onset</sub> = Onset of Melting Temperature; Tm = Melting Temperature; All values represent mean and standard deviation for three replicates unless otherwise noted. Compositional analysis and Tdeg tests only represent one measurement. Thickness measurements represent mean for 41 or 42 replicates per PE type; Letters (a–f) represent similarly grouped properties across PEs tested by a Tukey–Kramer Multiple Comparison test at α= 0.05.

\*Represents one measurement and that analysis halted after 5 hr because exothermic peak was not detected.

**Table 5–4 Time to Half Contaminant Saturation of Polyethylene Specimens**

Contaminant Class and Name <sup>1</sup>	Dipole Moment (Debye)	HDPE Resin	Time, hrs				
			Monomodal HDPE Pipe	Bimodal HDPE Pipe	PEX–A Pipe (MDPE)	PEX–B1 Pipe (HDPE)	PEX–B2 Pipe (HDPE)
<i>Polar Contaminants</i>							
Acetonitrile	3.92	99.5	82.7	54.4	31.0	142.0	65.1
2–Propanone	2.88	72.6	92.2	87.8	52.7	109.2	99.8
Benzaldehyde	2.80	139.8	191.6	229.2	113.6	226.6	242.3
2–Butanone	2.76	74.4	116.8	95.8	52.4	113.3	92.4
Benzyl Alcohol	1.71	118.0	167.6	117.5	231.5	246.9	142.6
1–Butanol	1.66	1324.6	966.7	302.2	342.9	1077.3	441.2
2–Propanol	1.56	347.8	185.7	312.2	304.8	392.4	194.6
<i>Nonpolar Contaminants</i>							
Dichloromethane	1.60	6.9	14.5	11.3	7.0	13.3	9.7
MTBE	1.36	74.3	134.2	101.3	73.4	163.6	135.6
Trichloromethane	1.01	8.9	15.8	14.7	10.1	15.1	14.8
Toluene	0.36	8.6	16.2	12.9	9.7	15.9	15.6
<i>m</i> –Xylene	0.30	12.7	24.9	21.1	14.8	24.8	26.0
<i>p</i> –Xylene	0.00	8.3	16.7	13.1	9.7	16.2	15.6

1. Mean values represent three replicates; Water diffusivity not shown since water was insoluble in all PEs; Coefficients of variation were < 60% for all PE–contaminant pairs except for benzyl alcohol (18–60%), 1–butanol (13–85%), 2–propanol (13–83%), and acetonitrile (13–92%).

**Table 5–5 Contaminant Solubility of Polyethylene Materials**

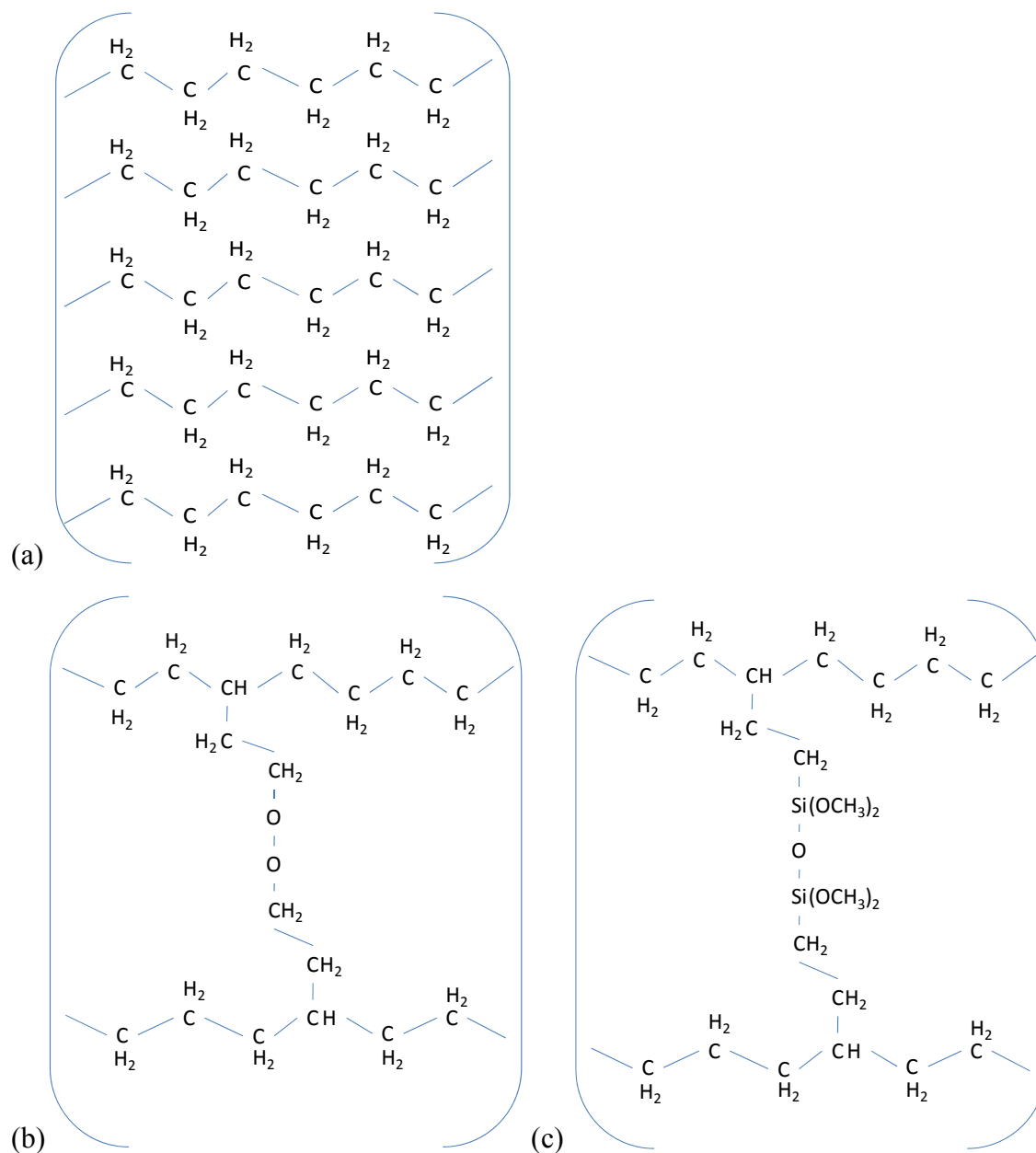
Contaminant Class and Name <sup>1</sup>	Dipole Moment (Debye)	HDPE Resin	Solubility, g/cm <sup>3</sup>				
			Monomodal HDPE Pipe	Bimodal HDPE Pipe	PEX-A Pipe (MDPE)	PEX-B1 Pipe (HDPE)	PEX-B2 Pipe (HDPE)
<i>Polar Contaminants</i>							
Acetonitrile	3.92	0.0012	0.0014	0.0018	0.0024	0.0027	0.0029
2-Propanone	2.88	0.0098	0.0101	0.0100	0.0120	0.0145	0.0143
Benzaldehyde	2.80	0.0204	0.0216	0.0214	0.0238	0.0263	0.0267
2-Butanone	2.76	0.0186	0.0190	0.0191	0.0219	0.0253	0.0237
Benzyl Alcohol	1.71	0.0051	0.0048	0.0036	0.0050	0.0063	0.0049
1-Butanol	1.66	0.0084	0.0053	0.0033	0.0053	0.0088	0.0056
2-Propanol	1.56	0.0047	0.0035	0.0031	0.0048	0.0054	0.0091
<i>Nonpolar contaminants</i>							
Dichloromethane	1.60	0.0685	0.0865	0.0854	0.0996	0.0862	0.0875
MTBE	1.36	0.0452	0.0546	0.0524	0.0591	0.0547	0.0534
Trichloromethane	1.01	0.1107	0.1428	0.1437	0.1655	0.1375	0.1417
Toluene	0.36	0.0660	0.0853	0.0859	0.0981	0.0807	0.0804
<i>m</i> -Xylene	0.30	0.0681	0.0875	0.0887	0.1010	0.0831	0.0836
<i>p</i> -Xylene	0.00	0.0691	0.0888	0.0896	0.1023	0.0844	0.0845

1. Mean values represent three replicates; Coefficients of variation were < 10% for all PE–contaminant pairs except for 1–butanol which was 39% for HDPE resin and 3–18% for other PEs; Water was not soluble in any PE.

**Table 5–6 Contaminant Diffusivity of Polyethylene Materials**

Contaminant Class and Name <sup>1</sup>	Dipole Moment (Debye)	HDPE Resin	Diffusivity, 10 <sup>-9</sup> cm <sup>2</sup> /s				
			Monomodal HDPE Pipe	Bimodal HDPE Pipe	PEX-A Pipe (MDPE)	PEX-B1 Pipe (HDPE)	PEX-B2 Pipe (HDPE)
<i>Polar Contaminants</i>							
Acetonitrile	3.92	3.76	11.5	14.2	30.0	6.38	14.2
2-Propanone	2.88	5.07	10.5	10.3	17.6	8.64	9.42
Benzaldehyde	2.80	2.65	4.77	4.02	8.11	4.29	3.92
2-Butanone	2.76	4.95	7.90	9.78	17.4	8.23	10.2
Benzyl Alcohol	1.71	3.17	5.52	7.40	4.03	3.89	6.66
1-Butanol	1.66	0.28	0.99	2.92	2.69	0.89	2.13
2-Propanol	1.56	1.07	4.97	2.78	2.99	2.42	4.82
<i>Nonpolar Contaminants</i>							
Dichloromethane	1.60	52.6	64.4	85.4	132	73.1	95.6
MTBE	1.36	5.00	6.65	8.75	12.6	5.96	6.92
Trichloromethane	1.01	41.2	58.2	66.3	91.9	61.7	63.9
Toluene	0.36	42.5	56.9	72.4	96.7	59.6	62.3
<i>m</i> -Xylene	0.30	29.7	37.1	45.9	62.7	38.1	36.1
<i>p</i> -Xylene	0.00	45.6	54.9	70.6	95.1	58.1	60.1

1. Mean values represent three replicates; Water diffusivity not shown since water was insoluble in all PEs; Coefficients of variation were < 60% for all PE–contaminant pairs except for benzyl alcohol (18–60%), 1–butanol (13–85%), 2–propanol (13–83%), and acetonitrile (13–92%).



**Figure 5-1 Two-Dimensional Molecular Structure of (a) HDPE, (b) Peroxide Crosslinked PE, and (c) Silane Crosslinked PE Materials.**

Electron beam crosslinked PE not shown.



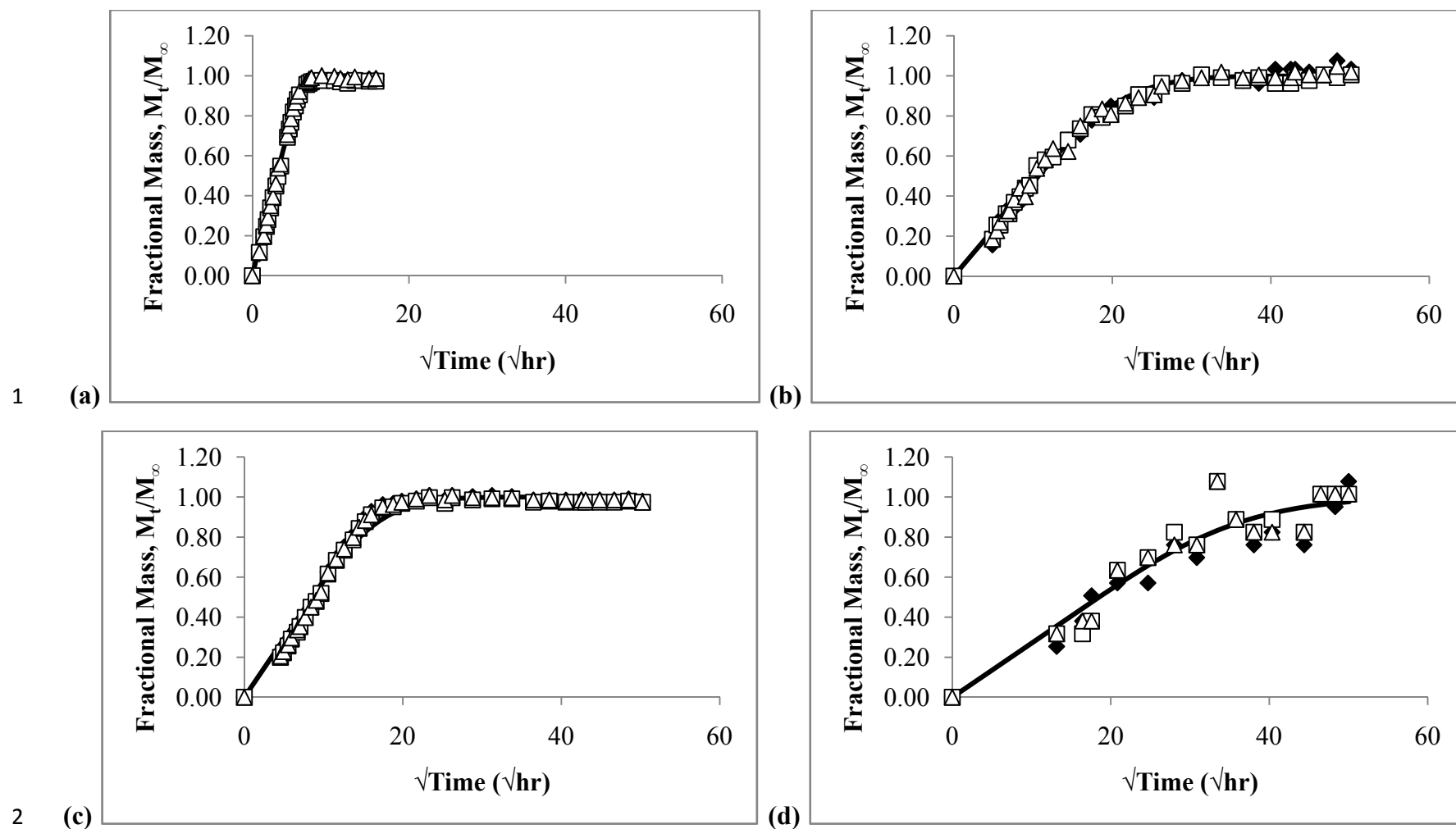
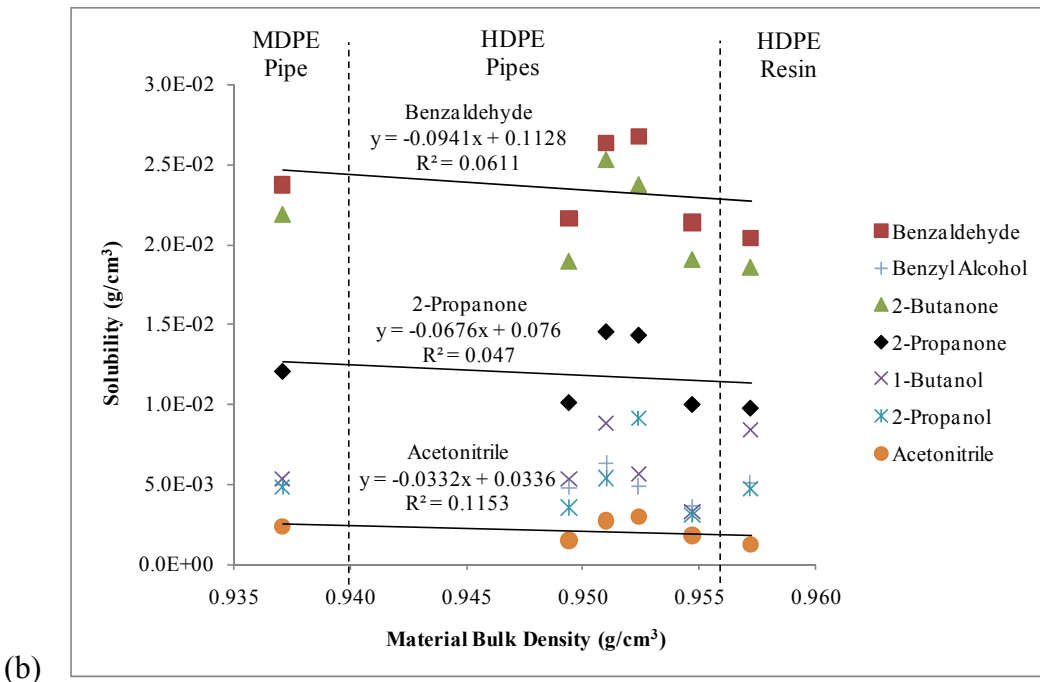
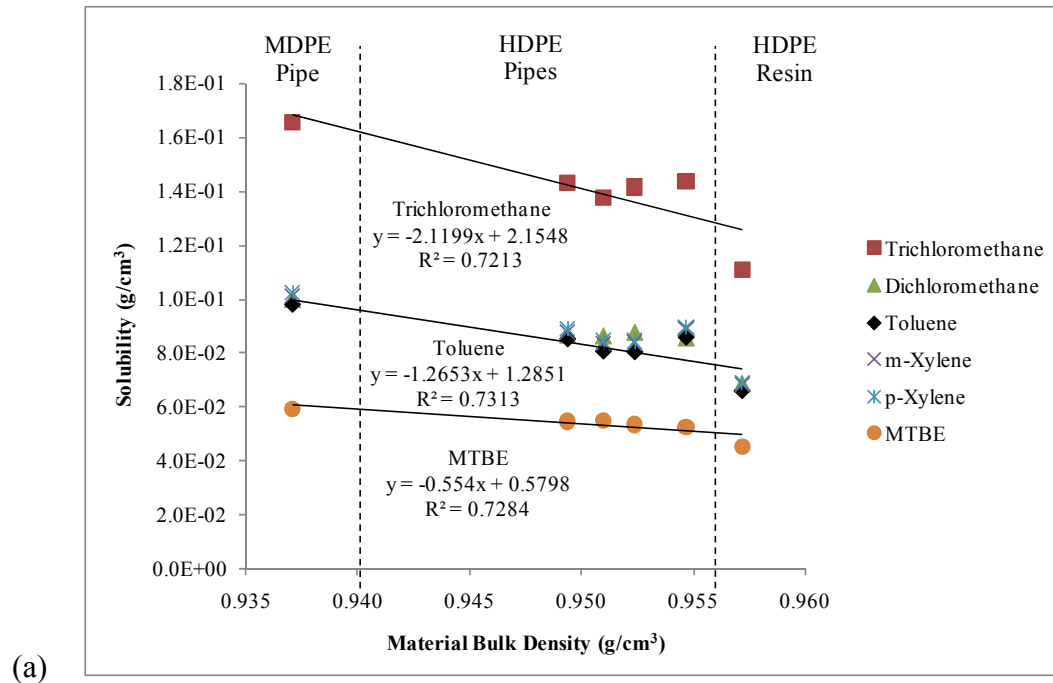


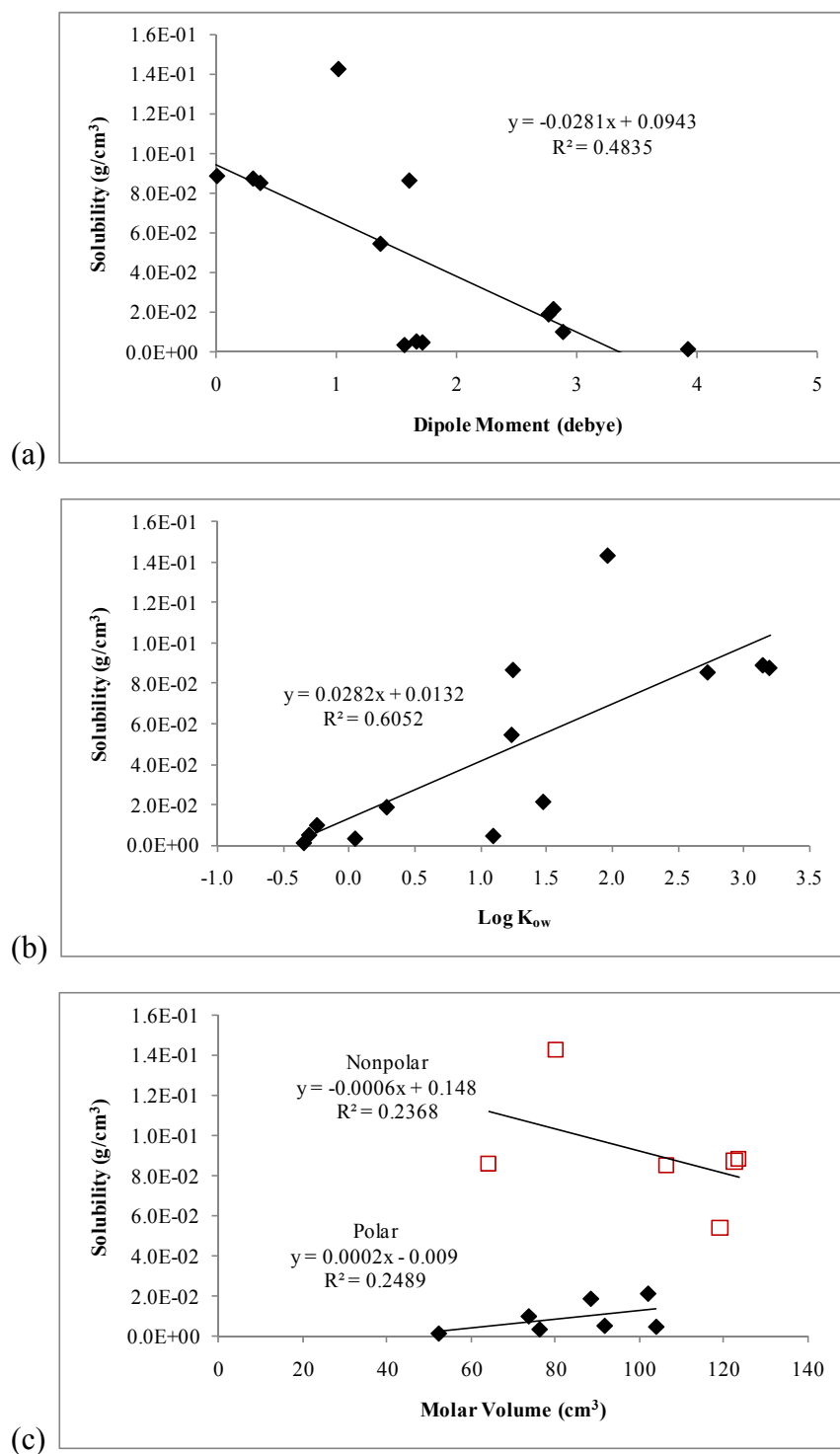
Figure 5-2 Sorption Data and Curves for (a) Toluene, (b) Benzaldehyde, (c) MTBE, and (d) 1-Butanol in PEX-A Pipe.

Triangles, squares, and diamonds represent data for each replicate. Three replicates for each contaminant-polymer pair.



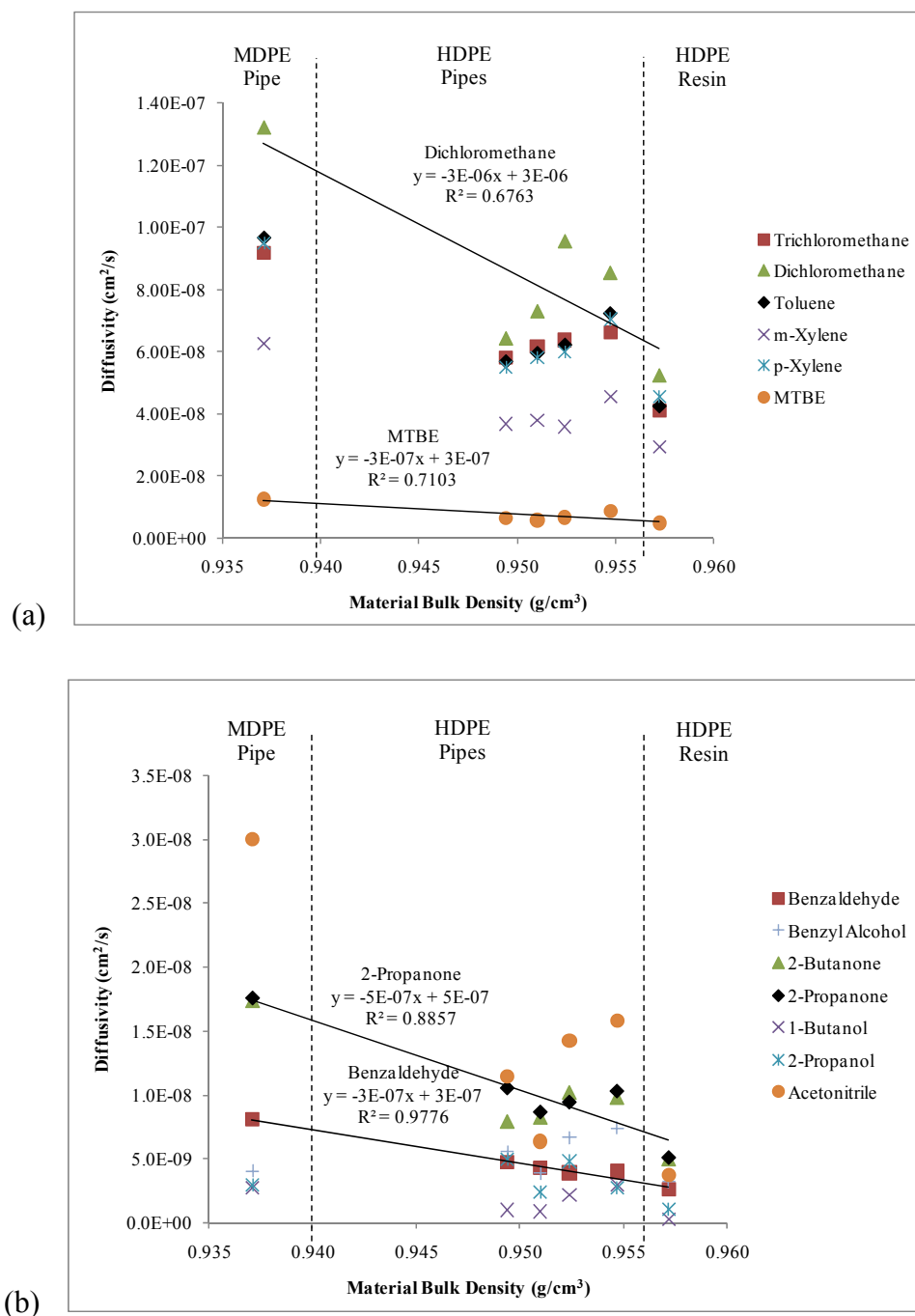
**Figure 5–3 Relationships between Material Bulk Density and Contaminant Solubility for (a) Nonpolar and (b) Polar Contaminants.**

Mean values shown. Trendlines for all nonpolar contaminants are statistically different than zero ( $p < 0.05$ ), all trendlines for polar contaminants were statistically equal to zero. Bulk density of materials shown left to right: PEX–A MDPE Pipe (0.9371 g/ cm<sup>3</sup>), Monomodal HDPE Pipe (0.9494 g/ cm<sup>3</sup>), PEX–B2 HDPE Pipe (0.9510 g/ cm<sup>3</sup>), PEX–B1 HDPE Pipe (0.9524 g/ cm<sup>3</sup>), Bimodal HDPE Pipe (0.9547 g/ cm<sup>3</sup>), and HDPE Resin (0.9572 g/cm<sup>3</sup>).



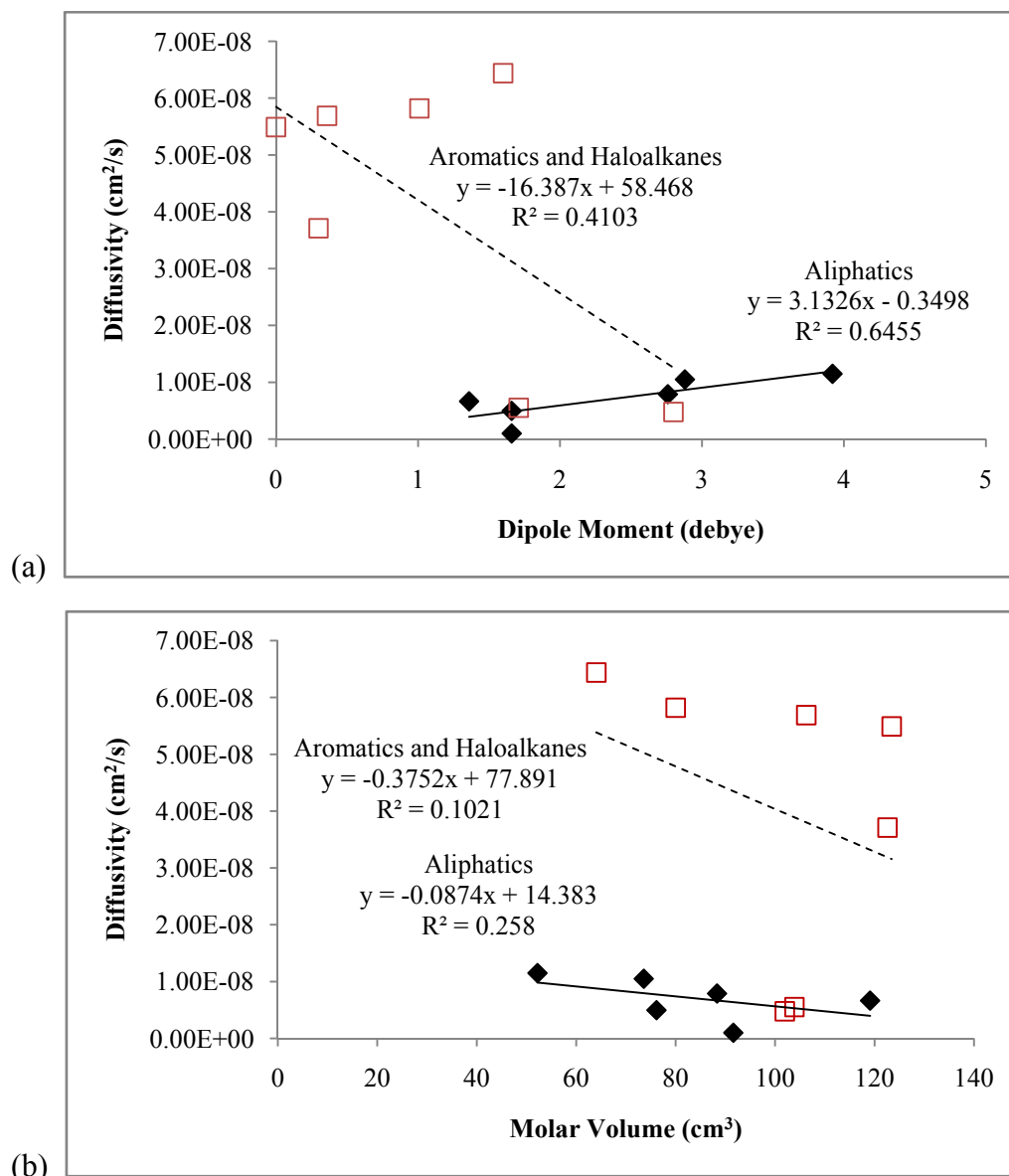
**Figure 5–4 HDPE Pipe Contaminant Solubility Relationships for (a) Dipole Moment, (b) Log  $K_{ow}$ , and (c) Molar Volume.**

All contaminants shown in Figures a and b. For Figure c, filled diamonds represent polar contaminants and white squares represent nonpolar contaminants where trendlines for each group of contaminants shown.



**Figure 5–5 Relationships between Material Bulk Density and Contaminant Diffusivity for (a) Nonpolar Contaminants and (b) Polar Contaminants.**

Mean values shown. Trendlines for all nonpolar contaminants are statistically different than zero ( $p < 0.05$ ). Trendlines for 2–butanone, 2–propanone, benzaldehyde, acetonitrile are statistically different than zero ( $p < 0.05$ ). All other trendlines for polar contaminants were statistically equal to zero. Bulk density of materials shown: PEX–A MDPE Pipe ( $0.9371 \text{ g/cm}^3$ ), Monomodal HDPE Pipe ( $0.9494 \text{ g/cm}^3$ ), PEX–B2 HDPE Pipe ( $0.9510 \text{ g/cm}^3$ ), PEX–B1 HDPE Pipe ( $0.9524 \text{ g/cm}^3$ ), Bimodal HDPE Pipe ( $0.9547 \text{ g/cm}^3$ ), and HDPE Resin ( $0.9572 \text{ g/cm}^3$ ).



**Figure 5–6 HDPE Pipe Contaminant Diffusivity Relationships for (a) Dipole Moment and (b) Molar Volume.**

Filled diamonds represent aliphatic contaminants and white squares represent haloalkane and aromatic contaminants. Trendlines for each group of contaminants shown. Two white squares near aliphatic contaminants represent benzaldehyde and benzyl alcohol.

## **Chapter 6 Impact of Chlorinated Water Exposure on Chemical Diffusivity and Solubility, Surface and Bulk Properties of HDPE and PEX Potable Water Pipe**

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*To be submitted to peer-review journal.*

### **6.1 Abstract**

The objectives of this work were to (1) artificially age polyethylene (PE) pipes in chlorinated water, (2) characterize the surface, bulk condition, contaminant diffusivity and solubility of new, lab aged, water utility pipes removed from a buried water distribution system, (3) identify contaminant and polymer relationships that influence diffusivity and solubility in aged PEs. Lab aged PE surfaces became more hydrophilic which enabled faster penetration of contaminants with a dipole moment  $\geq 1.66$  debye. Diffusivity increased greatest for alcohol > aldehyde > ketone containing compounds (50–162%). Solubility was weakly impacted by aging (0–40% change) and was not consistent across PEs. Chlorinated water exposure did not significantly alter nonpolar contaminant diffusivity or solubility. Nonpolar contaminant diffusivity and solubility in utility pipes was similar to those of new and lab aged HDPE pipe.

**Keywords:** Polyethylene, permeation, diffusion, MTBE, pipe, crosslink, HDPE, PEX

### **6.2 Introduction**

Polyethylene (PE) potable water pipes are increasingly being installed worldwide. They are lighter in weight, easier to install, and lower cost than their metallic counterparts and have an expected service life of 50–100 years (Davis et al. 2006). Two engineering concerns associated with PE pipes are that (1) long-term chlorinated water exposure changes PE surface and bulk properties leading to mechanical failure and (2) organic chemicals can diffuse in, out, and through these materials and adversely affect water quality. While the fate of nonpolar solvents, disinfectant byproducts, and pesticides have been studied in *new* PE pipes (Whelton et al. 2009; Ong et al. 2008; Watson 2006; Ginsberg et al. 2005; Moser et al. 2005; Hopman and Hoven 1992; Rigal et al. 1992; Thompson et al. 1992; Holsen et al. 1991; Selleck and Marinas 1991; Park et al. 1989; Thompson and Jenkins 1989; Vonk and Veenendaal 1983), the impact of PE pipe aging on contaminant fate has not been investigated. Because changes in pipe performance could impact water quality, material selection, and human exposure, this question deserves study.

Differences between new and aged PE pipe surface and bulk characteristics must be reviewed to determine how PE pipe aging impacts contaminant fate. Unfortunately, few buried PE water pipes have been analyzed so comparisons between laboratory results and buried pipes are difficult. According to previous laboratory experiments, chlorinated water exposure causes surface oxidation, polymer chain scission, and mechanical failure once a critical number of chains break whereby small cracks propagate through the pipe wall for high-density polyethylene (HDPE), medium-density polyethylene (MDPE) and crosslinked polyethylene (PEX) pipes (**Figure 6–1**). Accelerated aging in the lab has caused carbonyl [ $>C=O$ ] and sometimes chlorine [ $-Cl$ ], hydroxyl [ $-OH$ ], and vinyl [ $-CH=CH-$ ] bond formation on PE surfaces (Whelton and Dietrich, 2009; Karlsson et al. 1992). Though, carbonyl bonds were only detected in buried water pipes (Thompson et al. 1992). A reduction in PE oxidative resistance (referred to as Oxidation Induction Time or OIT) has been detected in both field and accelerated settings (Whelton, 2009; Campbell et al. 2008; Thompson et al. 1992). The OIT value of a polymer is important because once material OIT nears zero, it is thought that PE undergoes massive degradation whereby carbon-carbon bonds are broken Gedde et al. (1994). Carbon-carbon bond scission leads to an increase in pipe bulk density and reduction in mechanical strength due to polymer chain compaction and broken polymer chains do not crosslink (Gedde et al. 1994). Changes in pipe surface chemistry and bulk properties have the potential to impact the ability of contaminants to penetrate and reside in aged PE water pipes.

Contaminant fate in polymers is dependent on the interactions between the contaminant and polymer and is commonly described in terms of diffusivity (D) and solubility (S) (Crank and Park, 1968). Contaminants diffuse ( $cm^2/s$ ) through regions where polymer chain packing is less dense (amorphous) and diffusion stops once the contaminant-polymer achieve equilibrium. Solubility is commonly quantified at equilibrium as the mass of contaminant in the polymer per volume of polymer ( $g/cm^3$ ). Contaminant diffusion and solubility can be calculated by fitting data to a regression using **Equation 6–1** according to Crank (1975) as long as the sample thickness is known. Solubility can be calculated [ $S = (M_{\infty} - M_0) / (M_{t=0} / \rho_{Polymer})$ ] where  $M_{\infty}$  is the mass of contaminant in the saturated polymer,  $M_{t=0}$  is the mass of the polymer,  $M_0$  is the initial mass of contaminant in the polymer which is equal to zero, and  $\rho$  is the polymer's bulk density. Diffusion and solubility have been previously measured by others to describe neat contaminant interactions with buried HDPE and PEX pipes and some HDPE landfill liners

(Whelton et al. 2009; Chao et al. 2007; Chao et al. 2006; Joo et al. 2005; Joo et al. 2004; Aminabhavi and Naik 1999; Park and Nibras 1993).

**Equation 6–1**  $M_t / M_\infty = 1 - \sum_{n=0}^{\infty} [8/(2n+1)^2 \pi^2] \exp \{-D[(2n+1)^2 \pi^2 t]/4\ell^2\}$

where

$M_t$  = Mass of contaminant in polymer at time  $t$  (m)

$M_\infty$  = Mass of contaminant in polymer at equilibrium (m)

$t$  = Elapsed time (T)

$D$  = Diffusion coefficient ( $\text{m}^2/\text{T}$ )

$\ell$  = Half sample thickness (L)

Environmental conditions, contaminant, and polymer properties affect diffusivity and solubility (Crank and Park 1968; Comyn 1985). Diffusion and contaminant dissolution in polymers is restricted to polymer free volume or amorphous regions, and contaminants do not diffuse through (or reside in) highly crystalline/dense regions. An increase in PE bulk density results in a reduction of nonpolar contaminant diffusivity and solubility in HDPE and PEX–A and–B water pipes (Whelton et al. 2009). Polar contaminants are more soluble in PEX pipes than HDPE pipes due to the fact that polar contaminants associate with oxygen in PEX–A and PEX–B and not HDPE pipes that is incorporated in these materials during manufacture. Crosslinks generally inhibit contaminant transport (Guillot et al. 2004; Desai et al. 1998; Sheu et al. 1989) and contaminants can interact with polymer additives (e.g., carbon black) (Comyn 2004). Surface chemistry has also been shown to prevent or enable liquid penetration into polymers (Adamson and Gast 2006). Contaminant size, shape, symmetry, and polarity can also influence polymer interactions (Comyn 1985). Polar contaminants (e.g., water) are sparingly soluble in hydrophobic polymers like MDPE and HDPE (Comyn 1985) where nonpolar compounds (e.g., toluene and trichloromethane) have moderate to great solubility in PEs.

A literature review revealed that changes to polymer surface and bulk properties can cause changes to contaminant diffusivity and solubility, but no investigators have evaluated the impact of chlorinated water exposure on altering contaminant fate in PE water pipe. Park and



coworkers (1989, 1991) reported toluene diffusivity for poly(1-butene) (PB) water pipe purchased in 1989 and a 12-yr old PB buried water pipe were equal. However, the new and aged PB comparison is not appropriate since pipe crystallinity and surface chemistry were not examined and both material properties impact contaminant diffusion (Crank and Park 1968; Comyn 1985; Adamson and Gast 2006). It is possible that one PB pipe was less crystalline than the other which caused the differences in toluene diffusivity. Several investigators also found that water solubility increased as the oxygen content of a sheet of low-density polyethylene (LDPE) increased caused by oven aging (McCall et al. 1984; Jelinski et al. 1984). An increase in water solubility was also detected by Aristov et al. (1963) in a LDPE sheet after exposing the LDPE to a mixture of chromic acid and sulfuric acid at 20 °C. Cable technology researchers found that electrical current induced oxidation of HDPE and PEX pipes changed water contact angles from 82–88 degrees to values in the 70s (Khan and Hackman 1997; Khan and Hackman 1998; Deng and Hackman 1996). Contact angles are a measure of how well liquid “wets” a surface. Surfaces that contain polar groups ( $>C=O$ ,  $-OH$ ) will have strong liquid adhesive forces and low water contact angle (Adamson and Gast 1997). Large water contact angles indicate the water and surface do not interact as well. Changes in HDPE landfill liner surface chemistry and contaminant interaction were also examined by Sangam and Rowe (2005). These investigators discovered that surface fluorination of a new HDPE liner reduced diffusivity of nonpolar chlorinated and aromatic hydrocarbons 1.5–4.5 times at dilute aqueous concentration but solubility was unaffected. Sangam and Rowe (2005) attributed the diffusivity reduction to the ideas that fluorination: (1) increased surface crosslinking prevented large contaminant diffusion, (2) caused the surface to become more polar and prevented nonpolar contaminant diffusion, and (3) reduced free volume. In summary, the literature review implies that changes in surface and bulk properties caused by chlorinated water exposure could change HDPE and PEX water pipe contaminant diffusivity and solubility.

The aim of this work was to determine if exposure of HDPE and PEX water pipes to chlorinated water altered contaminant diffusivity and solubility. The objectives of this work were to (1) artificially age polyethylene (PE) pipes, (2) characterize the surface, bulk condition, contaminant diffusivity and solubility of new, lab aged, and pipes removed from a buried water distribution system, (3) identify contaminant and polymer relationships that influence diffusivity and solubility in aged PEs.

## **6.3 Methods**

### **6.3.1 Polymers & Water Utility Conditions**

HDPE resin sheets were obtained from McMaster–Carr, Inc. (Atlanta, GA) and new HDPE, PEX–A, and PEX–B pipes were obtained from a plumbing supply store. Three pipes were removed from a buried potable water distribution system operated by a public water utility in Florida, USA. These pipes had not mechanically failed, but were removed to assess the condition of polymer pipe bulk and surface properties and contaminant interactions. Dog–bone shaped samples were cut from polymers for all measurements using a microtensile die. All dog–bone samples were of equal length (9.0 mm) and width (2.5 mm) but differed slightly based on material thickness. The exposure history and water quality were cataloged by speaking with water system operations personnel.

### **6.3.2 Aging Condition and Solution Characterization**

Dog–bone shaped samples were immersed in aging solutions with an initial pH 6.5, 45 mg/L as  $\text{Cl}_2$ , 50 mg/L as  $\text{CaCO}_3$ , and stored in the dark at  $37 \pm 1^\circ\text{C}$  (Whelton and Dietrich, 2009; Whelton et al. 2009). Solutions were analyzed and changed–out every three days and samples in each bottle were rinsed thrice with reagent water and then placed in new aging solution in their constant temperature environments. Aging was halted after 3400 hr (141 days) of exposure. This aging condition was selected because of its reported minimal variations in pH, free chlorine, and alkalinity concentrations (Whelton and Dietrich, 2009). During the 141 day aging procedure, samples were periodically removed and analyzed for OIT and IR analysis. Aging solutions were prepared with reagent water from a Nanopure<sup>®</sup> ultrapure water system, 6.5% sodium hypochlorite, and  $\text{NaHCO}_3$ . Water pH was adjusted using  $\text{NaOH}$  and  $\text{HCl}$  and was measured using a bench–top Accumet<sup>™</sup> pH Meter 910 with probe. Alkalinity concentration was measured by titration using 0.025N sulfuric acid to an end–point pH of 4.5 in accordance with Standard Method 2320(B) (APHA, 2000). Free chlorine concentration was measured by titrating test solutions that contained potassium iodide and glacial acetic acid using 0.025N sodium thiosulfate according to Standard Method 4500–Cl(B) (APHA, 2000).

### **6.3.3 Polymer Characterization**

Methods used to quantify polymer surface chemistry, OIT, bulk density, crosslink density, and tensile properties are described in detail by Whelton (2009) and Whelton and

Dietrich (2009). Contact angles were determined by sessile drop method with distilled water using a FTA200 equipped with FTA 32 video (FTA, Inc., Portsmouth, VA) and a Newport benchtop vibration isolation system. Measurements were collected at two locations on each specimen (opposite ends of the dog–bone) at 23 °C 20–30 seconds after drop contact, and then at 5, 10, and 15 minute interval.

#### **6.3.4 Contaminant Interactions**

Contaminants examined were selected from those regulated under the Safe Drinking Water Act, those with desired chemical characteristics, and those containing functional groups of emerging contaminants (**Table 6–1**). Contaminant molar volume ( $M_v$ ) was calculated in Spartan (Version 5.0) (Wavefunction Inc., 1997) and all other contaminant properties were obtained from CHEMFATE (Syracuse Research Corporation, 2009). Contaminant diffusivity and solubility values were obtained for new, aged, and utility pipes by immersing dog–bone shaped samples in neat contaminants in 20 mL capped vials at  $22 \pm 1$  °C. Samples were removed periodically for weighing, and then returned to the vials until the polymer ceased to gain weight or 141 days had passed. Lab aged samples were exposed to chlorinated water on all sides during aging, while utility pipe samples had only 1 side (inner pipe wall) exposed to chlorinated water during service. Water sorption was quantified by measuring sample weight gain due to the aging condition.

Sample weight gain and contaminant mass in the polymer were calculated and plots of square root of time versus weight gain were created. These plots are similar to those commonly generated when determining diffusion and solubility to identify regions of linear mass increase and equilibrium (Crank and Park, 1968). Solubility and diffusivity coefficients were fit to the regression using **Equation 6–1**. An asymptotic 95% confidence interval was also calculated with a program designed for R Project version 2.7.1 (RFound, 2008). Type I error of 0.05 was applied in all statistical tests.

### **6.4 Results and Discussion**

#### **6.4.1 Lab Accelerated Aging Solution Stability**

Water quality results verify PE materials were exposed to uniform water chemistry (**Table 6–2**). Every three days, free chlorine and alkalinity concentrations were statistically

unchanged, but water pH slightly increased from 6.5 to 6.8 ( $p < 0.05$ ). This pH change did not substantially alter chlorine equilibrium since HOCl's  $pK_a$  is 7.5 and free chlorine concentration was unchanged every three days. Stoichiometric calculations revealed 93% of free available chlorine was HOCl [0.60M] at pH 6.5 and 84% HOCl [0.56M] at pH 6.8. Change in pH has been attributed to additive leaching from the polymer (Vibien et al. 2001).

#### **6.4.2 Lab Aged PE Surface and Bulk Characteristics**

New PEs showed no signs of surface oxidation, and surface chemistry changes were not consistent across lab aged PEs. Accelerated aging caused carbonyl bonds to form ( $\sigma=1713\text{ cm}^{-1}$ ) on all but PEX-A pipe surfaces. Detection of only carbonyl bonds during 4.5 month accelerated aging agrees with Whelton and Dietrich (2009) who examined HDPE pipe surfaces and Thompson et al. (1992) who analyzed surface and bulk properties of HDPE pipes removed from buried water distribution systems.

Surface and OIT results for lab aged PEs indicate that surface oxidation can occur before OIT is zero (**Figures 6-2 and 6-3**). This finding helps frame the significance of aged PE pipe contaminant interactions. Gedde et al. (1994) states that once polymer pipe antioxidants are depleted (OIT near zero) 5–10% of the polymer pipe's lifetime remains. If the surface chemistry of PE pipes that have an OIT  $> 0$  affects contaminant D and S, these changes should be expected to also occur in actual water distribution systems and before pipes enter their final life stage.

Results also demonstrate that a new pipe with the greatest initial oxidative resistance of several pipes does not necessarily indicate that it will have the greatest oxidative resistance among pipes after chlorinated water exposure. After 141 days, new PE oxidative resistance was reduced 30–95% depending on the PE and these oxidative resistance changes occurred at different times. PEX-B and HDPE pipe OIT reduced 95% and 69%, respectively during the first 3 months and then remained statistically unchanged until chlorinated water exposure was halted. PEX-A pipe OIT reduced 30% in the last month and HDPE Resin OIT reduce 40% in the final 2 months. The different oxidative resistance changes across PEs could be due to the different additives and bulk properties of the materials. Additives such as antioxidants and stabilizers in some PEs naturally migrate from the polymer into the water (Skjevra et al. 2003; Heim and Dietrich 2007) which may contribute to some OIT reduction. Polymer crosslinking and crystallinity could also prevent or enable additive reductions/consumption (Comyn, 1985). While

the exact PE additives are unknown, results show that initial oxidative resistance of new PEs varies greatly and that a pipe with the greatest initial OIT does not signify that this pipe will have the greatest OIT after chlorinated water exposure.

Accelerated aging also caused changes to polymer bulk density and mechanical strength which could imply chain scission has occurred (**Table 6–3**). New and lab aged PEs had similar bulk density resembling the HDPE density range of 0.941 to 0.965g/ cm<sup>3</sup>, except for PEX–A pipe which resembled the MDPE density range of 0.926 to 0.940 g/ cm<sup>3</sup>. Accelerated aging results demonstrated that HDPE pipe crystallinity increased. This phenomenon was also reported by Viebke and Gedde (1996) in Europe when MDPE pipe morphology was examined after chlorinated water exposure. Increased crystallinity can be caused by scission of tie molecules that link parallel chains and enables better chain compaction (**Figure 6–1**). Mechanical strength data for PEX–B pipe imply fracture of polymer chains or crosslinks occurred. An increase in bulk density could potentially reduce contaminant diffusivity and solubility while broken chains could also provide less tortuous path for contaminant transport.

#### **6.4.3 Lab Aged PE Contaminant Interactions**

**6.4.3.1 Equilibrium.** Generally, contaminants with low dipole moments such as trichloromethane, toluene, *m*-xylene, and MTBE achieved equilibrium the fastest of all contaminants in both new and aged PEs. Equilibrium for contaminants that did not achieve equilibrium by 2500 hr was predicted based on fitting data to a regression estimating diffusivity. **Figure 6–3** shows variability of measurements for select nonpolar and polar contaminants. Interestingly, more polar contaminants achieved equilibrium faster in aged PEs than in new PEs as contaminant dipole moment increased while time to equilibrium was relatively unchanged for nonpolar contaminants in new and aged PEs (**Table 6–4**). This finding is discussed in detail below. Solubility and diffusivity values obtained for HDPE and PEX materials are shown in **Tables 6–5 and 6–6**.

**6.4.3.2 Solubility.** Polymer aging had little to no impact on contaminant solubility. **Figure 6–5** shows a nearly 1:1 relationship between contaminant solubility for new and aged PEs. This finding was expected since polymer bulk density was not altered by chlorinated water exposure except for HDPE Pipe and solubility is governed by polymer crystallinity.

Contaminant dipole moment strongly influenced contaminant fate in aged PEs. While solubility of the most nonpolar contaminants toluene and *m*-xylene were unchanged, solubility changes ranged from 0–40% and were greatest as dipole moment increased (alcohol > aldehyde > ketone). Acetonitrile was barely soluble in new PEs but was insoluble in aged PEs and water sorption was not detected in new or aged PEs.

Contaminant solubility in aged PEX materials was significantly more impacted than in aged HDPE, but the regression implies that the magnitude of solubility changes was small. Contaminant solubility changes were more frequent in PEX pipes (13 of 20 contaminant–polymer pairs) than HDPE (3 of 20 pairs) where  $p < 0.05$ . Solubility changes detected in aged HDPE pipes were only found for contaminants with alcohol functional groups 1-butanol (–24%) and 2-propanol (–20%).

Contaminant solubility in PEX–A pipe mostly increased due to aging while solubility in PEX–B pipe generally decreased. These differences are difficult to explain because of the myriad differences between PEX–A and PEX–B pipes. PEX–A pipe was peroxide crosslinked [–O–O–] PE while PEX–B pipe was silane crosslinked PE [–Si(O)–O–Si(O)–]. PEX–A was significantly less dense (MDPE) than PEX–B (HDPE) and carbonyls were detected on aged PEX–B surfaces but not aged PEX–A surfaces. Finally, PEX–A pipe was 76% crosslinked and PEX–B pipe was 61% crosslinked.

Since aging hardly changed PE crystallinity, aged polymer and contaminant property relationships were very similar to those found for new PE materials. For example, solubility increased as octanol affinity increased but decreased as contaminant dipole moment increased (**Figure 6–6**) and crosslinking did not significantly alter this relationship. Whelton et al. (2009) also found similar octanol, dipole moment, molar volume, and crosslinking relationships with six new PE materials. Regression analysis revealed that the solubility of all nonpolar contaminants in new PEs in this work decreased as bulk density increased ( $p < 0.05$ ) and was similar to Whelton et al. (2009). However solubility of nonpolar contaminants was unchanged as aged PE bulk density increased.

Contaminants with alcohol, aldehyde, and ketone functional groups were more soluble in new and aged PEX compared to new and aged HDPE and results are similar to Whelton et al.

(2009). Increased polar contaminant solubility in polymers has been attributed to those polymers containing more oxygen (McCall et al. 1981; Jelinski et al. 1984; Comyn 1985). Results also revealed that contaminant solubility reduced as aromatic contaminant size increased and solubility increased as aliphatic contaminant size increased also reported by Crank and Park (1968). While more contaminant solubility–polymer pairs (16 of 40) were different for new and aged PEs than contaminant diffusivity–polymer pairs (13 of 40), solubility changes between new and aged PEs were relatively minor, while diffusivity differed moderately to greatly for compounds with great dipole moments.

**6.4.3.3 Diffusivity.** Aging had a moderate to great impact on contaminant diffusivity. Nonpolar contaminants diffused 5–38% faster in aged PEs, while polar contaminant diffusivity increased 50–162%. The greatest increases were for 1-butanol, 2-propanone, 2-butanone, and benzaldehyde (**Figure 6–7**). **Figure 6–5** shows the 1:1 relationship between contaminant diffusivity for new and aged PEs was invalid for polar contaminants and this finding is supported by water contact angle results for HDPE resin. HDPE resin water contact angle analysis showed a faster time-dependent wetting of water [after 15 minutes new HDPE resin  $75^{\circ} \pm 4.8$  and lab aged HDPE resin  $66.5^{\circ} \pm 5.6$ ]. These results imply that the oxygenated PE surface enabled contaminants with moderate to strong hydrogen bonding ability faster entry into the polymer. Water contact angles were not determined for new or aged pipe samples because pipe samples were not flat.

Aging did not affect  $D_{\text{Benzyl Alcohol}}$  or  $D_{\text{2-Propanol}}$  in any PE, but diffusivity results were highly variable making it difficult to discern differences. Contaminants with a dipole moment  $\geq 1.66$  debye diffused through aged PE differently in contrast to more nonpolar compounds (**Figure 6–9**).  $D_{\text{MTBE}}$  in aged PEX–B pipe was 20% less than  $D_{\text{MTBE}}$  in new PEX–B pipe. Since MTBE does not hydrogen-bond, one plausible reason for a reduction in  $D_{\text{MTBE}}$  in aged PEX–B pipe could be that carbonyl surface bonds prevented the bulky MTBE molecules from penetrating easily where toluene and *m*-xylene contaminants are more planar due to their benzene ring enabling easier entry and transport. Toluene and *m*-xylene diffused through all PEs approximately 5–13 times faster than MTBE.

Changes in polymer bulk characteristics may have impacted contaminant diffusivity and diffusivity changes numbered more in HDPE (10 polymer–contaminant pairs) than PEX pipes (6

pairs). Chain scission was indirectly implied by a reduction in aged PEX-B pipe mechanical strength and slight increase in aged HDPE pipe bulk density. The increase in nonpolar  $D_{\text{Toluene}}$  and  $D_{\text{m-Xylene}}$  in HDPE could be attributed to chain scission. Aging did not affect  $D_{\text{Trichloromethane}}$  in any PE and only  $D_{\text{MTBE}}$  in aged PEX-B pipe. Diffusivity was only different for one contaminant in the least dense material (aged PEX-A pipe), while diffusivity was changed for 4–6 contaminants in all other denser aged PEs. This finding could imply that polar contaminant diffusion is impacted to a greater degree in polymers with limited amorphous regions than with polymers where diffusion is less restricted.

Polymer–contaminant relationships identified for new PEs were similar for aged PEs. For both new and aged PEs, polar and nonpolar contaminant diffusivity decreased as bulk density increased as shown by regression analysis ( $p < 0.05$ ). **Figure 6–8** shows contaminants whose diffusivity decreased as bulk density of lab aged PE increased. This trend has also been reported by Crank and Park (1968), Comyn (1985), and Whelton et al. (2009). Crosslink density did not significantly reduce diffusivity since contaminant diffusion was fastest in the least dense and most crosslinked PE. Diffusivity also decreased as contaminant molecular volume and dipole moment increased.

#### **6.4.4 Water Utility PE (wu-PE) Pipe Comparison to Lab Aged PEs**

Water utility PE (wu-PE) pipes analyzed were removed from a buried water distribution system to assess their integrity. These pipes were removed from pressurized portions of the distribution system and had no known mechanical or contaminant permeation problems. In the laboratory, these pipes were determined to be HDPE and have surface and bulk characteristics indicative of oxidation. Hydroxyl, vinyl, and carbonyl bonds were detected on utility pipe surfaces and agree with MDPE surface chemistry findings by Karlsson et al. (1992) (**Figure 6–9**). Although, wu-PE surface chemistry changes were not consistent with lab aged PEs, or HDPE pipes removed from a buried water distribution system by Thompson et al. (1992). Detection of only carbonyl bonds during accelerated aging and on some buried water pipes may indicate that (1) carbonyl bonds form before hydroxyl, vinyl, and chlorine bonds, or (2) hydroxyl, vinyl, and chlorine bonds are caused by other water quality conditions (e.g., metals, other contaminants) not present in accelerated aging conditions or water utility service conditions of PEs analyzed in this work.



The three water utility pipes had little to no oxidative resistance after being in service for 7, 20, and 25 years and similar bulk density and crystallinity (**Table 6–7**). A reduction in OIT due to chlorinated water exposure was reproduced in the laboratory. Although, according to Gedde et al. (1994), the 7 year old PE pipe with the greatest thickness has reached the remaining 5–10% of its service life and will fail in the next 2 years. The wall thickness of wu–PE 1 was approximately 30% greater than all other pipes which should prolong its service life. Bulk density and crystallinity of wu–PE materials were not different than new and lab aged PEs (0.9504–0.9513 g/cm<sup>3</sup>). Since the initial utility pipe bulk density is unknown, it is not possible to draw conclusions regarding bulk density (crystallinity) changes throughout utility pipe lifetime.

Toluene and trichloromethane fate in water utility HDPE pipes were similar and were not significantly different than their fate in new and lab aged HDPE pipes.  $S_{\text{Toluene}}$  and  $S_{\text{Trichloromethane}}$  for wu–PE 1, wu–PE 2, wu–PE 3, new and lab aged HDPE pipes were all equal ( $p>0.05$ ). Diffusivity comparisons were much more complicated.  $D_{\text{Toluene}}$  and  $D_{\text{Trichloromethane}}$  for wu–PE 2 and wu–PE 3 were equal, and these contaminants diffused 19–25% faster and 18–23% more soluble in the thickest material, wu–PE 1.  $D_{\text{Trichloromethane}}$  for wu–PE 2 = aged HDPE pipe = aged PEX–B pipe and wu–PE 1 = aged PEX–A pipe.  $D_{\text{Toluene}}$  for wu–PE 2 = wu–PE 3 = aged HDPE pipe. Overall these results imply that nonpolar contaminant solubility and diffusivity are not significantly altered during buried water service, and toluene and trichloromethane fate in water utility pipes was similar to their fate in new and lab aged HDPE pipes.

## 6.5 Conclusion

In this work, surface, bulk, and contaminant interaction characteristics of water utility, new, and lab aged HDPE and PEX pipes were determined. All utility pipes had similar bulk density (0.950–0.951 g/cm<sup>3</sup>), little to no OIT (0–8 min) even for a pipe only installed for 7 years, and surfaces contained carbonyl, hydroxyl, and peroxide bonds. With the exception of new PEX–A pipe (0.938 g/cm<sup>3</sup>), all new HDPE and PEX pipes had similar bulk density (0.950–0.957 g/cm<sup>3</sup>) before and after aging. The oxidative resistance of *new* HDPE pipe (97 min.), PEX–B pipe (120 min.), and PEX–A pipe (33 min.) differed greatly. PEX–A pipe was 76% crosslinked while PEX–B pipe was 60% crosslinked. No surface oxidation was detected on new PEs before chlorinated water exposure.

Accelerated aging over 141 days reduced HDPE and PEX pipe OIT from 40–95% and PEX–B pipe had the least OIT of all materials after aging. Water sorption was not detected for any PE. The mechanical strength of PEX–B pipe was reduced and HDPE pipe bulk density increased likely due to chain scission caused by chlorinated water exposure. Carbonyl surface bonds were consistently detected on all HDPE and PEX–B pipes during aging, sporadically on HDPE resin, and not detected on PEX–A pipe during aging. However, contact angle analysis showed that chlorinated water changed PE surfaces were less hydrophobic than new PE surfaces even when oxygenation was not detected on aged PE surfaces by infrared spectroscopy.

Diffusivity and solubility values were measured for twelve contaminants in new and lab aged PEs and two contaminants in water utility PEs. Nonpolar contaminant diffusivity and solubility in *new* PE pipes was driven by bulk density, but bulk density was a good predictor of nonpolar contaminant solubility in lab aged PEs. Polar contaminant diffusivity and solubility was greater in *new* PEX than *new* HDPE pipes and can be attributed to the greater oxygen content of PEX. Diffusivity and solubility values calculated for utility and *new* PE pipes were similar to those reported by others for *new* HDPE and PEX water pipes. Toluene and trichloromethane diffusivity and solubility results for water utility HDPE pipes were similar and performed similar to *new* and lab aged HDPE pipe, but not PEX–A or PEX–B pipe.

Chlorinated water exposure changed polar contaminant diffusivity greatly and solubility slightly in lab aged PEs, but did not significantly alter nonpolar contaminant fate. Contaminant diffusivity increased when contaminant dipole moment was  $\geq 1.66$  debye and had the greatest impact for compounds with alcohol > aldehyde > ketone functional groups. In contrast to diffusivity in aged PEs, solubility was slightly affected. This finding is reasonable since chlorinated water induced oxidation is primarily a surface phenomenon and the majority of PE pipe amorphous regions are not affected during aging. Chlorinated water exposure caused PE surfaces to become hydrophilic which enabled faster penetration of polar contaminants.

The implications of this work are potentially far-reaching. Aged PE pipe surfaces can impact pipe performance and contaminant exposure risks posed to water users. Current water quality models are based on contaminant diffusion in *new* PE materials and do not consider contaminant polarity or PE pipe surface characteristics. *New* PE diffusivity data used for predicting contaminant fate for regulatory, security, emergency decontamination, and utility

operations purposes may over–or under–estimate contaminant transport in aged PE piping systems, especially contaminants capable of hydrogen–bonding. Existing potable water pipe performance standards and utility pipe acquisition criteria only consider a minimum mechanical strength/ service–life, and do not factor in how changes in polymer properties during service affect water quality (D or S) or oxidative resistance (OIT, bulk density). Finally, results of this work are representative for one chlorinated water exposure period and selected commercially available pipes. Changes in contaminant diffusivity or solubility in PE pipe and other polymeric materials at other exposure times could be more/less significant. Material and distribution network designers, utility and public health professionals benefit from this work.

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**Table 6–1 Contaminant Properties**

Contaminant	Contaminant	Contaminant Property						Hydrogen–Bonding Ability
Name <sup>1</sup>	Class	μ, Debye	M <sub>v</sub> , cm <sup>3</sup>	M <sub>m</sub> , g/mol	S <sub>w</sub> , mg/L	ρ, g/cm <sup>3</sup>	Log K <sub>ow</sub>	
Polar Contaminants								
Acetonitrile	Aliphatic nitrile	3.92	53.3	41.05	Miscible	0.786	−0.34	Poor
2–Propanone	Aliphatic ketone	2.88	73.1	58.08	Miscible	0.789	−0.24	Moderate
Benzaldehyde	Aromatic aldehyde	2.80	120.5	106.12	3000	1.041	1.48	Moderate
2–Butanone	Aliphatic ketone	2.76	91.4	72.11	223000	0.805	0.29	Moderate
Water	–	1.85	19.3	18.01	Miscible	1.000	–	Strong
Benzyl Alcohol	Aromatic alcohol	1.71	125.1	108.14	40000	1.041	1.10	Strong
1–Butanol	Aliphatic alcohol	1.66	96.2	74.12	74000	0.809	−0.30	Strong
2–Propanol	Aliphatic alcohol	1.56	77.8	60.10	Miscible	0.789	0.05	Strong
Nonpolar Contaminants								
MTBE	Aliphatic ether	1.36	119.1	88.15	51000	0.740	1.24	Poor
Trichloromethane	Chlorinated alkane	1.01	74.4	119.37	7290	1.492	1.97	Poor
Toluene	Methylated aromatic	0.36	117.7	92.14	526	0.867	2.73	Poor
<i>m</i> –Xylene	Methylated aromatic	0.30	135.9	106.16	161	0.864	3.20	Poor

1. All properties represent conditions at 25 °C; MTBE = Methyl *t*-butyl ether;  $\mu$  = Dipole moment;  $\delta$  = Solubility parameter;  $M_v$  = Calculated molar volume;  $M_m$  = Molar mass;  $S_w$  = Water solubility;  $\rho$  = Density;  $K_{ow}$  = Octanol–water partition coefficient;  $M_m$ ,  $S_w$ , Log  $K_{ow}$ , and  $\rho$  values obtained from *CHEMFATE* (Syracuse Research Corporation 2009);  $M_v$  calculated molar volume using *Spartan* (Wavefunction 1997)



**Table 6–2 Stability of Accelerated Aging Solution during Test Periods**

Aging Condition Parameter	Control Initial	Aging Solution Characteristic Measured at End of Three Day Exposure				
		Control (no PE)	HDPE	HDPE	PEX–A	PEX–B
			Resin	Pipe	Pipe	Pipe
Water pH, SU	$6.54 \pm 0.02$	$6.77 \pm 0.13$	$6.79 \pm 0.12$	$6.80 \pm 0.11$	$6.82 \pm 0.11$	$6.82 \pm 0.13$
Free available chlorine concentration, mg/L	$53.18 \pm 4.28$	$53.56 \pm 3.47$	$51.54 \pm 4.52$	$51.25 \pm 4.73$	$52.89 \pm 4.01$	$51.83 \pm 5.11$
Alkalinity concentration, mg/L	$53.49 \pm 4.98$	$54.72 \pm 6.59^*$	$55.11 \pm 6.87^*$	$54.59 \pm 6.45^*$	$55.84 \pm 6.95^*$	$55.07 \pm 7.04^*$

1. Aging solutions stored in a dark constant temperature room:  $22 \pm 1$  °C; Values represent mean and standard deviation of 46 water changes over 141 days. Water pH and free chlorine concentration represent 46 measurements, while an asterisk (\*) indicates 44 measurements for alkalinity concentration.

**Table 6–3 Bulk and Mechanical Properties for New and Lab Aged Polyethylene**

Polymer Type	Condition	Bulk Property <sup>1</sup>					
		Bulk Density <sup>3</sup> , g/cm <sup>3</sup>	Crystallinity <sup>3</sup> , %	Tensile Strength at Yield <sup>4</sup> , MPa	Tensile Strength at Break <sup>4</sup> , MPa	Elongation at Break <sup>4</sup> , %	Oxidation Induction Time <sup>3</sup> , min.
HDPE Resin	New	0.9578 ± 0.0001	71.5 ± 0.1	45.8 ± 0.8	26.8 ± 3.8	615 ± 199	22.4 ± 2.3†
	Aged	0.9581 ± 0.0000	71.7 ± 0.0	44.2 ± 1.9	24.2 ± 6.3	529 ± 69	13.5 ± 2.2†
HDPE Pipe	New	0.9503 ± 0.0004†	66.4 ± 0.2†	30.1 ± 0.8	21.8 ± 6.6	491 ± 174	97.1 ± 1.8†
	Aged	0.9513 ± 0.0002†	67.1 ± 0.1†	31.5 ± 1.2	22.4 ± 5.1	491 ± 181	29.7 ± 6.7†
PEX–A Pipe <sup>2</sup>	New	0.9385 ± 0.0002	58.4 ± 0.1	30.6 ± 1.2	35.0 ± 2.7	569 ± 44	33.5 ± 3.9†
	Aged	0.9389 ± 0.0001	58.7 ± 0.1	31.8 ± 1.9	34.8 ± 2.4	536 ± 19	27.2 ± 5.7†
PEX–B Pipe <sup>2</sup>	New	0.9524 ± 0.0001	67.8 ± 0.1	37.4 ± 1.9	34.9 ± 2.0†	379 ± 38†	119.6 ± 12.3†
	Aged	0.9527 ± 0.0000	68.1 ± 0.0	36.0 ± 1.0	23.7 ± 3.8†	154 ± 18†	5.4 ± 0.6†

1. Mean and standard deviation shown for all measurements; † represent statistical differences were detected between new and aged materials using a student's t-test ( $p < 0.05$ ). 2. PEX–A pipe was  $76.1 \pm 5.5$  % crosslinked while PEX–B Pipe was  $60.4 \pm 2.2$  % crosslinked. 3. Three replicates per polymer; Crystallinity was calculated based on bulk density values. 4. Five replicates per polymer.

**Table 6–4 Change in Time to Half–Equilibrium for New and Lab Aged Polyethylene**

Contaminant Name <sup>1</sup>	Dipole Moment, Debye	Time, hrs			
		HDPE Resin	HDPE Pipe	PEX–A Pipe	PEX–B Pipe
<i>Polar Contaminants</i>					
2–Propanone	2.88	32.9	46.4	17.5	50.8
Benzaldehyde	2.80	33.0	33.1	12.0	38.4
2–Butanone	2.76	21.7	40.1	2.7	31.8
Benzyl Alcohol	1.71	76.4	79.4	191.0	185.0
2–Propanol	1.56	90.5	−53.0	−97.3	−111.2
1–Butanol	1.66	653.6	617.7	−86.5	618.1
<i>Nonpolar Contaminants</i>					
MTBE	1.36	3.0	−3.0	−6.5	−42.2
Trichloromethane	1.01	−0.3	1.0	−0.1	−0.6
Toluene	0.36	0.9	2.6	0.3	0.7
<i>m</i> –Xylene	0.30	0.7	4.9	0.8	0.8

1. Equilibrium is the point at which the polymer no longer gains weight when immersed in neat contaminant; The time to half equilibrium is commonly reported in polymer diffusion studies; Mean values shown and represent three replicates; Change = Time<sub>New</sub>–Time<sub>Aged</sub>; Mean and standard deviation of specimen thickness is: HDPE resin (1.65 ± 0.02), HDPE pipe (2.61 ± 0.05), PEX–A pipe (2.60 ± 0.02), and PEX–B pipe (2.64 ± 0.03). Specimen thickness did not change during lab aging.

**Table 6–5 Contaminant Solubility in New and Lab Aged Polyethylene**

Contaminant Name <sup>1</sup>	Dipole Moment, debye	Solubility, g/cm <sup>3</sup>							
		HDPE Resin		HDPE Pipe		PEX–A Pipe		PEX–B Pipe	
		New	Aged	New	Aged	New	Aged	New	Aged
<i>Polar Contaminants</i>									
Acetonitrile	3.92	0.0012	—	0.0014	—	0.0023	—	0.0026	—
2–Propanone	2.88	0.0097	0.0098	0.0101	0.0107	0.0120†	0.0126†	0.0145†	0.0128†
Benzaldehyde	2.80	0.0204	0.0206	0.0216	0.0216	0.0237†	0.0250†	0.0263†	0.0250†
2–Butanone	2.76	0.0186	0.0185	0.0189	0.0199	0.0218†	0.0232†	0.0253†	0.0225†
Benzyl Alcohol	1.71	0.0051	0.0039	0.0048†	0.0036†	0.0050†	0.0038†	0.0063†	0.0038†
1–Butanol	1.66	0.0084†	0.0064†	0.0053	0.0045	0.0053†	0.0062†	0.0088†	0.0063†
2–Propanol	1.56	0.0047†	0.0037†	0.0035	0.0030	0.0048	0.0048	0.0054	0.0051
<i>Nonpolar Contaminants</i>									
MTBE	1.36	0.0452	0.0449	0.0546	0.0575	0.0591†	0.0611†	0.0547†	0.0634†
Trichloromethane	1.01	0.1106	0.1091	0.1426	0.1425	0.1652†	0.1590†	0.1373	0.1372
Toluene	0.36	0.0660	0.0656	0.0852	0.0853	0.0979	0.0961	0.0806	0.0812
<i>m</i> –Xylene	0.30	0.0680	0.0685	0.0874	0.0873	0.1009	0.0984	0.0830	0.0827

1. †Indicates new and aged contaminant values were statistically different at  $p < 0.05$ ; Acetonitrile was not soluble in aged materials and water was not soluble in either new or aged materials; All measurements had a coefficient of variation  $\leq 10\%$  except for 1–butanol (3–39%).

**Table 6–6 Contaminant Diffusivity in New and Lab Aged Polyethylene**

Contaminant Name <sup>1</sup>	Dipole Moment, debye	Diffusivity, 10 <sup>-9</sup> cm <sup>2</sup> /s							
		HDPE Resin		HDPE Pipe		PEX–A Pipe		PEX–B Pipe	
		New	Aged	New	Aged	New	Aged	New	Aged
<i>Polar Contaminants</i>									
2–Propanone	2.88	5.07†	9.73†	10.52†	19.72†	17.57†	26.41†	8.64†	16.18†
Benzaldehyde	2.80	2.65†	3.67†	4.77†	6.04†	8.11	9.30	4.29†	5.09†
2–Butanone	2.76	4.95†	7.32†	7.90†	12.32†	17.40	18.58	8.23†	11.63†
Benzyl Alcohol	1.71	3.17	8.99	5.52	9.92	4.03	23.31	3.89	14.98
1–Butanol	1.66	0.28	0.58	0.99†	2.61†	2.69	2.15	0.89†	2.05†
2–Propanol	1.56	1.07	1.52	4.97	4.03	2.99	2.27	2.42	1.86
<i>Nonpolar Contaminants</i>									
MTBE	1.36	5.00	5.58	6.65	7.15	12.64	11.76	5.96†	4.71†
Trichloromethane	1.01	41.22	42.60	58.20	61.42	91.92	91.02	61.73	61.11
Toluene	0.36	42.55†	50.24†	56.92	68.82	96.73	99.24	59.62	61.35
<i>m</i> –Xylene	0.30	29.68	32.77	37.06†	44.04†	62.71	66.43	38.10	39.44

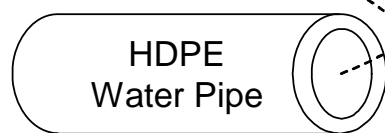
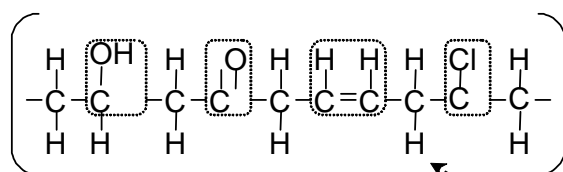
1. †Indicates new and aged contaminant values were statistically different at  $p < 0.05$ ; Mean values shown; All measurements had a coefficient of variation  $< 8\%$  except for benzyl alcohol (18–60%), 1–butanol (11–86%), and 2–propanol (16–27%).

**Table 6–7 Attributes of Water Utility Polyethylene Pipes**

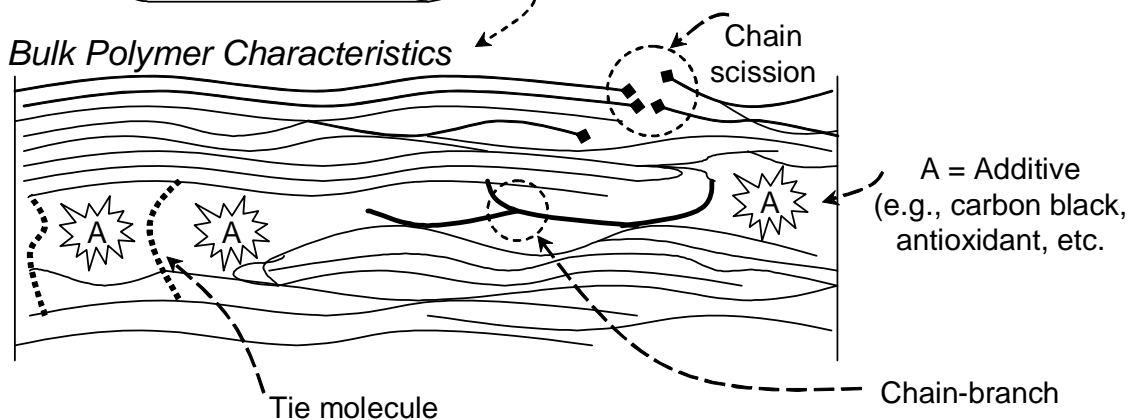
Characteristic <sup>1</sup>	wu–PE 1	wu–PE 2	wu–PE 3
<b><i>Service and Disinfectant Exposure History</i></b>	7 yr in service: combined chlorine only	20 yr in service: 18 yr free available chlorine; 2 yr combined chlorine	25 yr in service: free available chlorine only
<b><i>Bulk Properties</i></b>			
Thickness, mm.	3.37 ± 0.06	2.52 ± 0.03	2.65 ± 0.03
Bulk density, g/cm <sup>3</sup>	0.9504 ± 0.0003 (HDPE)	0.9513 ± 0.0001 (HDPE)	0.9504 ± 0.0004 (HDPE)
Crystallinity, %	66.4 ± 0.2	67.0 ± 0.0	66.5 ± 0.2
OIT, min.	0.0 ± 0.0	4.8 ± 4.2	8.3 ± 4.0
<b><i>Contaminant Interactions</i></b>			
Toluene			
D x 10 <sup>-9</sup> , cm <sup>2</sup> /s	78.1 ± 2.9	80.1 ± 4.4	70.9 ± 1.2
S, g/cm <sup>3</sup>	0.0865 ± 0.0013	0.0866 ± 0.0016	0.0858 ± 0.0006
Trichloromethane			
D x 10 <sup>-9</sup> , cm <sup>2</sup> /s	70.1 ± 2.2	80.6 ± 2.6	66.1 ± 1.3†
S, g/cm <sup>3</sup>	0.1440 ± 0.0018	0.1431 ± 0.0014	0.1453 ± 0.0012

1. (wu) represents water utility; Total chlorine residual concentration typically varied from 2.0 to 4.8 mg/L as Cl<sub>2</sub> during service, pH varied from 7.4 to 7.9, and temperature ranged from 20 to 24 °C; Bulk property results represent the mean and standard deviation of three replicates; Standard error for contaminant properties reported; † indicates the diffusivity was statistically less than the other utility PEs.

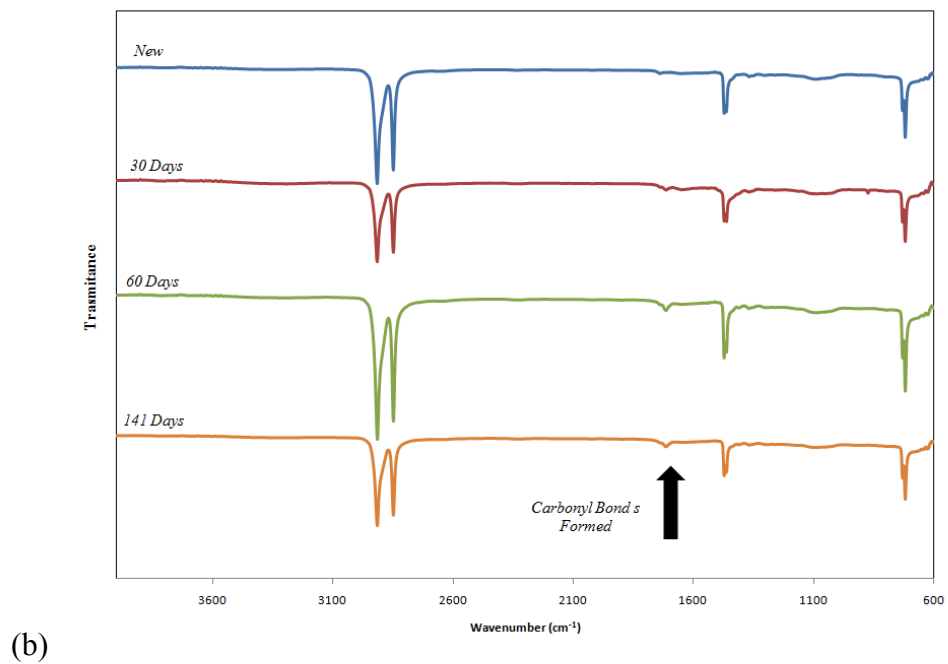
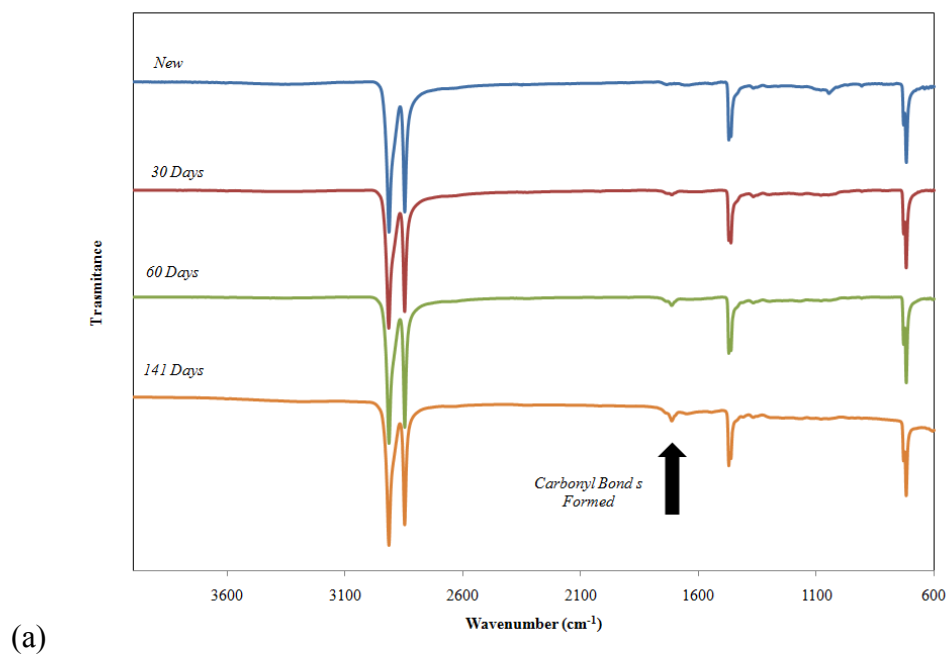
*Bonds Present on Surface*



*Bulk Polymer Characteristics*



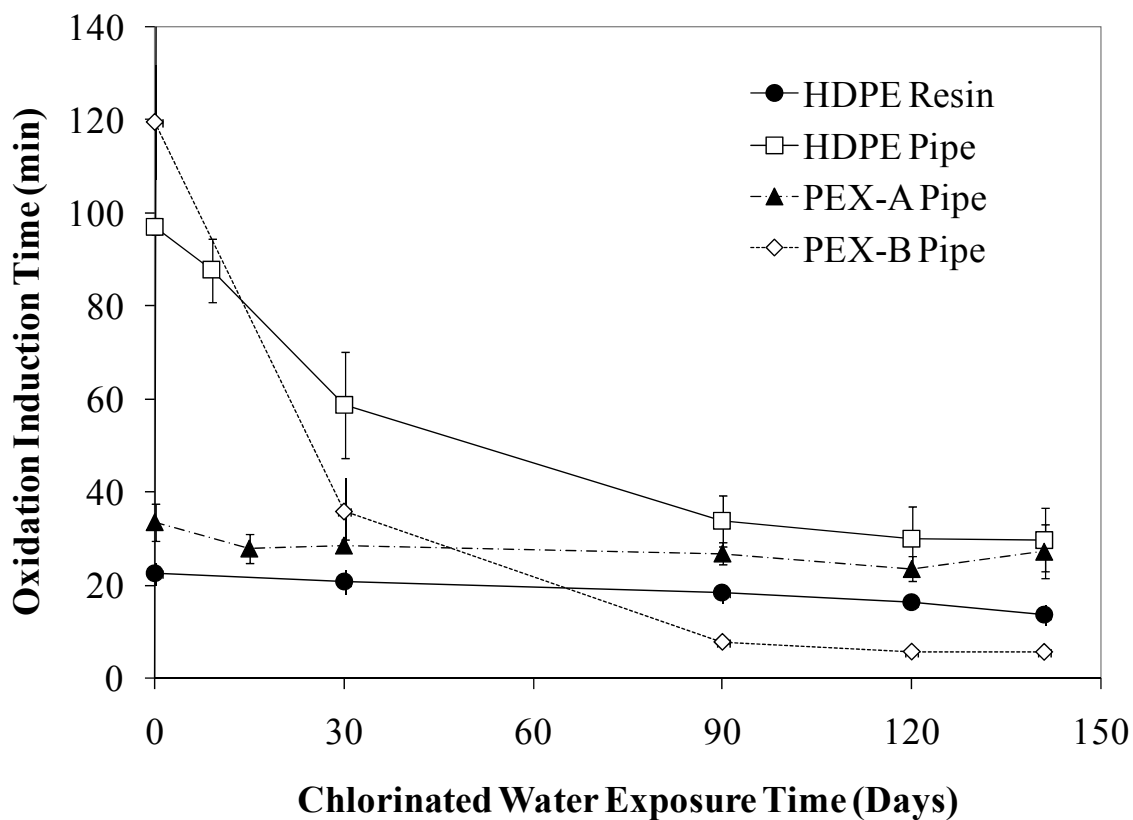
**Figure 6–1 Representation of Polyethylene Degradation due to Chlorinated Potable Water Exposure**



**Figure 6–2 Infrared Spectra for (a) HDPE Pipe and (b) PEX–B Pipe Surfaces during Accelerated Aging in 45 mg/L as  $\text{Cl}_2$ , 50 mg/L as  $\text{CaCO}_3$  at 37 °C**

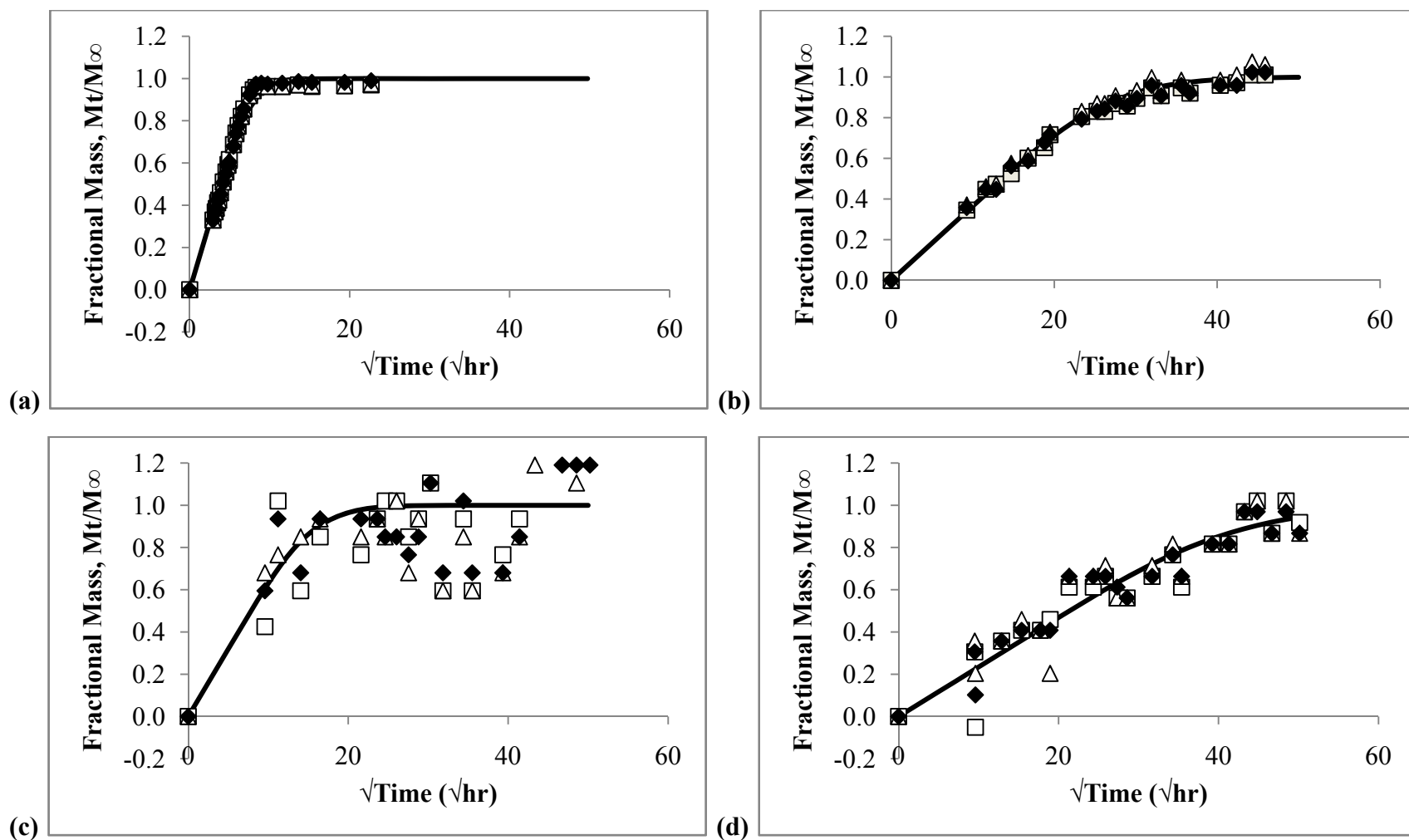
Solutions were replaced every three days. Carbonyl bonds [ $>\text{C}=\text{O}$ ] ( $\sigma = 1713 \text{ cm}^{-1}$ ) were formed on aged PE surfaces due to chlorinated water exposure.





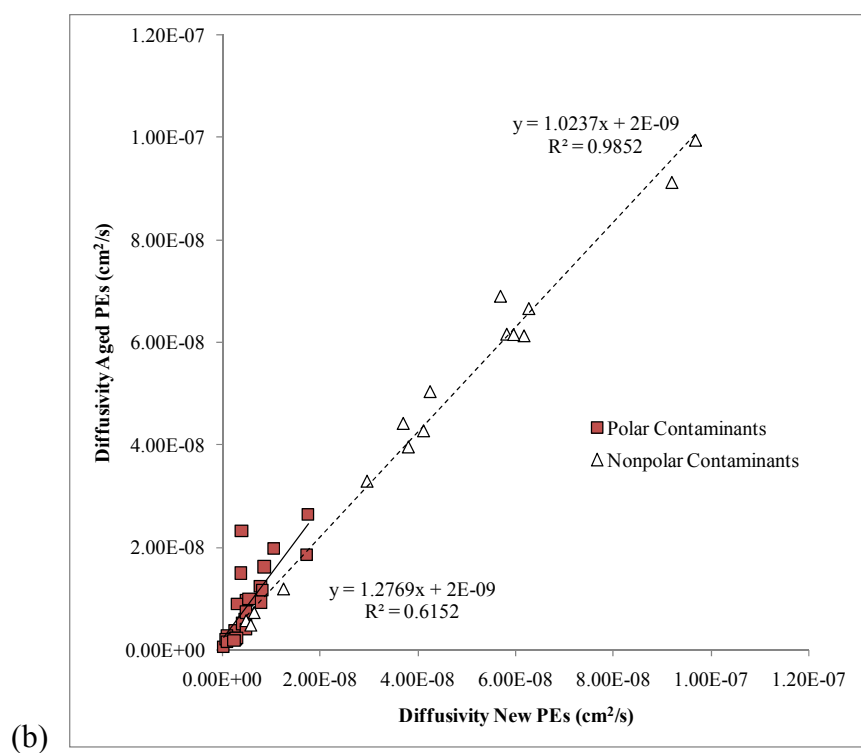
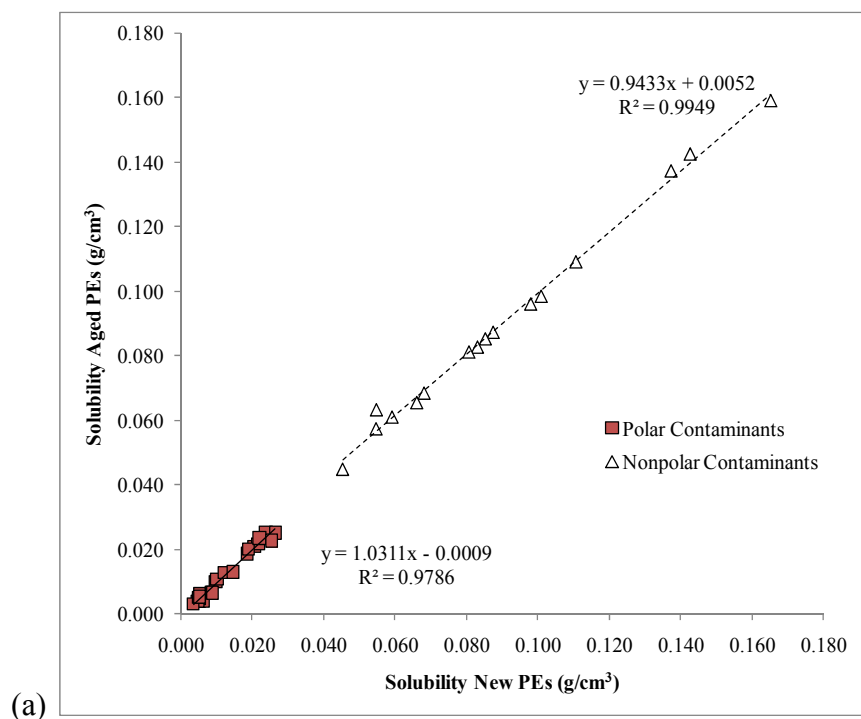
**Figure 6–3 Change in Oxidation Induction Time for HDPE Resin, HDPE Pipe, PEX–A Pipe, and PEX–B Pipe during Accelerated Aging in 45 mg/L as  $\text{Cl}_2$ , 50 mg/L as  $\text{CaCO}_3$  at 37 °C**

Solutions were replaced every three days. Mean and standard deviation of three replicates shown.



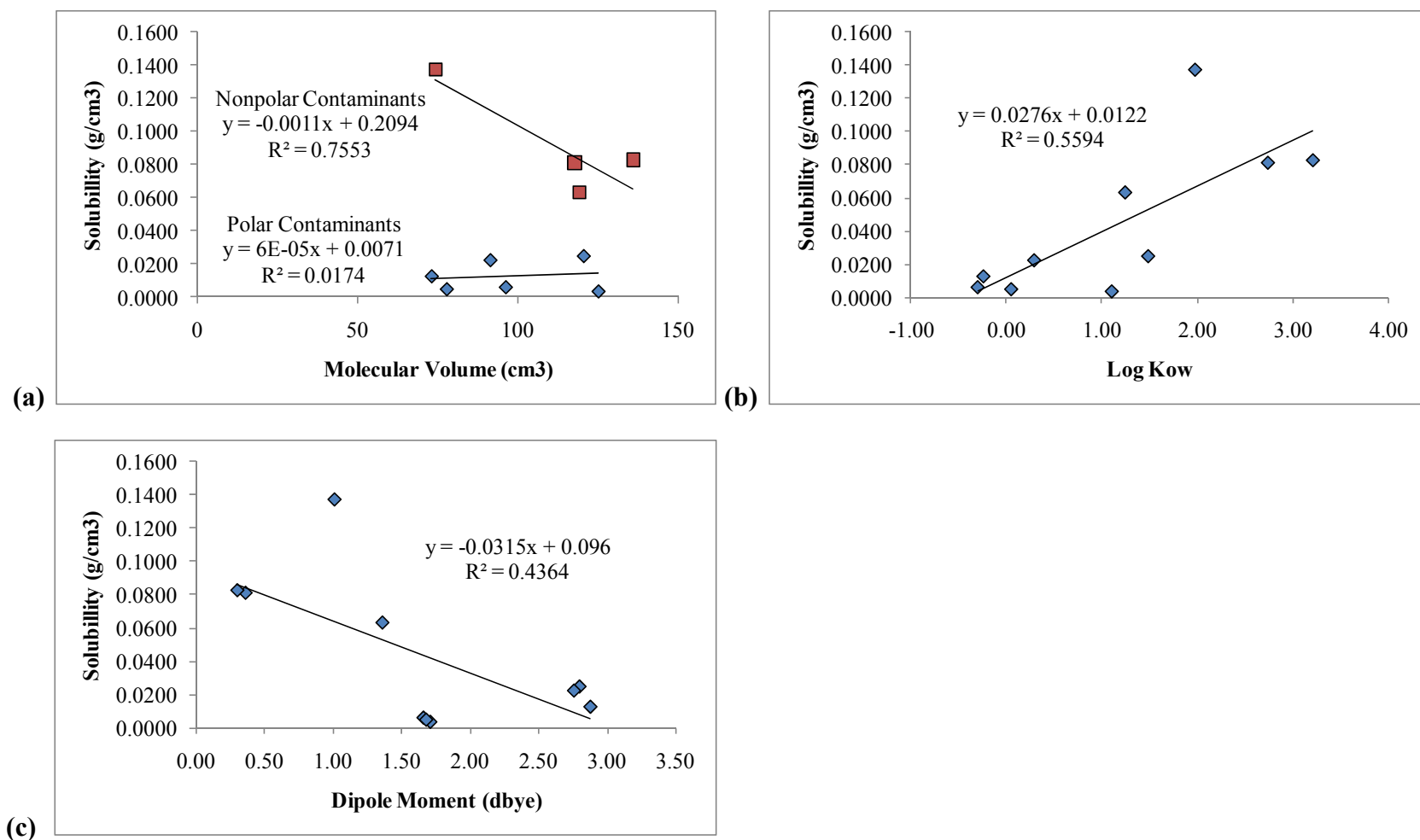
**Figure 6-4 Sorption Data and Curves for (a) Toluene, (b) Benzaldehyde, (c) Benzyl Alcohol, and (d) 1-Butanol in New PEX-A Pipe**

Triangles, squares, and diamonds represent data for each replicate. Three replicates for each contaminant–polymer pair.



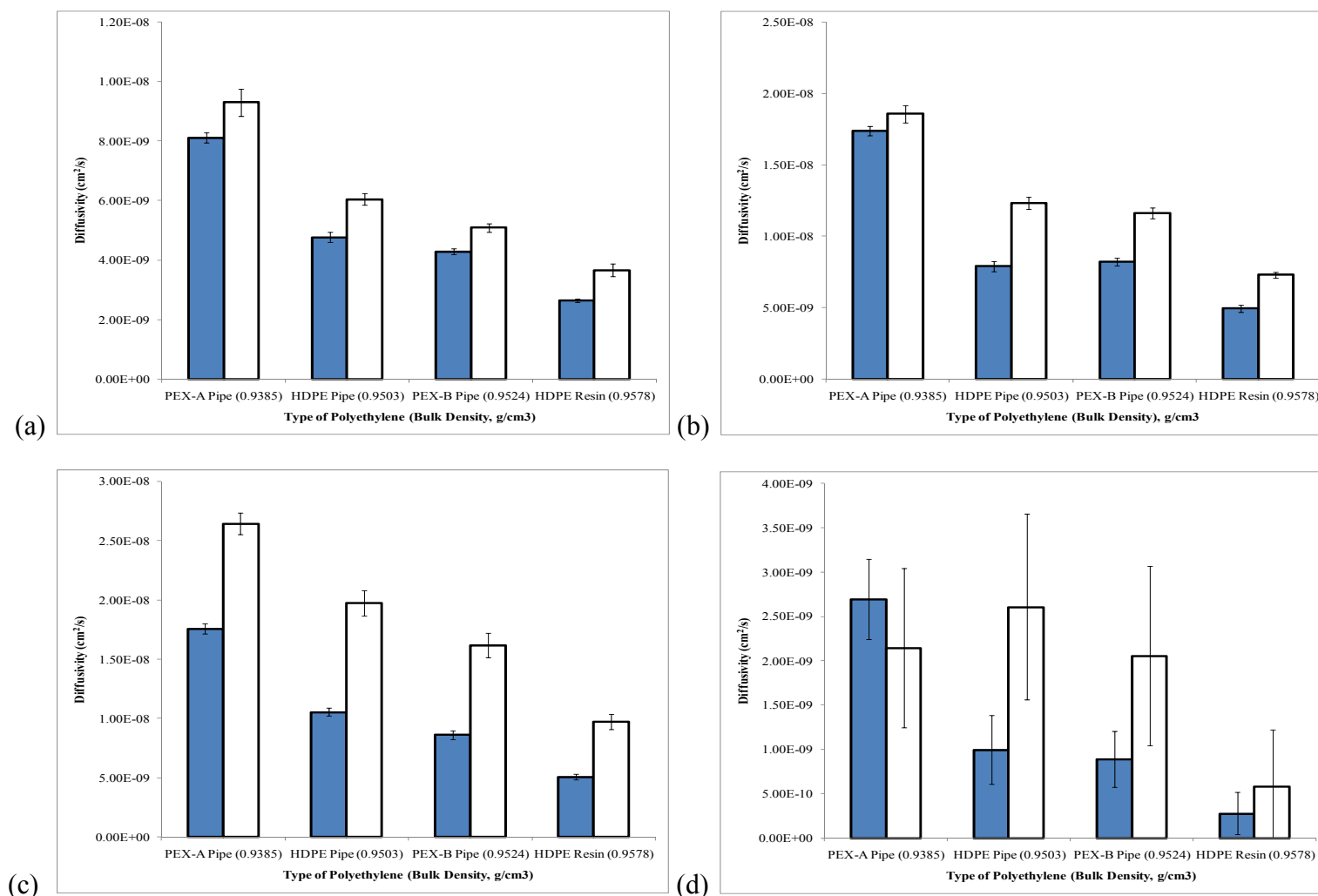
**Figure 6–5 Relationship between Contaminant (a) Solubility and (b) Diffusivity in New and Lab Aged PEs for Nonpolar and Polar Contaminants**

The magnitude of contaminant diffusivity changed as dipole moment increases. Regression slopes of Figure (b) are statistically different. ( $p < 0.05$ ), but Figure (a) slopes are not different.



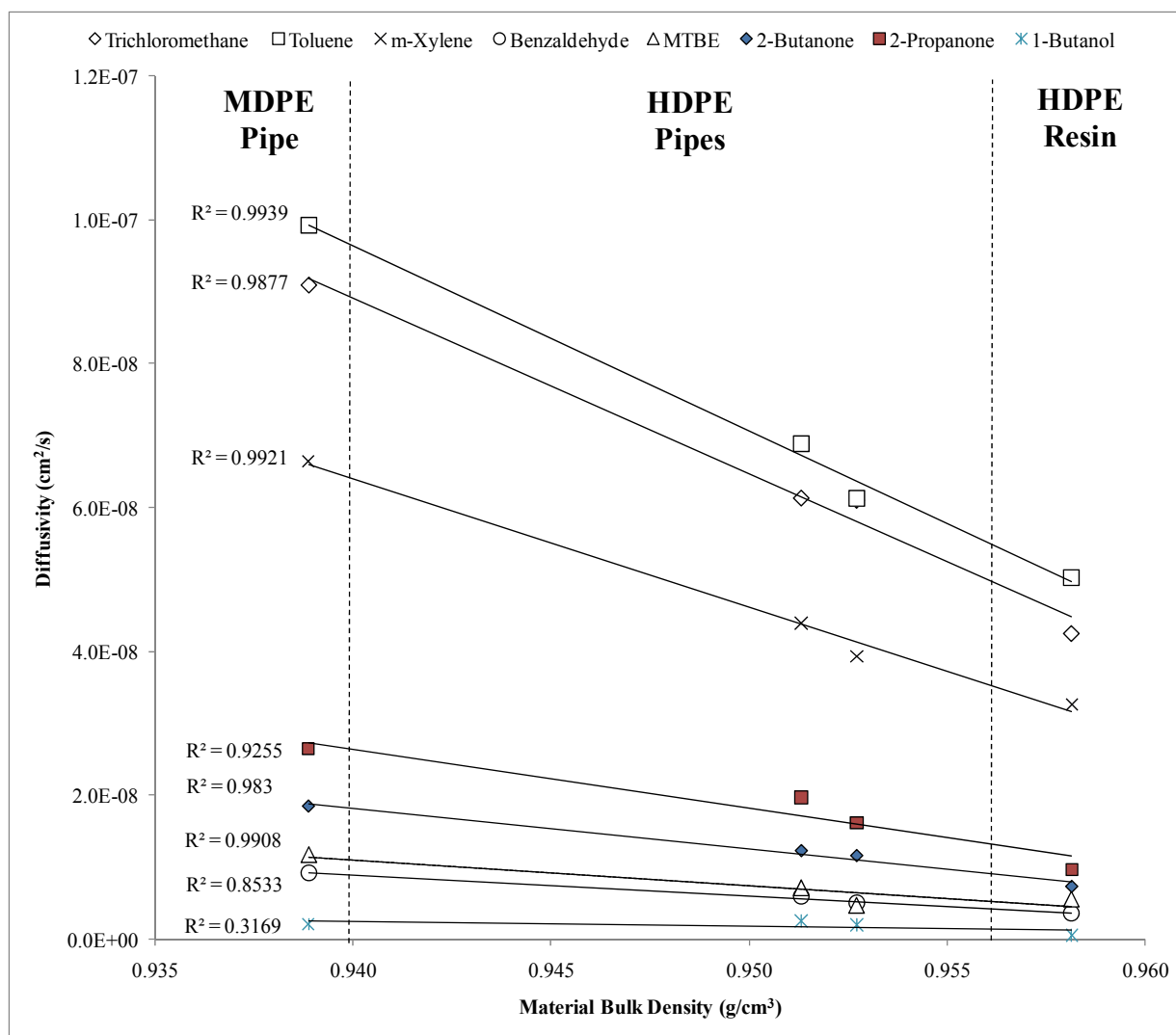
**Figure 6–6 Relationship between Lab Aged PEX–B Pipe Contaminant Solubility and Contaminant (a) Molar Volume, (b) Log K<sub>ow</sub>, and (c) Dipole Moment**

Mean solubility values for all contaminants shown.



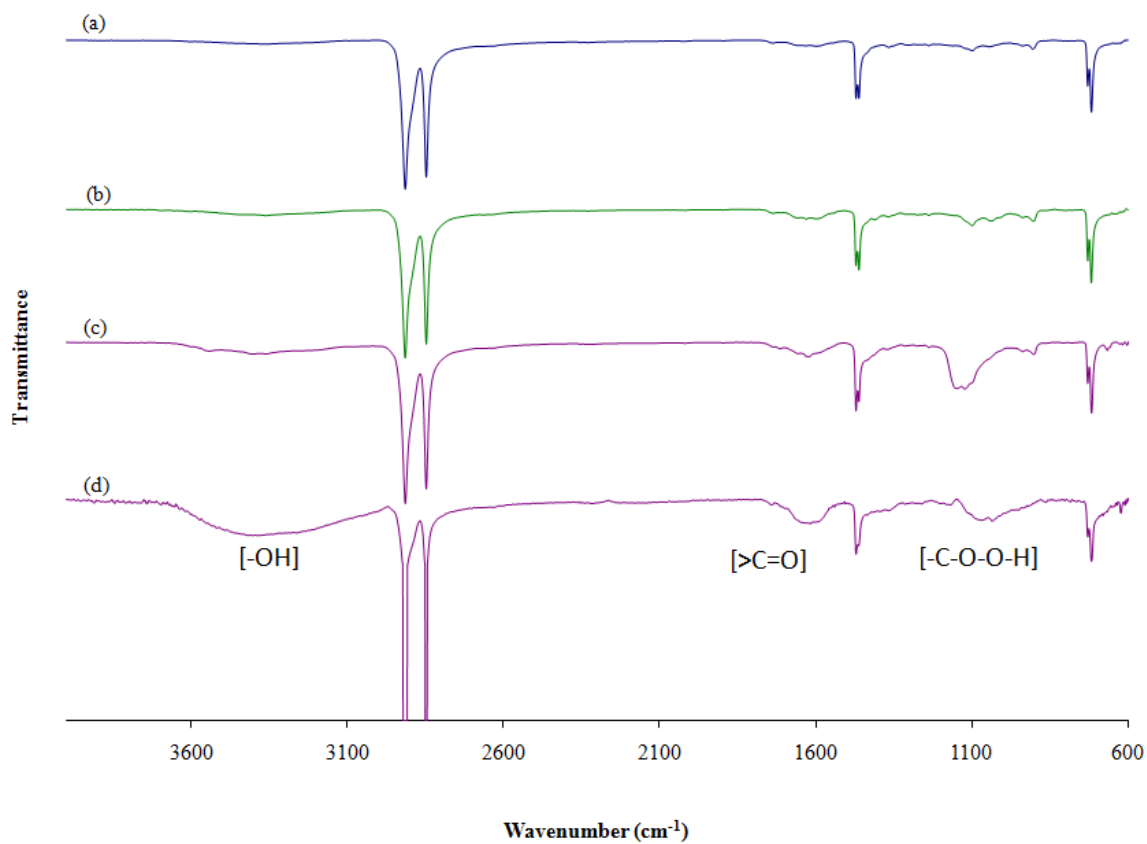
**Figure 6–7 Comparison of New and Lab Aged Polyethylene Diffusivity for (a) Benzaldehyde, (b) 2–Butanone, (c) 2–Propanone, and (d) 1–Butanol**

Mean and standard error shown. Shaded bars represent new polymer and white/open bars represent polymer exposed to 45 mg/L as Cl<sub>2</sub>, 50 mg/L as CaCO<sub>3</sub> at 37 °C for 4.5 months. Bulk density values shown represent aged PE.



**Figure 6–8 Statistically Significant Relationships between Lab Aged Polymer Bulk Density and Contaminant Diffusivity**

Mean shown for three replicates per data point. Regression line slopes are statistically different than zero ( $p < 0.05$ ). Regression line slopes for all other contaminants were equal to zero. The bulk density of aged materials shown is: PEX-A [MDPE] Pipe ( $0.938 \text{ g/cm}^3$ ), HDPE Pipe ( $0.951 \text{ g/cm}^3$ ), PEX-B [HDPE] Pipe ( $0.952 \text{ g/cm}^3$ ), and HDPE Resin ( $0.958 \text{ g/cm}^3$ ).



**Figure 6–9 Infrared Spectrum for (a) New HDPE Pipe from a Plumbing Supply Store and Water Utility PE (wu-PE) Pipe Samples Removed from a Buried Water Distribution System after Chlorinated Water Exposure, (b) wu-PE 1 (7 year exposure), (c) wu-PE 2 (20 year exposure), (d) wu-PE 3 (25 year exposure)**

## **Chapter 7 Organic Contaminant Desorption from New and Aged Polyethylene and Poly(1-butene) Potable Water Pipes**

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*To be submitted to peer-review journal.*

### **7.1 Abstract**

Organic contaminant desorption was characterized at 23 °C for ten different new and lab aged polyethylene (PE) as well as four PE and poly(1-butylene) (PB) pipes removed from a water distribution system after 7–30 year service. Nonpolar contaminants desorbed the fastest from new and lab aged PEs (10–79 hr to achieve 50% desorption), while the time for hydrogen-bonding contaminants to desorb 50% was 1000–2000 hr. Chlorinated water exposure significantly extended the time for PEs to reach 50% desorption of alcohol and ketone containing contaminants (95–406 hr). Extended desorption can be attributed to contaminants hydrogen-bonding with oxygen on the polymer surface. PE pipes removed from a water distribution had similar bulk and contaminant desorption properties to new and lab aged PE pipes. Desorption from PB pipe was significantly faster than desorption from PEs, and immersion of PE and PB in two contaminants resulted in 1.4, 2.6, and 3.0% weight loss. Contaminant diffusivity was reduced for 10 aromatic and aliphatic compounds as new and lab aged PE bulk density/crystallinity increased.

**Key words:** Water, pipe, desorption, plastic, polyethylene, PE, PB

### **7.2 Introduction**

#### **7.2.1 Existing Knowledge–Gaps and Need for Research**

In the last 10 years, the fate and transport of pollutants accidentally or maliciously injected into potable water systems has received much attention (USEPA 2008; Ginsberg et al. 2006; Watson 2006; Welter et al. 2006; USEPA 2004; Whelton et al. 2003; Burrows and Renner 1999). A major concern is that organic chemicals will penetrate or adhere to water pipe inner walls and leach back into drinking water posing health risks to water users (CDC 2003). Previous investigators have validated this concern and found that the ability to remove contaminants from material *in-situ* or leach from them into the water they transport depends on environmental and temporal conditions as well as water pipe and chemical properties. Polymeric water pipes are



especially vulnerable to organic chemical penetration and are increasingly being installed in buried and premise potable water applications. These materials are cheaper, easier to install than their metallic counterparts and have predicted 50 year service lives (Burn et al. 2005; Davis et al. 2007).

In 2008, public health and water sector leaders reaffirmed the need for research that clarifies how to decontaminate premise and buried potable water pipes following contamination events (CIPAC, 2008). Unfortunately, little is known about the time required and polymer pipe properties affecting contaminant desorption. In response, a few studies have been conducted to quantify contaminant removal from a number of different infrastructure materials (Lemieux 2004; USEPA, 2004; Welter et al. 2006). While these prior studies reported organic chemical desorption data for poly(vinyl chloride) (PVC), their results do not identify key material or chemical properties necessary for predicting desorption in other materials under other conditions. The consequence of not understanding organic chemical fate in water pipe networks was underscored during a 1980 public health response to the intentional injection of the pesticide chlordane into a Pennsylvanian drinking water distribution system (Moser et al. 2005; Welter et al. 2006). This event affected 3400 people, required more than 9 months to desorb pesticide from buried and premise pipes, and some polymers had to be removed and replaced entirely. With the looming massive buried water pipe replacement effort on the horizon and continued installation of polymer pipes into piping inventories, public health and water production officials would be well-served by research that elucidates challenges associated with contaminant desorption from polymer water pipes (AWWASC 2002; Raynaud 2004; USEPA 2005; USDOC 2006).

Polyethylene (PE) materials are rapidly gaining popularity in premise and buried water service applications and PE represents 33.5% of the global plastic pipe demand (Raynaud, 2004). High-density polyethylene (HDPE) pipes have been used in premise plumbing since 1940s (NAHB 2006) and represent 70% of some utilities total buried water pipe inventory (AWWA 1996; AWWA 2003). Crosslinked polyethylene (PEX) piping has been used in premise plumbing since the 1980s, constitutes 40% of potable water piping in buildings (BGLLC, 2007; Raynaud, 2004; Long 2005), and was recently approved for buried water service in 2007 (AWWA 2007). Poly(1-butene) (PB) pipes can also be found in premise and buried water pipe networks, but their installation was halted in the 1990s due to mechanical failure problems

(CPRC 2009). Aside from the popularity of HDPE and PEX and existence of PB pipes, they are particularly amenable for study because they share similar polymer characteristics.

PE ( $[-CH_2-CH_2-]_n$ ) and PB ( $[-CH_2-C(CH_3)_2-]_n$ ) pipes are semi-crystalline thermoplastics that contain amorphous and crystalline regions. Crystalline regions are those areas where the polymer chains are densely packed. Dense regions improve polymer strength, reduce flexibility, and do not enable contaminants to penetrate. Amorphous regions enable flexibility but are vulnerable to permeation due to the less densely packed polymer chains. Bulk density is another indirect measure of polymer crystallinity and PE water pipe is generally classified into one of three density categories: low (LDPE), medium (MDPE), or high (HDPE) (Bensason et al. 1996). PE water pipe is typically 46–66% crystalline (Lundback 2005; Karlsson et al. 1992). PB pipe bulk density is 0.930–0.935 g/cm<sup>3</sup> (Park et al. 1989) and is 40–65% crystalline (Lundback 2005; Karlsson et al. 1993). PEX pipes are very different from HDPE and PB materials in that they have undergone an additional manufacturing step. PEX-A and PEX-B pipes are two of the most popular PEX in the USA. During manufacturing, polymer chains are crosslinked (connected) with oxygen atoms to improve their resistance to mechanical failure at high-temperature (Peacock 2001; Pexcon 2004). PEX pipe crosslink density can be > 60% and PEX materials are typically manufactured using resin with densities similar to HDPE and MDPE (Pexcon 2004).

Organic chemical fate in HDPE, PEX, and PB pipes can be described using several terms and is impacted by polymer and chemical properties. Sorption is the condition when chemical diffuses into the polymer and desorption takes place when contaminant leaves the polymer. Equilibrium occurs when contaminant no longer diffuses in or out of the polymer. Diffusivity (D) (cm<sup>2</sup>/s) describes contaminant migration through the polymer and is a function of polymer and contaminant properties. Crank and Park (1978) and Comyn (1985) reported that contaminant diffusivity decreases as polymer bulk density, crystallinity, crosslink density, and contaminant molecular volume increases. Contaminant diffusion coefficients are typically determined using weight gain-immersion, time lag, and diffusion/ permeation methods (Aminabhavi and Naik 1999; Crank 1975) and can be calculated by fitting weight gain/loss data to a regression identified by Crank (1975) (**Equation 7-1**). In contrast to polymer weight gain during contaminant sorption, weight loss during desorption is a combination of contaminant diffusion

through the polymer to the surface and volatilization from the surface into air. By fitting weight loss data to **Equation 7–1**, the overall contaminant desorption value is obtained. Contaminant desorption is slower than contaminant sorption if the rate of chemical loss from the polymer's surface is greater than the rate at which additional chemical moves to the surface.

**Equation 7–1**  $M_t / M_\infty = A - \sum_{n=0}^{\infty} [8/(2n+1)^2 \pi^2] \exp \{-D[(2n+1)^2 \pi^2 t]/4\ell^2\}$

where

$A = 1$  for sorption;  $A = 0$  for desorption with no minus sign following

$t$  = Elapsed time (T)

$M_t$  = Mass of contaminant in polymer at time  $t$  (m)

$M_\infty$  = Mass of contaminant in polymer at equilibrium (m)

$D$  = Diffusion coefficient ( $\text{m}^2/\text{T}$ )

$\ell$  = Half sample thickness (L)

Few studies have focused on understanding contaminant desorption from HDPE, PEX, and PB pipes, while most prior research has focused on contaminant sorption *into* these polymers (Whelton et al. 2009b; Whelton et al. 2009c; Ong et al. 2008; Glaza and Park 1992; Hopman and van de Hoven 1992; Rigal et al. 1992; Thompson et al. 1992; Holsen et al. 1991; Selleck and Marinas 1991; Park et al. 1989; Vonk and Veenedaal 1983). Park et al. (1989) reported that neat toluene diffused into PB pipe much faster than it desorbed and diffusion into and out of PB were both faster than in HDPE pipes. Welter et al. (2006) found that several pesticides did not readily desorb from PVC pipe into water. A related study of contaminant desorption from a HDPE landfill liner was conducted by Aminabhavi and Naik (1999a, 1999b). These investigators evaluated desorption of 14 organic contaminants from 1.6 mm thick HDPE landfill liner into air at “room temperature.” Aromatic and aliphatic compounds used were in liquid state and unfortunately result variability was not reported. Results showed that  $D_{\text{Benzene}}$ ,  $D_{\text{Toluene}}$ , and  $D_{p\text{-xylene}}$  were faster during desorption than sorption. Interestingly, desorption of aliphatic compounds were slightly to significantly slower than sorption. Aminabhavi and Naik (1999a) attributed their findings “to the different drying mechanisms included especially by higher

boiling liquids,” but did not provide any quantitative or statistical evidence. Moreover, no relationships between desorption, contaminant properties, or polymer characteristics were examined in any of these polymer material investigations.

The goal of this work was to quantify contaminant diffusion during desorption for new, lab aged, and polymeric pipes removed from a water distribution system. The bulk properties of the polymer pipes were previously documented by Whelton et al. (2009a, 2009b, 2009c) and Dietrich and Whelton (2009). Specific objectives of this work were to (1) characterize diffusivity for organic compounds and water during sorption and desorption for new and lab aged PE potable water pipes at room temperature, (2) Determine the diffusivity of two nonpolar contaminants for three HDPE and one PB pipe removed from a buried water distribution system, and (3) Identify time necessary to desorb contaminants as well as polymer and contaminant characteristics that can be used to predict desorption and aide in public health risk and infrastructure decontamination assessments.

### **7.2.2 Previously Reported Polymer Characteristics for New and Lab Aged Polyethylene Examined in this Work**

The bulk properties of new and lab aged PEs examined in this work were previously reported by Whelton et al. (2009a, b, c). Whelton et al. (2009a, b, c) found that all new PEs were within the typical HDPE density range of 0.941–0.965 g/cm<sup>3</sup> except for PEX–A pipe, which resembled the density range of MDPE (0.926–0.940 g/cm<sup>3</sup>) (**Table 7–2**). Crystalline content followed a similar trend across all HDPE materials and for PEX–A pipe. Crosslink density of PEX–A and PEX–B1 pipes was 76% and 60%, respectively.

Chlorinated water exposure changed the surface chemistry and bulk properties of some new PEs. Carbonyl bonds ( $\sigma = 1713 \text{ cm}^{-1}$ ) were detected on all but PEX–A pipe surfaces after chlorinated water exposure. Carbonyl bonds have been previously detected on the surfaces of PE pipes removed from buried water distribution systems after 7–25 years of service and during accelerated aging experiments (Whelton and Dietrich, 2009; Whelton et al. 2009a, b; Gedde et al. 1994; Karlsson et al. 1992; Thompson et al. 1992). The increase in HDPE pipe bulk density/crystallinity due to chlorinated water exposure was statistically significant, while the bulk density/crystallinity of all other polymers were unchanged. Chlorinated water exposure had no affect on sample thickness. A more detailed discussion of mechanical, oxidative resistance

and compositional properties of PE pipes examined in this work can be found in Whelton and Dietrich (2009), Whelton et al. (2009a, b) and Whelton (2009).

### **7.3 Materials and Methods**

#### **7.3.1 Materials and Preparation**

HDPE resin was obtained in square prepressed sheet form (30.0 x 30.0 cm) from an industrial supplier. Five different brands of new PE potable water pipe were purchased from a local plumbing supply store and are referred to as monomodal HDPE, bimodal HDPE, PEX-A, PEX-B1, and PEX-B2. Markings on external pipe walls indicated that all purchased pipes complied with pipe classification and performance codes for the American Standards for Testing and Materials and National Sanitation Foundation. Four polymeric water pipes were removed from buried water distribution system in South Florida, USA and were analyzed by the authors one week after their receipt. A microtensile die was used to cut dog-bone shaped samples (0.2 x 0.8 cm) from all polymeric materials before any testing was conducted. Next, all specimens were rinsed in distilled water and underwent desiccation for 48 hr at 23 °C. Sample thickness was determined using a micrometer.

#### **7.3.2 Accelerated Aging in Chlorinated Water**

Four *new* polyethylene materials were exposed to chlorinated water for 3400 hr (141 days): HDPE resin, monomodal HDPE pipe, PEX-A pipe, and PEX-B1 pipe. The accelerated aging technique developed and validated by Whelton and Dietrich (2009) and Whelton et al. (2009b) was applied. Die-cut polymer specimens approximately 0.3 g were immersed in aging solutions with 45 mg/L as Cl<sub>2</sub>, 50 mg/L as CaCO<sub>3</sub> at pH 6.5. Aging took place in a dark constant temperature oven ( $37 \pm 1$  °C) and aging solutions were replaced every three days to make certain that PE samples were exposed to consistent free available chlorine, alkalinity, and pH levels. Water quality characterization methods used are described in Whelton and Dietrich (2009a, 2009c). Polymers were removed intermittently during aging and analyzed for oxidative resistance and surface chemistry. Chlorinated water solutions were prepared with reagent water from a Nanopure<sup>®</sup> ultrapure water system, 6.5% sodium hypochlorite, and NaHCO<sub>3</sub>. Water pH was adjusted using NaOH and HCl and was measured using a pH meter with probe. Alkalinity concentration was measured by titration to an end-point pH of 4.5 compliant with Standard Method 2320(B) (APHA, 2000). Free chlorine concentration was measured by titration of

solutions that contained potassium iodide and glacial acetic acid according to Standard Method 4500–Cl(B) (APHA, 2000).

### **7.3.3 Polymer Characterization, Contaminant Sorption and Desorption**

Techniques used to quantify surface chemistry, bulk density, crystallinity, and crosslink density are described in Whelton et al. (2009a, 2009b). Contaminant diffusion coefficients were obtained for 11–14 contaminants in new and lab aged PEs, and two nonpolar contaminants for each water utility pipe. Die-cut specimens were immersed in neat contaminant at  $22 \pm 1$  °C using 20 mL amber glass, PTFE sealed vials. Periodically, specimens were removed from contaminant, quickly blotted with KIMWIPES<sup>®</sup>, weighed on a Vernier scale, and then returned to the contaminant. Contaminant desorption was carried out by allowing sorbed contaminant to evaporate into air from the polymers at  $23 \pm 1$  °C and these samples were intermittently weighed. Three replicates were used for each polymer–contaminant pair.

Unlike sorption testing, the weight change during desorption is a measure of two processes: (1) contaminant migration through the polymer to the surface and (2) contaminant volatilization from the surface into air. Desorption diffusivity values represent both of these processes and the latter is notable because contaminants had varying volatility (e.g., dichloromethane vs. 1-butanol). Sorption values represent contaminant migration through the polymer occurring in neat contaminant solutions so there is no volatilization component. While there is an inherent difference between desorption and sorption diffusivity values measured in this work, the results are useful for quantifying the actual time required for desorption and comparing the gain and loss of contaminant from polymer water pipes.

Contaminant sorption and desorption testing was conducted using two experiments in parallel. New PE specimens were immersed in neat contaminant for 1000 to 3500 hr. When polymers no longer gained mass, polymers were removed from solutions and desorption commenced. Lab aged PE specimens were immersed in neat contaminant for a maximum of 2500 hr. Polymers that ceased to gain mass before 2500 hr immersion were removed from the neat contaminant and desorption was initiated. At 2500 hr all of the remaining polymers were removed from contaminant and began desorption. Desorption experiments for new and lab aged pipes were conducted for 900–16,360 hr and 900–5600 hr, respectively. Calculation of

desorption diffusivity values was conducted if two criteria were met for each polymer–contaminant pair and is explained below.

Diffusion coefficients were calculated using the quantity of contaminant in the polymer during sorption and desorption and sample thickness (**Equation 7–1**). Plots of fractional uptake of contaminant ( $M_t/M_\infty$ ) versus the square root of time ( $\sqrt{t}$ ) were created for each polymer–contaminant pair. This practice is commonly used to identify regions of linear mass increase (where diffusion is constant) and the time to half–equilibrium ( $T_{0.5}$ ) which is also used to describe sorption and desorption phenomena. This methodology is further described by Crank and Park (1968) and Comyn (1985).

Contaminant diffusivity mean and standard error were calculated for each polymer–contaminant pair and an asymptotic 95% confidence interval was the basis of all contaminant diffusivity statistical comparisons. All confidence interval and regression model calculations were carried out using R Project version 2.7.1 (RFound, 2008). A Type I error of 0.05 was applied in all statistical tests.

#### **7.3.4 Assessment of Immersion and Air Drying Equilibrium for Each Polymer–Contaminant Pair**

Contaminant diffusivity was calculated for a polymer–contaminant pair if the pair met two criteria. First, equilibrium during sorption ( $M_\infty$ ) must have been reached. The equilibrium mass of contaminant in the polymer during sorption was determined using the model (**Equation 7–1**). The model output ( $M_\infty$ ) was compared against the final experimental measurements for the polymer–contaminant pair. Contaminant diffusivity values were calculated for polymer–contaminant pairs that achieved 100% of the model predicted equilibrium.

The second criterion the polymer–contaminant pair had to meet was that polymers did not lose weight during contaminant exposure. The polymer mass before sorption and after desorption was compared. Desorption diffusivity calculations are based on the assumption that the polymer’s mass does not change. If polymers lost mass then contaminant desorption results would represent a combination of both contaminant and additive leaving the polymer. Contaminant diffusivity values were calculated for polymer–contaminant pairs that did not lose > 0.1% weight due to contaminant exposure.

## 7.4 Results and Discussion

### 7.4.1 Sorption and Desorption Equilibrium for New and Lab Aged PEs

Sorption data for each polymer–contaminant pair (e.g., HDPE pipe–Toluene, PEX–A Pipe–Acetonitrile, etc.) was analyzed. Results indicated that 78 of 78 new PE–contaminant pairs achieved 100% equilibrium during immersion, but 5 of 40 lab aged PE–contaminant pairs did not. Polymer–nonpolar contaminant pairs achieved equilibrium faster than polymer–polar contaminant pairs and some results are shown in **Figure 7–1**. The lab aged PE–contaminant pairs that did not reach equilibrium during sorption and their percent of equilibrium achieved include HDPE resin (86%), monomodal HDPE pipe (81%), PEX–A pipe (79%), and PEX–B1 pipe (75%) in benzyl alcohol and PEX–B1 pipe (82%) in 1–butanol. Because these polymer–contaminant pairs did not reach equilibrium, their diffusivity values for desorption were not calculated.

Each polymer that was immersed in contaminant was independently weighed following desorption experiments. Results show that weight variability for new and lab aged PEs did not significantly differ from control specimens in air ( $\pm 0.1\%$ ) (**Table 7–3**). Desorption diffusivity values were calculated for each contaminant–polymer pair that passed both aforementioned sorption and desorption criteria. Desorption results for several contaminants in lab aged PEX–A pipe are shown in **Figure 7–1** and regression lines fit were good to excellent. Variability between polymer mass measurements over time for both sorption and desorption experiments was most variable for polar contaminants and least variable for nonpolar contaminants. Desorption data did not fit the predicted curve as well as sorption results. This could be due to the fact that desorption results represent a two step process (contaminant migration through polymer and volatilization from the surface), while sorption only involved migration of the contaminant into the polymer.

### 7.4.2 Time Required to Desorb 50% of the Contaminant for New and Lab Aged PEs

The time required to desorb 50% of contaminant ( $T_{0.5}$ ) from new PEs differed greatly (**Table 7–4**). HDPE resin (1.6 mm thickness) desorbed all contaminants faster than all pipe samples (2.6 mm thickness) and PEX–A pipe with MDPE density desorbed all contaminants faster than PEX–B pipes with HDPE density. Comyn (1985) reported that contaminants diffuse through less dense MDPE faster than HDPE and thin samples achieve equilibrium faster than thick samples. It should also be noted that the less dense pipe with the greatest crosslink density



(PEX–A pipe, 76%) desorbed contaminants faster than the lesser crosslinked, more dense pipe (PEX–B1 pipe, 61%). While Comyn (1985) and Crank and Park (1968) reported that increased crosslink density decreases contaminant diffusivity, results from this work imply that the great difference between MDPE and HDPE bulk density controlled desorption, not crosslink density.

The time required to desorb 50% of contaminants that can hydrogen–bond from new PEs was much longer for all nonpolar contaminants. New pipes generally required 1000–2000 hr to desorb 50% of polar contaminant mass, while the time to desorb 50% of nonpolar contaminant ranged from 10–79 hr. The time to desorb 50% of MTBE was 4–14 times longer than other nonpolar contaminants. This is surprising since the MTBE vapor pressure is greater and molecular volume is less than the aromatic contaminants which achieved  $T_{0.5}$  faster.

Aging of PE due to chlorinated water exposure significantly increased the time to reach  $T_{0.5}$  desorption for some polymer–contaminant pairs, but was not consistent across all PEs. The time to desorb 50% of 2–propanone, 2–butanone, 1–butanol for PEX–B1 pipe along with benzaldehyde and 2–propanol for PEX–A pipe was extended by 95–406 hr. Unlike HDPE pipes and resin, PEX pipes contain oxygen atoms in the chemical structure. Polar contaminants diffusing out of lab aged PEX water pipes may interact with these oxygen atoms changing their diffusivity much like Jelinski et al. (1984) and McCall et al. (1984) imply. These results are further discussed below in terms of contaminant diffusivity.

### **7.4.3 Contaminant Diffusivity during Sorption and Desorption and their Relationships**

#### ***7.4.3.1 Contaminant Sorption into New and Lab Aged PEs***

Contaminant sorption tests for the same polymers in this work were described in detail previously (Whelton et al. 2009a, 2009b; Dietrich and Whelton 2009). These results will be briefly reviewed so that comparisons can be drawn to desorption data reported in this work.

Whelton et al. (2009a) found that diffusion of the same 13 contaminants as listed in **Table 7–5** in new HDPE resin, HDPE pipe, PEX–A and PEX–B pipes was dependent on both polymer and contaminant properties. Nonpolar contaminant diffusivity decreased as new PE bulk density increased. This finding is similar to observations by Crank and Park (1968) and Comyn (1985). Nonpolar compounds also diffused into new PEX–A pipe faster than all other PEs likely due to its significantly lower bulk density. Diffusion of only a few polar contaminants decreased

as bulk density increased (2-butanone, 2-propanone, and benzaldehyde) in new PEs. Contaminant diffusivity was reduced by increasing molecular volume for nonpolar contaminants, but molecular volume changes had no impact on polar compound diffusivity.

Whelton et al. (2009b) reported that chlorinated water exposure did not significantly alter the fate of four nonpolar contaminants in HDPE resin, HDPE pipe, PEX-A and PEX-B pipes, but greatly changed diffusivity for seven contaminants capable of hydrogen-bonding. Contaminant diffusivity increased 50–162% for contaminants with alcohol > aldehyde > ketone functional groups and was attributed to oxidation of PE pipe surfaces which enabled faster penetration of polar contaminants into the hydrophobic matrix. Regression analyses revealed that an increase in lab aged PE bulk density decreased diffusivity for trichloromethane, toluene, *m*-xylene, benzaldehyde, MTBE, 2-butanone, 2-propanone, and 1-butanol. Like *new* PE materials, contaminant diffusivity was reduced as molecular volume of nonpolar contaminants increased in lag aged PEs and this relationship was not significant for contaminants capable of hydrogen-bonding.

#### **7.4.3.2 Contaminant Desorption from New and Lab Aged PEs**

Some polymer and contaminant characteristics influenced contaminant diffusion during desorption. Regression analyses revealed that desorption diffusivity decreased as new and lab aged polymer bulk density increased for some but not all contaminants (**Figure 7-2**). Toluene, acetone, dichloromethane, and benzaldehyde diffusivity decreased as the bulk density of new PE increased, and all other contaminant-bulk density relationships were insignificant ( $p < 0.05$ ). Dichloromethane and acetone are some of the most volatile contaminants examined (greatest vapor pressure), followed by toluene, and benzaldehyde is slightly volatile (LaGrega et al. 2001). Regression analysis also showed that diffusivity decreased as the lab aged PE bulk density increased for trichloromethane, *m*-xylene, MTBE, 2-butanone, 2-propanone, and benzaldehyde. Desorption of contaminants with alcohol functional groups were unaffected by bulk density.

Regression analyses also revealed that contaminant properties (Log  $K_{ow}$ , dipole moment, vapor pressure, or molecular volume) did not significantly impact desorption diffusivity in either new or lab aged PEs ( $p > 0.05$ ). Desorption diffusivity results varied for each contaminant by roughly 7%, but were sometimes highly variable which may have contributed to this finding (1-butanol 10–63%, 2-propanol 8–17%, acetonitrile 25–100%). Even when bulk density was

examined for groups of nonpolar and polar contaminants, a relationship between density and contaminant diffusivity was not detected.

With the exception of MTBE, nonpolar contaminants diffused the fastest from all PEs and some structural characteristics of contaminants inhibited diffusion. **Figure 7–3** shows nonpolar contaminant diffusivity was greater than polar contaminant diffusivity in both new and aged PE, and there was no clear relationship between diffusivity in new and lab aged PEs. The following relationships were found for both new and lab aged materials:  $D_{\text{Toluene}} = D_{p\text{-Xylene}} > D_{m\text{-Xylene}} > D_{\text{Benzaldehyde}} > D_{\text{Benzyl Alcohol}}$ .  $D_{p\text{-Xylene}} > D_{m\text{-Xylene}}$  because the meta-methyl group inhibited transport while the para-methyl group made the aromatic molecule more linear and easier to migrate through the polymer (Joo et al. 2005).  $D_{\text{Dichlormethane}} > D_{\text{Trichlormethane}}$  for all new and aged PEs and this is likely because the extra chlorine atom inhibited migration and decreased volatility. These findings are similar to contaminant properties that cause reduced diffusion in polymers reported by Crank and Park (1968) and Comyn (1985) that impact contaminant diffusion in polymers. Generally,  $D_{2\text{-Propanone}} > D_{2\text{-Butanone}} > D_{\text{MTBE}} > D_{1\text{-Butanol}} = D_{2\text{-Propanol}}$  for all new and lab aged PEs.  $D_{\text{Acetonitrile}}$  was equal to all contaminants in new PEs due to great variability in measurements.  $D_{\text{Acetonitrile}}$  in lab aged PEs was not calculated because lab aged PEs did not sorb a detectable amount of acetonitrile during immersion.

#### ***7.4.3.3 Comparing Contaminant Diffusion during Sorption and Desorption in New and Lab Aged PEs***

As mentioned previously, diffusion coefficients calculated for desorption in this work represent the migration of the contaminant to the polymer surface and volatilization of the contaminant to the air. In contrast, sorption only involves contaminant diffusion from the neat solution into the polymer. Knowing this difference enables an informed comparison of contaminant fate during sorption and desorption.

Generally, contaminant sorption into new and lab aged PEs was 20–75 % and 36–68 % faster than desorption, respectively. This phenomena was also observed by Comyn (1985) and implies that desorption is driven by the rate at which sorbed contaminant migrates to/ volatilizes from the polymer surface. Contaminant diffusion during sorption and desorption were statistically equal for 1-butanol and 2-propanol in both new and lab aged PEs.

Chlorinated water exposure significantly altered contaminant desorption for several hydrogen-bonding contaminants and PEX pipes (**Table 7-5**). **Figure 7-4** shows that polar contaminants diffused in and out of new PEs at the same rate (1:1). After PE specimens were exposed to chlorinated water, the nearly 1:1 relationship between polar contaminant diffusion in and out of polymers was invalid. Jelinski et al. (1984) and McCall et al. (1984) suggested that as a water molecule diffuses “through an oxidized polyethylene, it moves rapidly through the hydrocarbon matrix but spends part of its time restricted in oxygen-sites/traps” due to hydrogen-bonding. If we extend this reasoning to hydrogen-bonding contaminants in this work, polar contaminant-lab aged PE results imply that chlorinated water exposure produced “oxygen sites” on the pipe that lengthened the time required for polar contaminants to desorb. Detection of carbonyl bonds on lab aged PE surfaces by IR spectroscopy support this assertion.

Aging significantly changed  $D_{\text{Benzaldehyde}}$ ,  $D_{2\text{-Butanone}}$ , and  $D_{2\text{-Propanol}}$  for all PEs and this change was greatest for alcohol containing contaminants.  $D_{2\text{-Butanone}}$  and  $D_{2\text{-Propanol}}$  was increased in lab aged HDPEs and was reduced in lab aged PEX-A pipe. Changes in contaminant diffusivity numbered most for crosslinked pipes (PEX-B1 pipe > PEX-A pipe > HDPE Resin > MonoHDPE Pipe). Nonpolar contaminant diffusivity was unchanged in all PEs except for PEX-A pipe, the most crosslinked and least dense material. Aging reduced  $D_{\text{MTBE}}$  16% and slightly increased  $D_{\text{Trichloromethane}}$  5% in PEX-A pipe. Chlorinated water exposure altered  $D_{2\text{-Propanone}} = D_{2\text{-Butanone}}$  for lab aged monomodal HDPE and PEX-A, PEX-B1 pipes.

#### 7.4.4 Pipes Removed from a Buried Water Distribution Network

Bulk property results for the water utility (wu-) PB pipe examined in this work can be found in **Table 7-6** along with wu-PE pipes reported by Whelton et al. (2009b). Four pipes were received of which three were classified as HDPE according to infrared spectroscopy analysis, thermal analysis, and density gradient column results. A Tukey-Kramer multiple comparison test revealed the following bulk density and crystallinity relationships:  $wu\text{-PE } 2 > wu\text{-PE } 1 = wu\text{-PE } 3$  ( $p < 0.05$ ). Bulk density and crystallinity of water utility PE pipes was similar to new and lab aged HDPE pipes. The fourth pipe was classified as PB based on IR and thermal analysis by differential scanning calorimetry. The 30 year old  $wu\text{-PB}$  was significantly less crystalline than all PEs which agreed with density measurements by Thompson et al. (1992) and Park et al. (1989).

Water utility pipe chemical interaction results are provided in **Table 7-7**. All polymer-contaminant pairs achieved 100% equilibrium during sorption. A Tukey-Kramer multiple comparison test revealed that *wu*-PE pipes sorbed a similar amount of toluene and trichloromethane and the *wu*-PB pipe sorbed the greatest amount of both contaminants even though its thickness was 44–93% less than all other utility pipes. Moreover, the *wu*-PB pipe attained 50% equilibrium after only 2.4 hr immersion compared to all other pipes which achieved 50% equilibrium after 10–21 hr. Toluene and trichloromethane diffused through the *wu*-PB pipe significantly faster than all other pipes and this has been reported by others who examined PB pipes removed from buried water distribution systems (Thompson et al. 1992; Park et al. 1989). Diffusion through PB pipes is faster than PE pipes because PB pipes are less crystalline due to the butyl functional group that inhibits chain packing.

Polymer weight measurements after desorption revealed that a few water utility pipes lost weight. *wu*-PB samples lost 2.6 and 3.0% weight due to exposure to both contaminants, while the weight of *wu*-PE 2 pipe was reduced 1.4% after toluene exposure. Because these polymers lost weight, diffusivity values were not calculated for desorption. Weight loss could be due to dissolution and extraction of polymer additives and residual monomer.

Contaminant desorption from water utility pipes was significantly different than contaminant sorption into these materials. Toluene diffusivity was 9.7% slower during desorption than sorption for *wu*-PE 1, but 24% faster during desorption than sorption for *wu*-PE 3. This finding is perplexing since both materials were of equal crystallinity, though *wu*-PE 1 was in service for 7 years while *wu*-PE 3 was in service for 25 years. Trichloromethane desorption was 36–93% slower than sorption for all utility pipes. The 25 year old pipe was 93% slower and this was the greatest difference between sorption and desorption.

Toluene and trichloromethane desorption results revealed great variability between HDPE pipes and results were difficult to explain since many of the PEs were similar in bulk density and crystallinity but the history of the pipes was poorly documented. Toluene desorbed from *wu*-PE 1 faster than *wu*-PE 3 and all new and lab aged HDPE pipes. Specifically,  $D_{wu-PE\ 1}$  was  $70\text{ cm}^2/\text{s}$  and was greater than  $D_{wu-PE\ 3}$  ( $29\text{ cm}^2/\text{s}$ ) and  $D_{\text{New\&LabAged HDPEs}}$  ( $28\text{--}30\text{ cm}^2/\text{s}$ ). The pipe *wu*-PE 1 was seven years old, was the thickest material, but similar in bulk density and crystallinity to all other HDPEs. Trichloromethane desorbed from the 25 year old *wu*-PE 3 pipe

seven to ten times slower than all other HDPE pipes ( $D_{\text{wu-PE 3}} = 4.2 \text{ cm}^2/\text{s}$ ) and desorption was fastest for wu-PE 1 ( $D_{\text{wu-PE 1}} = 44.5 \text{ cm}^2/\text{s}$ ). All new and aged HDPE pipes were similar in  $D$  to wu-PE 2 ( $D = 25\text{--}35 \text{ cm}^2/\text{s}$ ).

## 7.5 Conclusion

Organic chemical desorption was evaluated for ten different polymeric water pipes at 23 °C. Polymers included new and lab aged HDPE, PEX-A, and PEX-B pipes as well as HDPE and PB pipes removed from a buried water distribution after 7–30 years in service. The bulk density of all HDPE based materials was similar ( $0.949\text{--}0.951 \text{ g/cm}^3$ ), while PEX-A ( $0.938 \text{ g/cm}^3$ ) and PB pipes ( $0.938 \text{ g/cm}^3$ ) were significantly less dense. Slight differences in density resulted in major changes for the time required to desorb contaminants and their diffusivity.

Contaminant desorption from polymer water pipes at 23 °C revealed many relationships between contaminant and polymer properties. The time to achieve 50% contaminant desorption for new and aged PEs can be explained in terms of contaminant polarity. Nonpolar contaminants desorbed the fastest from new and lab aged PEs (10–79 hr to reach 50% desorption), while the time for hydrogen-bonding contaminants to desorb 50% was 1000–2000 hr in the same polymers. Exposing PEs to chlorinated water significantly extended the time for these materials to reach 50% desorption of alcohol and ketone containing contaminants (95–406 hr). This extended duration can be attributed to the contaminants hydrogen-bonding with oxygen detected on the polymer surface by IR spectroscopy. This finding implies that polar contaminants sorbed into actual water distribution pipes desorb slower from aged PEX pipes than HDPE materials.

Some polymer and contaminant properties can be used to predict contaminant desorption. Contaminant diffusivity was reduced as new PE bulk density/crystallinity decreased for toluene, 2-propanone, dichloromethane, benzaldehyde, and with lag aged PE bulk density for trichloromethane, *m*-xylene, MTBE, 2-butanone, 2-propanone, and benzaldehyde. These contaminants did not share any common properties except that none were alcohols. Contaminant molecular volume had no impact on desorption. The addition of methyl groups on aromatic contaminants and chlorine atoms on aliphatic contaminants inhibited diffusion.

HDPE pipes removed from an actual water distribution had similar bulk properties to new and lab aged HDPE pipes. Contaminant desorption from water utility HDPEs were highly

variable  $D_{\text{Toluene}}$  (29 and 70  $\text{cm}^2/\text{s}$ ) and  $D_{\text{Trichloromethane}}$  (4–44  $\text{cm}^2/\text{s}$ ). Desorption from PB pipe was significantly faster, but several PB–contaminant pairs resulted in weight loss. It was not determined if the 2.6 and 3.0% PB pipe weight loss changed the structural integrity of the pipe.

Results of this work are unique, incremental but provide important scientific contributions to understanding organic contaminant desorption from new, lab aged, and water utility PE and PB pipes. Results can be used by public health officials, infrastructure managers, regulators, and emergency responders to quantify risks posed to contaminated water pipe users as well as evaluate and develop pipe decontamination methods. Several critical aspects of this work should be considered when assessing contaminant desorption: (1) All data in this work is based on a contaminant–polymer pair achieving equilibrium and desorbing contaminant into air at 23 °C; (2) Desorption of polar contaminants from HDPE and PEX pipes exposed to chlorinated water was significantly longer than new HDPE and PEX pipes because polar contaminants hydrogen–bonded with oxygen on the chlorinated water exposed surface; (3) Nonpolar contaminants desorb significantly faster than polar contaminants in both new and lab aged HDPE and PEX pipes, and (4) Polymer bulk density/crystallinity is useful for predicting the desorption for some contaminants, but no contaminant properties were found useful for predicting desorption; and (5) Exposure of some HDPE and PB pipes to neat contaminants can reduce polymer weight.

## **7.6 Acknowledgement**

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**Table 7–1 Contaminant Characteristics at 25 °C**

Contaminant	Contaminant	$\mu$ , Debye	Contaminant Property <sup>1</sup>				
Name	Class		$M_m$ , g/mol	$M_v$ , cm <sup>3</sup>	$S_w$ , mg/L	Log $K_{ow}$	Hydrogen Bonding Power
<i>Polar Contaminants</i>							
Acetonitrile	Aliphatic nitrile	3.92	41.05	53.3	Miscible	−0.34	Poor
2-Propanone	Aliphatic ketone	2.88	58.08	73.1	Miscible	−0.24	Moderate
Benzaldehyde	Aromatic aldehyde	2.80	106.12	120.5	3000	1.48	Moderate
2-Butanone	Aliphatic ketone	2.76	72.11	91.4	223000	0.29	Moderate
Water	—	1.85	18.01	19.3	Miscible	—	Strong
Benzyl Alcohol	Aromatic alcohol	1.71	108.14	125.1	40000	1.10	Strong
1-Butanol	Aliphatic alcohol	1.66	74.12	96.2	74000	−0.30	Strong
2-Propanol	Aliphatic alcohol	1.56	60.10	77.8	Miscible	0.05	Strong
<i>Nonpolar Contaminants</i>							
Dichloromethane	Chlorinated alkane	1.60	84.93	60.6	13030	1.25	Poor
MTBE	Aliphatic ether	1.36	88.15	119.1	51000	1.24	Poor
Trichloromethane	Chlorinated alkane	1.01	119.37	74.4	7290	1.97	Poor
Toluene	Methylated aromatic	0.36	92.14	117.7	526	2.73	Poor
<i>m</i> -Xylene	Methylated aromatic	0.30	106.16	135.9	161	3.20	Poor
<i>p</i> -Xylene	Methylated aromatic	0.00	106.16	135.8	162	3.15	Poor

1. MTBE = Methyl *t*-butyl ether; NP = Nanopure water;  $\mu$  = Dipole moment;  $M_v$  = Molar volume;  $M_m$  = Molar mass;  $S_w$  = Water solubility;  $\rho$  = Density;  $K_{ow}$  = Octanol–water partition coefficient;  $M_m$ ,  $S_w$ , Log  $K_{ow}$  values obtained from *CHEMFATE* (Syracuse Research Corporation 2009);  $M_v$  calculated molar volume using *Spartan* (Wavefunction 1997)

**Table 7–2 Bulk Characteristics of New and Lab Aged Polyethylene**

Polymer Type	Polymer Condition	Polymer Property <sup>1</sup>			
		Thickness, mm	Bulk Density, g/cm <sup>3</sup>	Crystallinity, %	Crosslink Density, %
<i>HDPE Resin</i>	<i>New</i>	1.65	0.9578	71.5	—
	<i>Aged</i>	1.65	0.9581	71.7	—
<i>Monomodal HDPE Pipe</i>	<i>New</i>	2.61	0.9503†	66.4†	—
	<i>Aged</i>	2.61	0.9513†	67.1†	—
<i>Bimodal HDPE Pipe</i>	<i>New</i>	2.59	0.9547	72.7	—
<i>PEX–A Pipe</i>	<i>New</i>	2.60	0.9385	58.4	76.1
	<i>Aged</i>	2.60	0.9389	58.7	—
<i>PEX–B1 Pipe</i>	<i>New</i>	2.64	0.9524	67.8	60.4
	<i>Aged</i>	2.64	0.9527	68.1	—
<i>PEX–B2 Pipe</i>	<i>New</i>	2.63	0.9510	70.4	—

1. Mean of three replicates shown; The standard deviation was: Thickness (0.02–0.08), bulk density (0.0002–0.0008), and crystallinity (0.1–0.3); Standard deviation for crosslink density was  $\pm 5.5$  for PEX–A and  $\pm 2.2$  for PEX–B1, crosslink density was not determined after polymer aging because broken polymer chains do not crosslink; † indicates new and lab aged property is statistically different ( $p < 0.05$ ).

**Table 7–3 Weight Gain as Percent of New and Lab Aged Polyethylene due to Contaminant Sorption**

Contaminant Name	Dipole Moment, Debye	Weight Gain, percent <sup>1</sup>													
		HDPE Resin		Monomodal HDPE Pipe		Bimodal HDPE Pipe		PEX-A Pipe (MDPE)		PEX-B1 Pipe (HDPE)		PEX-B2 Pipe (HDPE)			
								New	Aged	New	Aged	New	Aged	New	Aged
<i>Polar Contaminants</i>															
Acetonitrile	3.92	0.1	—	0.1	—	0.1	—	0.2	—	0.3	—	0.2	—		
2-Propanone	2.88	0.9	0.9	1.0	1.0	0.9	—	1.1	1.2	1.4	1.3	1.3	—		
Benzaldehyde	2.80	2.0	2.0*	2.0	2.1*	2.1*	—	2.3	2.4*	2.5	2.4*	2.6	—		
2-Butanone	2.76	1.8	1.7	1.8	1.8	1.7	—	2.0	2.1	2.4	2.1	2.2	—		
Benzyl Alcohol <sup>#</sup>	1.71	0.5	0.4*	0.5	0.4*	0.3	—	0.4	0.5*	0.6	0.5*	0.5*	—		
1-Butanol <sup>#</sup>	1.66	0.4*	0.3	0.3*	0.3	0.3	—	0.5	0.4	0.5*	0.4*	0.4	—		
2-Propanol	1.56	0.4	0.5	0.3	0.4	0.3	—	0.5	0.5*	0.5	0.5*	0.5	—		
<i>Nonpolar Contaminants</i>															
Dichloromethane	1.60	6.6	—	8.1	—	8.0	—	9.2	—	8.1	—	8.2	—		
MTBE	1.36	4.2	4.1*	5.1	4.9*	4.9	—	5.5	5.5*	5.1	5.0*	4.9	—		
Trichloromethane	1.01	10.6	10.2	13.4	13.2	13.4	—	15.2	14.6	13.1	12.7	13.2	—		
Toluene	0.36	6.3	6.3	7.9	7.9	8.0	—	9.0	8.8	7.5	7.6	7.5	—		
<i>m</i> -Xylene	0.30	6.4	6.5	8.0	8.1	8.2	—	9.2	9.0	7.6	7.7*	7.6	—		
<i>p</i> -Xylene	0.00	6.6	—	8.3	—	8.3	—	9.4	—	7.9	—	7.9	—		

1. Results are based on polymer weight before immersion; Mean values for three replicates shown and standard deviation varied 0–0.3%; (\*) asterisk means polymer did not return to initial mass when desorption halted; Water did not sorb into any PE; (#) During sorption no lab aged PEs achieved equilibrium in benzyl alcohol and lab aged PEX–B1 pipe did not achieve equilibrium in 1–butanol.



**Table 7–4 Time to Desorb 50% of the Contaminant from New and Lab Aged Polyethylene**

Contaminant Name	Time to 50% Desorption of Contaminant, hours <sup>1</sup>											
	HDPE Resin		Monomodal HDPE Pipe		Bimodal HDPE Pipe		PEX–A Pipe (MDPE)		PEX–B1 Pipe (HDPE)		PEX–B2 Pipe (HDPE)	
	New	Aged	New	Aged	New	Aged	New	Aged	New	Aged	New	Aged
<b><i>Polar Contaminants</i></b>												
Acetonitrile	5.7	–	15.3	–	7.9	–	7.8	–	24.4	–	19.6	–
2–Propanone	59.2	68.2	119.6	100.1	97.5	–	62.0	69.0	94.2	164.0	160.1	–
Benzaldehyde	119.0	192.4	226.1	291.9	554.6	–	138.0	186.2	359.1	353.4	288.0	–
2–Butanone	93.2	66.9	151.4	104.6	82.7	–	47.6	67.6	110.5	145.2	213.6	–
Benzyl Alcohol <sup>#</sup>	325.0	–	18.5	–	355.1	–	244.0	–	2136.2	–	201.9	–
1–Butanol <sup>#</sup>	477.6	467.1	510.6	464.9	156.1	–	164.9	410.3	673.1	–	1664.0	–
2–Propanol	765.5	558.8	1090.3	364.8	71.3	–	100.4	385.0	754.6	666.4	1866.9	–
<b><i>Nonpolar Contaminants</i></b>												
Dichloromethane	9.7	–	16.4	–	17.9	–	11.8	–	21.8	–	17.4	–
MTBE	326.3	278.5	435.2	407.6	272.5	–	206.4	248.8	393.0	654.3	653.4	–
Trichloromethane	15.4	15.7	27.1	25.9	38.6	–	26.5	18.7	51.0	32.6	28.8	–
Toluene	17.2	19.2	31.8	31.1	33.0	–	25.11	23.5	51.4	164.3	33.8	–
<i>m</i> –Xylene	23.3	29.3	50.9	45.0	49.8	–	38.6	33.8	78.9	60.4	53.0	–
<i>p</i> –Xylene	17.0	–	35.5	–	36.5	–	26.5	–	55.4	–	38.7	–

1. Mean values for three replicates shown. Confidence intervals not calculated for  $T_{0.5}$ ; Coefficients of variation (= standard error / mean) were generally < 7%. Three contaminants had great variations in coefficient of variation: 1–Butanol (10–63%), 2–Propanol (8–17%), Acetonitrile (25–100%); (#) Benzyl alcohol did not achieve equilibrium in any PE and 1–butanol did not achieve equilibrium in PEX–B1 pipe.

**Table 7–5 Contaminant Diffusivity during Desorption for New and Lab Aged Polyethylene**

Contaminant Name	Dipole Moment, Debye	Diffusivity, cm <sup>2</sup> /s <sup>1</sup>											
		HDPE Resin		Monomodal HDPE Pipe		Bimodal HDPE Pipe		PEX-A Pipe (MDPE)		PEX-B1 Pipe (HDPE)		PEX-B2 Pipe (HDPE)	
		New	Aged	New	Aged	New	Aged	New	Aged	New	Aged	New	Aged
<i>Polar Contaminants</i>													
Acetonitrile	3.92	65.12	—	61.46	—	108.52	—	117.80	—	45.82	—	37.85	—
2-Propanone	2.88	6.17†	5.65†	8.10	9.01	9.25	—	14.92	13.49	5.87	5.76	9.97	—
Benzaldehyde	2.80	3.10†	2.04†	4.03†	3.28†	1.66	—	6.67†	5.07†	3.36†	2.71†	2.64	—
2-Butanone	2.76	3.91†	5.76†	6.07†	9.03†	11.34	—	19.15†	13.66†	4.34†	6.52†	8.51	—
Benzyl Alcohol <sup>#</sup>	1.71	1.14	—	49.60	—	2.45	—	3.82	—	4.74	—	0.44	—
1-Butanol <sup>#</sup>	1.66	0.77	0.84	1.87	1.96	5.64	—	5.60	2.24	0.58	—	1.39	—
2-Propanol	1.56	0.49†	0.70†	0.85†	2.64†	12.15	—	9.08†	2.37†	0.51†	1.43†	1.24	—
<i>Nonpolar Contaminants</i>													
Dichloromethane	1.60	37.11	—	56.51	—	54.10	—	77.28	—	55.41	—	42.24	—
MTBE	1.36	1.13	1.43	2.04	2.41	3.25	—	4.50†	3.78†	1.49	1.48	2.39	—
Trichloromethane	1.01	23.66	25.01	33.67	35.21	25.16	—	35.00	49.54	32.27	29.36	18.56	—
Toluene	0.36	21.18	20.16	29.00	30.16	28.32	—	37.25	39.47	27.96	5.68	18.89	—
<i>m</i> -Xylene	0.30	16.16	13.42	18.99	19.57	18.54	—	23.98	27.46	17.83	15.66	11.88	—
<i>p</i> -Xylene	0.00	22.28	—	25.78	—	25.29	—	34.66	—	24.33	—	16.96	—

1. Mean values for three replicates shown and coefficients of variation (= standard error / mean) were generally < 7%. Three contaminants had great variations in coefficient of variation: 1–Butanol (10–63%), 2–Propanol (8–17%), Acetonitrile (25–100%); (†) Diffusivity in new and aged PE were statistically different for the polymer–contaminant pair ( $p < 0.05$ ); (#) Benzyl alcohol did not achieve equilibrium in any PE and 1–butanol did not achieve equilibrium in PEX–B1 pipe.

**Table 7–6 Water Utility Pipe Bulk Properties**

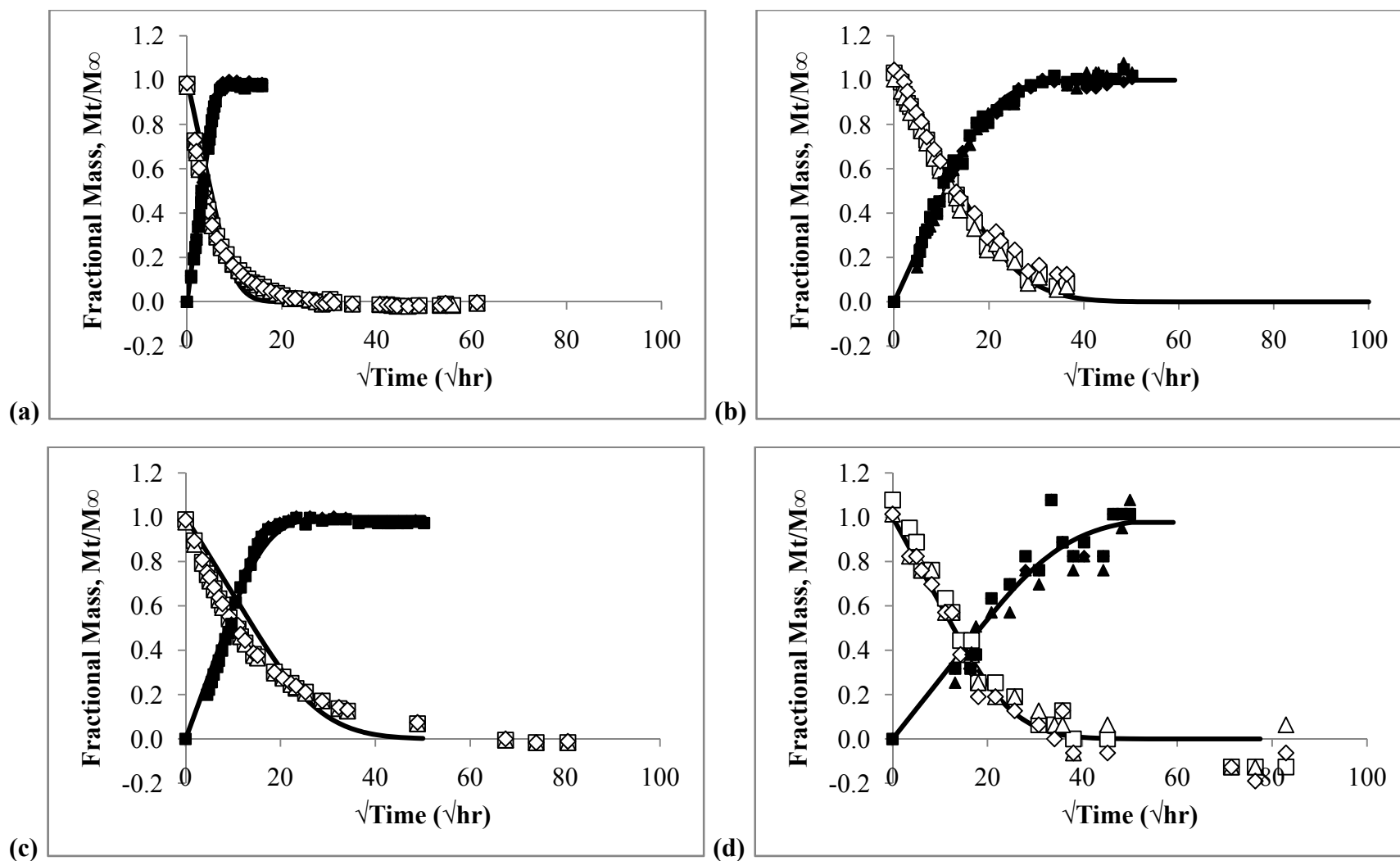
Polymer Type	Polymer Aging History	Polymer Property <sup>1</sup>		
		Thickness, mm.	Bulk Density, g/cm <sup>3</sup>	Crystallinity, %
<i>wu-PE 1</i>	7 yr service: chloramines only	3.37	0.9504 (HDPE)	70.0
<i>wu-PE 2</i>	20 yr service: 18 yr free available chlorine and 2 yr chloramines	2.52	0.9513 (HDPE)	70.0
<i>wu-PE 3</i>	25 yr service: free available chlorine only	2.65	0.9504 (HDPE)	70.5
<i>wu-PB</i>	30 yr service: 28 yr free available chlorine and 2 yr chloramines	1.74	0.9348	44.2*

1. Mean values for three replicates shown; Standard deviation was: Thickness (0.03–0.07), bulk density (0.0001–0.0004), and crystallinity (0.1–0.2); (\*) Crystallinity of PE samples was calculated based on density gradient column measurements, while the crystallinity of *wu-PB* was calculated using thermal analysis data; PE data reported by Whelton et al. (2009c).

**Table 7–7 Toluene and Trichloromethane Sorption and Desorption Results for Water Utility Pipes**

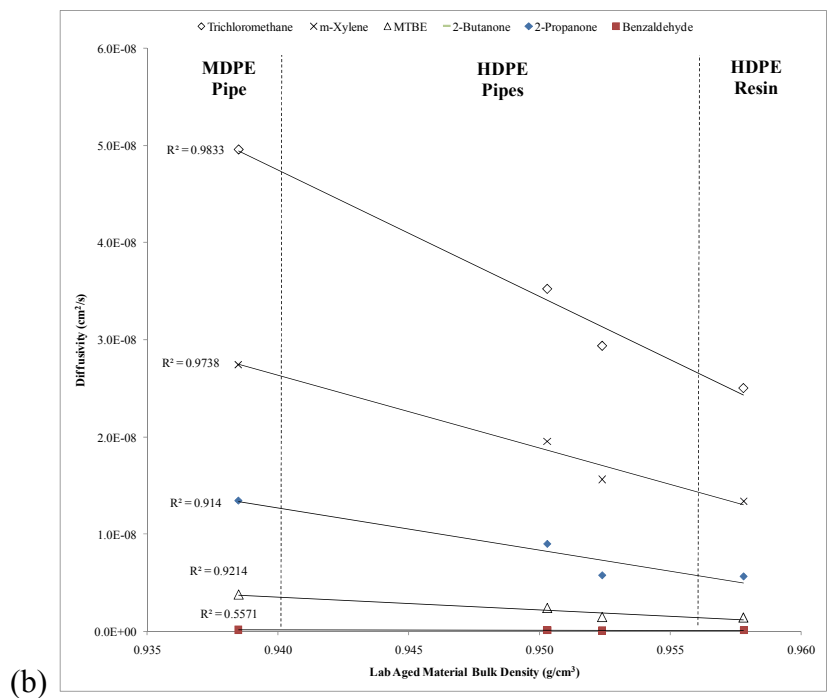
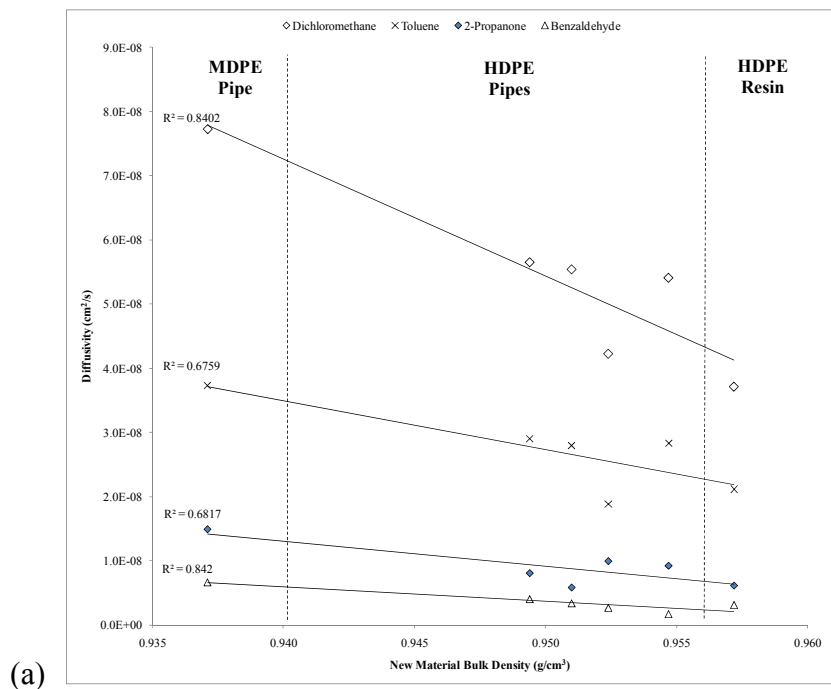
Contaminant and Polymer Pair		Measurement Method and Values					
		Sorption by Immersion			Desorption by Air Drying		
		Weight Gain, %	D, cm <sup>2</sup> /s	T <sub>0.5</sub> , hr	Weight Loss, %	D, cm <sup>2</sup> /s	T <sub>0.5</sub> , hr
<i>Toluene</i>							
	<i>wu</i> –PE 1	7.5	78.1	20.0	–0.1	70.5	22.2
	<i>wu</i> –PE 2	7.6	95.6	11.6	–1.4*	–	–
	<i>wu</i> –PE 3	8.0	70.9	13.3	–0.3	29.8	31.8
	<i>wu</i> –PB	11.7	173.6	2.4	–2.6*	–	–
<i>Trichloromethane</i>							
	<i>wu</i> –PE 1	11.0	70.1	21.8	–0.1	44.5	34.3
	<i>wu</i> –PE 2	13.5	80.6	10.5	–0.2	28.8	5.0
	<i>wu</i> –PE 3	12.7	66.1	14.6	–0.2	4.2	231.3
	<i>wu</i> –PB	27.0	255.1	1.6	–3.0*	–	–

1. Units for contaminant diffusivity (D) are 10<sup>–9</sup> cm<sup>2</sup>/s; T<sub>0.5</sub> is the time to half-contaminant sorption or desorption; Mean values for three replicates shown; Weight gain and loss standard deviation varied from 0–0.3%; Coefficient of variation for diffusivity was 0.02–2.0; (\*) Diffusivity not calculated because material weight loss was detected for the contaminant–polymer pair.



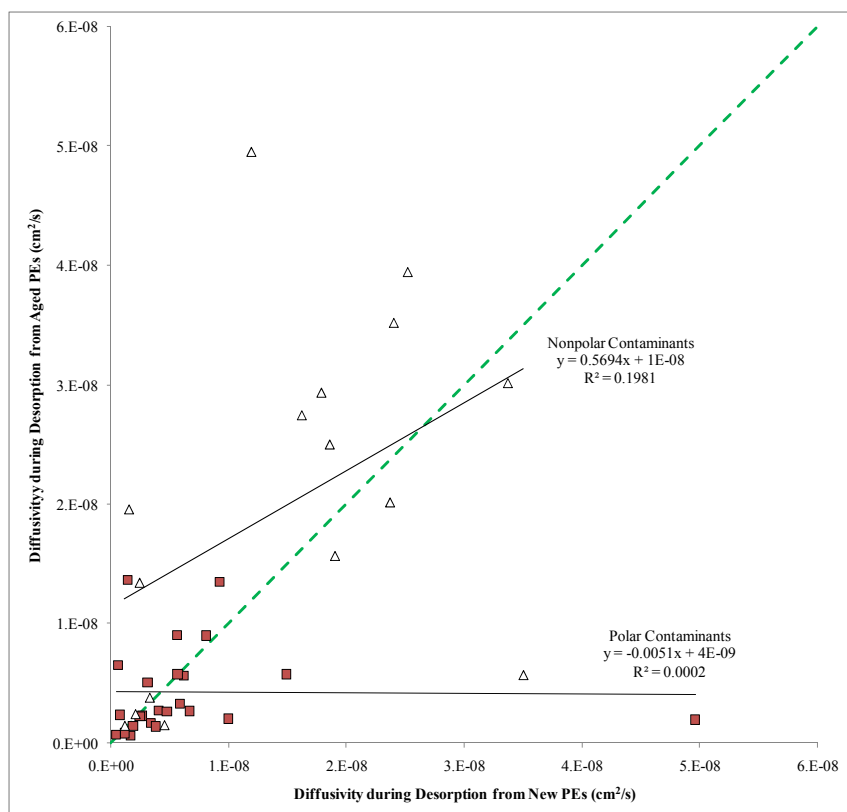
**Figure 7-1 Sorption and Desorption Data and Curves for (a) Toluene, (b) Benzaldehyde, (c) MTBE, and (d) 1-Butanol in New and Lab Aged PEX-A Pipe**

Triangles, squares, and diamonds represent data for each replicate. Three replicates for each contaminant-polymer pair. Filled symbols represent sorption and unfilled symbols represent desorption.



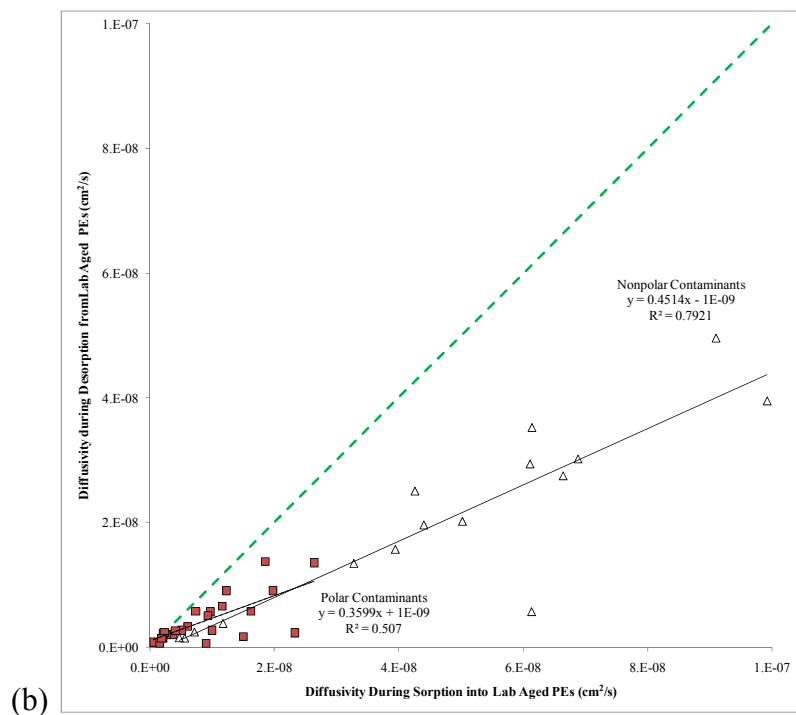
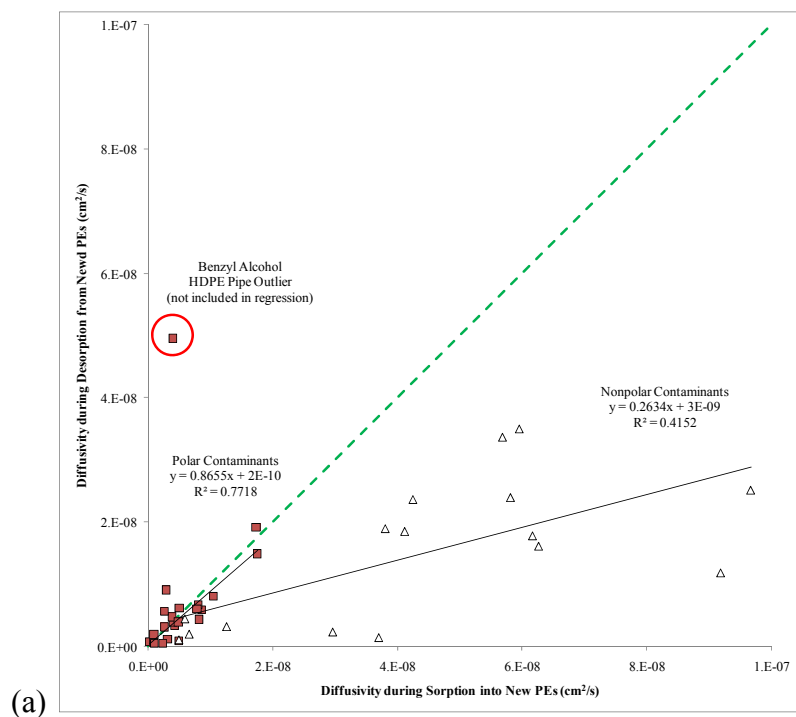
**Figure 7–2 Statistically Significant Relationships between Material Bulk Density and Contaminant Diffusivity for (a) New and (b) Lab Aged Polyethylene**

Mean diffusivity values shown for three replicates. Regression analysis show that slopes were statistically different than zero ( $p < 0.05$ ). Regression line slopes for all other contaminants not shown were equal to zero. Six materials used for new PEs and four materials used for lab aged PEs.



**Figure 7–3 Relationship for Contaminant Diffusivity during Desorption with New and Lab Aged Polyethylene**

Mean of three replicates shown. Trendlines for each group of contaminants shown. Squares represent polar contaminants and triangles represent nonpolar contaminants. The dotted line represents 1:1 relationship between the x- and y-axes.



**Figure 7-4 Relationship between Contaminant Diffusivity during Sorption and Desorption for (a) New and (b) Lab Aged Polyethylene**

Mean of three replicates shown. Trendlines for each group of contaminants shown. Squares represent polar contaminants and triangles represent nonpolar contaminants. The dotted line represents 1:1 relationship between the x- and y-axes.

## Limitations and Future Work

The limitations of experimental methods used in this research and recommendations for future work are briefly described. This information should be considered when evaluating past research, this work, as well as designing future polymer aging and performance investigations.

### *Polymer Condition and Aging Assessments using Oxidation Induction Time*

Oxidative induction time (OIT) has been used for many years in polymer pipe oxidation assessments and represents a polymer's ability to "resist" oxidation when the polymer is isothermally exposed to oxygen at  $\geq 180$  °C. OIT is a measure of the time (minutes) required to start breaking C–C bonds. Both OIT method descriptions and OIT industry standards are provided in Chapters 4–6. While the method used to determine polymer OIT is the same for lab aged and water utility polymer pipes, there are several limitations of OIT data: (1) there are inherent differences between lab aging conditions and water distribution system conditions, (2) there is a knowledge–gap as to what oxidation mechanisms cause PE degradation in potable water distribution systems and if these same mechanisms influence OIT reduction, and (3) there is a lack of data regarding initial OIT of new and water utility PE water pipes.

Environmental and water quality conditions in a real water distribution system significantly differ than those of lab accelerated aging. Depending on the hot– or cold–water pipe application in the USA, temperatures encountered by real–water pipes would be 4–60 °C and water would likely contain a disinfectant either free available chlorine or chloramines at low concentration (0–4 mg/L as  $\text{Cl}_2$ ). In contrast, many accelerated aging methods use temperatures  $\geq 70$  °C to cause oxidation. Some prior work has shown that additives thermally degrade at high temperatures and additives can also leach into water both contributing to OIT reduction. Also, results described in Chapter 4 clearly show that OIT reduction is a function of water quality and environmental exposure conditions. So by simply selecting an accelerated aging condition, the investigator influences the outcome of the results. Results in Chapter 6 also show that even when the same aging condition with stable water quality is applied, OIT reduction can also vary across PE pipes. Unfortunately, PE oxidation and additive loss mechanisms occurring at different aging conditions have not been well–defined. Additional research should focus on determining PE



water pipe degradation mechanisms and correlating those to an acceptable accelerated aging approach.

The usefulness of using OIT values in signifying the oxidative state of PE water utility pipes removed from water distribution systems is also up for debate. In this research, HDPE water utility pipes were removed from the ground to assess their condition and at the time these pipes were performing well (had not mechanically failed). Results show that these utility HDPE pipes had OIT level 0–8 min. after 7–25 years service. While the exposure of HDPE pipes to water containing free available chlorine has proven to cause surface and bulk pipe oxidation, the 7 year old water utility HDPE pipe exposed to chloramines had an OIT of 0 min. This was surprising because chloramines are reportedly not aggressive towards PE pipes based on a recent investigation:

Chung S; Oliphant K; Vibien P; Zhang J. 2007. An examination of the relative impact of common potable water disinfectants (chlorine, chloramines, and chlorine dioxide) on plastic piping system components. *Proc of ANTEC*. **5**, 2894–2898.

The water and pipe manufacturing industries would be well-served by understanding what OIT really signifies, if it truly correlates to potable water pipe service-life, and what controls OIT reduction. Based on the peer-reviewed and non-peer reviewed literature reports, it seems these questions have not yet been answered. In spite of this, OIT measurements continue to be conducted and reported as a basis of assessing pipe integrity.

Finally, because the initial OIT of water utility pipes examined in this work were unknown, OIT measurements on the utility pipes did not provide insight into the degree of OIT reduction. Information also not provided by OIT is what caused the OIT reduction during service life (e.g., disinfectant exposure, additive migration into water, thermal degradation, other). A more descriptive polymer analysis technique should be developed that enables investigators to identify the age of the material, its remaining life, and truly understand how oxidant exposure affects pipe characteristics.

Future work could focus on comparing the similarity and differences between mechanisms responsible for PE pipe oxidation under different accelerated aging conditions, or

oxygen gas at high-temperature to the mechanisms that cause oxidation when PE pipes are installed in an actual water distribution system. Another study could focus on identifying a more effective method to predict pipe age, the remaining pipe service-life, and what polymer pipe characteristic(s) would best correlate to polymer pipe life. Ideally, a method could be developed that answers to the previously described questions without having to conduct a multi-month or multi-year accelerated aging experiment. Another idea would be to characterize the OIT of new PE pipes, install them in different water distribution systems, and periodically remove sections to monitor the actual OIT reduction overtime. This approach would provide information under the most realistic environmental and water quality conditions.

#### *Water Sorption into PE*

In Chapter 4, several accelerated aging conditions were selected to age HDPE resin and pipe based on a literature review. Aging solution chemistry and polymer characteristics were evaluated before, during, and after aging. Results showed that several aging conditions caused HDPE to sorb water. Water sorption was determined by measuring HDPE sample weight change during dessicator drying at 23°C and 8 hour convection oven drying at 70 °C. Before specimens were placed in these drying environments they were blotted with KIM Wipes® to remove residual water from the polymer surface and were weighed using the balance with Vernier scale. The exact location of the water molecules was not identified (surface or bulk) in this work. DSC freezing and thawing methods and a moisture analyzer used were unable to quantify the amount of water sorbed into or onto the PE. References cited in the Chapter 4 Introduction explain the concept of bound and free water. Research in this dissertation did not identify where the water was located. Future work could apply more precise analytical techniques to identify if the water molecules are “in” the polymer or bonded to the surface.

One accelerated aging method evaluated in Chapter 4 was used to age HDPE and PEX pipes in Chapter 6. This aging condition was selected because it did not cause water sorption in Chapter 4 (45 mg/L as Cl<sub>2</sub>, pH 6.5, 50 mg/L as CaCO<sub>3</sub>, 37 °C, 3 day water changes, 20 week exposure). To determine if HDPE and PEX pipe samples in Chapter 6 sorbed water, two approaches were taken. First, polymer specimens were aged in batch 1L solutions (e.g., 150 pieces of the same polymer per bottle). After 20 week aging, polymer samples were placed in a dessicator at 23°C and were periodically weighed to determine if they lost weight (like the

method used in Chapter 4). Second, at the start of 1L batch aging experiment single polymer specimens were placed in 20 mL glass and capped vials with the same aging solution used in the batch aging. Aging solution in these individual vials was replaced every three days like the large 1L bottles and this aging was also conducted for 20 weeks. The weight of each polymer in each vial was measured before and after the 20 week aging. We concluded the accelerated aging method used in Chapter 6 did not cause water sorption because HDPE and PEX samples did not lose weight during 23 °C desiccation and the weight of polymers stored in individual vials before and after 20 weeks was unchanged.

#### *Polymer Characterization Methods that Could Enhance Future Investigations*

Depth profiling of crystalline content was not conducted and bulk density was used to describe the overall PE crystalline content. However, if polymers were annealed differently during manufacture, varying degrees of crystallinity may be present at the surface compared to the inner polymer pipe regions. Differences between contaminant solubility and diffusivity in polymers of similar bulk density could be due in part to surface and depth profile crystallinity differences. Microtoming PE pipe sections by depth and analysis by X-ray diffraction (XRD) has been used by others to examine crystalline content as a function of depth and could be used in future work. Like others, OIT variation as a function of depth could also be quantified by analyzing microtomed PE pipe sections.

Results of this work imply that pipe composition (e.g., oxygen content) influenced contaminant fate and other techniques could also provide supportive data. Elemental analysis may help describe the composition of the materials. Antioxidants could be extracted by solvent and then analyzed by high-performance liquid chromatography (HPLC) and elemental analysis. Secondary ion mass spectrometry (SIMS) and environmental scanning electron microscopy (ESEM) could also provide useful information about elemental surface characteristics for new and lab aged PEs; however, the change in surface elements would need to be greater than the technique detection limit.  $C^{13}$  Nuclear Magnetic Resonance (NMR) could also be used to assess chain-branching (number of ethyl groups per 1000 main chain carbon atoms). High-temperature Gel Permeation Chromatography (GPC) could also be used to assess molar mass distribution changes in HDPE resin and pipes before and after chlorinated water exposure.

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Ms. Xi van Fleet, Manager Information Services

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March 23, 2009

Dear Ms. van Fleet:

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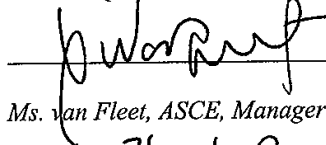
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Marcia Lacey

Editor, Journal of the American Water Works Association

American Water Works Association, Denver, CO

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March 18, 2009

Dear Ms. Lacey:

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## Chapter 4

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**Sent:** Friday, March 27, 2009 11:37 AM  
**To:** Andrew J. Whelton  
**Subject:** RE: Permission Request, Graduation Deadline April 10

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Sincerely,

Andrew J. Whelton

**Andrew Whelton**

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