

**BTEX REMOVAL FROM PRODUCED WATER USING SURFACTANT-
MODIFIED ZEOLITE**

by

John Michael Ranck

Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Science in Hydrology

New Mexico Institute of Mining and Technology
Socorro, New Mexico

December 2003

ABSTRACT

Produced water contains large amounts of various hazardous organic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX). With increasing regulations governing disposal of this water, low-cost treatment options are necessary. This study evaluated the effectiveness of surfactant-modified zeolite (SMZ) for removal of BTEX from produced water. The long-term effectiveness of SMZ for BTEX removal was investigated along with how sorption properties change with long-term use. The results from these investigations showed that SMZ successfully removes BTEX from produced water, and that SMZ can be regenerated via air-sparging without loss of sorption capacity. The BTEX compounds break through laboratory columns in order of decreasing water solubility and of increasing K_{ow} . The most soluble compound, benzene, began to elute from the column at 8 pore volumes (PV), while the least soluble compounds, ethylbenzene and xylenes, began to elute at 50 PV. After treating 4500 pore volumes of water in the column system over 10 sorption/regeneration cycles, no significant reduction in sorption capacity of the SMZ for BTEX was observed. The mean K_d from these column experiments ranged from a low value of 18.3 L/kg for benzene to the highest value of 95.0 L/kg for p-&m-xylene. Batch sorption experiments confirmed the column results showing no significant loss of capacity for BTEX sorption after 10 sorption/regeneration cycles, although the batch K_d values were consistently lower than

K_{ds} from the column experiments. Batch K_{ds} ranged from a low of 6.71 L/kg for benzene to a high of 39.4 L/kg for o-xylene.

Laboratory columns were upscaled to create a field-scale SMZ treatment system. The field-scale system was tested at a produced water treatment facility near Wamsutter, Wyoming. We observed greater sorption of BTEX in field columns tests than predicted from laboratory column studies. In the field column, initial benzene breakthrough occurred at 10 PV and toluene breakthrough began at 15 PV, and no breakthrough of ethylbenzene or xylenes occurred throughout the 80 PV experiment. These results, along with the low cost of SMZ, indicate that SMZ has a potential role in a cost-effective produced water treatment system.

ACKNOWLEDGEMENTS

I would like to thank the many people who have assisted me during my time at New Mexico Tech. To those who have helped with homework, listened to me bouncing ideas and frustrations around, helped out in the lab, and helped take my mind off of school sometimes; thank you. Special thanks go to Dr. Robert Bowman for introducing me to SMZ and assisting me all along the way. I would like to recognize Sarah Loughney for her help with sampling columns and keeping the lab in order. Thanks to Dr. E. Jeri Sullivan and Jim Smith for training me and helping me with the SEM analysis. In addition, I would like to thank Fei Zhang and Alana Fuierer for helping me during my first few weeks of learning the necessary experimentation and analysis techniques.

Thanks to all of my friends and family who have supported and encouraged me, whether it be from here in Socorro or from across the country.

TABLE OF CONTENTS

	Page
TABLE OF CONTENTS.....	iii
LIST OF FIGURES	v
LIST OF TABLES.....	vi
LIST OF APPENDICES FIGURES	vii
LIST OF APPENDICES TABLES.....	x
INTRODUCTION	1
PAPER ENTITLED "BTEX REMOVAL FROM PRODUCED WATER USING SURFACTANT-MODIFIED ZEOLITE"	2
ABSTRACT.....	2
INTRODUCTION	4
MATERIALS AND METHODS.....	8
RESULTS AND DISCUSSION.....	17
CONCLUSIONS.....	25
ACKNOWLEDGEMENTS.....	25
APPENDIX I. REFERENCES.....	26
APPENDIX II. NOTATION	29
FIGURE CAPTIONS.....	34
INTRODUCTION TO APPENDICES.....	42
APPENDIX A . PRELIMINARY LAB COLUMN DISCUSSION AND DATA.....	44

APPENDIX B . COLUMN FLOW PROPERTIES, SMZ LOSS, AND SCANNING ELECTRON MICROSCOPY INVESTIGATION OF SMZ PARTICLE BREAKDOWN.....	59
APPENDIX C . LABORATORY COLUMN BTC DATA.....	79
APPENDIX D . BATCH EXPERIMENT RESULTS.....	132
APPENDIX E . FIELD COLUMN METHODS AND RESULTS	146
APPENDIX F . ADDITIONAL ORGANIC MATERIAL IN PRODUCED WATER..	153
APPENDIX G . APPLICABLE PRODUCED WATERS FOR AN SMZ TREATMENT SYSTEM.....	165

LIST OF FIGURES

	Page
Figure 1. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 10A.....	35
Figure 2. Observed and fitted BTEX breakthrough curves on virgin SMZ (Column 10A). The lines were based on the best fit of eq. 10 to the observed data, as described in the text.....	36
Figure 3. BTCs of benzene and p-&m-xylene in Columns 10A and 10B for (a) virgin SMZ and (b) during the fifth sorption cycle in columns 10A and 10B.....	37
Figure 4. (a) Benzene BTCs for Column 10A over 10 sorption/regeneration cycles and (b) p-&m-xylene BTCs for Column 10A over 10 sorption/regeneration cycles.....	38
Figure 5. Cumulative masses of benzene, toluene, and p-&m-xylene removed relative to masses sorbed during first regeneration in Column 10A.....	39
Figure 6. Comparison of benzene and toluene BTC for virgin SMZ in lab column 10A and field column.....	40
Figure 7. Benzene and toluene breakthrough on virgin and regenerated SMZ in field column.....	41

LIST OF TABLES

	Page
Table 1. Analysis of produced water used in laboratory experiments.....	31
Table 2. Dimensions and operating parameters for field and laboratory columns.	32
Table 3. Mean K_d values determined by laboratory column and batch experiments. Standard deviations are shown in parentheses. “n” indicates the number of measurements for each mean.	33

LIST OF APPENDICES FIGURES

	Page
Appendix Figure B-1. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 10B.....	61
Appendix Figure B-2. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 5A.	62
Appendix Figure B-3. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 5B.....	63
Appendix Figure B-4. SEM image of virgin SMZ (35X).....	70
Appendix Figure B-5. SEM image of virgin SMZ (190X). Large particle in upper-center is quartz.....	71
Appendix Figure B-6. SEM image of virgin SMZ (4500X).....	72
Appendix Figure B-7. SEM image of Column 5A SMZ (35X).	73
Appendix Figure B-8. SEM image of Column 5A SMZ (190X).	74
Appendix Figure B-9. SEM image of Column 5A SMZ (4500X).	75
Appendix Figure B-10. SEM image of Column 10B SMZ (35X).....	76
Appendix Figure B-11. SEM image of Column 10B SMZ (190X).....	77
Appendix Figure B-12. SEM image of Column 10A SMZ (4500X).	78
Appendix Figure C-1. Toluene BTCs for Column 10A over 10 sorption/regeneration cycles.	81
Appendix Figure C-2. Ethylbenzene BTCs for Column 10A over 10 sorption/regeneration cycles.	82
Appendix Figure C-3. o-xylene BTCs for Column 10A over 10 sorption/regeneration cycles.	83

Appendix Figure C-4. Benzene BTCs for Column 10B over 10 sorption/regeneration cycles.	84
Appendix Figure C-5. Toluene BTCs for Column 10B over 10 sorption/regeneration cycles.	85
Appendix Figure C-6. Ethylbenzene BTCs for Column 10B over 10 sorption/regeneration cycles.	86
Appendix Figure C-7. p-&m-xylene BTCs for Column 10B over 10 sorption/regeneration cycles.	87
Appendix Figure C-8. o-xylene BTCs for Column 10B over 10 sorption/regeneration cycles.	88
Appendix Figure D-1. Benzene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.....	133
Appendix Figure D-2. Toluene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.....	134
Appendix Figure D-3. Ethylbenzene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.....	135
Appendix Figure D-4. p-&m-xylene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.....	136
Appendix Figure D-5. o-xylene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.....	137
Appendix Figure E-1. Observed BTEX breakthrough on virgin SMZ in smaller field column.	148
Appendix Figure F-1. PID measurements with BTEX BTCs on virgin SMZ in smaller field column.	158
Appendix Figure F-2. PID measurements with BTEX BTCs on virgin SMZ in larger field column.....	159

Appendix Figure F-3. PID measurements with BTEX BTCs on regenerated SMZ
in larger field column..... 160

LIST OF APPENDICES TABLES

	Page
Appendix Table A-1. BTEX BTC data on virgin SMZ in preliminary lab column.	46
Appendix Table A-2. Benzene removal data.....	48
Appendix Table A-3. Toluene removal data.....	50
Appendix Table A-4. Ethylbenzene removal data.....	52
Appendix Table A-5. p-&m-xylene removal data.....	54
Appendix Table A-6. o-xylene removal data.....	56
Appendix Table A-7. BTEX BTC data for preliminary lab column with regenerated SMZ.....	58
Appendix Table B-1. Hydrodynamic properties of laboratory columns before sorption cycles.	60
Appendix Table B-2. Tritium breakthrough data for virgin SMZ.....	64
Appendix Table B-3. Hydrodynamic properties of laboratory columns after sorption cycles.	65
Appendix Table B-4. Tritium breakthrough data after sorption cycles.....	66
Appendix Table C-1. Data for BTEX BTC 1 from Column 10A.....	89
Appendix Table C-2. Data for BTEX BTC 2 from Column 10A.....	90
Appendix Table C-3. Data for BTEX BTC 3 from Column 10A.....	91
Appendix Table C-4. Data for BTEX BTC 4 from Column 10A.....	92
Appendix Table C-5. Data for BTEX BTC 5 from Column 10A.....	93
Appendix Table C-6. Data for BTEX BTC 6 from Column 10A.....	94

Appendix Table C-7. Data for BTEX BTC 7 from Column 10A.....	95
Appendix Table C-8. Data for BTEX BTC 8 from Column 10A.....	96
Appendix Table C-9. Data for BTEX BTC 9 from Column 10A.....	97
Appendix Table C-10. Data for BTEX BTC 10 from Column 10A.....	98
Appendix Table C-11. Data for BTEX BTC 1 from Column 10B.....	99
Appendix Table C-12. Data for BTEX BTC 2 from Column 10B.....	100
Appendix Table C-13. Data for BTEX BTC 3 from Column 10B.....	101
Appendix Table C-14. Data for BTEX BTC 4 from Column 10B.....	102
Appendix Table C-15. Data for BTEX BTC 5 from Column 10B.....	103
Appendix Table C-16. Data for BTEX BTC 6 from Column 10B.....	104
Appendix Table C-17. Data for BTEX BTC 7 from Column 10B.....	105
Appendix Table C-18. Data for BTEX BTC 8 from Column 10B.....	106
Appendix Table C-19. Data for BTEX BTC 9 from Column 10B.....	107
Appendix Table C-20. Data for BTEX BTC 10 from Column 10B.....	108
Appendix Table C-21. BTEX removal data from Column 10A during first sparging cycle.	109
Appendix Table C-22. BTEX removal data from Column 10A during second sparging cycle.	110
Appendix Table C-23. BTEX removal data from Column 10A during third sparging cycle.	111
Appendix Table C-24. BTEX removal data from Column 10A during fourth sparging cycle.	112

Appendix Table C-25. BTEX removal data from Column 10A during fifth sparging cycle.	113
Appendix Table C-26. BTEX removal data from Column 10A during sixth sparging cycle.	114
Appendix Table C-27. BTEX removal data from Column 10A during seventh sparging cycle.	115
Appendix Table C-28. BTEX removal data from Column 10A during eighth sparging cycle.	116
Appendix Table C-29. BTEX removal data from Column 10A during ninth sparging cycle.	117
Appendix Table C-30. BTEX removal data from Column 10A during tenth sparging cycle.	118
Appendix Table C-31. BTEX removal data from Column 10B during first sparging cycle.	119
Appendix Table C-32. BTEX removal data from Column 10B during second sparging cycle.	120
Appendix Table C-33. BTEX removal data from Column 10B during third sparging cycle.	121
Appendix Table C-34. BTEX removal data from Column 10B during fourth sparging cycle.	122
Appendix Table C-35. BTEX removal data from Column 10B during fifth sparging cycle.	123
Appendix Table C-36. BTEX removal data from Column 10B during sixth sparging cycle.	124
Appendix Table C-37. BTEX removal data from Column 10B during seventh sparging cycle.	125
Appendix Table C-38. BTEX removal data from Column 10B during eighth sparging cycle.	126

Appendix Table C-39. BTEX removal data from Column 10B during ninth sparging cycle.	127
Appendix Table C-40. BTEX removal data from Column 10B during tenth sparging cycle.	128
Appendix Table C-41. K _d , Mass sorbed, mass removed, and cumulative mass remaining for BTEX compounds on Column 10A.	129
Appendix Table C-42. K _d , Mass sorbed, mass removed, and cumulative mass remaining for BTEX compounds on Column 10B.	130
Appendix Table C-43. CXTFIT 2.1 calculations used to create manuscript Figure 2.	131
Appendix Table D-1. Benzene sorption on virgin SMZ.	138
Appendix Table D-2. Benzene sorption on Column 5A/5B SMZ.	138
Appendix Table D-3. Benzene sorption on Column 10A/10B SMZ.	139
Appendix Table D-4. Toluene sorption on virgin SMZ.	139
Appendix Table D-5. Toluene sorption on Column 5A/5B SMZ.	140
Appendix Table D-6. Toluene sorption on Column 10A/10B SMZ.	140
Appendix Table D-7. Ethylbenzene sorption on virgin SMZ.	141
Appendix Table D-8. Ethylbenzene sorption on Column 5A/5B SMZ.	141
Appendix Table D-9. Ethylbenzene sorption on Column 10A/10B SMZ.	142
Appendix Table D-10. p-&m-xylene sorption on virgin SMZ.	142
Appendix Table D-11. p-&m-xylene sorption on Column 5A/5B SMZ.	143
Appendix Table D-12. p-&m-xylene sorption on Column 10A/10B SMZ.	143
Appendix Table D-13. o-xylene sorption on virgin SMZ.	144

Appendix Table D-14. o-xylene sorption on Column 5A/5B SMZ.....	144
Appendix Table D-15. o-xylene sorption on Column 10A/10B SMZ.....	145
Appendix Table E-1. Data for BTEX BTC on virgin SMZ in larger field column.....	149
Appendix Table E-2. Data for BTEX BTC on regenerated SMZ in larger field column.....	150
Appendix Table E-3. Data for BTEX BTC on virgin SMZ in smaller field column.....	151
Appendix Table E-4. BTEX removal data from 14-inch field column during air sparging.....	152
Appendix Table F-1. TPH and semi-volatile analysis of untreated produced water collected during field testing (only noting compounds present above detectable limits).....	153
Appendix Table F-2. TOC analysis of produced water used in laboratory column experiments.....	155
Appendix Table F-3. Semi-volatile breakthrough at 2.4 PV from smaller field column.....	156
Appendix Table F-4. PID measurements recorded on virgin SMZ in smaller field column.....	161
Appendix Table F-5. PID measurements recorded on virgin SMZ in larger field column.....	162
Appendix Table F-6. PID measurements recorded on regenerated SMZ in larger field column.....	163

INTRODUCTION

This document is the result of a thesis project and contains a journal article and supporting appendices. The thesis project partially fulfills the requirements for the Degree of Master of Science in Hydrology at the New Mexico Institute of Mining and Technology. The study evaluated the use of surfactant-modified zeolite for removal of benzene, toluene, ethylbenzene, and xylenes from produced water. The objectives of the study were to evaluate the long-term effectiveness of surfactant-modified zeolite to remove these compounds from produced water, investigate how the sorption characteristics of surfactant-modified zeolite change with progressive sorption and regeneration cycles, and to evaluate our ability to predict results in a field system by scaling from a laboratory system.

The following manuscript, entitled “BTEX Removal from Produced Water Using Surfactant-Modified Zeolite,” was prepared for submission to the Journal of Environmental Engineering, and follows the editorial guidelines set by the publisher (American Society of Civil Engineers). The article presents the results of laboratory column and batch experiments and field column experiments that were designed to fulfill the objectives stated above.

The appendices contain information on preliminary and unreported studies, more detailed descriptions of experimental procedures, and the results from the experiments I have performed.

BTEX REMOVAL FROM PRODUCED WATER USING SURFACTANT-MODIFIED ZEOLITE

J. Michael Ranck¹, Robert S. Bowman², Jeffrey L. Weeber³, Lynn E. Katz⁴, and Enid J. Sullivan⁵

ABSTRACT

Produced water contains large amounts of various hazardous organic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX). With increasing regulations governing disposal of this water, low-cost treatment options are necessary. This study evaluated the effectiveness of surfactant-modified zeolite (SMZ) for removal of BTEX from produced water. The long-term effectiveness of SMZ for BTEX removal was investigated along with how sorption properties change with long-term use. The results from these investigations showed that SMZ successfully removes BTEX from produced water, and that SMZ can be regenerated via air-sparging without loss of sorption capacity. The BTEX compounds break through laboratory columns in order of decreasing water solubility and of increasing K_{ow} . The most soluble compound, benzene, began to elute from the column at 8 pore volumes (PV), while the least soluble compounds, ethylbenzene and xylenes, began to elute at 50 PV. After treating 4500 pore volumes of water in the column system over 10 sorption/regeneration cycles, no

¹ Department of Earth and Environmental Science, New Mexico Tech, Socorro, NM 87801.

² Department of Earth and Environmental Science, New Mexico Tech, Socorro, NM 87801 (corresponding author). E-mail: bowman@nmt.edu

³ Department of Civil Engineering, University of Texas-Austin, Austin, TX 78712.

⁴ Department of Civil Engineering, University of Texas-Austin, Austin, TX 78712.

⁵ Los Alamos National Laboratory, RRES Division, Los Alamos, NM 87545.

significant reduction in sorption capacity of the SMZ for BTEX was observed. The mean K_d from these column experiments ranged from a low value of 18.3 L/kg for benzene to the highest value of 95.0 L/kg for p-&m-xylene. Batch sorption experiments confirmed the column results showing no significant loss of capacity for BTEX sorption after 10 sorption/regeneration cycles, although the batch K_d values were consistently lower than K_{dS} from the column experiments. Batch K_{dS} ranged from a low of 6.71 L/kg for benzene to a high of 39.4 L/kg for o-xylene.

Laboratory columns were upscaled to create a field-scale SMZ treatment system. The field-scale system was tested at a produced water treatment facility near Wamsutter, Wyoming. We observed greater sorption of BTEX in field columns tests than predicted from laboratory column studies. In the field column, initial benzene breakthrough occurred at 10 PV and toluene breakthrough began at 15 PV, and no breakthrough of ethylbenzene or xylenes occurred throughout the 80 PV experiment. These results, along with the low cost of SMZ, indicate that SMZ has a potential role in a cost-effective produced water treatment system.

INTRODUCTION

A significant amount of fossil water is generated during petroleum production. This produced water represents the largest volume waste stream in the production process, and can exceed the total volume of hydrocarbon produced by a factor of ten (Stephenson 1992). In 1995, the volume of produced water generated in onshore wells throughout the United States was approximately 17.9 trillion barrels (bbls) (2.8 trillion m³) (API 2000). Produced water contains an assortment of chemicals including inorganic salts, metals, and organic substances. Dissolved benzene, toluene, ethylbenzene, and xylenes (BTEX) are the most abundant hydrocarbons, with BTEX concentrations ranging from 68 to 600,000 µg/L in various produced waters (Neff and Sauer 1996). Benzene levels in produced water can surpass the U.S. drinking water standard of 5 µg/L by a factor of 7000.

Produced water is currently excluded from the Federal Resource Conservation and Recovery Act (RCRA) Subtitle C regulation of hazardous waste (40 CFR Part 261.4), but is subject to other RCRA sections (40 CFR Parts 260 to 279), the Clean Water Act (40 CFR Parts 100-129 and 400-503), the Safe Drinking Water Act (40 CFR Parts 141-148), and various state regulations. Surface discharge is governed by the Clean Water Act and is permitted by the National Pollutant Discharge Elimination System (NPDES) (40 CFR Part 435). NPDES permits are not issued for onshore discharges of produced water except for small-volume stripper wells (10 bbls of oil or less per day) or for discharge water that can be of beneficial use in areas west of the 98th meridian. NPDES regulations also do not allow coastal discharge of produced water, except for

Cook Inlet, Alaska, which is subject to offshore limits. NPDES regulations do allow offshore produced water discharge with dissolved oil and grease limits of 29 mg/L (monthly average) and 42 mg/L (daily average). These limits were reduced in 1994 from previous levels of 48 mg/L (monthly average) and 72 mg/L (daily average) (Otto and Arnold 1996). Many states are adopting new regulations favoring deep well injection for produced water disposal (Boysen et al. 2002). With increasing regulations, producers in situations where injection is not cost-efficient, such as offshore and stripper wells, could require the development of new treatment options (Lawrence et al. 1995). The changing regulatory environment has stimulated interest in developing inexpensive techniques for removing target produced water contaminants from systems of all scales, from isolated, single-well operations to large oil fields and offshore rigs.

Currently 92% of onshore produced water is disposed via reinjection (API 2000). However, this is geologically infeasible in some areas and economically infeasible for many small producers (less than 10 bbl/day). According to the U.S. EPA (2000), the remaining onshore produced water is disposed of by irrigation (west of the 98th meridian only) (4%), evaporation/percolation pits (2%), treatment and discharge (1%), and application to roads (<1%). For offshore producers, discharge to the ocean is far more practical and cost-effective than reinjection. Current treatment methods (primarily oil/water separation, hydrocyclones, and gas flotation) focus on separation of oil and grease from water and are not effective on dissolved organic components including BTEX.

These dissolved organic compounds occur in produced water at levels that are dangerous to the environment when discharged, and can reach levels that are thousands

of times higher than U.S. drinking water standards. Benzene is just one example of a known carcinogen found at high concentrations in produced water. Lawrence et al. (1995) indicated that future regulations will likely require additional removal of dissolved organic compounds before discharge. Treatment methods for the removal of dissolved hydrocarbons include chemical clarification, membrane filtration, bubble separation, photocatalytic oxidation, phytoremediation, and sorption on altered clay minerals, carbonaceous sorbents, or granular activated carbon (GAC). Tao et al. (1993) reported a treatment system that utilized chemical clarification, softening, filtration, and reverse osmosis methods to satisfy California drinking water standards. This method was quite expensive with high capital and operating costs. Santos and Wiesner (1997) concluded that membrane filtration (ultrafiltration) results varied with influent water samples and were unable to report on the overall technical and economic effectiveness. Thoma et al. (1999) tested bubble separation and found 40% removal of dissolved toluene and ethylbenzene, but did not report system costs. Bessa et al. (2001) reported on the use of titanium oxide semiconductors for photocatalytic oxidation of BTEX. While this method reduces BTEX levels, the expense of the semiconductors would likely inhibit the use of this technique for smaller producers. Negri and Hinchman (1997) discussed phytoremediation of produced water, which may prove to be low cost and low maintenance, but is dependent on local climate and season. Gallup et al. (1996) reported the commercially available carbonaceous sorbent Ambersorb® exhibits higher sorption capacity for BTEX than GAC and certain altered clay minerals, and has an operating cost that is 15-25% that of GAC, although Ambersorb® showed a 1-40% capacity loss after

regeneration. No additional information concerning capital and operating costs was provided.

An additional candidate low-cost sorbent for BTEX removal is surfactant-modified zeolite (SMZ). SMZ has been studied previously for its ability to sorb contaminants from various aqueous solutions. Janks and Cadena (1992), Huddleston (1990), Neel and Bowman (1992), and Bowman et al. (1995) evaluated the ability of SMZ to sorb organic molecules such as benzene, toluene, and p-xylene. Haggerty and Bowman (1994) and Bowman et al. (1995) investigated the use of SMZ to sorb divalent oxyanions such as chromate, sulfate, and selenate. Bowman et al. (2001) have shown the use of SMZ in an in-situ permeable barrier for remediation of chromate and perchloroethylene.

Zeolites are natural aluminosilicate minerals that are characterized by cage-like structures, high surface areas, and high cation-exchange capacities. Large cationic surfactant molecules, such as hexadecyltrimethylammonium (HDTMA), have a strong affinity for the zeolite surface and replace positively charged inorganic counterions that neutralize the negative surface charge of the zeolite. The surfactant molecules impart hydrophobic properties to the zeolite surface, allowing the zeolite to retain organic compounds including BTEX (Bowman et al. 2000). Once SMZ is saturated with volatile organic compounds, it can be regenerated using air sparging (Li and Bowman 2001). The ability to regenerate SMZ and the low cost of the material (on the order of \$460 per metric ton) increases its economic feasibility in a produced water treatment system.

This study evaluated the use of SMZ as a sorbent for BTEX removal from produced water. The objectives of this study were to (1) determine the sorptive capacity

of SMZ for BTEX, (2) evaluate the long-term effectiveness of SMZ to sorb BTEX over multiple sorption/regeneration cycles, and (3) build and field test a prototype SMZ produced water treatment system.

MATERIALS AND METHODS

SMZ Preparation

The zeolite used in this study was a natural clinoptilolite-rich tuff obtained from the St. Cloud mine near Winston, NM. The mineral composition was 74% clinoptilolite, 5% smectite, 10% quartz/cristobalite, 10% feldspar, and 1% illite. The zeolite had an external surface area of 15.7 m²/g. The internal cation exchange capacity was 800 meq/kg and the external cation exchange capacity was 90-110 meq/kg (Bowman et al. 2000). The zeolite was crushed and sieved to two different grain sizes: 1.4 to 0.4 mm (14-40 mesh) for the field test and 0.18 to 0.15 mm (80-100 mesh) for the laboratory batch and column experiments.

The SMZ used in the laboratory experiments was produced by treating 1000 g of zeolite with 3000 mL of a 0.10 M HDTMA-Cl (Aldrich, Milwaukee, WI) solution and shaking for 24 h. The HDTMA-zeolite was rinsed with two 180 mL aliquots of Type I water (purified with Milli-Q system, Millipore Corp., Bedford, MA) and air-dried. The final HDTMA loading was 157 mmol HDTMA/kg zeolite. The SMZ for the field test, bulk produced at the St. Cloud mine and described by Bowman et al. (2001), had an HDTMA loading of 180 mmol HDTMA/kg zeolite.

Produced Water

The site selected for the field test was a produced water treatment facility operated by Crystal Solutions, LLC. The facility is located near Wamsutter, Wyoming, where a large natural gas reservoir exists. Produced water from the region is delivered to the facility by tanker truck, where it is unloaded into an oil/water separation tank. Overflow from this tank is transferred into a second separation tank. From the second tank, oil is sent into an oil condensate tank for later processing, while water flows into a lined separation pond and is then pumped through a series of lined evaporation ponds.

Produced water for use in the laboratory studies was collected from the separation tanks at this site in December 2002 and stored in sealed 208 L drums. The composition of this water is shown in Table 1.

BTEX Sorption/Regeneration in Laboratory Columns

Laboratory columns were scaled based upon a proposed field treatment design using the rapid small-scale column test method, developed for sorption of organic compounds onto granular activated carbon (Crittenden et al. 1986). The scaling method is based on the Dispersed Flow Pore and Surface Diffusion Model (DFPSDM) and incorporates advective flow, axial dispersion and diffusion, liquid phase mass transfer resistance, local adsorption equilibrium at the exterior surface of the adsorbent, surface diffusion, pore diffusion, and competitive equilibrium of solutes on the surface (Crittenden et al. 1986). For perfect similitude between small-scale and large-scale systems, dimensionless parameters contained in the DFPSDM must be equal in both systems, and the scaling law is defined as:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{SC}}{d_{LC}} \right]^2 \quad (1)$$

where: SC = small column

LC = large column

$EBCT$ = empty bed contact time (bed volume/volumetric flow rate)

d = particle diameter

Table 2 contains the parameters from the proposed field treatment design that were used in Eq. 1 to determine the volumetric flow rate in the laboratory column. The EBCT ratio is 0.0330 and the square of the particle diameter ratio is 0.0332. SMZ particle size in the laboratory column was chosen to be close to the minimum requirement of a 50-to-1 column diameter-to-particle size ratio to avoid channeling (Crittenden et al. 1991).

Four glass columns (Ace Glass, Vineland, NJ) with a 4 mm radius and 100 mm length (Table 2) were packed with 80-100 mesh SMZ. Precision made PTFE end-fittings were designed for use with these columns and provided a leak-tight seal. Four-way valves (Cole-Parmer, Vernon Hills, IL) were connected to the end-fittings with Luer fittings. These valves served as sampling ports and could seal the columns shut between experiments. Once packed, the columns were purged with CO₂ for 24 hours to displace air in the columns. They were then saturated from the bottom with an organic-free synthetic brine (3110 mg/L HCO₃⁻, 4400 mg/L Cl⁻, 4020 mg/L Na⁺) which approximated the inorganic composition of the produced water (Table 1). The brine was injected with 10-mL gastight syringes (Hamilton, Reno, NV) loaded in a syringe pump (Harvard Apparatus, Holliston, MA) at an average flow rate of 2.3 * 10⁻³ L/min (approximately 70 mm/min). These flow conditions were maintained for the duration of the experiments.

The columns were assumed to be at steady state when no gas bubbles were visible and the water-filled column weights remained constant.

A 2 pore-volume (PV) slug of tritiated water tracer (tritium) was injected into each column to determine the flow velocity and column dispersion coefficient. Effluent samples were collected every 0.2 PV in 7 mL vials. One-half milliliter of effluent solution was combined with 4.5 mL of scintillation cocktail solution (ICN Biomedicals, Inc., Irvine, CA) for analysis with an LS6500 liquid scintillation counter (Beckman Coulter, Inc., Fullerton, CA).

Produced water for the column experiments was transferred to a collapsible 30 L Tedlar® Gas Sampling Bag (Alltech Associates, Inc., Deerfield, IL) with a barbed on/off valve for injection into the columns. The water in the bag was spiked with additional ethylbenzene and o-xylene (Aldrich, Milwaukee, WI) to yield concentrations of approximately 15 mg/L, similar to the benzene concentration. The produced water was continuously injected into the columns until an air-sparging cycle was begun (see below). To remove iron oxide precipitates from the influent water, 0.45 µm and 0.2 µm nylon syringe-tip filters (Supelco, Bellefonte, PA) were added in series to the influent tubing just upstream of the columns. Using the four-way valves, influent and effluent samples were collected in 10-mL gastight syringes and sealed in 10-mL glass headspace vials with Teflon-faced butyl septa (Supelco) for subsequent analysis via gas chromatography. The columns were sampled at 3 PV intervals for the first 20 PV of effluent, 15 PV intervals for the next 60 PV of effluent, and 50 PV intervals for the remaining effluent. Flow was terminated when the effluent BTEX concentrations were approximately equal to influent concentrations (after 450-500 PV).

The spent SMZ was regenerated by air-sparging. A compressed air tank and 65-mm single-float flow controller (Cole-Parmer) were attached to the effluent end of the columns, reversing the flow direction from the water injection stage. A soap film flowmeter (Hewlett-Packard, Palo Alto, CA) was attached to the exhaust end. No water was removed during gravity drainage prior to air-sparging, but most retained water was removed during the first minute of sparging. The compressed air tank regulator was set to 30 psi and the flow controller was used to control air flow rate through the columns. Flow rate was set at 20 mL/min (6 PV/min). Using a 1.0-mL gastight syringe, samples were collected by withdrawing 0.2 mL from the effluent gas stream and analyzed immediately by direct injection into the gas chromatograph. Air-sparging continued until the concentration of each BTEX compound in the effluent gas stream was reduced to 2% or less of its initial concentration observed during regeneration (approximately 3500 PV of air).

The regenerated SMZ was again saturated with produced water under the same conditions as the original saturation, except the columns were not purged with CO₂ or leached with organic-free brine prior to produced water injection. This cycle of produced water injection/regeneration was repeated for a total of ten repetitions in two duplicate columns (columns 10A and 10B), while the injection/regeneration cycle was repeated for a total of five repetitions in two other duplicate columns (columns 5A and 5B). Columns 5A and 5B were operated simultaneously with columns 10A and 10B. Influent and effluent samples were not collected for columns 5A and 5B, which were used for batch sorption studies (see below).

Sorption Characteristics of Virgin and Regenerated SMZ

Sorption isotherms were prepared using virgin SMZ (no exposure to produced water), SMZ from columns 5A/5B (SMZ from both columns was combined), and SMZ from columns 10A/10B (combined). Batch experiments were performed using produced water. In order to achieve desired initial BTEX concentrations, the produced water was placed in uncovered beakers for several hours to allow BTEX volatilization, then spiked with the desired levels of BTEX. Initial concentrations were 3, 6, 9, 12, and 15 mg/L for benzene, ethylbenzene, p-&m-xylene combined, and o-xylene. Initial concentrations of toluene were 6, 12, 18, 24, and 30 mg/L. These values were chosen so that the maximum concentration of each compound was similar to the influent concentration during the column experiments. Three milliliters of produced water and 0.75 g of SMZ were combined in 10-mL headspace vials (in duplicate) and shaken for 24 hours at 25°C, conditions which have been previously shown sufficient to attain sorption equilibrium (Neel and Bowman 1992). Each sample was centrifuged at $900\times g$ for 20 min, and 1 mL of the supernatant transferred to a 10-ml headspace vial containing 2 mL Type I water for gas chromatography analysis. To monitor volatilization losses, two sets of duplicate blank samples containing produced water at each initial BTEX concentration but no SMZ were prepared, shaken, and centrifuged. One set of blank samples was analyzed without transferring the water to a separate vial, and the other set of blank samples was analyzed after transferring 1 mL of water to a separate vial containing 2 mL Type I water, following the same procedure as the samples containing SMZ. The two sets of blank samples allowed determination of volatilization losses during the shaking/centrifugation processes, and during the transfer of supernatant to a vial for analysis.

Field Test of a Prototype SMZ Treatment System

The field treatment system consisted of a fiberglass column designed for use in ion exchange systems with SMZ substituted for the ion exchange resin. The column design dispersed the influent stream at the top of the SMZ and collected the effluent via a perforated plate and tube at the bottom. The column dimensions are given in Table 2. The system was filled to the top with 87.1 kg of 14-40 mesh SMZ.

The field column was connected to the second separation tank at the Crystal Solutions facility on a 102-mm diameter valve located about 610 mm from the bottom of the tank. Flow through the SMZ system was driven by approximately 4.5 m of produced water head in the tank. A flowmeter was installed at the influent end of the column, and sampling valves were installed at the influent and effluent ends.

Influent and effluent water samples were collected using 10-mL gastight syringes and stored in 10-mL glass headspace vials sealed with Teflon-faced butyl septa for later analysis via gas chromatography. A portable photoionization detector (MiniRAE 2000 PID, RAE Systems, Sunnyvale, CA) was used to estimate total concentrations of volatiles in water and air during produced water treatment and SMZ regeneration. Air samples were collected during regeneration by affixing Tygon® tubing to the effluent end of the column and filling 10-mL glass headspace vials with the effluent gas stream until all the original air in the vial had been displaced. Each vial was quickly closed and sealed with a Teflon-faced butyl septum.

Produced water was passed through the SMZ system for about 46 hours. The flow rate began at 85 L/hr (1.6 PV/hr), increased to 108 L/hr (2.1 PV/hr), then dropped to

66 L/hr (1.3 PV/hr) at the end of the run. This drop in flow rate was caused by clogging of the SMZ pores inside the column by particles in the unfiltered water.

Regeneration was performed in the field by attaching a portable air compressor to the influent port on the column. Air-sparging was performed for 8.5 hours at air flow rates between 85 and 100 L/min (1.6 to 1.9 PV/min). Following regeneration, another sorption cycle was performed by passing produced water through the system for an additional 47 hours. The flow rate ranged from 91 L/hr (1.7 PV/hr) at the beginning of the run to 62 L/hr (1.2 PV/hr) at the end.

Analytical Methods

Aqueous BTEX concentrations from the laboratory column and batch experiments were measured using a Hewlett-Packard (HP) Model 7694 headspace sampler attached to a HP Model 5890A gas chromatograph (GC) with a 10-m, 0.53-mm I.D. HP-5 capillary column and flame ionization detector. The carrier gas (He) had a flow rate of 35 mL/min and the split gas (He) flow rate was 28 mL/min. No makeup gas was utilized. The analyses were performed isothermally at 55°C, with an injector temperature of 210°C and detector temperature of 240°C. The GC was calibrated during each run with five BTEX standards of varying concentrations over a linear response range from 0.5 mg/L to 40 mg/L. p-xylene and m-xylene were not resolved by this method and were treated as a single compound. For headspace analysis, a 3-mL aqueous sample was sealed in a 10-mL headspace vial fitted with a Teflon-faced butyl septum. The headspace sampler run conditions were as follows: Oven temperature 70°C, loop temperature 75°C, transfer line temperature 75°C, equilibration time 1.0 min,

pressurization time 1.0 min, loop fill time 1.0 min, loop equilibration time 0.5 min, injection time 0.09 min.

The BTEX concentrations in gas samples from both lab and field air-sparging were analyzed by direct injection into the HP 5890A GC. Calibration standards in Milli-Q water were prepared in 10-mL headspace vials fitted with Teflon face butyl septum. Based on the Henry's constants and the known aqueous concentration, the BTEX mass removed from the headspace and injected into the GC was calculated. All GC operating conditions were the same as above, with the split flow increased to 63 mL/min.

Aqueous BTEX concentrations in samples from the field columns were measured using a Tekmar 7000 headspace sampler attached to a HP Model 5890 gas chromatograph with a 30-m, 0.53-mm I.D. Restek capillary column (RTX-624) and flame ionization detector. The carrier gas (He) had a flow rate of 36 mL/min and nitrogen was added as a makeup gas. No split flow was utilized. The analyses were performed with an initial temperature of 40°C for 1 minute, followed by a 20°C/min ramp to 85°C, and then increased at 0.5°C/min to a final temperature of 90°C held for 1 minute. The injector temperature was 250°C and detector temperature was 275°C. The GC was calibrated during each run with eleven BTEX standards of varying concentrations over a linear response range up to 1.5 mg/L of each BTEX compound. p-xylene and m-xylene were not resolved by this method and were treated as a single compound. For headspace analysis, a 50- μ L sample was diluted with 5 mL of Milli-Q water and sealed in a 22-mL headspace vial fitted with a Teflon-faced butyl septum. The headspace sampler run conditions were as follows: Oven temperature 80°C, loop temperature 170°C, transfer line temperature 170°C, equilibration time 15.0 min, mixing

time 10.0 min, pressurization time 1.0 min, pressure equilibration time 0.25 min, loop fill time 1.0 min, loop equilibration time 0.25 min, injection time 1.0 min.

RESULTS AND DISCUSSION

BTEX Sorption/Regeneration in Laboratory Columns

The tritium BTCs for the columns were well described by the simple 1-dimensional advection-dispersion equation:

$$R \frac{\partial C^*}{\partial p} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (2)$$

where:

$$C^* = \frac{C}{C_0} \quad (3)$$

$$P = \frac{vL}{D} \quad (4)$$

$$R = 1 + \left(\frac{\rho}{\theta} \right) K_d \quad (5)$$

$$p = \frac{vt}{L} \quad (6)$$

$$X = \frac{x}{L} \quad (7)$$

and C is the effluent solute concentration (M/L^3), C_0 is the influent solute concentration (M/L^3), C^* is the dimensionless solute concentration, D is the dispersion coefficient (L^2/T), v is the pore-water velocity (L/T), x is the distance (L), L is the column length (L), p is dimensionless time (pore volumes), ρ is bulk density (M/L^3), θ is volumetric water

content, K_d is the linear equilibrium sorption constant (L^3/M), P is the Peclet number, and R is the retardation factor.

Equation 2 was fitted to the observed tritium data using the nonlinear, least-squares optimization program CXTFIT 2.1 under flux-type boundary conditions (Toride et al. 1999). The pore-water velocity v was treated as a fixed value and R and D were fitted. All four columns yielded similar tritium BTCs with symmetrical shapes and R values in the range 0.955 to 1.13. The BTC for column 10A is shown in Figure 1. A dip in C^* was observed at about 2 PV for all columns, corresponding to the time at which flow through the columns was interrupted to change the influent from tritiated to non-tritiated brine. When flow was stopped, a pressure drop throughout the system likely allowed the tritiated brine in effluent end of the column to mix with lower-tritium brine residing in the column end-fitting.

Figure 2 shows the results of BTEX breakthrough on virgin SMZ in column 1. The equilibrium one-dimensional advection-dispersion equation (Eq. 2) did not adequately fit the observed data, so sorption of BTEX in the column experiments was analyzed with a bicontinuum model.

The bicontinuum model can be used to describe both physical and chemical nonequilibrium. Because the tritium BTCs did not exhibit early breakthrough or significant tailing, physical nonequilibrium was likely not significant and the processes causing nonequilibrium behavior in the BTEX BTCs are probably related to sorption nonequilibrium (Brusseau and Rao 1989). The mechanisms behind slow sorption are not fully understood, but it is often attributed to diffusion control (Pignatello and Xing 1996). We assume slow sorption involves diffusion of BTEX within the hydrophobic region

created by the surfactant molecules on the surface of SMZ. Under the first-order mass transfer model described by Brusseau et al. (1991), sorption occurs in two regions characterized by either instantaneous or rate-limited sorption:

$$S_1 = FK_d C \quad (8)$$

$$\frac{dS_2}{dt} = k_f S_1 - k_r S_2 \quad (9)$$

where S_1 is the sorbed concentration (M/M) in the instantaneous sorption region, S_2 is the sorbed concentration (M/M) in the rate-limited sorption region, F is the fraction of instantaneous sorption sites, t is time, and k_f and k_r are forward and reverse first-order rate constants (1/T), respectively.

The 1-dimensional advective-dispersive transport equation accounting for kinetically limited sorption and assuming steady-state water flow and a homogeneous porous medium, leads to the following equations (Brusseau et al. 1991):

$$\frac{\partial C^*}{\partial p} + (\beta R - 1) \frac{\partial C^*}{\partial p} + (1 - \beta) R \frac{\partial S^*}{\partial p} = (1/P) \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (10)$$

$$(1 - \beta) R \frac{\partial S^*}{\partial p} = \omega (C^* - S^*) \quad (11)$$

where:

$$S^* = \frac{S_2}{(1 - F)} K_d \quad (12)$$

$$\beta = \frac{\left[1 + F \left(\frac{\rho}{\theta} \right) K_d \right]}{R} \quad (13)$$

$$\omega = \frac{k_2 (1 - \beta) R L}{v} \quad (14)$$

S^* is the dimensionless sorbed concentration in the rate-limited domain, ω is the Damkohler number, the ratio of characteristic sorption time to hydrodynamic residence time.

The solution to Eqs. 10 and 11 requires estimation of four parameters (P , R , ω , and β). The value of P was determined from the tritium BTCs using Eq. 4. The value for R was determined from Eq. 5 by estimating K_d directly from the BTEX breakthrough curves, using the areas between the influent and effluent BTEX concentrations to determine S ($S=S_1+S_2$). The parameter S was then related to K_d by Eq. 8 assuming equilibrium had been reached and $F=1$. Benzene and toluene had reached equilibrium and the actual value of C was used in Eq. 8 for these compounds. For ethylbenzene and the xylenes, which had not reached equilibrium by the end of each sorption cycle, we used the average of the final values of C and C_0 as a measure of C . The other two sorption parameters, ω and β , were optimized by fitting Eq. 10 to the experimental data with CXTFIT 2.1.

As shown in Figure 2, benzene breakthrough occurs first because of its high solubility in water and low octanol-water partition coefficient K_{ow} (Table 1), while the other compounds elute in order of increasing K_{ow} . The BTCs of ethylbenzene and xylenes are similar due to their similar K_{ow} values (Table 1). Benzene begins to elute from the column after approximately 8 PV of produced water have been injected, while the xylenes and ethylbenzene do not rise above initial effluent concentrations until after 50 PV of water have been injected.

Reproducibility between the BTCs for replicate columns was good. Figures 3a and 3b show the BTCs for benzene and p-&m-xylene during the first and fifth sorption cycles in duplicate columns.

Figures 4a and 4b show the breakthrough of benzene and p-&m-xylene, respectively, in Column 10A over 10 sorption/regeneration cycles. The BTCs for each BTEX compound changed little over these 10 cycles, indicating little reduction in the sorption capacity of SMZ upon repeated saturation and air-stripping. In fact, the BTC during the first injection shows the earliest breakthrough (least sorption and retardation) for each compound. The removal efficiency may have increased because of the retention of low volatility components in produced water during regeneration which could create an additional sorption medium for the partitioning of BTEX (Jaynes and Vance 1996). During these 10 cycles, approximately 4500 PV of water passed through each column.

With repeated sorption cycles, backpressures increased in each column. This was investigated after completion of the ten sorption/regeneration cycles by examining virgin SMZ and SMZ from Columns 10A/10B and 5A/5B with a scanning electron microscope (SEM). The SEM results showed that the SMZ particles were breaking apart, creating finer particles which reduced column permeability and increased backpressure. Many particles from Columns 10A/10B were 10% of the size of the virgin SMZ grains. The cause of the particle breakdown is not understood and could be either mechanical or chemical in origin. With no significant reduction in sorption capacity after 10 sorption/regeneration cycles, the breakdown of SMZ particles and subsequent increase in column backpressure may play the largest role in determining the lifetime of SMZ in a produced-water treatment system.

Table 3 shows the K_d values calculated for each BTEX compound in Columns 10A and 10B. The K_d values determined by the tenth sorption cycle were not considered because sorption was not completed during this cycle due to high column backpressures. Using a regression coefficient significance test (Edwards 1984), the K_d values for benzene and toluene showed no statistically significant trends throughout the first nine sorption/regeneration cycles, while there was a decreasing trend in K_d for ethylbenzene and xylenes. The average decrease in K_d for ethylbenzene and the xylenes was approximately 2.7 L/kg per sorption cycle in Column 10a and 7.2 L/kg per sorption cycle in Column 10b. T-tests showed that the mean K_d values for each BTEX compound were statistically equivalent (95% confidence level) between replicate columns 10A and 10B throughout the first nine sorption cycles.

The mass of BTEX removed from Column 10A by air-sparging after the first injection of BTEX is shown in Figure 5. The compounds with the highest aqueous solubility were the most readily removed. Air-sparging effectively stripped approximately 100% of the benzene from the columns, 90% of the toluene, and 75% of the lowest solubility BTEX compounds (only p-&m-xylene shown). Air-sparging results throughout the remaining nine regeneration cycles showed similar patterns as in Figure 5. Duplicate columns showed comparable sparging results.

Sorption Characteristics of Virgin and Regenerated SMZ

The batch sorption study performed on virgin SMZ (no prior BTEX exposure), SMZ that had experienced 5 sorption/regeneration cycles, and SMZ that had undergone 10 sorption/regeneration cycles confirmed that the SMZ had not lost any significant

sorption capacity for BTEX after 5 and 10 cycles. Sorption data for each SMZ batch were well-described by the linear sorption model (Eq. 8 with $F = 1$), with all $R^2 \geq 0.77$ and most $R^2 \geq 0.92$. The K_{ds} for each BTEX compound on virgin and exposed SMZ were statistically indistinguishable. The means and standard deviations of K_d for each BTEX compound are shown in Table 3. These batch sorption results are consistent with our column results showing SMZ does not lose sorption capacity for BTEX over 10 sorption/regeneration cycles (> 4500 PV of exposure to produced water). Table 3 shows that K_d values determined from batch experiments were, however, significantly lower than K_d values determined from column experiments. Results from other studies have shown disagreement in K_d between batch and column experiments. Several different reasons for the differences have been hypothesized, including immobile water in the column (MacIntyre et al. 1991), failure to reach sorption equilibrium in batch experiments (Streck et al. 1995), destruction of particles while shaking (Schweich et al. 1983), reduction in column particle spacing (Celorie et al. 1989), and inappropriate application of an equilibrium sorption model (Altfelder et al. 2001). The reasons for the discrepancies between batch and column K_{ds} in our experiments are unclear.

Field Test of a Prototype SMZ Treatment System

The breakthrough of benzene and toluene on virgin SMZ in the field column is shown in Figure 6. The effluent concentration of ethylbenzene and xylenes remained near zero after 80 PV (not shown in Figure 6). Figure 6 includes a comparison of the BTC for benzene and toluene on virgin SMZ in the laboratory columns. The field column exhibited later breakthrough and stronger retention of BTEX than the laboratory

column. Although the two systems are scaled, the likely reason for this is that the 14-40 mesh SMZ used in the field column has a higher surfactant loading (180 mmol HDTMA/kg zeolite) than the 80-100 mesh SMZ used in the laboratory columns (157 mmol HDTMA/kg zeolite).

Figure 7 shows the BTCs for benzene and toluene on virgin and regenerated SMZ in the field column. The effluent concentrations for ethylbenzene and the xylenes were again very low and are not shown in Figure 7. The initial effluent concentrations of toluene (and ethylbenzene and xylenes) were above zero, which was higher than during any stage of the initial sorption experiment. These relatively high effluent concentrations were likely due to incomplete regeneration of the SMZ. During regeneration, air flow was in the same direction as water flow in the column, pushing the BTEX toward the effluent end of the column. The compounds with higher K_{ow} were likely not completely removed during sparging, but instead were concentrated toward the effluent end of the column. When produced water was reintroduced to the column for the second sorption cycle, these higher concentrations eluted. By reversing flow during air-sparging as in the laboratory columns, this problem could be eliminated as BTEX would be concentrated toward the influent end of the column if sparging was incomplete. Aside from the high concentration of toluene initially, Figure 7 shows that the regenerated SMZ was even more effective at BTEX removal than the virgin SMZ, similar to the trend observed in the laboratory columns.

CONCLUSIONS

Surfactant-modified zeolite successfully removed BTEX from produced water with components eluting from columns in order of decreasing water solubility/increasing K_{ow} . The SMZ was regenerated by air-sparging and continued to remove BTEX from produced water. After 10 cycles of sorption/regeneration with a total of > 4500 pore volumes of water treated, SMZ showed no significant reduction in sorption capacity. In fact, the earliest breakthrough (least sorption) of BTEX compounds was observed on virgin zeolite. Batch experiments provided further evidence that surfactant-modified zeolite did not lose any significant capacity for BTEX sorption after 10 sorption/regeneration cycles. However, as the column experiments progressed, the SMZ particles were breaking down into finer grained particles which reduced the column permeability and increased the backpressure.

Field-scale tests supported laboratory column test data, showing even greater sorption of BTEX from produced water than was observed in the laboratory columns. The results of this study along with the low cost of SMZ suggest that surfactant-modified zeolite may have use in cost-effective produced-water treatment systems.

ACKNOWLEDGEMENTS

This work was funded by the U.S. Department of Energy (DE-AC26-99BC15221). We thank Mr. John Boysen of B.C. Technologies (Laramie, WY) for the use of their facilities. Guifang Tan of the University of Texas-Austin prepared the SMZ, performed

the gas chromatography analyses of the field-test samples, and provided assistance with the field test. Sarah Loughney of New Mexico Tech assisted with laboratory column experiments. Jim Smith of Los Alamos National Laboratory assisted with SEM analysis. Alana Fuierer of New Mexico Tech aided with the setup of the laboratory column system.

APPENDIX I. REFERENCES.

- Altfelder, S., Streck, T., Maraqa, M. A., and Voice, T. C. (2001). "Nonequilibrium sorption of dimethylphthalate--compatibility of batch and column techniques." *Soil Sci. Soc. Am. J.*, 65(1) 102-111.
- American Petroleum Institute. (2000). "Overview of exploration and production waste volumes and waste management practices in the United States." Washington, DC.
- Bessa, E., Sant'Anna, G. L. Jr., and Dezotti, M. (2001). "Photocatalytic/H₂O₂ treatment of oil field produced waters." *Applied Catalysis B: Environmental*, 29(2) 125-134.
- Bowman, R. S., Haggerty, G. M., Huddleston, R. G., Neel, D., and Flynn, M. M. (1995). "Sorption of nonpolar organic compounds, inorganic cations, and inorganic oxyanions by surfactant-modified zeolites." *Surfactant-enhanced subsurface remediation*, D. A. Sabatini, R. C. Knox, and J. H. Harwell, eds., American Chemical Society, Washington, DC, 54-64.
- Bowman, R. S., Li, Z., Roy, S. J., Burt, T., Johnson, T. L., and Johnson, R. L. (2001). "Pilot test of a surfactant-modified zeolite permeable barrier for groundwater remediation." *Physicochemical groundwater remediation*, S. A. Burns, ed., Kluwer Academic/Plenum Publishers, New York, 161-185.
- Bowman, R. S., Sullivan, E. J., and Li, Z. (2000). "Uptake of cations, anions, and nonpolar organic molecules by surfactant-modified clinoptilolite-rich tuff." *Natural zeolites for the third millennium*, C. Colella and F. A. Mumpton, eds., De Frede Editore, Napoli, Italy, 287-297.
- Boysen, D. B., Boysen, J.E., and Boysen, J.A. (2002) "Creative strategies for produced water disposal in the Rocky Mountain region." *Proc., 9th Annu. International Petroleum Environmental Conference*, Integrated Petroleum Environmental Consortium, Albuquerque, NM.

- Brusseau, M. L., Jessup, R.E., and Rao, P.S.C. (1991). "Nonequilibrium sorption of organic chemicals: elucidation of rate-limiting processes." *Environ. Sci. Technol.*, 25(1), 134-142.
- Brusseau, M. L., and Rao, P.S.C. (1989). "Sorption nonideality during organic contaminant transport in porous media." *CRC Crit. Rev. Environ. Control*, 19(1), 33-99.
- Celorie, J. A., Woods, S. L., Vinson, T. S., and Istok, J. D. (1989). "A comparison of sorption equilibrium distribution coefficients using batch and centrifugation methods." *J. Environ. Qual.*, 18(3) 307-313.
- Code of Federal Regulations*. (2002). Title 40, Pt. 100-129 and 400-503.
- Code of Federal Regulations*. (2002). Title 40, Pt. 141-148.
- Code of Federal Regulations*. (2002). Title 40, Pt. 260-279.
- Code of Federal Regulations*. (2002). Title 40, Pt. 261, 4.
- Code of Federal Regulations*. (2002). Title 40, Pt. 435.
- Crittenden, J. C., Berrigan, J.K, and Hand, D.W. (1986). "Design of rapid small-scale adsorption tests for a constant diffusivity." *Journal WPCF*, 58(4), 312-319.
- Crittenden, J. C., Reddy, P. S., Arora, H., Trynoski, J., Hand, D. W., Perram, D. L., and Summers, R. S. (1991). "Predicting GAC performance with rapid small-scale column tests." *Journal AWWA*, 83(1), 77-87.
- Edwards, A. L. (1984). *An Introduction to Linear Regression and Correlation*, 2nd Ed. W. H. Freeman and Co., New York.
- Gallup, D. L., Isacoff, E. G., and Smith, D. N. III. (1996). "Use of Amborsorb® carbonaceous adsorbent for removal of BTEX compounds from oil-field produced water." *Environ. Progress*, 15(3) 197-203.
- Haggerty, G. M., and Bowman, R. S. (1994). "Sorption of chromate and other inorganic anions by organo-zeolite." *Environ. Sci. Technol.*, 28(3), 452-458.
- Huddleston, R. (1990). "Surface-altered hydrophobic zeolites as sorbents for hazardous organic compounds." MS Thesis, New Mexico Institute of Mining and Technology, Socorro, NM.

- Janks, J.S., and Cadena, F. (1992). "Investigations into the use of modified zeolites for removing benzene, toluene, and xylene from saline produced water." *Produced Water*, J.P. Ray and F.R. Engelhart, eds., Plenum Press, New York, 473-487.
- Jaynes, W. F., and Vance, G. F. (1996). "BTEX sorption by organo-clays: cosorptive enhancement and equivalence of interlayer complexes." *Soil Sci. Soc. Am. J.*, 60(6), 1742-1749.
- Lawrence, A. W., Miller, J.A., Miller, D.L., and Hayes, T.D. (1995). "Regional assessment of produced water treatment and disposal practices and research needs." Proc., *SPE/EPA Exploration and Production Environmental Conference*, Society of Petroleum Engineers, Houston, Texas, 373-392.
- Li, Z., and Bowman, R. S. (2001). "Regeneration of surfactant-modified zeolite after saturation with chromate and perchloroethylene." *Wat. Res.*, 35(1), 322-326.
- MacIntyre, W. G., Stauffer, T. B., and Antworth, C. P. (1991) "A comparison of sorption coefficients determined by batch, column, and box methods on a low organic carbon aquifer material." *Ground Water*, 29(6) 908-913.
- Mackay, D., Shiu, W. Y., and Ma, K. C. (1992). "Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals," Lewis Publishers, Chelsea, MI.
- Neel, D., and Bowman, R. S. (1992). "Sorption of organics to surface-altered zeolites." *Proc.*, 36th Annual New Mexico Water Conference, New Mexico Water Resources Research Institute, Las Cruces, NM, 57-61.
- Neff, J. M., and Sauer, Jr, T.C. (1996). "Aromatic hydrocarbons in produced water." *Produced Water 2: Environmental Issues and Mitigation Technologies*, M. Reed and S. Johnsen, eds., Plenum Press, New York, 163-175.
- Negri, M. C., and Hinchman, R. C. (1997). "Biotreatment of produced waters for volume reduction and contaminant removal." *Proc.*, 4th Annual International Petroleum Environmental Conference: Issues and Solutions, Production and Refining. Integrated Petroleum Environmental Consortium, San Antonio, Texas.
- Otto, G. H., and Arnold, K. E. (1996). "U.S. produced water discharge regulations have tough limits." *Oil and Gas J.*, 94(29) 54-61.
- Pignatello, J. J., and Xing, B. (1996). "Mechanisms of slow sorption of organic chemicals to natural particles." *Environ. Sci. Technol.*, 30(1), 1-11.
- Santos, S. M., and Wiesner, M. R. (1997). "Ultrafiltration of water generated in oil and gas production." *Water Environ. Res.*, 69(6) 1120-1127.

- Schweich, D., Sardin, M., and Guedent, J. P. (1983). "Measurement of a cation exchange isotherm from elution curves obtained in a soil column: Preliminary results." *Soil Sci. Soc. Am. J.*, 47(1) 32-37.
- Stephenson, M. T. (1992). "A survey of produced water studies." *Produced Water*, J. P. Ray and F. R. Engelhart, eds., Plenum Press, New York, 1-11.
- Streck, T., Poletika, N. N., Jury, W. A., and Farmer, W. J. (1995). "Description of simazine transport with rate-limited, two-stage, linear and nonlinear sorption." *Water Resour. Res.*, 31(4) 811-822.
- Tao, F. T., Curtice, S., Hobbs, R. D., Sides, J. L., Wieser, J. D., Dyke, C. A., Tuohey, D., and Pilger, P. F. (1993). "Reverse osmosis process successfully converts oil field brine into freshwater." *Oil and Gas J.*, 91(38) 88-91.
- Thoma, G. J., Bowen, M. L., and Hollensworth, D. (1999). "Dissolved air precipitation/solvent sublimation for oil-field produced water treatment." *Separation and Purification Tech.*, 16(2) 101-107.
- Toride, N., Leij, F.J., and van Genuchten, M.T. (1999). "The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, version 2.1." Research Report No. 137, U.S. Salinity Laboratory, USDA, ARS, Riverside, CA.
- U.S. EPA. (2000). "Profile of the oil and gas extraction industry." *EPA/310-R-99-006*, Washington, DC.

APPENDIX II. NOTATION

The following symbols are used in this paper:

C = liquid-phase concentration (M/L^3);

C^* = dimensionless solute concentration;

D = dispersion coefficient (L^2/T);

d = particle diameter (mm);

F = fraction of instantaneous sorption sites (dimensionless);

K_d = equilibrium sorption constant (L^3/M);

K_{ow} = octanol-water partition coefficient (dimensionless);
 k = first-order rate constant (dimensionless);
 L = column length (L);
 P = Peclet number (dimensionless);
 p = dimensionless time (pore volumes);
 R = retardation factor (dimensionless);
 S = sorbed concentration (M/M);
 S^* = dimensionless sorbed concentration in rate-limited sorption region;
 t = time (T);
 v = pore-water velocity (L/T);
 x = distance (L);
 θ = volumetric water content (dimensionless);
 ρ = bulk density (M/L³);
 ω = Damkohler number (dimensionless);

SUBSCRIPTS

f = forward;
 r = reverse;
 0 = influent concentration;
 1 = instantaneous sorption region;
 2 = rate-limited sorption region;

Table 1. Analysis of produced water used in laboratory experiments.

Analysis¹	Amount (mg/L)	log K_{ow}²	Solubility (mg/L) 25°C²
Benzene	15.8	2.13	1850
Toluene	36.7	2.69	470
Ethylbenzene	1.4	3.15	140
p-xylene & m-xylene	6.4	3.15, 3.20	200, 173
o-xylene	3.4	3.15	204
<hr/>			
Cl ⁻	4,400		
HCO ₃ ⁻	3,120		
F ⁻	57		
Br ⁻	22		
SO ₄ ⁻	13		
Na ⁺	4,100		
K ⁺	44		
Ca ²⁺	30		
Mg ²⁺	6.4		
Total Dissolved Solids	11,792		
Total Organic Carbon	1,000		

¹ Inorganic anions determined by ion chromatography. Inorganic cations determined by flame atomic absorption. TDS determined by addition of anions and cations. TOC determined by combustion. BTEX compounds determined as described in Methods section.

² Mackay, D., et al. (1992).

Table 2. Dimensions and operating parameters for field and laboratory columns.

	Field Column	Laboratory Column
Column radius (mm)	178	4.0
Column length (mm)	1220	100
Bed volume (L)	102 ¹	5.03 * 10 ⁻³
Ave. SMZ particle size (mm)	0.90	0.164
Volumetric flow rate (L/min)	1.67	2.92 * 10 ⁻³
EBCT (min)	52.3	1.74

¹ Bed volume (total volume of grains and voids) is less than volume calculated from column dimensions because of internal column plumbing.

Table 3. Mean K_d values determined by laboratory column and batch experiments. Standard deviations are shown in parentheses. “n” indicates the number of measurements for each mean.

Compound	Mean Column K_d (L/kg) (n=18)	Mean Batch K_d (L/kg) (n=6)
Benzene	18.3 (4.70)	6.71 (0.57)
Toluene	37.5 (5.27)	15.6 (1.32)
Ethylbenzene	88.0 (10.9)	33.5 (2.87)
p-&m-xylene	95.0 (11.3)	36.5 (2.61)
o-xylene	87.7 (11.5)	39.4 (3.37)

FIGURE CAPTIONS

- Figure 1. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 10A.
- Figure 2. Observed and fitted BTEX breakthrough curves on virgin SMZ (Column 10A). The lines were based on the best fit of eq. 10 to the observed data, as described in the text.
- Figure 3. BTCs of benzene and p-&m-xylene in Columns 10A and 10B for (a) virgin SMZ and (b) during the fifth sorption cycle.
- Figure 4. (a) Benzene BTCs for Column 10A over 10 sorption/regeneration cycles and (b) p-&m-xylene BTCs for Column 10A over 10 sorption/regeneration cycles.
- Figure 5. Cumulative masses of benzene, toluene, and p-&m-xylene removed relative to masses sorbed during first regeneration in Column 10A.
- Figure 6. Comparison of benzene and toluene BTC for virgin SMZ in lab column 10A and field column.
- Figure 7. Benzene and toluene breakthrough on virgin and regenerated SMZ in field column.

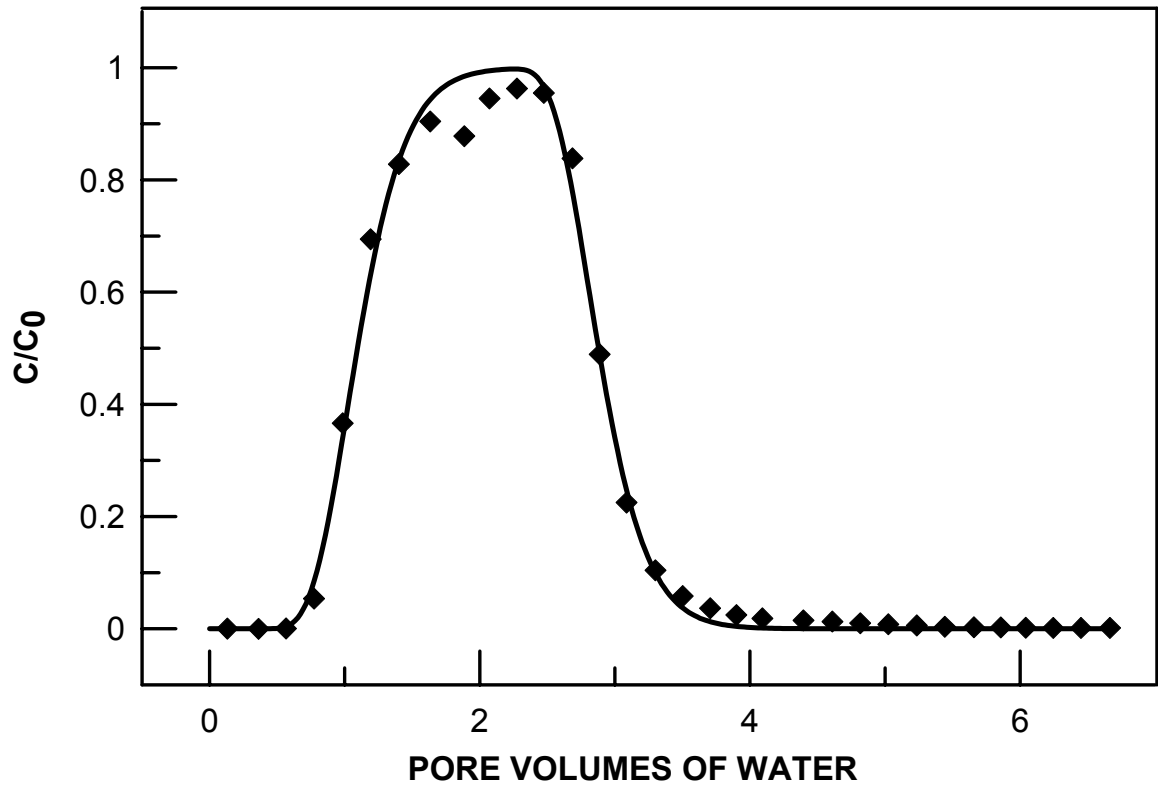


Figure 1. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 10A.

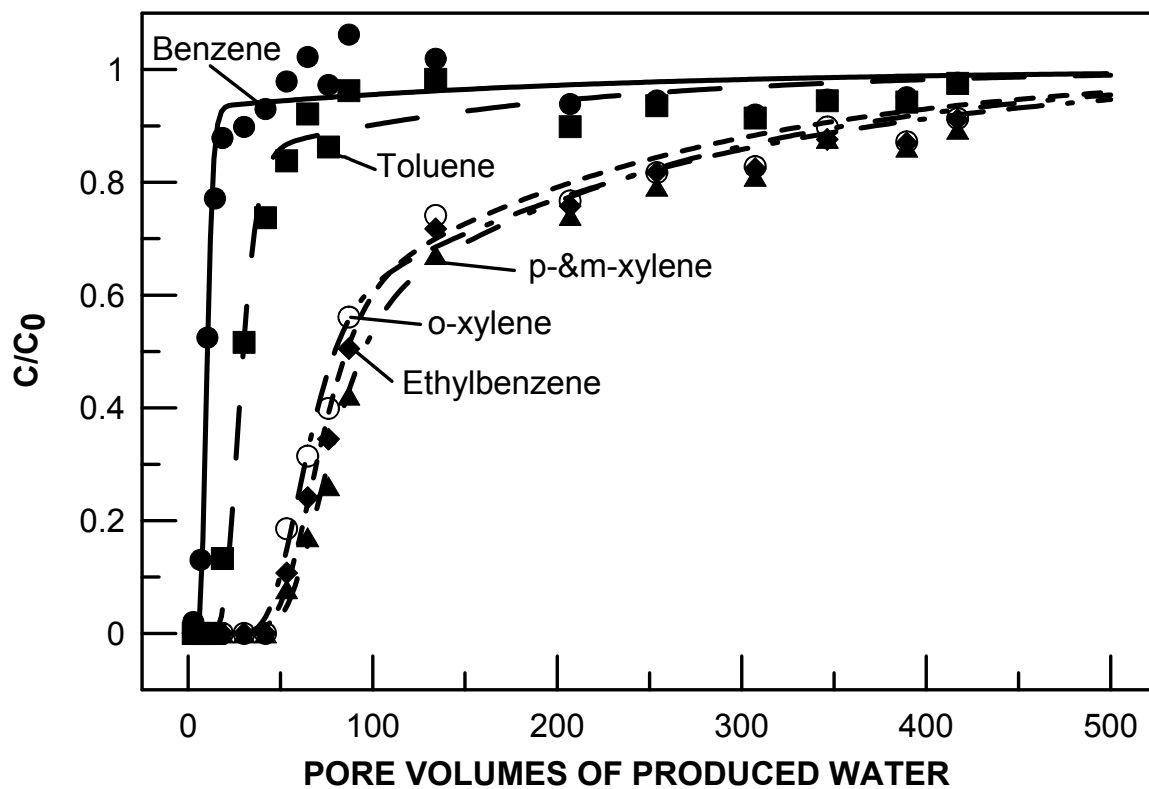


Figure 2. Observed and fitted BTEX breakthrough curves on virgin SMZ (Column 10A). The lines were based on the best fit of eq. 10 to the observed data, as described in the text.

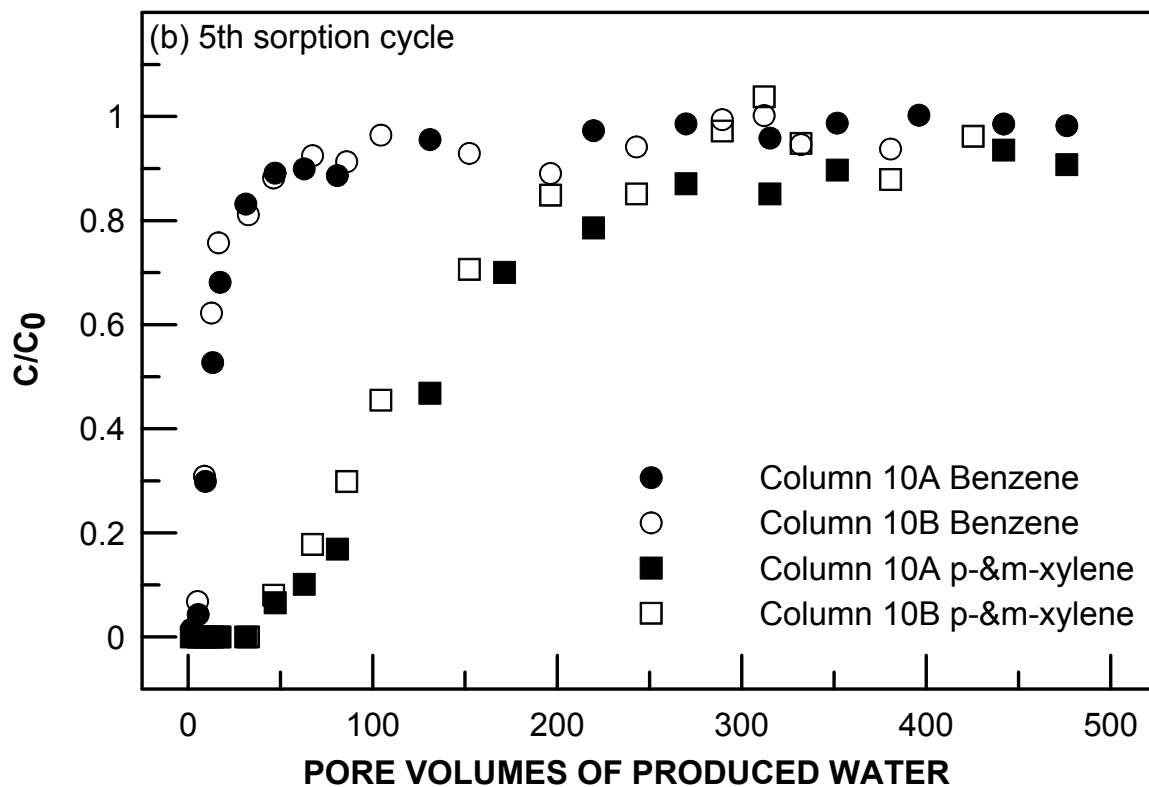
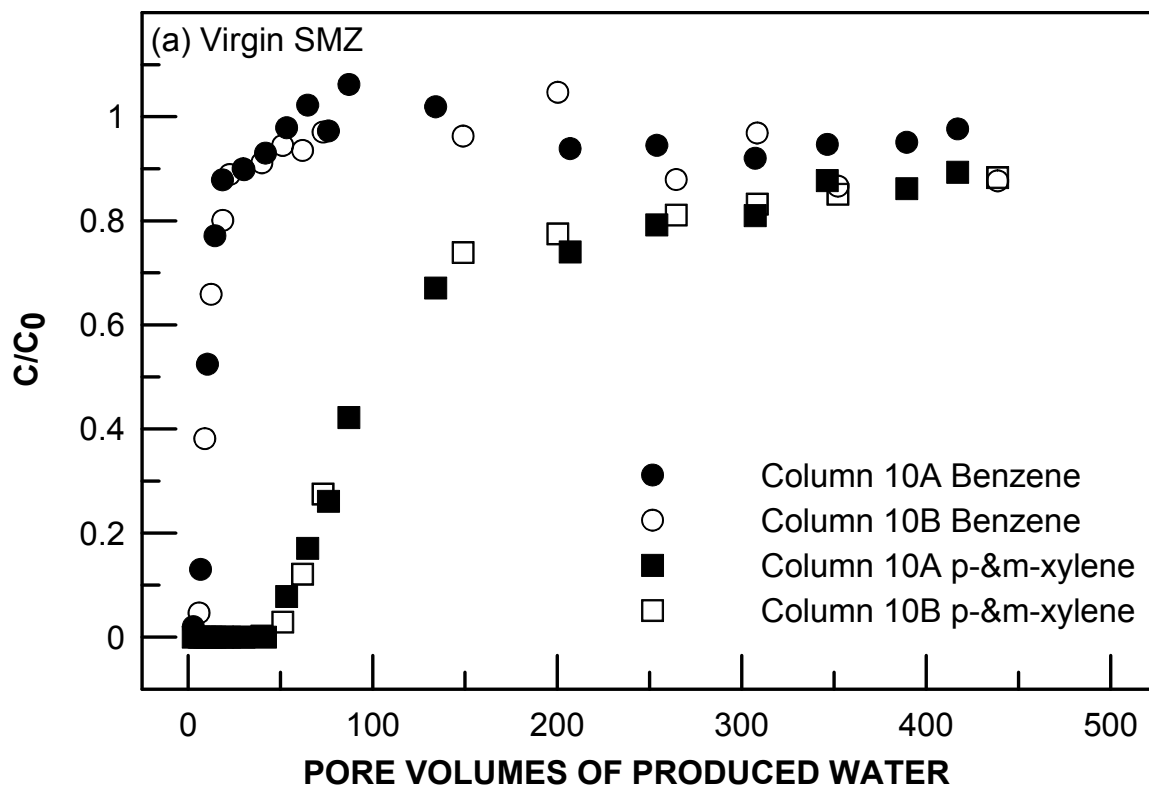


Figure 3. BTCs of benzene and p-&m-xylene in Columns 10A and 10B for (a) virgin SMZ and (b) during the fifth sorption cycle in columns 10A and 10B.

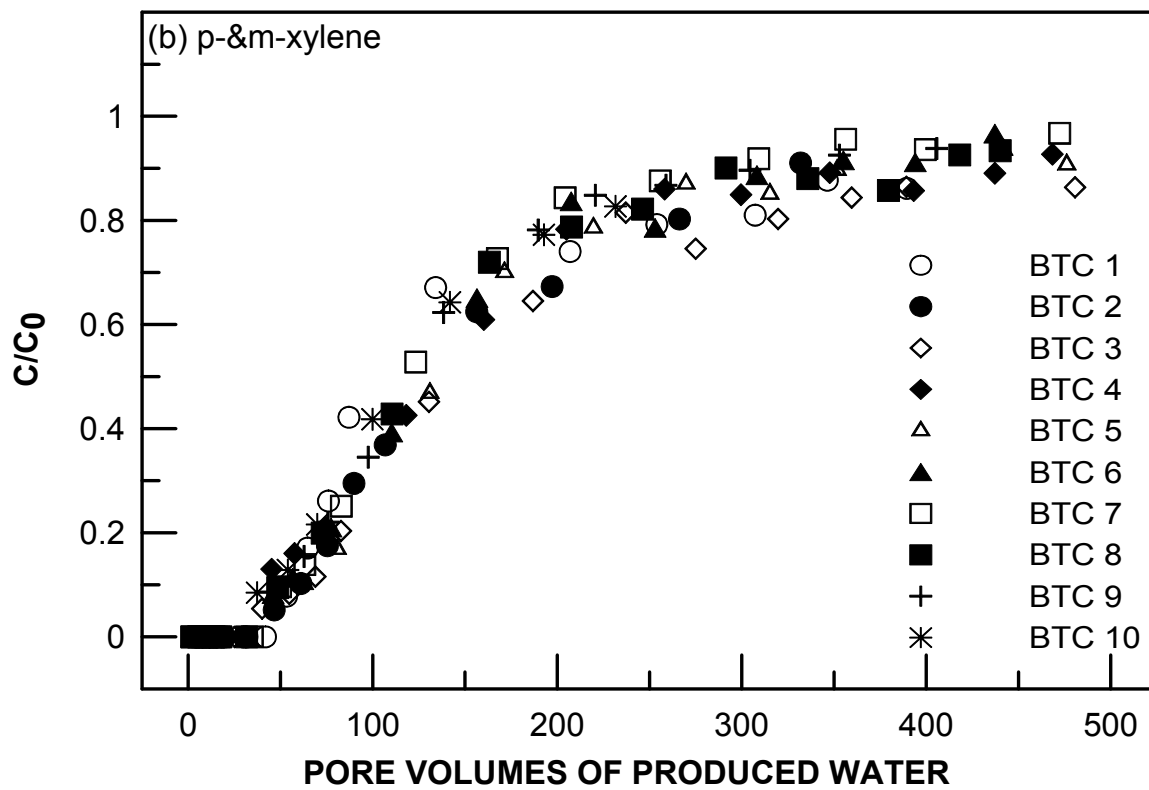
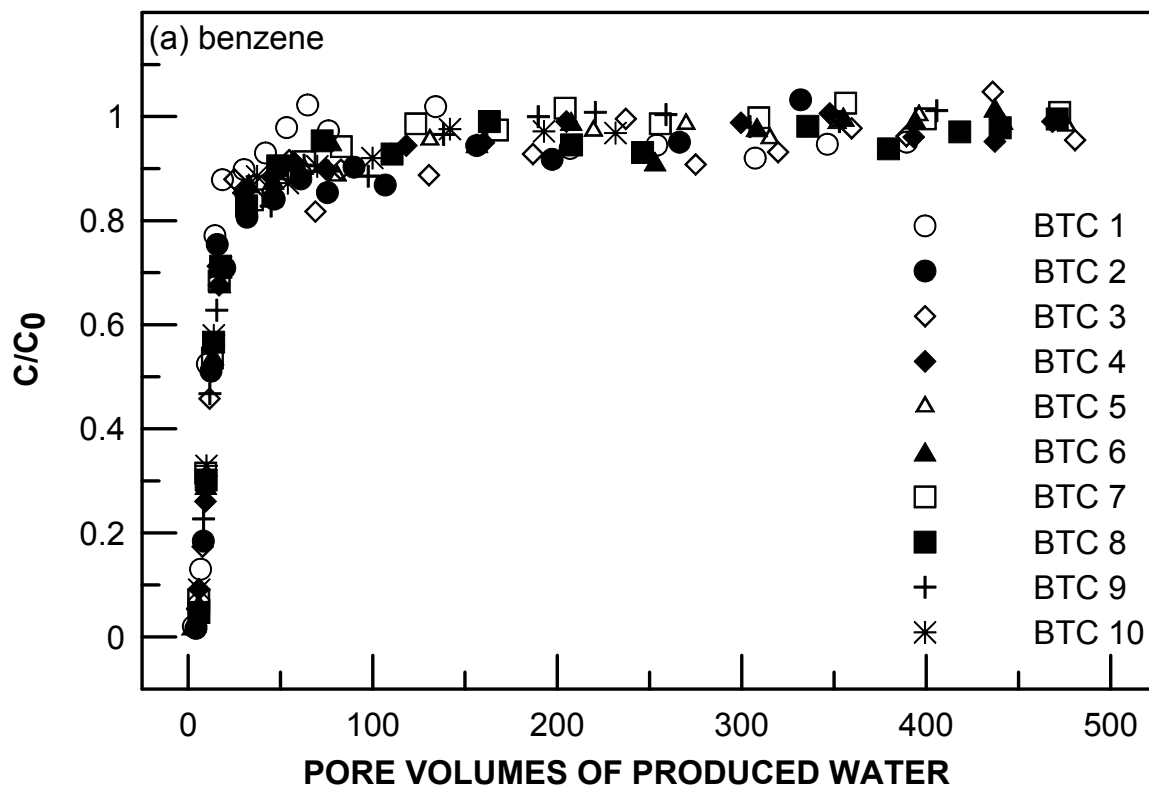


Figure 4. (a) Benzene BTCs for Column 10A over 10 sorption/regeneration cycles and (b) p-&m-xylene BTCs for Column 10A over 10 sorption/regeneration cycles.

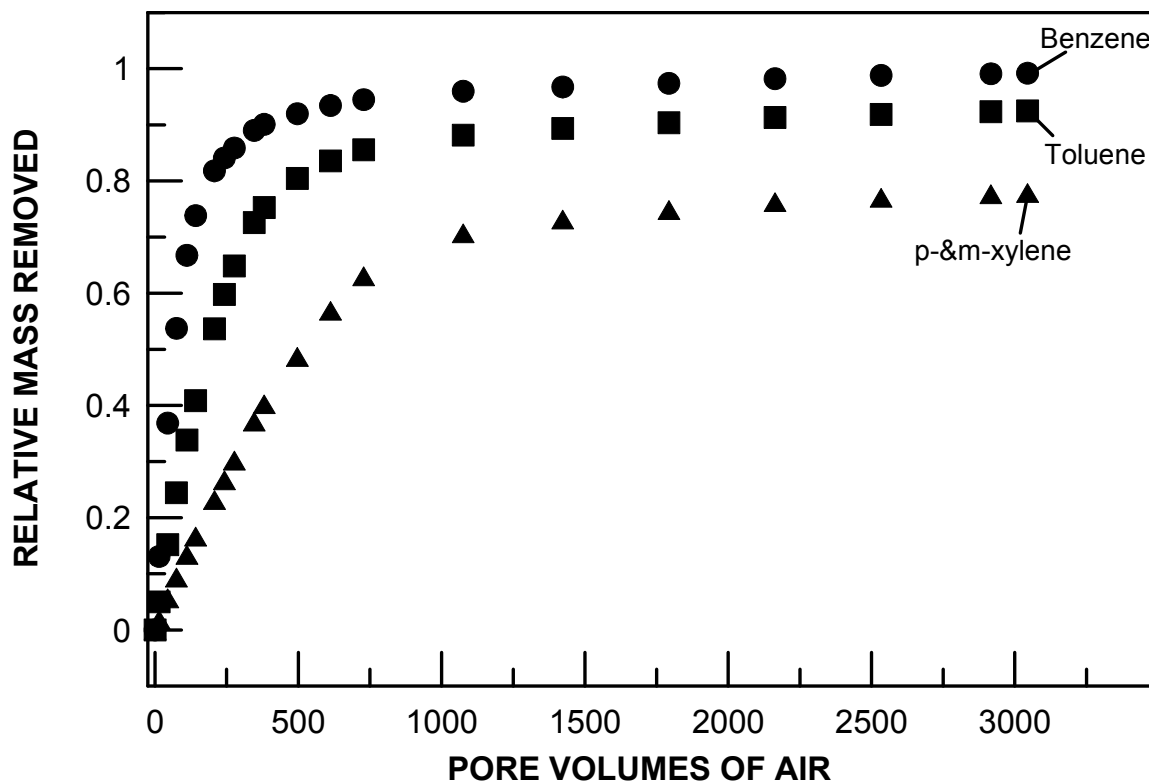


Figure 5. Cumulative masses of benzene, toluene, and p-&m-xylene removed relative to masses sorbed during first regeneration in Column 10A.

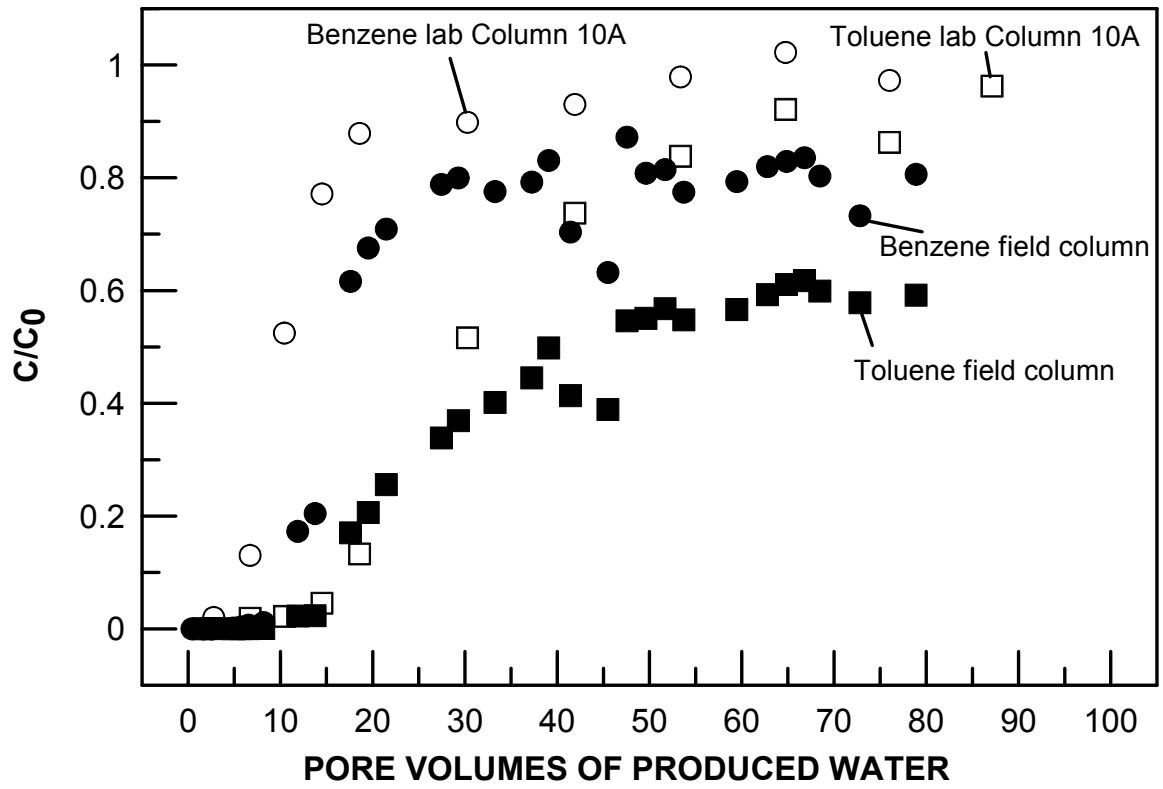


Figure 6. Comparison of benzene and toluene BTC for virgin SMZ in lab column 10A and field column.

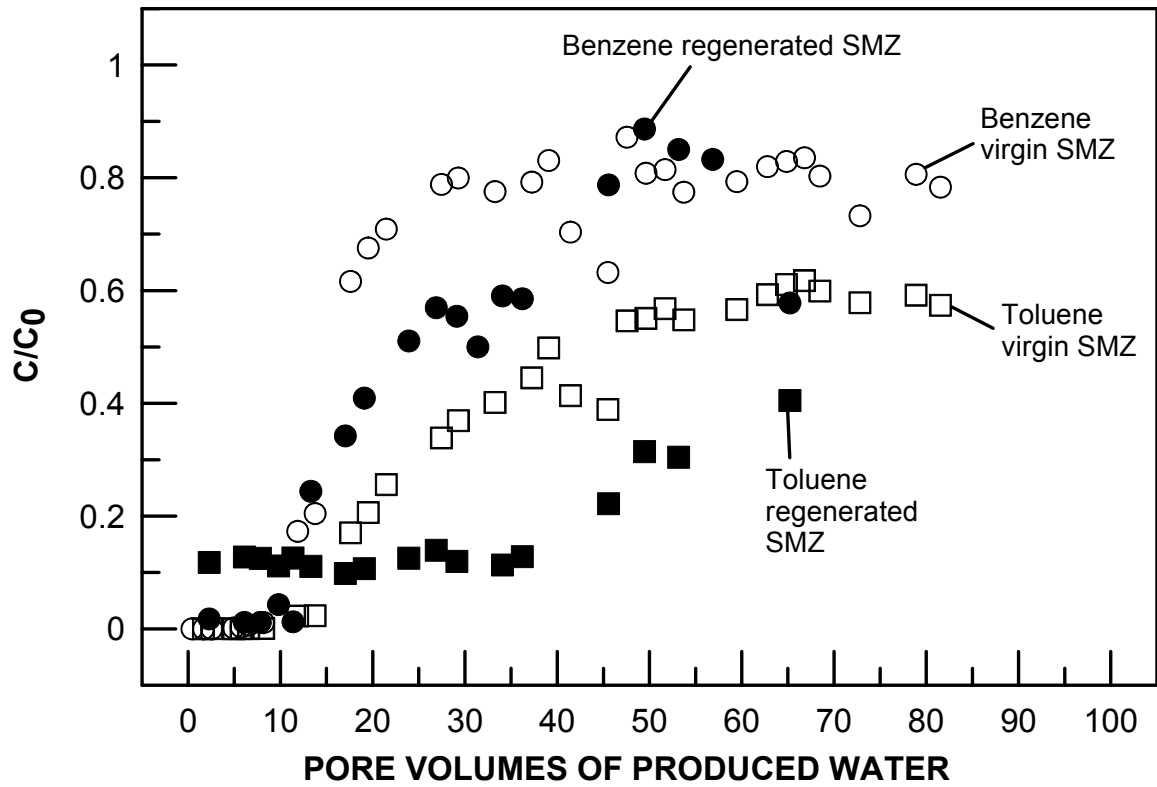


Figure 7. Benzene and toluene breakthrough on virgin and regenerated SMZ in field column.

INTRODUCTION TO APPENDICES

The following appendices provide descriptions of preliminary and unreported studies, further information on methods used, and the experimental data collected throughout the thesis project.

Appendix A contains a description of the preliminary laboratory column experiments and results.

Appendix B contains the tabulated results of the tritium tracer tests in the laboratory columns. This includes the tracer tests described in the manuscript and also unreported tracer tests performed following the completion of the sorption/regeneration cycle tests. A discussion of SMZ loss from the columns is provided. The discussion continues with the results of the investigation of the causes of high backpressures in the column during the late sorption cycles by comparison of virgin SMZ, SMZ from Columns 5A/5B, and SMZ from Columns 10A/10B using a scanning electron microscope.

Appendix C provides the BTC data for the 10 sorption/regeneration cycles for Columns 10A and 10B.

Appendix D presents the data from the batch experiments.

Appendix E contains a more detailed explanation of the field treatment system and the full results from these experiments.

Appendix F presents information about organic compounds present in this produced water in addition to BTEX. A discussion of known semi-volatiles in the produced water is provided, along with a discussion of potential unquantified compounds

and how the presence of other organic compounds may affect the use of SMZ in a treatment system.

Appendix G contains a discussion outlining applicable produced waters for use in an SMZ treatment system.

APPENDIX A. PRELIMINARY LAB COLUMN DISCUSSION AND DATA

In the early stages of this project, a study was conducted using a column not discussed in the preceding manuscript. The column dimensions were scaled from a proposed field treatment design using the rapid small-scale column test method as described in the manuscript. The proposed field setup and scaling parameters are described by Tan (2002). The field system was then re-designed after experiments with this column had been performed, leading to re-scaling for the columns described in Chapter 2. The column (Ace Glass) had a 0.8 cm diameter, 25 cm length, and was packed with 80-100 mesh SMZ. The end-fittings and sampling port fixtures were identical to the setup described in the manuscript, although no syringe-tip filters were required as no iron oxide precipitates were present in the influent water. Once packed, the column was purged with CO₂ gas and saturated from the bottom with purified water (Type I). The water was injected using the same syringe pump setup described in the manuscript. No tritium tracer test was completed for this column, and no duplicate columns were operated. The influent BTEX solution was prepared by combining BTEX and Type I water in a collapsible 10-L (12" x 19") Tedlar® Gas Sampling Bag (Alltech) with a barbed on/off valve. The BTEX concentration was 16 mg/L for each of the six compounds. The BTEX solution was injected into the saturated column at a flow rate of 1.19 cm/min. Influent and effluent samples were collected in the same manner as described previously.

Once the effluent BTEX concentrations were approximately equal to influent concentrations, flow was terminated and the column was then regenerated by air-sparging

in the same manner as the method described in previously. In this study, however, the air flowrate was 2.3 mL/min. Following regeneration, a second sorption/regeneration cycle was completed with this column. The results of these two sorption/regeneration cycles follow. Appendix Table A-1 contains the BTC data on virgin SMZ in the preliminary column. Appendix Tables A-2 through A-6 contain the air-sparging data for this column. The BTC data on regenerated SMZ in the preliminary lab column are presented in Appendix Table A-7.

Results from these column experiments are further discussed by Ranck et al. (2002).

APPENDIX A REFERENCE

Ranck, J.M., J.L. Weeber, G. Tan, E.J. Sullivan, L.E. Katz, and R.S. Bowman. (2002)

“Removal of BTEX from produced waters using surfactant-modified zeolite.”

Proc., 9th Annu. International Petroleum Environmental Conference, Integrated

Petroleum Environmental Consortium, Albuquerque, NM.

Appendix Table A-1. BTEX BTC data on virgin SMZ in preliminary lab column.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	0.0	0.000	0.000	0.000	0.000	0.000
2	3.1	0.000	0.001	0.001	0.002	0.000
3	5.1	0.000	0.001	0.001	0.001	0.000
4	6.8	0.007	0.001	0.001	0.001	0.000
5	8.6	0.161	0.001	0.001	0.001	0.000
6	10.4	0.578	0.001	0.001	0.001	0.000
7	12.8	0.763	0.001	0.001	0.001	0.000
8	14.3	0.744	0.000	0.001	0.001	0.000
9	16.1	0.858	0.003	0.001	0.000	0.000
10	18.0	0.583	0.017	0.001	0.001	0.000
11	19.9	0.876	0.060	0.001	0.001	0.000
12	21.7	0.850	0.129	0.001	0.001	0.000
13	23.7	0.837	0.206	0.001	0.001	0.000
14	25.5	1.281	0.465	0.001	0.001	0.000
15	27.4	0.948	0.421	0.001	0.001	0.000
16	29.4	0.961	0.507	0.001	0.001	0.000
17	31.3	0.959	0.568	0.001	0.001	0.000
18	33.3	0.958	0.617	0.001	0.001	0.000
19	35.2	0.957	0.647	0.001	0.001	0.000
20	38.6	1.006	0.725	0.002	0.001	0.000
21	40.7	0.907	0.659	0.002	0.001	0.002
22	42.7	1.033	0.783	0.003	0.001	0.005
23	44.7	0.795	0.601	0.001	0.001	0.007
24	46.6	1.081	0.851	0.016	0.003	0.019
25	48.7	1.002	0.772	0.022	0.004	0.026
26	51.3	1.094	0.867	0.043	0.009	0.048
27	54.5	0.969	0.745	0.053	0.013	0.061
28	57.9	0.998	0.794	0.088	0.027	0.098
29	60.5	1.006	0.814	0.113	0.070	0.125
30	63.1	0.889	0.670	0.114	0.045	0.125
31	65.9	0.897	0.691	0.136	0.061	0.149
32	67.2	0.872	0.665	0.137	0.063	0.153
33	72.5	0.962	0.800	0.215	0.115	0.229
34	75.8	no data	no data	no data	no data	no data
35	79.8	no data	no data	no data	no data	no data
36	83.5	no data	no data	no data	no data	no data
37	87.5	no data	no data	no data	no data	no data
38	91.3	no data	no data	no data	no data	no data
39	95.5	no data	no data	no data	no data	no data

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
40	100.2	no data	no data	no data	no data	no data
41	103.7	no data	no data	no data	no data	no data
42	110.9	no data	no data	no data	no data	no data
43	115.4	no data	no data	no data	no data	no data
44	118.2	no data	no data	no data	no data	no data
45	121.5	no data	no data	no data	no data	no data
46	125.0	no data	no data	no data	no data	no data
47	132.5	no data	no data	no data	no data	no data
48	138.4	0.965	0.886	0.609	0.551	0.607
49	144.6	0.873	0.767	0.553	0.495	0.545
50	149.0	0.937	0.850	0.628	0.580	0.636
51	155.3	0.951	0.863	0.663	0.618	0.665
52	162.1	0.891	0.807	0.630	0.585	0.632
53	173.8	0.877	0.810	0.636	0.599	0.630
54	187.2	0.958	0.940	0.800	0.774	0.772
55	196.2	1.023	1.021	0.904	0.867	0.877
56	199.2	0.901	0.867	0.757	0.736	0.736
57	204.7	0.864	0.798	0.695	0.686	0.694
58	210.5	0.877	0.845	0.760	0.738	0.740
59	226.3	0.896	0.886	0.843	0.821	0.822
60	231.2	0.956	0.925	0.901	0.892	0.876
61	239.1	1.038	1.035	1.016	1.038	0.990
62	244.8	0.981	0.955	0.959	0.968	0.944
63	248.3	0.969	0.955	0.968	0.981	0.946
64	252.6	1.170	1.273	1.327	1.365	1.293
65	265.9	1.028	1.087	1.138	1.180	1.109
66	276.4	0.987	1.023	1.069	1.122	1.060
67	281.0	0.928	0.900	0.902	0.937	0.877
68	284.3	0.985	1.010	1.058	1.104	1.065
69	294.6	0.933	0.923	0.962	0.986	0.936
70	308.9	1.167	1.182	1.304	1.333	1.238
71	313.2	0.916	0.895	0.995	1.014	0.957

Appendix Table A-2. Benzene removal data

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
Start	0.0	0.000	0.000
1	1.5	2.322	0.025
2	9.9	1.977	0.148
3	18.4	1.540	0.244
4	27.7	2.280	0.401
5	35.5	1.840	0.506
6	46.1	2.550	0.705
7	53.7	1.610	0.795
8	63.1	1.370	0.890
9	72.0	1.297	0.975
10	81.6	1.364	1.071
11	90.2	1.681	1.178
12	99.0	1.351	1.265
13	108.4	1.198	1.349
14	120.9	0.542	1.398
15	129.2	0.443	1.425
16	138.0	0.328	1.447
17	147.4	0.370	1.472
18	156.8	0.259	1.490
19	166.2	0.180	1.503
20	175.8	0.135	1.512
21	185.2	0.102	1.519
22	194.7	0.101	1.526
23	205.7	0.078	1.533
24	216.8	0.058	1.537
25	226.4	0.045	1.540
26	252.2	0.051	1.550
27	261.8	0.041	1.553
28	272.5	0.037	1.556
29	281.2	0.032	1.558
30	292.0	0.023	1.560
31	300.7	0.018	1.561
32	310.4	0.023	1.563
33	320.1	0.014	1.564
34	329.9	0.022	1.565

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
35	339.6	0.011	1.566
36	349.3	0.009	1.567
37	358.9	0.008	1.567
38	371.7	0.008	1.568
39	384.5	0.007	1.569
40	396.1	0.005	1.569
41	410.2	0.006	1.570
42	459.2	0.002	1.570
43	476.1	0.005	1.571
44	490.8	0.003	1.571
45	503.7	0.003	1.572
46	518.6	0.000	1.572
47	533.1	0.000	1.572
48	547.3	0.000	1.572
49	561.6	0.000	1.572
50	591.1	0.000	1.572
51	605.8	0.000	1.572
52	635.6	0.000	1.572
53	665.3	0.000	1.572
54	692.6	0.000	1.572
55	721.9	0.000	1.572
56	889.7	0.000	1.572
57	1231.2	0.000	1.572
59	1252.9	0.000	1.572
60	1508.6	0.000	1.572
61	1609.8	0.000	1.572
62	2047.8	0.000	1.572
63	2270.6	0.000	1.572

Appendix Table A-3. Toluene removal data

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
Start	0.0	0.000	0.000
1	1.5	3.066	0.033
2	9.9	2.685	0.200
3	18.4	2.094	0.330
4	27.7	3.154	0.548
5	35.5	2.494	0.690
6	46.1	3.476	0.962
7	53.7	2.260	1.088
8	63.1	1.991	1.225
9	72.0	1.930	1.353
10	81.6	2.130	1.502
11	90.2	2.856	1.684
12	99.0	2.683	1.857
13	108.4	2.933	2.061
14	120.9	1.909	2.236
15	129.2	2.026	2.360
16	138.0	1.960	2.488
17	147.4	2.861	2.684
18	156.8	2.489	2.856
19	166.2	2.331	3.017
20	175.8	2.203	3.173
21	185.2	2.028	3.314
22	194.7	2.423	3.483
23	205.7	2.279	3.668
24	216.8	2.023	3.832
25	226.4	1.896	3.967
26	252.2	1.919	4.331
27	261.8	1.547	4.441
28	272.5	1.358	4.548
29	281.2	1.159	4.622
30	292.0	0.996	4.701
31	300.7	0.880	4.757
32	310.4	0.783	4.813
33	320.1	0.717	4.865
34	329.9	0.611	4.908

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
35	339.6	0.530	4.946
36	349.3	0.417	4.976
37	358.9	0.403	5.004
38	371.7	0.331	5.036
39	384.5	0.290	5.063
40	396.1	0.239	5.083
41	410.2	0.227	5.107
42	459.2	0.135	5.156
43	476.1	0.159	5.176
44	490.8	0.111	5.188
45	503.7	0.097	5.197
46	518.6	0.080	5.205
47	533.1	0.074	5.213
48	547.3	0.069	5.220
49	561.6	0.073	5.228
50	591.1	0.044	5.238
51	605.8	0.040	5.242
52	635.6	0.043	5.251
53	665.3	0.025	5.257
54	692.6	0.024	5.262
55	721.9	0.022	5.267
56	889.7	0.014	5.284
57	1231.2	0.000	5.284
59	1252.9	0.000	5.284
60	1508.6	0.000	5.284
61	1609.8	0.000	5.284
62	2047.8	0.000	5.284
63	2270.6	0.000	5.284

Appendix Table A-4. Ethylbenzene removal data

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
Start	0.0	0.000	0.000
1	1.5	2.403	0.026
2	9.9	2.293	0.168
3	18.4	1.811	0.281
4	27.7	2.773	0.473
5	35.5	2.118	0.593
6	46.1	2.958	0.824
7	53.7	1.998	0.936
8	63.1	1.762	1.058
9	72.0	1.687	1.169
10	81.6	1.879	1.301
11	90.2	2.564	1.464
12	99.0	2.338	1.615
13	108.4	2.559	1.793
14	120.9	1.672	1.946
15	129.2	1.836	2.058
16	138.0	1.781	2.174
17	147.4	2.629	2.355
18	156.8	2.194	2.507
19	166.2	2.068	2.650
20	175.8	2.003	2.791
21	185.2	1.842	2.919
22	194.7	2.278	3.078
23	205.7	2.191	3.256
24	216.8	2.034	3.421
25	226.4	2.122	3.572
26	252.2	2.625	4.070
27	261.8	2.400	4.240
28	272.5	2.258	4.418
29	281.2	2.251	4.563
30	292.0	2.116	4.729
31	300.7	2.096	4.865
32	310.4	2.134	5.017
33	320.1	2.315	5.183
34	329.9	2.232	5.342

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
35	339.6	2.262	5.503
36	349.3	1.935	5.642
37	358.9	2.045	5.787
38	371.7	1.973	5.972
39	384.5	2.081	6.169
40	396.1	1.949	6.335
41	410.2	2.036	6.547
42	459.2	1.980	7.260
43	476.1	2.167	7.531
44	490.8	1.892	7.735
45	503.7	1.915	7.917
46	518.6	1.674	8.101
47	533.1	1.690	8.281
48	547.3	1.655	8.453
49	561.6	1.826	8.646
50	591.1	1.120	8.889
51	605.8	0.991	8.997
52	635.6	0.958	9.206
53	665.3	0.498	9.315
54	692.6	0.433	9.402
55	721.9	0.365	9.481
56	889.7	0.151	9.667
57	1231.2	0.087	9.885
59	1252.9	0.017	9.885
60	1508.6	0.006	9.887
61	1609.8	0.006	9.899
62	2047.8	0.000	9.903
63	2270.6	0.000	9.903

Appendix Table A-5. p-&m-xylene removal data

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
Start	0.0	0.000	0.000
1	1.5	2.340	0.025
2	9.9	2.486	0.180
3	18.4	2.002	0.304
4	27.7	3.018	0.513
5	35.5	2.343	0.646
6	46.1	3.222	0.898
7	53.7	2.202	1.021
8	63.1	1.959	1.156
9	72.0	1.880	1.280
10	81.6	2.089	1.427
11	90.2	2.807	1.606
12	99.0	2.565	1.771
13	108.4	2.779	1.964
14	120.9	1.865	2.135
15	129.2	2.046	2.260
16	138.0	1.987	2.390
17	147.4	2.861	2.586
18	156.8	2.405	2.753
19	166.2	2.286	2.910
20	175.8	2.216	3.067
21	185.2	2.028	3.208
22	194.7	2.505	3.383
23	205.7	2.419	3.579
24	216.8	2.248	3.762
25	226.4	2.344	3.928
26	252.2	2.881	4.475
27	261.8	2.659	4.664
28	272.5	2.487	4.859
29	281.2	2.489	5.019
30	292.0	2.338	5.204
31	300.7	2.303	5.352
32	310.4	2.353	5.520
33	320.1	2.564	5.704
34	329.9	2.481	5.881

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
35	339.6	2.516	6.060
36	349.3	2.150	6.214
37	358.9	2.275	6.375
38	371.7	2.216	6.584
39	384.5	2.327	6.804
40	396.1	2.225	6.993
41	410.2	2.318	7.235
42	459.2	2.429	8.109
43	476.1	2.677	8.444
44	490.8	2.508	8.715
45	503.7	2.621	8.963
46	518.6	2.432	9.230
47	533.1	2.591	9.506
48	547.3	2.700	9.788
49	561.6	3.124	10.118
50	591.1	2.237	10.603
51	605.8	2.120	10.833
52	635.6	2.234	11.322
53	665.3	1.283	11.603
54	692.6	1.147	11.834
55	721.9	0.959	12.040
56	889.7	0.343	12.464
57	1231.2	0.176	12.905
59	1252.9	0.042	12.905
60	1508.6	0.015	12.912
61	1609.8	0.015	12.940
62	2047.8	0.006	12.952
63	2270.6	0.000	12.972

Appendix Table A-6. o-xylene removal data

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
Start	0.0	0.000	0.000
1	1.5	1.652	0.018
2	9.9	1.664	0.121
3	18.4	1.319	0.203
4	27.7	2.010	0.342
5	35.5	1.544	0.430
6	46.1	2.117	0.595
7	53.7	1.458	0.677
8	63.1	1.298	0.767
9	72.0	1.233	0.848
10	81.6	1.376	0.944
11	90.2	1.865	1.063
12	99.0	1.669	1.171
13	108.4	1.809	1.297
14	120.9	1.216	1.408
15	129.2	1.343	1.490
16	138.0	1.308	1.575
17	147.4	1.892	1.705
18	156.8	1.558	1.813
19	166.2	1.471	1.915
20	175.8	1.437	2.016
21	185.2	1.304	2.107
22	194.7	1.624	2.220
23	205.7	1.559	2.347
24	216.8	1.451	2.465
25	226.4	1.530	2.573
26	252.2	1.878	2.930
27	261.8	1.750	3.054
28	272.5	1.590	3.179
29	281.2	1.632	3.284
30	292.0	1.504	3.403
31	300.7	1.473	3.498
32	310.4	1.513	3.606
33	320.1	1.683	3.726
34	329.9	1.642	3.843

Sample	Pore Volumes	Concentration (mg/L)	Total Mass Removed (mg)
35	339.6	1.663	3.962
36	349.3	1.377	4.060
37	358.9	1.450	4.163
38	371.7	1.410	4.296
39	384.5	1.531	4.440
40	396.1	1.461	4.565
41	410.2	1.504	4.722
42	459.2	1.537	5.275
43	476.1	1.724	5.490
44	490.8	1.636	5.667
45	503.7	1.767	5.835
46	518.6	1.649	6.016
47	533.1	1.820	6.210
48	547.3	1.957	6.414
49	561.6	2.391	6.667
50	591.1	1.998	7.099
51	605.8	2.083	7.326
52	635.6	2.747	7.927
53	665.3	1.983	8.361
54	692.6	2.118	8.787
55	721.9	2.038	9.226
56	889.7	0.554	9.911
57	1231.2	0.200	10.413
59	1252.9	0.019	10.413
60	1508.6	0.006	10.416
61	1609.8	0.007	10.428
62	2047.8	0.000	10.433
63	2270.6	0.000	10.433

Appendix Table A-7. BTEX BTC data for preliminary lab column with regenerated SMZ.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.0	0.000	0.001	0.004	0.007	0.005
2	8.0	0.034	0.001	0.004	0.007	0.006
3	15.5	0.747	0.002	0.004	0.006	0.005
4	23.0	0.961	0.159	0.004	0.006	0.004
5	28.6	0.976	0.441	0.003	0.005	0.001
6	36.0	0.952	0.675	0.003	0.004	0.003
7	46.8	0.964	0.763	0.015	0.007	0.023
8	55.7	0.961	0.772	0.075	0.024	0.096
9	64.5	0.901	0.717	0.183	0.082	0.210
10	84.0	0.995	0.805	0.388	0.269	0.414
11	100.9	1.003	0.922	0.529	0.441	0.555
12	110.5	0.983	0.939	0.602	0.523	0.629
13	119.4	1.014	1.002	0.669	0.600	0.688
14	130.5	1.029	1.004	0.720	0.663	0.741
15	141.9	1.002	0.979	0.733	0.682	0.754
16	152.6	0.941	0.976	0.764	0.709	0.778
17	165.1	1.054	1.038	0.838	0.798	0.854
18	186.1	1.001	0.816	0.833	0.811	0.850
19	205.0	1.001	0.941	0.810	0.785	0.805
20	213.1	0.963	0.864	0.742	0.742	0.750
21	224.7	0.997	0.906	0.759	0.750	0.768
22	235.7	0.954	0.941	0.792	0.776	0.810
23	247.5	0.934	0.926	0.745	0.731	0.761
24	259.6	0.965	0.949	0.743	0.726	0.751
25	269.9	0.976	0.936	0.746	0.724	0.753
26	289.4	1.001	0.954	0.775	0.750	0.787
27	309.7	1.028	0.989	0.832	0.790	0.827
28	320.3	1.023	0.997	0.838	0.813	0.838
29	333.8	1.011	0.980	0.834	0.818	0.825
30	351.0	1.024	0.995	0.869	0.846	0.862
31	370.6	1.012	0.986	0.863	0.837	0.866
32	405.9	0.994	0.945	0.822	0.808	0.816

**APPENDIX B. COLUMN FLOW PROPERTIES, SMZ LOSS, AND SCANNING
ELECTRON MICROSCOPY INVESTIGATION OF SMZ PARTICLE
BREAKDOWN**

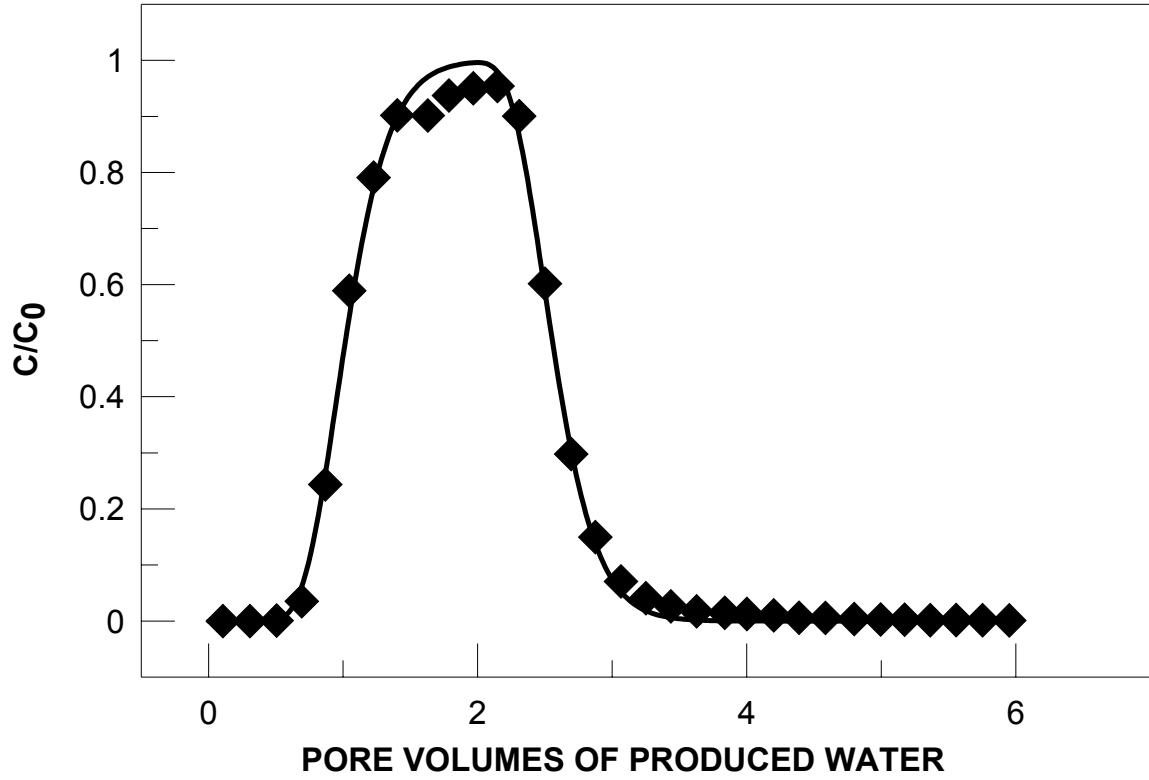
COLUMN FLOW PROPERTIES: TRITIUM TRACER TEST

As described in the manuscript, a tritium tracer test was performed in each column prior to the first sorption/regeneration cycle. The hydrodynamic properties of each column determined from this test are presented in Appendix Table B-1. The tritium BTCs on virgin SMZ for Columns 10B, 5A, and 5B are shown in Appendix Figures B-1, B-2, and B-3, along with the fitted BTC for each column (using Eq. 2 described in the manuscript). The tritium BTC for Column 10A is shown in the manuscript. The data obtained from the virgin SMZ tritium tests in all four columns and the CXTFIT 2.1 fitted data are shown in Appendix Table B-2.

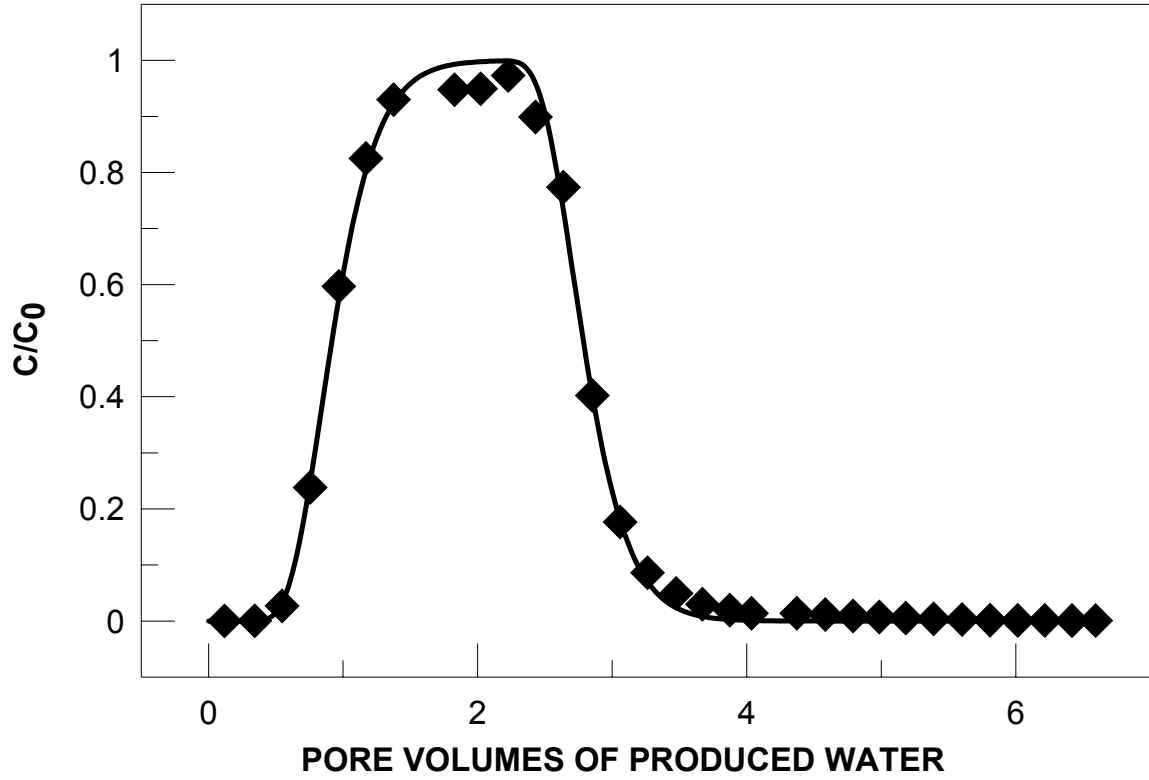
At the conclusion of the sorption/regeneration cycles, before the SMZ was removed from the columns for use in the batch sorption experiments, a second tritium tracer test was conducted in each column. Because of high backpressures in the columns, it was difficult to maintain a constant flow rate. The syringe pumps stalled occasionally throughout the experiment, but they were restarted immediately in an attempt to maintain a constant flow rate. The final hydrodynamic properties for each column are shown in Appendix Table B-3, and the data from the second tracer test and CXTFIT 2.1 fitted data are presented in Appendix Table B-4.

Appendix Table B-1. Hydrodynamic properties of laboratory columns before sorption cycles.

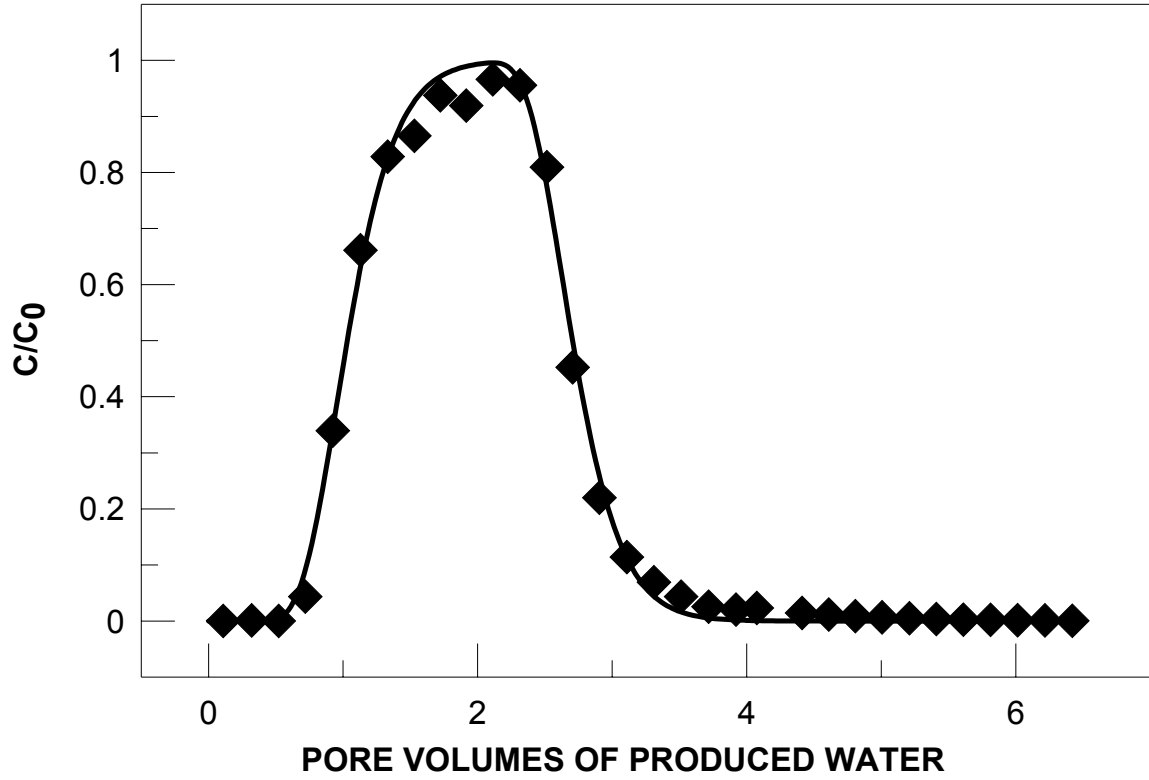
	Mass SMZ (g)	Pore Volume (mL)	<i>R</i>	<i>P</i>	θ	ρ (g/cm ³)
Column 10A	5.11	3.24	1.13	30.5	0.64	1.016
Column 10B	5.09	3.43	1.05	31.2	0.68	1.012
Column 5A	4.90	3.20	0.955	24.1	0.64	0.974
Column 5B	5.12	3.28	1.07	26.4	0.65	1.018



Appendix Figure B-1. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 10B.



Appendix Figure B-2. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 5A.



Appendix Figure B-3. Observed and fitted (Eq. 2) breakthrough curves for tritiated water in Column 5B.

Appendix Table B-2. Tritium breakthrough data for virgin SMZ.

Column 10A			Column 10B			Column 5A			Column 5B		
PV	Obs. C/C₀	Fit C/C₀	PV	Obs. C/C₀	Fit C/C₀	PV	Obs. C/C₀	Fit C/C₀	PV	Obs. C/C₀	Fit C/C₀
0.131	0.000	0.000	0.107	0.000	0.000	0.119	0.000	0.000	0.109	0.000	0.000
0.362	0.000	0.000	0.307	0.000	0.000	0.342	0.000	0.000	0.320	0.001	0.000
0.565	0.000	0.004	0.507	0.001	0.002	0.546	0.027	0.033	0.521	0.000	0.005
0.773	0.054	0.085	0.693	0.035	0.063	0.755	0.238	0.247	0.718	0.043	0.092
0.986	0.366	0.341	0.867	0.243	0.265	0.968	0.597	0.575	0.924	0.340	0.346
1.192	0.694	0.633	1.046	0.589	0.548	1.170	0.825	0.803	1.129	0.661	0.633
1.401	0.828	0.836	1.227	0.791	0.775	1.375	0.930	0.923	1.331	0.828	0.828
1.633	0.904	0.944	1.403	0.902	0.902	1.829	0.948	0.993	1.530	0.865	0.928
1.885	0.878	0.985	1.629	0.902	0.971	2.022	0.949	0.998	1.722	0.938	0.972
2.072	0.945	0.995	1.787	0.937	0.989	2.226	0.973	0.999	1.915	0.919	0.990
2.275	0.963	0.998	1.967	0.950	0.996	2.430	0.899	0.959	2.113	0.966	0.996
2.474	0.955	0.967	2.148	0.954	0.982	2.638	0.774	0.732	2.315	0.956	0.960
2.686	0.838	0.777	2.309	0.901	0.875	2.853	0.402	0.403	2.514	0.810	0.772
2.888	0.489	0.486	2.500	0.602	0.601	3.058	0.177	0.181	2.706	0.453	0.496
3.086	0.225	0.246	2.695	0.298	0.314	3.263	0.086	0.070	2.905	0.220	0.255
3.300	0.104	0.099	2.875	0.150	0.143	3.475	0.049	0.024	3.109	0.114	0.111
3.502	0.058	0.037	3.066	0.071	0.054	3.670	0.030	0.008	3.310	0.069	0.044
3.705	0.037	0.013	3.250	0.041	0.019	3.874	0.019	0.003	3.512	0.044	0.016
3.899	0.024	0.004	3.436	0.026	0.006	4.035	0.014	0.001	3.716	0.026	0.005
4.092	0.019	0.001	3.627	0.017	0.002	4.372	0.014	0.000	3.920	0.020	0.002
4.396	0.015	0.000	3.836	0.015	0.001	4.584	0.012	0.000	4.075	0.023	0.001
4.610	0.013	0.000	4.001	0.013	0.000	4.790	0.009	0.000	4.412	0.014	0.000
4.816	0.010	0.000	4.201	0.010	0.000	4.985	0.007	0.000	4.609	0.012	0.000
5.024	0.008	0.000	4.389	0.006	0.000	5.181	0.005	0.000	4.807	0.009	0.000
5.235	0.006	0.000	4.585	0.006	0.000	5.388	0.004	0.000	5.006	0.007	0.000
5.442	0.004	0.000	4.799	0.004	0.000	5.600	0.002	0.000	5.209	0.005	0.000
5.658	0.003	0.000	4.995	0.003	0.000	5.809	0.001	0.000	5.409	0.003	0.000
5.857	0.002	0.000	5.174	0.002	0.000	6.013	0.001	0.000	5.610	0.002	0.000
6.041	0.002	0.000	5.363	0.001	0.000	6.214	0.001	0.000	5.812	0.002	0.000
6.245	0.001	0.000	5.557	0.002	0.000	6.417	0.001	0.000	6.013	0.001	0.000
6.451	0.001	0.000	5.753	0.001	0.000	6.593	0.001	0.000	6.217	0.001	0.000
6.665	0.001	0.000	5.951	0.001	0.000				6.421	0.001	0.000

Appendix Table B-3. Hydrodynamic properties of laboratory columns after sorption cycles.

	Mass SMZ (g)	% SMZ Lost	<i>R</i>	<i>P</i>	θ	ρ (g/cm ³)
Column 10A	5.06	0.98	0.94	17.1	0.70	1.012
Column 10B	3.65	28.3	0.88	6.85	0.87	1.726
Column 5A	4.83	1.43	0.93	15.6	0.76	0.960
Column 5B	4.72	7.81	0.93	14.2	0.70	0.938

Appendix Table B-4. Tritium breakthrough data after sorption cycles.

Column 10A			Column 10B			Column 5A			Column 5B		
PV	Obs. C/C ₀	Fit C/C ₀	PV	Obs. C/C ₀	Fit C/C ₀	PV	Obs. C/C ₀	Fit C/C ₀	PV	Obs. C/C ₀	Fit C/C ₀
0.281	0.000	0.000	0.081	0.000	0.000	0.091	0.000	0.000	0.089	0.000	0.000
0.464	0.008	0.025	0.240	0.000	0.008	0.272	0.000	0.000	0.267	0.000	0.000
0.650	0.125	0.177	0.397	0.027	0.097	0.448	0.013	0.028	0.449	0.005	0.032
0.837	0.413	0.432	0.553	0.230	0.263	0.620	0.119	0.167	0.633	0.133	0.191
1.024	0.665	0.665	0.712	0.477	0.444	0.787	0.378	0.390	0.819	0.462	0.433
1.302	0.858	0.873	0.874	0.554	0.599	0.959	0.640	0.609	1.007	0.718	0.652
1.471	0.929	0.934	1.034	0.733	0.717	1.130	0.784	0.771	1.193	0.812	0.803
1.654	0.956	0.967	1.196	0.808	0.803	1.412	0.930	0.916	1.378	0.867	0.894
1.834	0.912	0.922	1.394	0.838	0.875	1.579	0.943	0.956	1.554	0.882	0.943
2.143	0.518	0.555	1.553	0.881	0.902	1.752	0.942	0.957	1.732	0.932	0.970
2.305	0.313	0.353	1.714	0.830	0.827	1.926	0.784	0.838	1.918	0.943	0.965
2.464	0.198	0.209	1.872	0.699	0.672	2.098	0.641	0.618	2.107	0.880	0.832
2.636	0.123	0.111	2.030	0.475	0.508	2.266	0.405	0.403	2.298	0.591	0.593
2.931	0.059	0.034	2.191	0.311	0.367	2.436	0.229	0.239	2.484	0.338	0.370
3.104	0.044	0.016	2.354	0.209	0.257	2.603	0.135	0.135	2.670	0.194	0.212
3.278	0.032	0.008	2.518	0.149	0.178	2.771	0.080	0.072	2.857	0.128	0.114
3.564	0.021	0.002	2.684	0.110	0.122	2.946	0.050	0.037	3.046	0.091	0.058
3.726	0.018	0.001	2.849	0.090	0.083	3.120	0.040	0.018	3.234	0.071	0.029
3.900	0.015	0.001	3.012	0.075	0.057	3.291	0.028	0.009	3.420	0.054	0.015
4.067	0.012	0.000	3.175	0.066	0.039	3.587	0.022	0.003	3.608	0.043	0.007
4.223	0.009	0.000	3.324	0.058	0.028	3.750	0.017	0.001	3.780	0.035	0.004
4.380	0.007	0.000	3.480	0.057	0.019	3.925	0.013	0.001	3.965	0.030	0.002
			3.654	0.053	0.013	4.101	0.011	0.000	4.161	0.026	0.001
			3.819	0.055	0.009	4.276	0.009	0.000	4.341	0.022	0.000
			3.982	0.046	0.006	4.450	0.007	0.000	4.525	0.020	0.000
			4.148	0.037	0.004	4.624	0.006	0.000	4.715	0.015	0.000
			4.308	0.026	0.003	4.800	0.003	0.000	4.910	0.011	0.000
			4.470	0.018	0.002	4.971	0.004	0.000	5.099	0.008	0.000
			4.636	0.014	0.001	5.147	0.003	0.000	5.288	0.006	0.000
			4.797	0.013	0.001	5.326	0.002	0.000	5.478	0.005	0.000
			4.959	0.011	0.001	5.500	0.002	0.000	5.664	0.006	0.000
			5.123	0.010	0.001	5.655	0.002	0.000	5.850	0.004	0.000

SMZ LOSS AND SMZ PARTICLE BREAKDOWN: SCANNING ELECTRON MICROSCOPY

With increasing sorption cycles, loss of SMZ from Columns 10B, 5A, and 5B was apparent. It is believed that the nylon mesh placed just inside the column end-fittings became dislodged, allowed SMZ to escape out the end-fittings. Some SMZ was observed in both influent and effluent tubing from these columns. As shown in Appendix Table B-3, all four columns had lost SMZ ranging in amount from 0.98% to 28.3% of the initial amount. The nylon mesh covering the end-fittings in Column 10A had not dislodged and this column experienced little SMZ loss (0.98%). This indicates that the nylon does hold most of the SMZ inside the columns, and should be more permanently attached the end-fittings in the future to prevent it from moving out of place.

Another concern that arose with increasing sorption cycles performed was that backpressures increased in each column. This issue was discussed briefly in the manuscript. The SEM images used to investigate the backpressure increase are presented below, along with additional conclusions from this work not discussed in the manuscript.

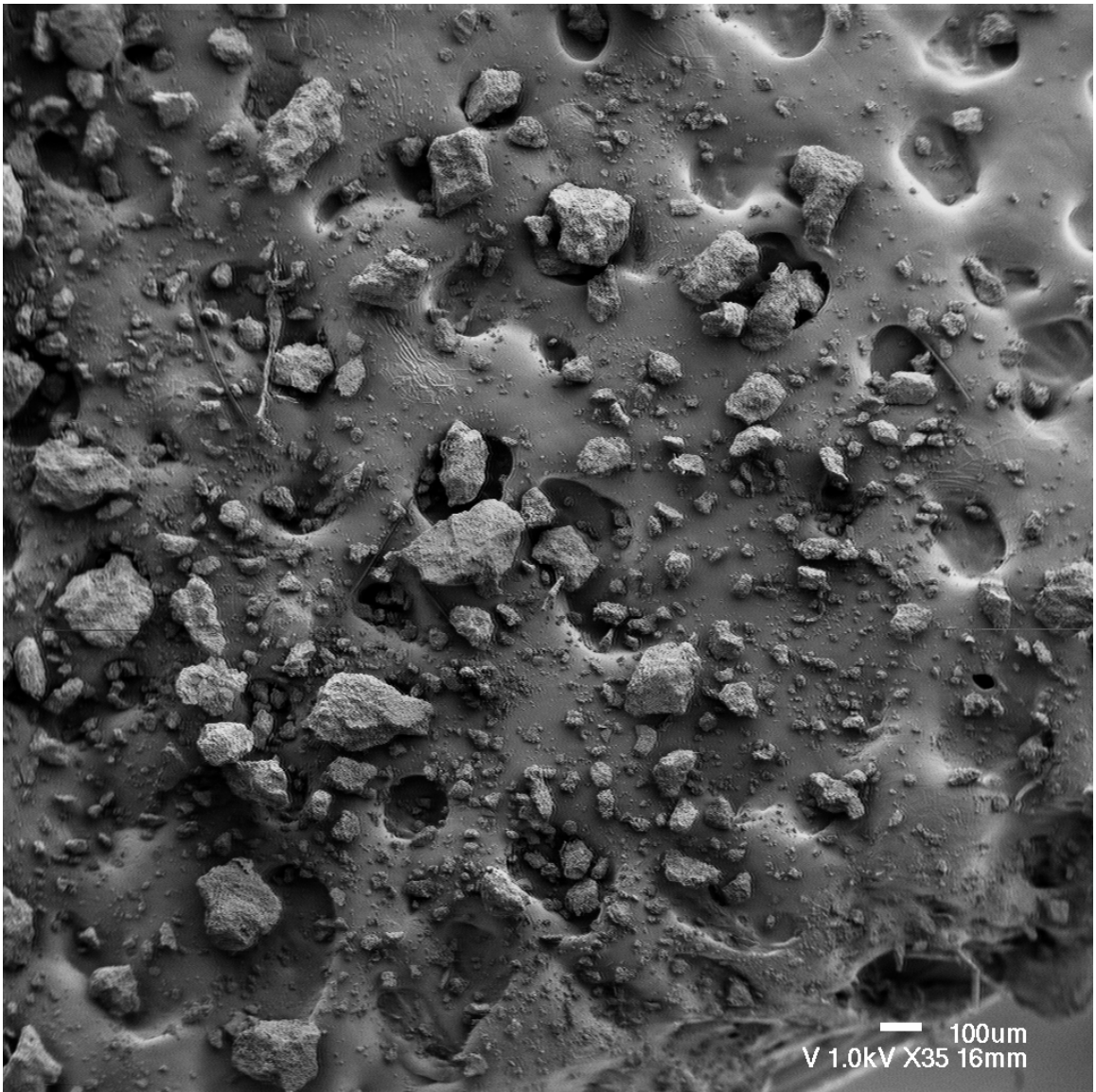
To investigate the reason for the increase of backpressure in the laboratory columns during the final sorption/regeneration cycles, the SMZ removed from each column was examined with a scanning electron microscope (SEM). The following series of images were acquired from SMZ that had not been previously exposed to SMZ, SMZ from Column 5A, and SMZ from Columns 10A and 10B. The three image series were obtained at 3 different magnifications, 35X, 190X, and 4500X.

The 35X and 190X images show that the average particle size of SMZ in Columns 5A, 10A, and 10B has decreased significantly from the virgin SMZ. Continued use of the SMZ in the column systems likely led to grain damage, creating abundant fine grained particles which reduced the column permeability and raised backpressures. Appendix Figure B-4 shows that many virgin SMZ particles are 100 μm or greater in diameter, while Appendix Figure B-10 shows that few SMZ particles from column 10B are this large. Closer inspection of the largest grains in Appendix Figure B-10 revealed that many of these particles are not SMZ, but are other material including quartz and volcanic glass. Appendix Figure B-11 shows that in Column 10B, a significant portion of SMZ particles are 10 μm or less in diameter, while fewer virgin SMZ particles are this small (Appendix Figure B-5). The images at 4500X (Appendix Figures B-6, B-9, and B-12) show that the SMZ particles consist of the same structure in all the SMZ samples. Zeolite (clinoptilolite) crystals are the cubes and plates seen in the images, and each figure contains other minerals (likely clays or other amorphous zeolites) present on the SMZ surface.

The cause of the particle breakdown could be either mechanical or chemical in origin. Future work addressing this issue is necessary, as the high backpressures were the limiting factor determining the length of use of the laboratory system. If the reason is mechanical, a system design that would reduce the differential stress on the SMZ particles and therefore reduce the likelihood of significant SMZ particle breakdown is needed. However, if the reason is chemical, additional work is needed to determine the specific reasons for particle breakdown and possible solutions. To potentially delay the high backpressure effects of SMZ particle breakdown, using an initial SMZ grain size

with larger pores could allow more fine-grained particles to pass through the system before clogging pores and raising permeability. However, this practice could result in buildup of fine particles on the nylon mesh covering the column end-fittings or the loss of SMZ material from the columns.

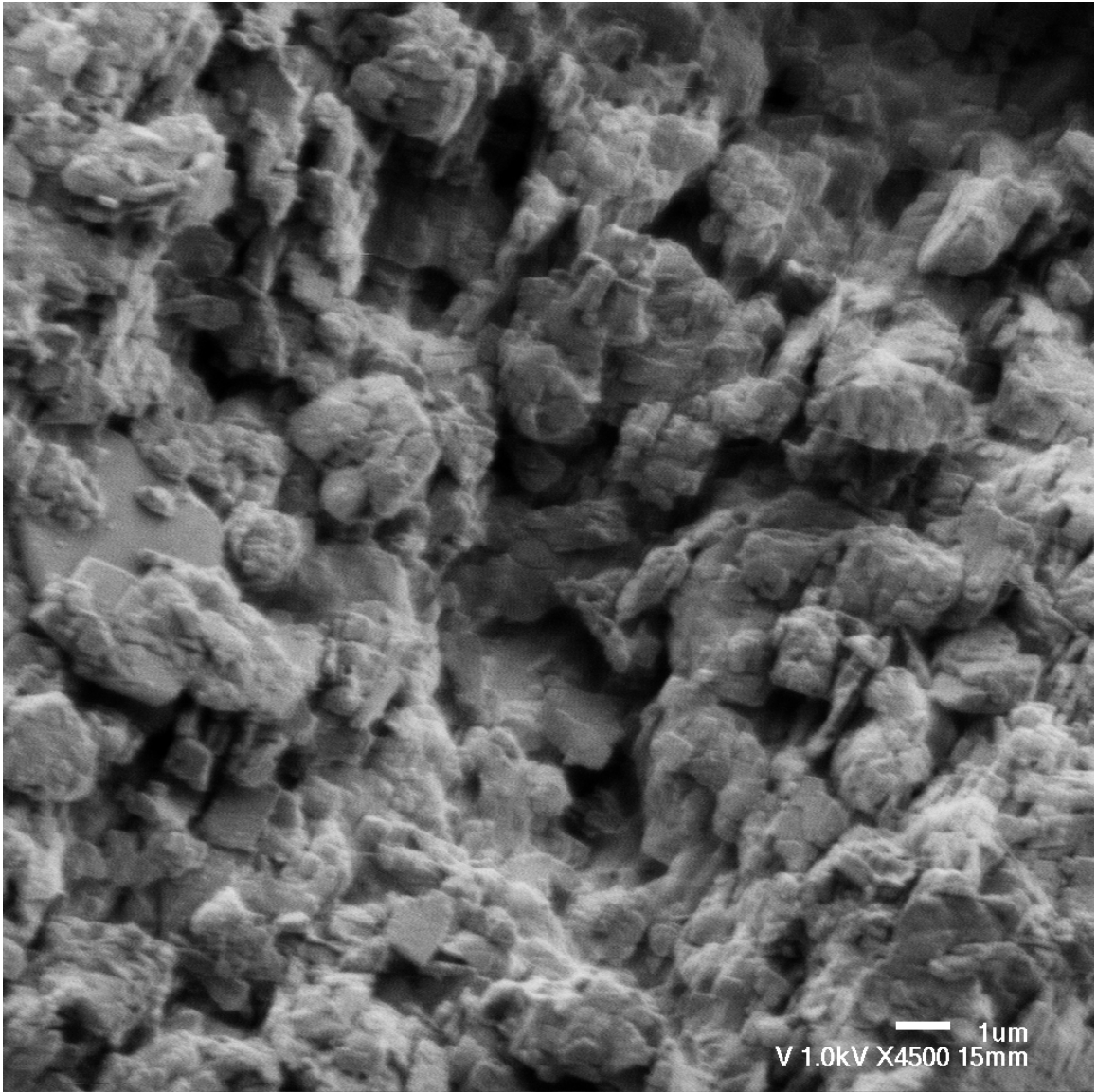
The SEM work was conducted at Los Alamos National Laboratory (LANL), using a JEOL Model JSM-6300FXV SEM. Jim Smith and E. Jeri Sullivan of LANL assisted with the analysis. The samples were prepared for microscopy by affixing the SMZ to double-sided carbon tape and coating the samples with carbon. The following images were acquired at 1.0 kV accelerating voltage using secondary imaging and a working distance of 15 mm.



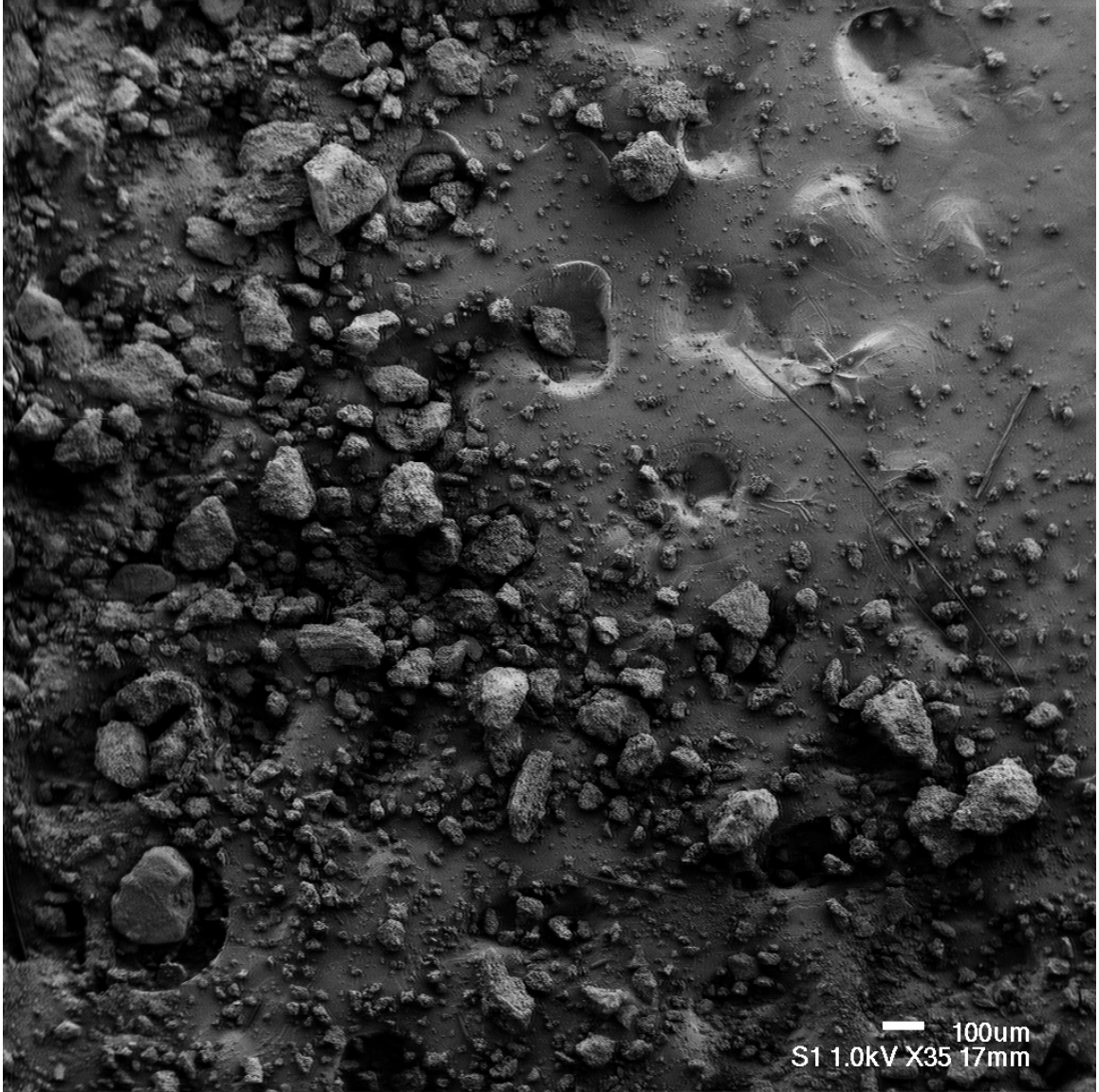
Appendix Figure B-4. SEM image of virgin SMZ (35X).



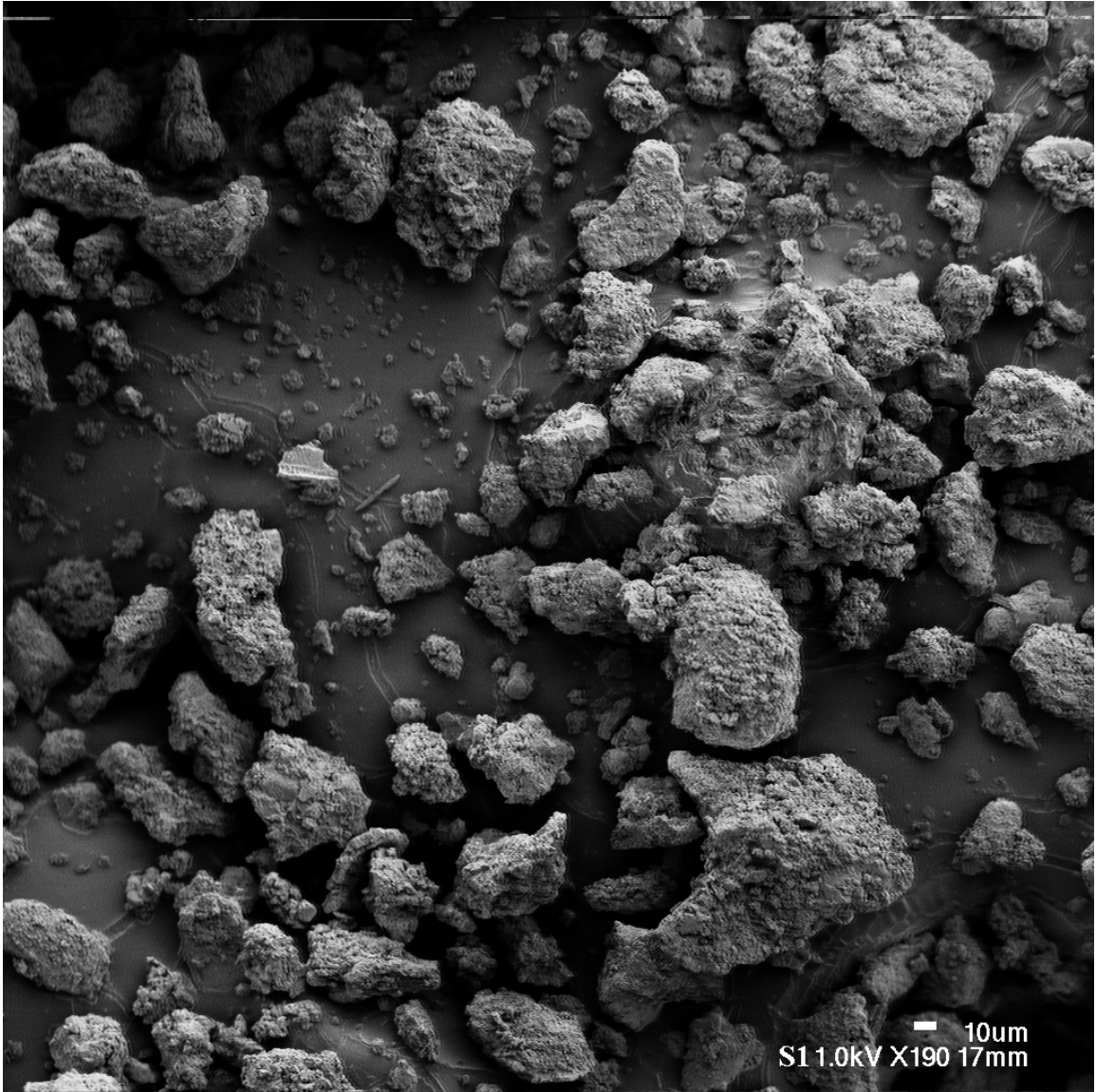
Appendix Figure B-5. SEM image of virgin SMZ (190X). Large particle in upper-center is quartz.



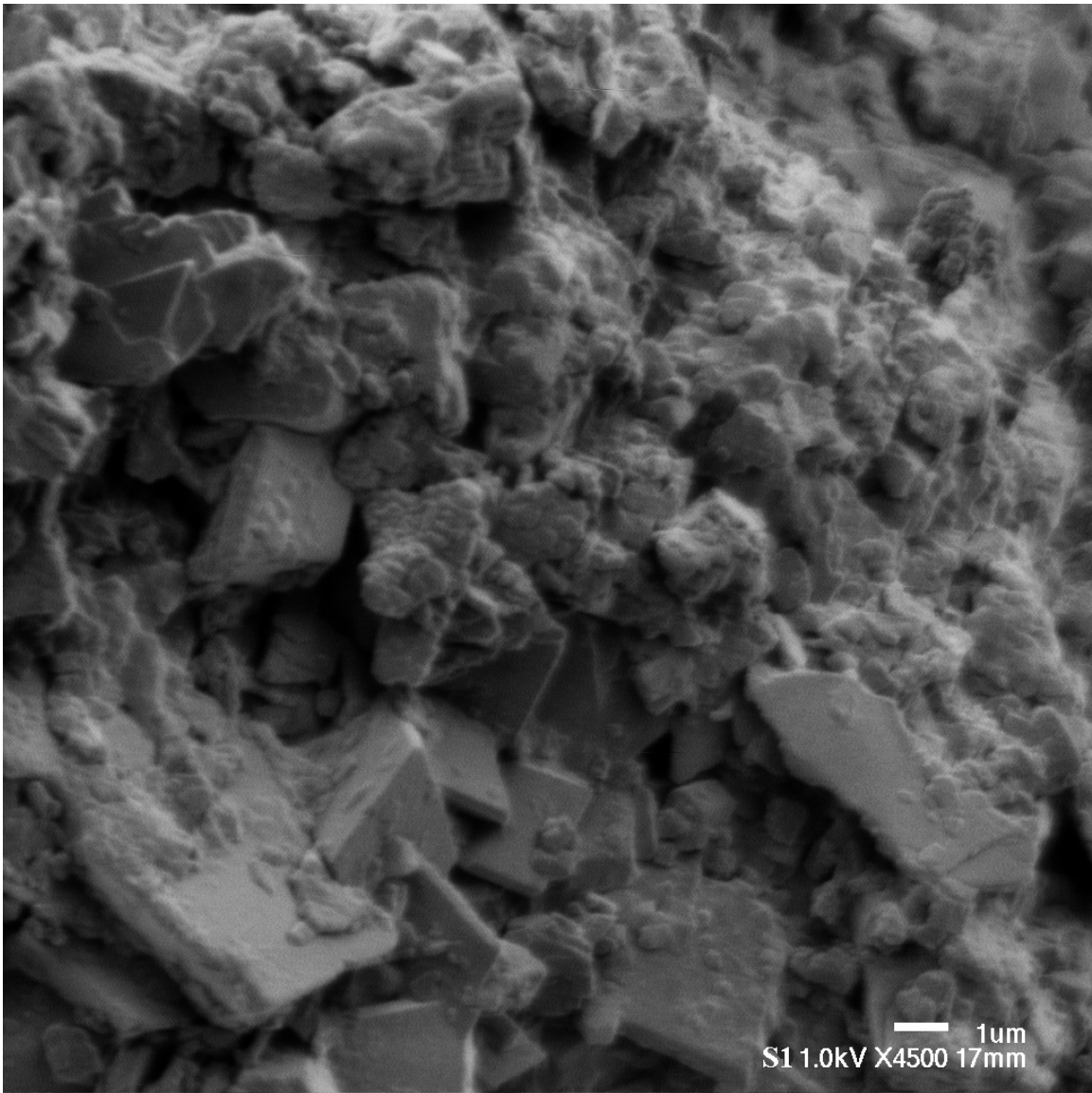
Appendix Figure B-6. SEM image of virgin SMZ (4500X).



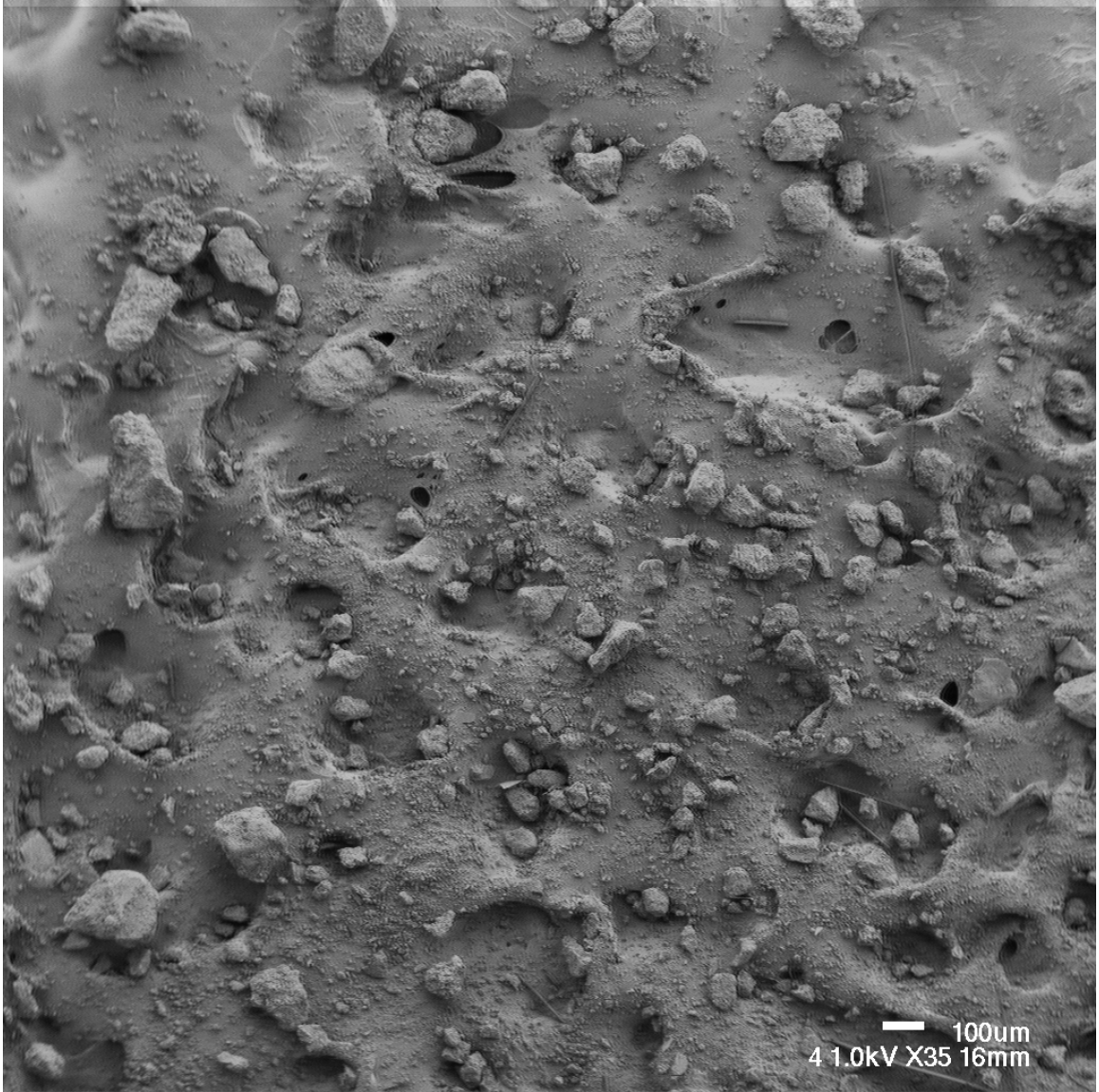
Appendix Figure B-7. SEM image of Column 5A SMZ (35X).



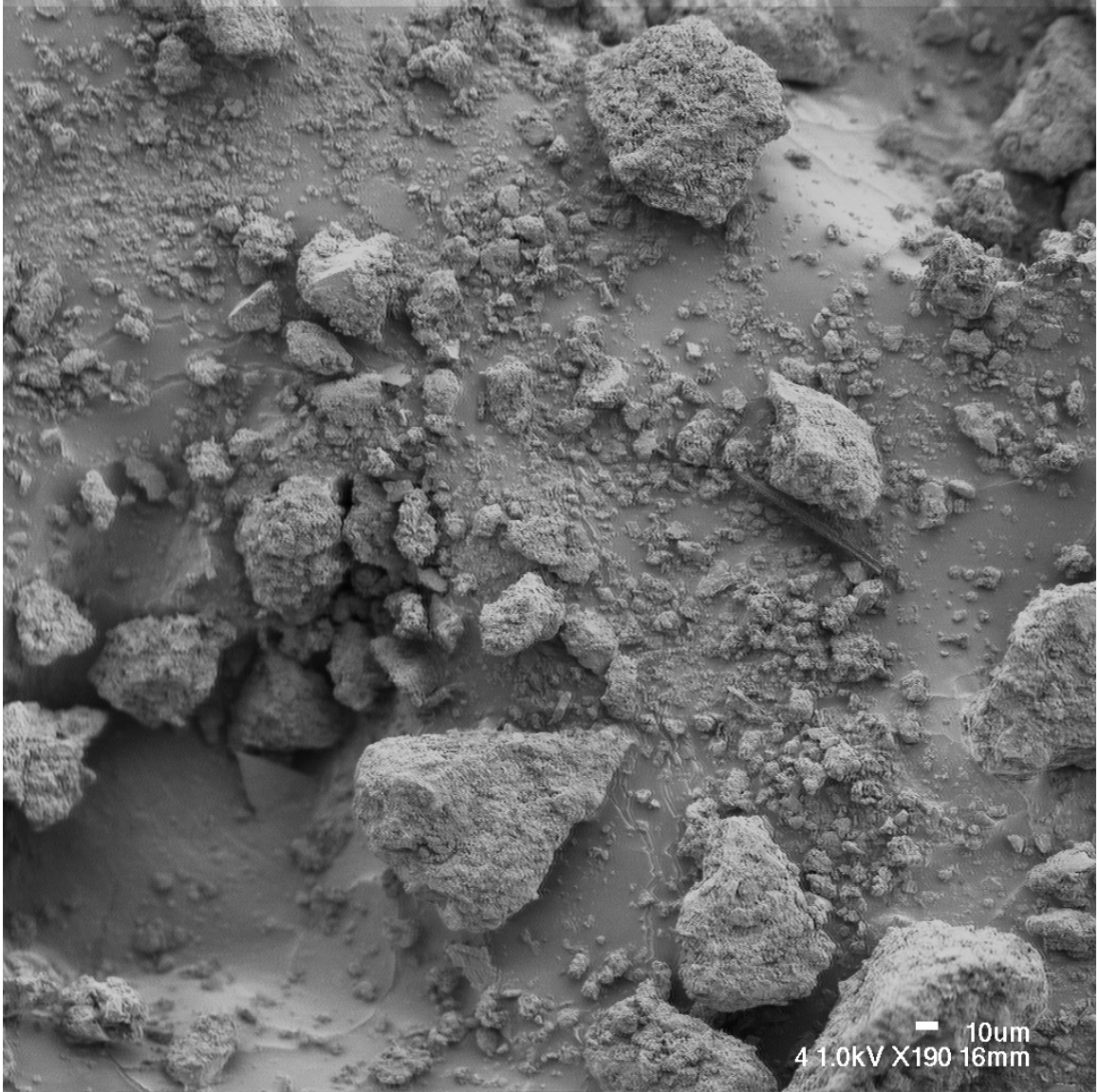
Appendix Figure B-8. SEM image of Column 5A SMZ (190X).



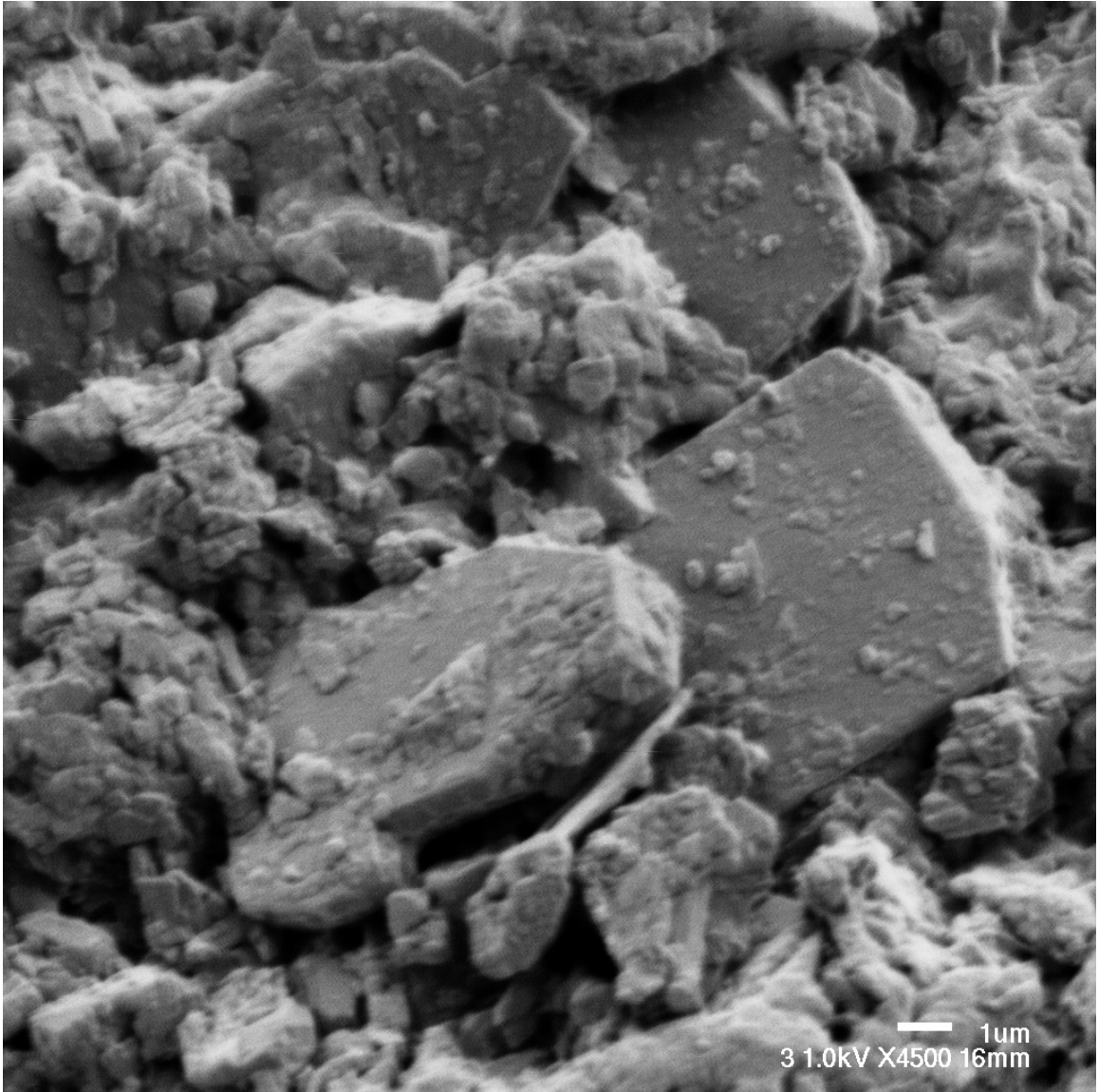
Appendix Figure B-9. SEM image of Column 5A SMZ (4500X).



Appendix Figure B-10. SEM image of Column 10B SMZ (35X).



Appendix Figure B-11. SEM image of Column 10B SMZ (190X).



Appendix Figure B-12. SEM image of Column 10A SMZ (4500X).

APPENDIX C. LABORATORY COLUMN BTC DATA

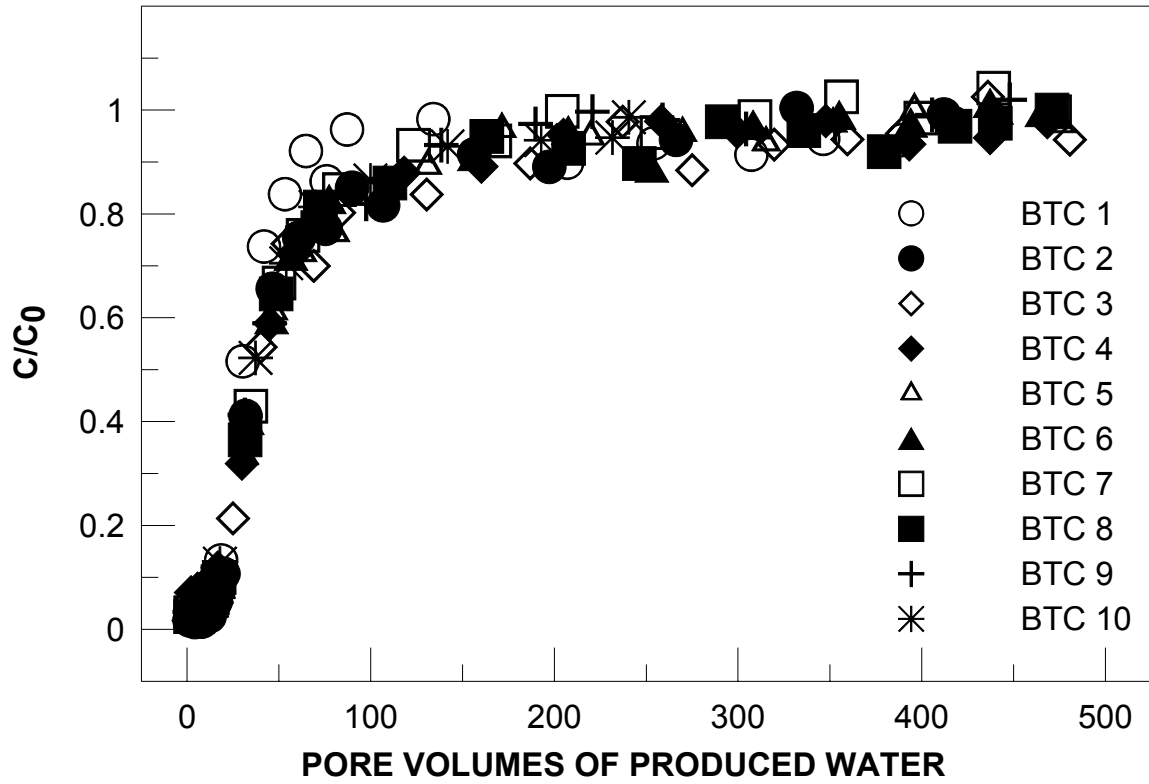
Figure 4 of the manuscript shows the 10 BTCs of benzene and p-&m-xylene in Column 10A. The BTCs for the other compounds in Column 10A are shown in Appendix Figures C-1 through C-3. The BTCs for each compound in Column 10B are plotted in Appendix Figures C-4 through C-8. As discussed in the manuscript, the column experiments show no significant loss of SMZ sorption capacity after 10 sorption/regeneration cycles. However, during the third sorption cycle in Columns 10A and 10B, ethylbenzene and o-xylene do have a different BTC than during the other cycles. The reason the C/C_0 measurements for these two compounds are lower than expected during BTC 3 is because additional ethylbenzene and o-xylene were added to the produced water in the bag, as discussed in the manuscript. During BTC 3, these compounds were not equilibrated in the sampling bag and their influent concentrations were increasing throughout the injection cycle. Because C_0 was rising, C/C_0 was decreased, lowering the points on the BTC.

Appendix Tables C-1 through C-10 contain the data for the 10 BTEX BTCs from Column 10A, and Appendix Tables C-11 through C-20 contain the data for the 10 BTEX BTCs from Column 10B. Appendix Tables C-21 through C-30 provide the data from the 10 sparging cycles for Column 10A, and Appendix Tables C-31 through C-40 contain the data from the 10 sparging cycles for Column 10B.

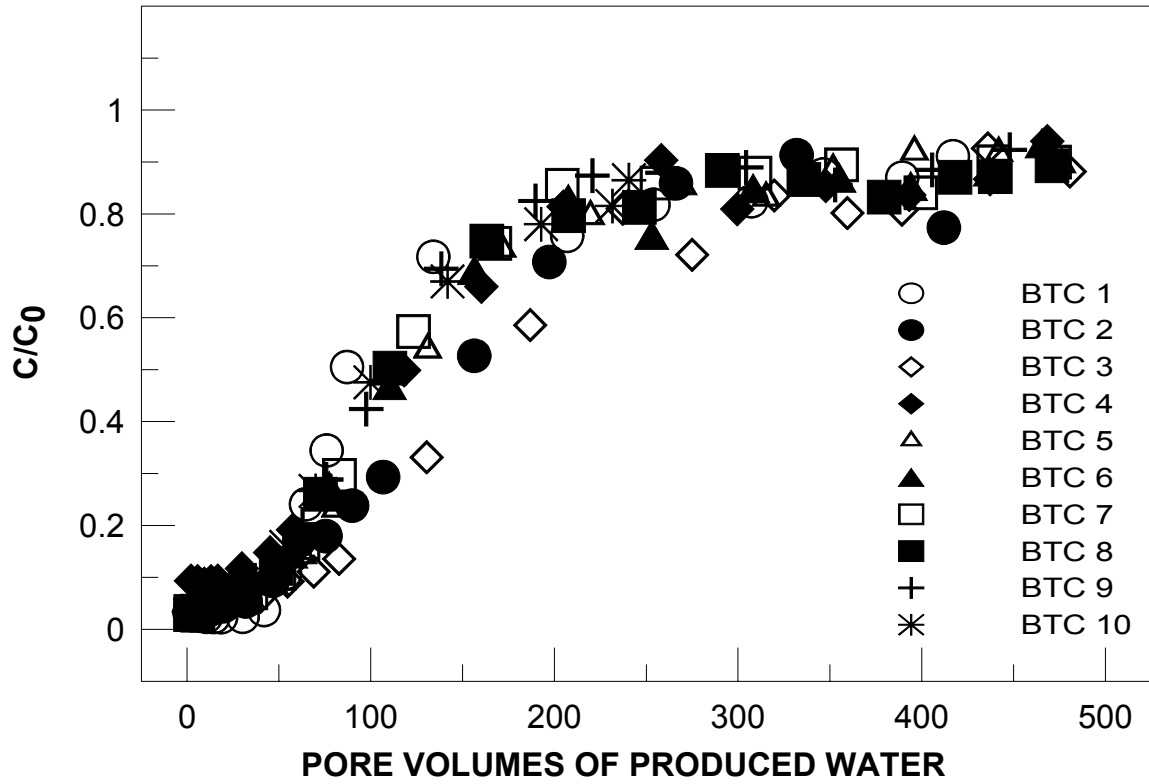
Appendix Tables C-41 and C-42 contains the K_d determined during each sorption cycle in Columns 10A and 10B, and also the estimated mass of each BTEX compound retained by the SMZ during sorption, the estimated mass of each BTEX compound

removed from the SMZ during each regeneration cycle, and the apparent cumulative mass of each compound present on the SMZ following the sorption/regeneration cycle. The reason why more o-xylene is removed during sparging than is sorbed is unclear, although it is hypothesized that another compound present in the exhaust gas co-elutes with o-xylene in the GC analysis.

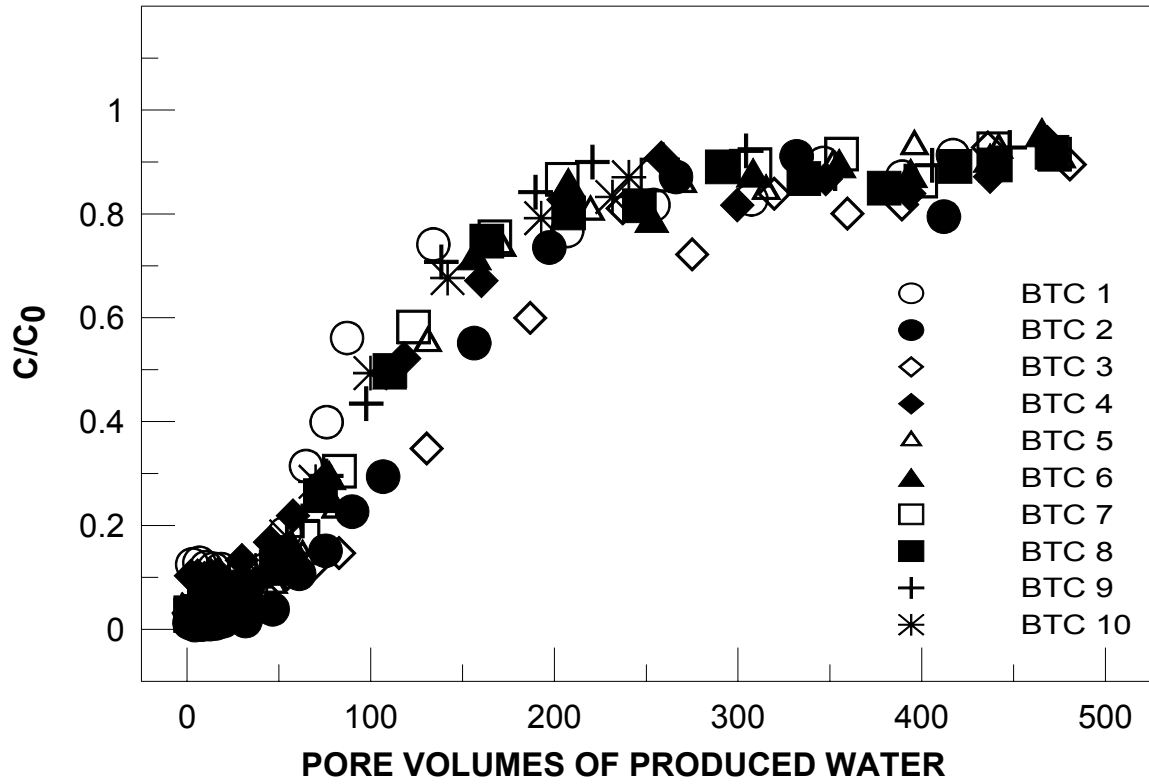
Appendix Table C-43 contains the CXTFIT 2.1 calculations used to create Figure 2 in the manuscript.



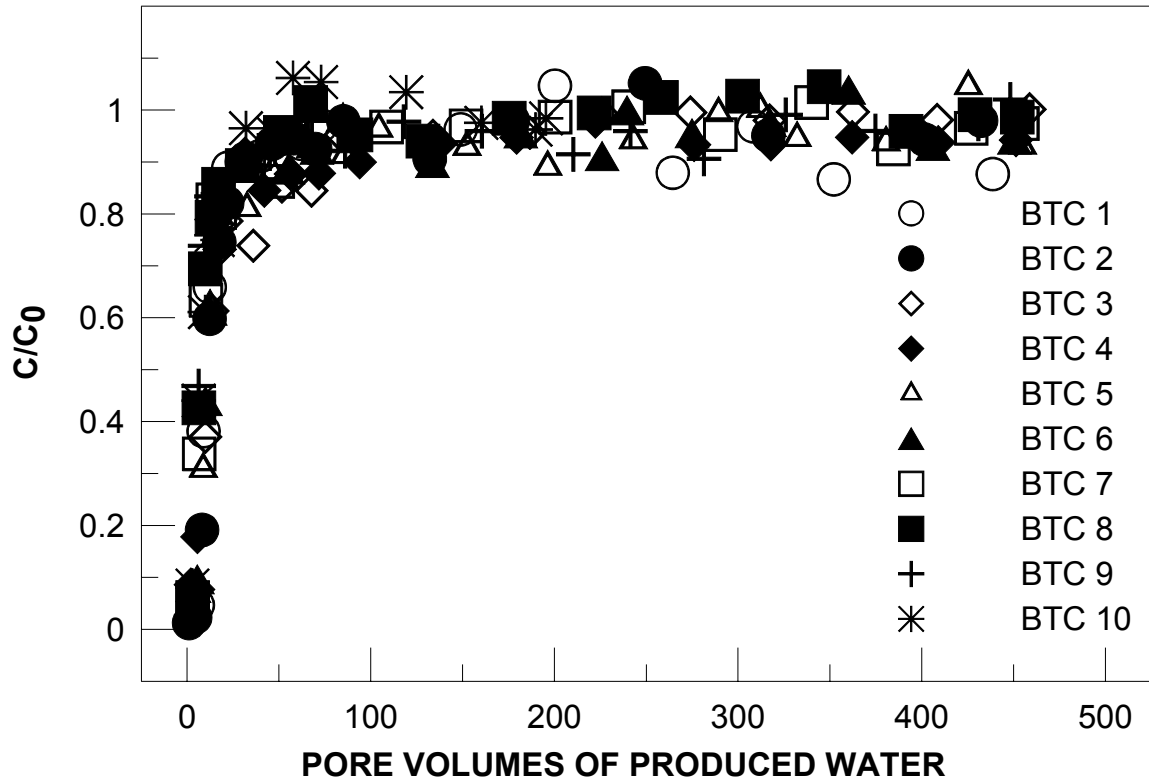
Appendix Figure C-1. Toluene BTCs for Column 10A over 10 sorption/regeneration cycles.



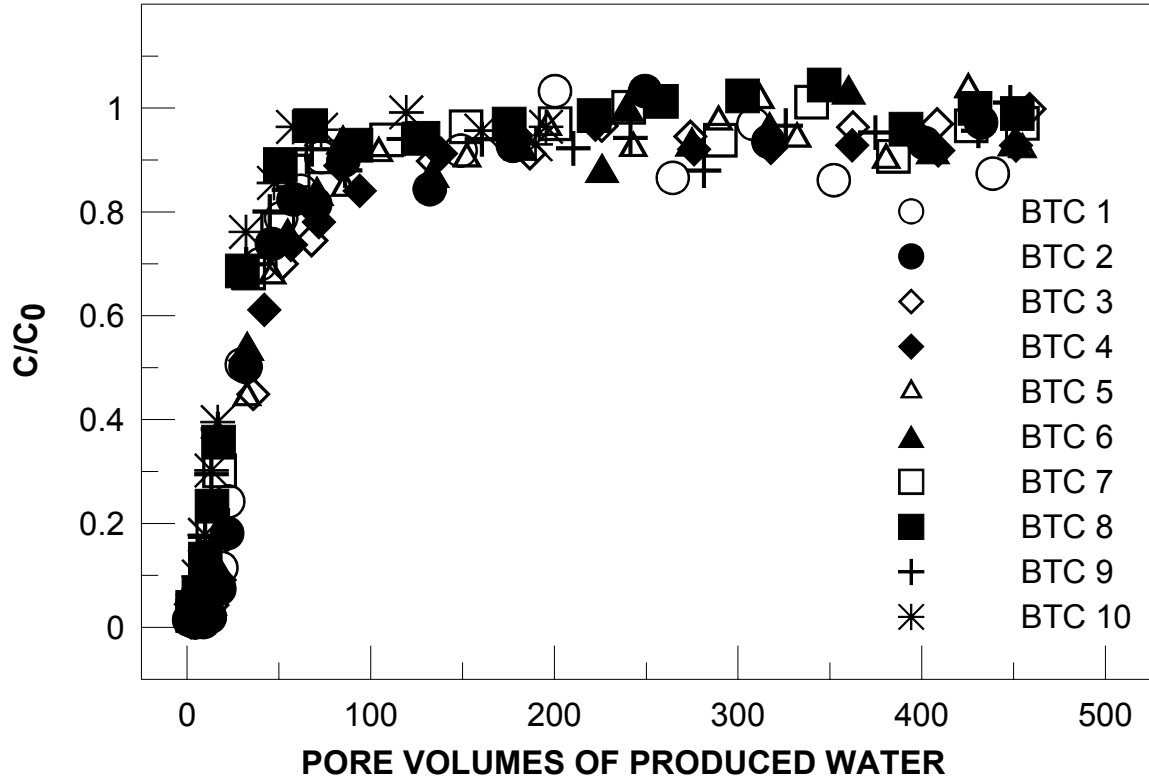
Appendix Figure C-2. Ethylbenzene BTCs for Column 10A over 10 sorption/regeneration cycles.



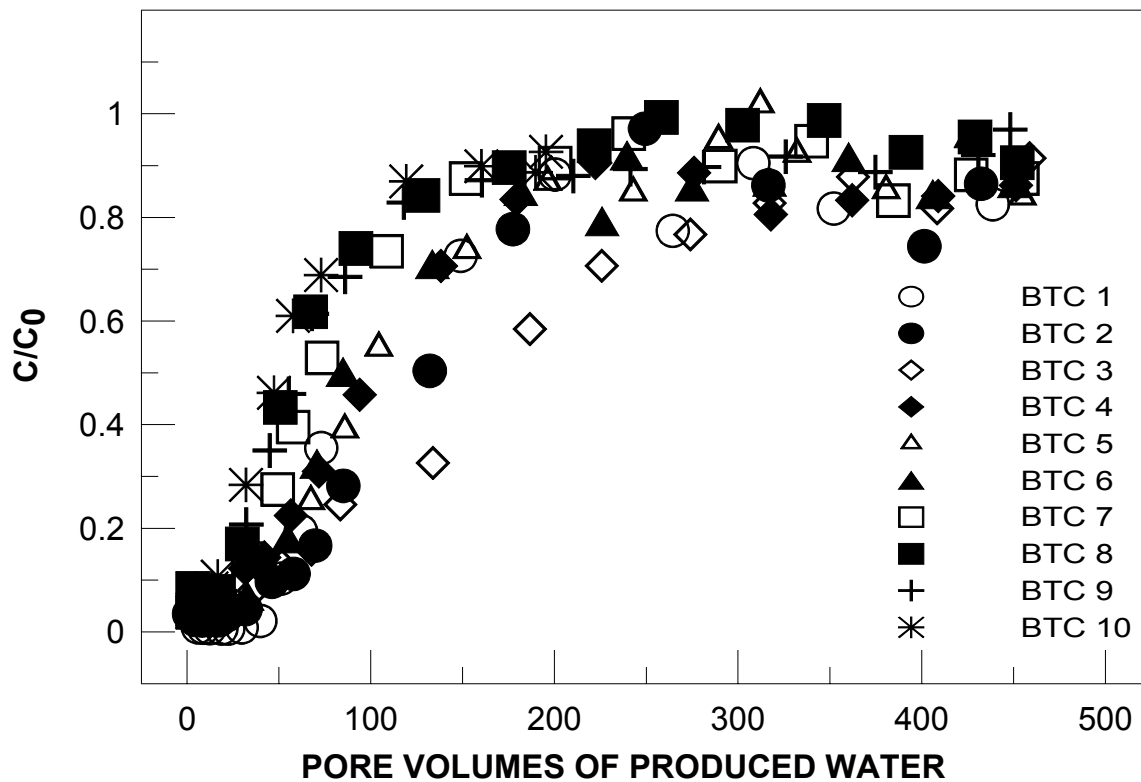
Appendix Figure C-3. o-xylene BTCs for Column 10A over 10 sorption/regeneration cycles.



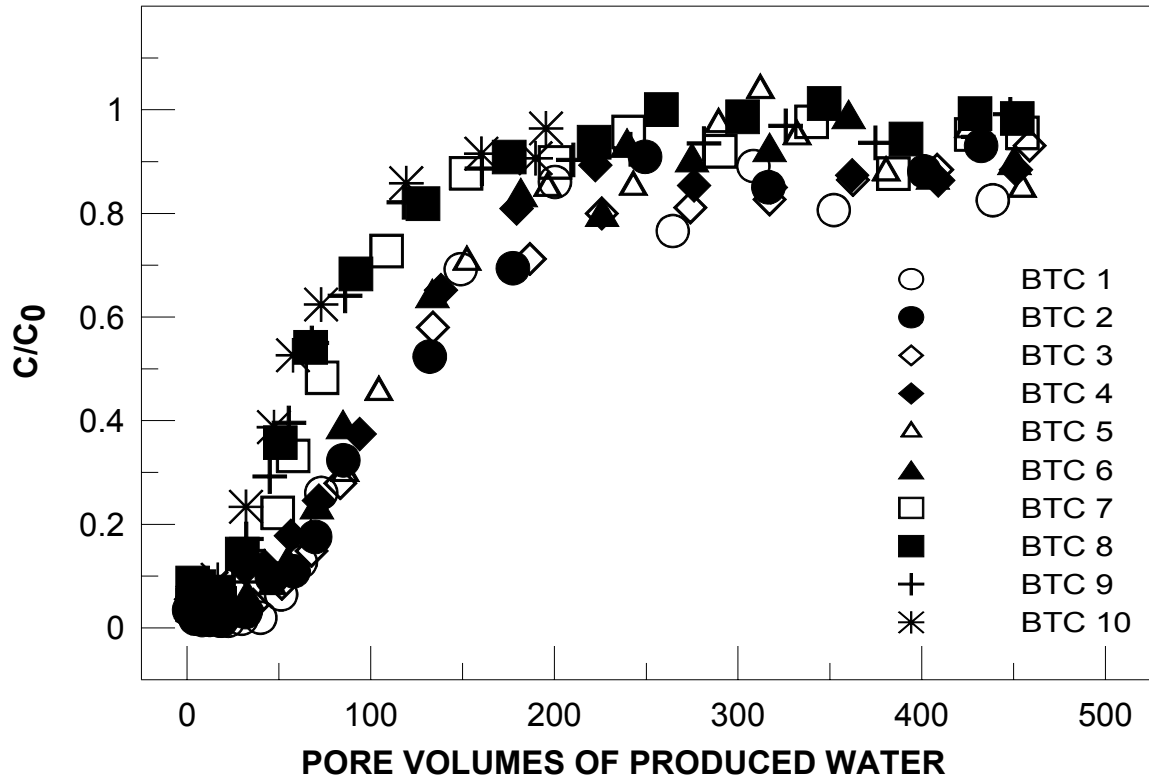
Appendix Figure C-4. Benzene BTCs for Column 10B over 10 sorption/regeneration cycles.



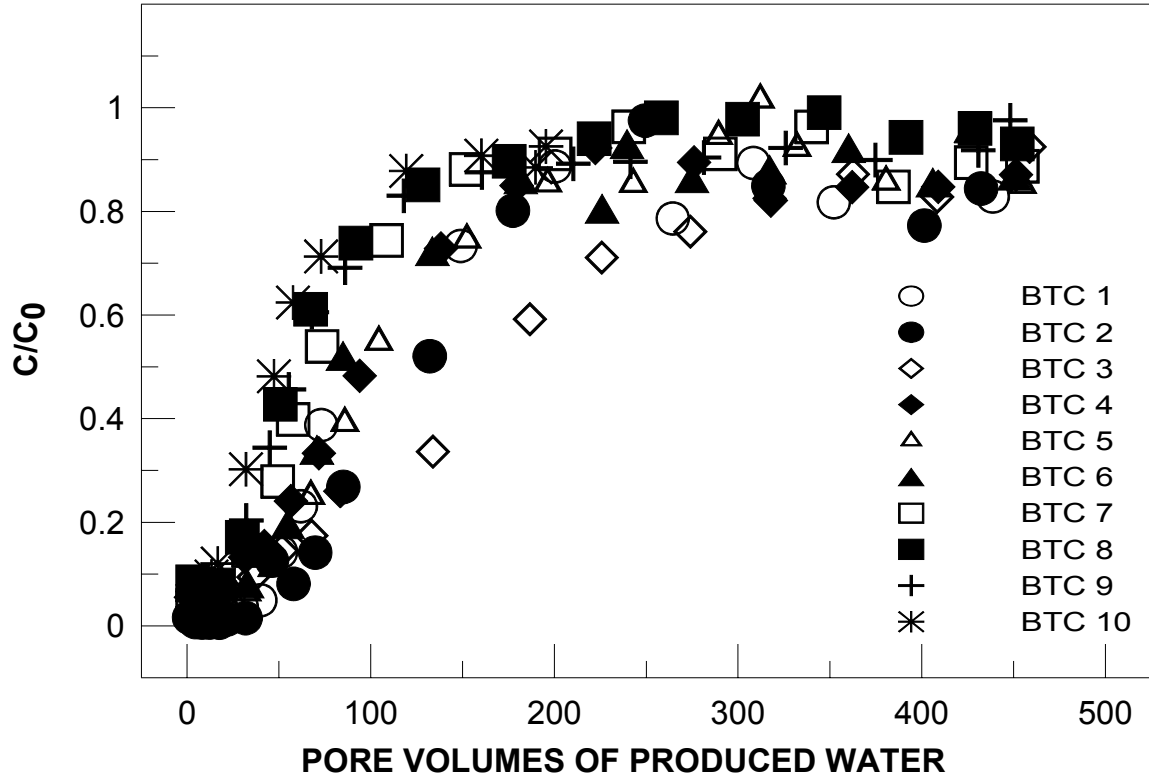
Appendix Figure C-5. Toluene BTCs for Column 10B over 10 sorption/regeneration cycles.



Appendix Figure C-6. Ethylbenzene BTCs for Column 10B over 10 sorption/regeneration cycles.



Appendix Figure C-7. p-&m-xylene BTCs for Column 10B over 10 sorption/regeneration cycles.



Appendix Figure C-8. o-xylene BTCs for Column 10B over 10 sorption/regeneration cycles.

Appendix Table C-1. Data for BTEX BTC 1 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.8	0.020	0.018	0.027	0.052	0.125
2	6.7	0.130	0.019	0.026	0.051	0.128
3	10.4	0.524	0.022	0.024	0.046	0.120
4	14.5	0.771	0.046	0.024	0.045	0.117
5	18.6	0.879	0.133	0.023	0.045	0.116
6	30.3	0.898	0.516	0.024	0.051	0.111
7	41.9	0.930	0.737	0.037	0.043	0.114
8	53.4	0.979	0.838	0.107	0.078	0.186
9	64.8	1.022	0.921	0.241	0.171	0.315
10	76.0	0.973	0.863	0.344	0.261	0.399
11	87.1	1.062	0.963	0.505	0.422	0.561
12	134.1	1.019	0.983	0.717	0.671	0.741
13	207.0	0.939	0.899	0.758	0.740	0.767
14	254.0	0.945	0.936	0.818	0.792	0.817
15	307.3	0.920	0.914	0.824	0.810	0.828
16	346.4	0.947	0.945	0.876	0.877	0.898
17	389.4	0.951	0.942	0.870	0.862	0.872
18	417.0	0.977	0.976	0.911	0.893	0.913

Appendix Table C-2. Data for BTEX BTC 2 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	1.3	0.013	0.017	0.032	0.028	0.012
2	4.2	0.017	0.014	0.029	0.020	0.008
3	8.2	0.184	0.015	0.035	0.021	0.009
4	12.3	0.511	0.025	0.037	0.022	0.010
5	15.7	0.754	0.055	0.043	0.025	0.011
6	19.8	0.709	0.107	0.045	0.033	0.016
7	31.8	0.807	0.411	0.054	0.031	0.016
8	46.6	0.841	0.656	0.093	0.052	0.039
9	61.1	0.880	0.754	0.170	0.103	0.107
10	75.4	0.854	0.771	0.180	0.175	0.151
11	89.9	0.903	0.850	0.238	0.295	0.227
12	106.8	0.868	0.816	0.293	0.369	0.294
13	156.4	0.944	0.915	0.527	0.624	0.551
14	197.2	0.918	0.891	0.707	0.673	0.735
15	266.2	0.951	0.943	0.859	0.803	0.871
16	331.9	1.032	1.004	0.913	0.910	0.911
17	412.0	1.001	0.991	0.774	0.919	0.795

Appendix Table C-3. Data for BTEX BTC 3 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	0.9	0.016	0.017	0.034	0.030	0.031
2	4.3	0.022	0.018	0.032	0.022	0.034
3	7.8	0.174	0.022	0.046	0.028	0.051
4	11.6	0.458	0.028	0.051	0.031	0.059
5	16.1	0.713	0.050	0.054	0.037	0.065
6	25.1	0.880	0.214	0.065	0.056	0.078
7	40.1	0.867	0.544	0.063	0.054	0.075
8	54.7	0.916	0.742	0.092	0.083	0.107
9	69.0	0.817	0.700	0.111	0.116	0.125
10	82.8	0.898	0.802	0.136	0.204	0.147
11	130.5	0.887	0.837	0.331	0.452	0.348
12	186.8	0.928	0.897	0.586	0.645	0.600
13	237.2	0.996	0.977	0.810	0.815	0.811
14	275.0	0.908	0.884	0.721	0.746	0.722
15	319.7	0.932	0.933	0.835	0.803	0.839
16	359.6	0.977	0.943	0.801	0.844	0.801
17	389.3	0.962	0.955	0.808	0.865	0.818
18	436.0	1.047	1.026	0.926	0.943	0.928
19	480.6	0.955	0.943	0.881	0.864	0.895

Appendix Table C-4. Data for BTEX BTC 4 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.2	0.067	0.071	0.093	0.099	0.103
2	5.8	0.092	0.078	0.093	0.095	0.103
3	9.4	0.261	0.083	0.088	0.087	0.099
4	13.1	0.523	0.099	0.092	0.090	0.104
5	16.7	0.676	0.119	0.093	0.090	0.106
6	29.9	0.853	0.319	0.117	0.114	0.133
7	45.2	0.884	0.589	0.148	0.130	0.168
8	57.7	0.911	0.723	0.191	0.160	0.219
9	74.6	0.899	0.775	0.259	0.209	0.287
10	118.2	0.944	0.879	0.499	0.426	0.522
11	160.3	0.950	0.891	0.660	0.609	0.671
12	205.0	0.990	0.952	0.814	0.783	0.827
13	258.1	1.020	0.978	0.903	0.860	0.908
14	299.6	0.988	0.958	0.809	0.849	0.817
15	347.7	1.006	0.979	0.854	0.892	0.867
16	393.2	0.961	0.934	0.837	0.857	0.839
17	437.2	0.952	0.946	0.867	0.890	0.872
18	468.4	0.990	0.977	0.940	0.927	0.938

Appendix Table C-5. Data for BTEX BTC 5 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	1.7	0.015	0.022	0.029	0.032	0.023
2	5.4	0.043	0.023	0.030	0.027	0.026
3	9.3	0.299	0.030	0.043	0.037	0.040
4	13.3	0.527	0.038	0.045	0.039	0.044
5	17.3	0.681	0.069	0.051	0.044	0.050
6	31.2	0.832	0.333	0.060	0.053	0.060
7	47.1	0.891	0.612	0.085	0.066	0.086
8	62.9	0.899	0.724	0.142	0.101	0.141
9	80.8	0.887	0.763	0.232	0.169	0.231
10	131.0	0.956	0.892	0.539	0.469	0.551
11	171.5	1.008	0.963	0.733	0.701	0.735
12	219.7	0.973	0.949	0.795	0.786	0.804
13	269.8	0.986	0.956	0.853	0.871	0.858
14	315.3	0.958	0.937	0.831	0.851	0.844
15	351.7	0.987	0.974	0.885	0.897	0.893
16	396.0	1.002	1.001	0.920	0.943	0.930
17	441.9	0.986	0.989	0.917	0.936	0.923
18	476.2	0.982	0.972	0.895	0.907	0.905

Appendix Table C-6. Data for BTEX BTC 6 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	1.9	0.026	0.037	0.032	0.051	0.043
2	5.8	0.063	0.031	0.036	0.041	0.043
3	9.6	0.292	0.036	0.043	0.046	0.053
4	13.4	0.541	0.052	0.049	0.051	0.061
5	17.2	0.679	0.088	0.052	0.053	0.065
6	32.9	0.872	0.403	0.071	0.076	0.089
7	46.0	0.878	0.597	0.096	0.082	0.114
8	56.6	0.917	0.719	0.146	0.113	0.165
9	77.4	0.952	0.829	0.276	0.210	0.297
10	110.3	0.931	0.859	0.470	0.392	0.491
11	156.5	0.949	0.911	0.692	0.651	0.720
12	207.6	0.991	0.961	0.829	0.837	0.861
13	253.0	0.914	0.889	0.760	0.786	0.793
14	308.2	0.979	0.972	0.849	0.887	0.880
15	355.1	0.999	0.990	0.870	0.916	0.897
16	394.0	0.994	0.976	0.854	0.912	0.878
17	437.2	1.017	1.013	0.882	0.967	0.908
18	465.4	1.007	0.996	0.936	0.963	0.957

Appendix Table C-7. Data for BTEX BTC 7 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.0	0.022	0.032	0.034	0.042	0.032
2	5.7	0.071	0.035	0.035	0.036	0.034
3	9.4	0.315	0.041	0.044	0.043	0.045
4	13.1	0.536	0.055	0.049	0.049	0.053
5	16.8	0.684	0.092	0.054	0.054	0.059
6	34.8	0.840	0.430	0.070	0.074	0.078
7	50.1	0.900	0.667	0.108	0.096	0.117
8	63.1	0.913	0.759	0.167	0.139	0.177
9	83.0	0.942	0.847	0.297	0.251	0.305
10	123.3	0.986	0.932	0.573	0.528	0.582
11	167.6	0.974	0.941	0.744	0.727	0.756
12	204.3	1.016	0.998	0.855	0.843	0.867
13	255.8	0.986	0.957	0.859	0.876	0.875
14	309.2	0.998	0.988	0.879	0.919	0.895
15	356.3	1.026	1.025	0.894	0.956	0.915
16	399.5	0.995	0.984	0.841	0.936	0.863
17	439.2	1.026	1.042	0.900	1.011	0.925
18	472.3	1.008	0.997	0.900	0.967	0.915

Appendix Table C-8. Data for BTEX BTC 8 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.0	0.016	0.024	0.028	0.035	0.027
2	5.8	0.047	0.024	0.028	0.028	0.028
3	9.8	0.302	0.042	0.055	0.051	0.055
4	13.8	0.567	0.060	0.064	0.059	0.065
5	17.6	0.712	0.100	0.068	0.063	0.071
6	31.7	0.828	0.365	0.078	0.076	0.081
7	48.5	0.905	0.646	0.117	0.095	0.121
8	72.6	0.953	0.813	0.260	0.199	0.257
9	110.5	0.928	0.860	0.503	0.428	0.498
10	163.2	0.990	0.949	0.747	0.719	0.748
11	207.7	0.946	0.926	0.797	0.787	0.802
12	246.2	0.931	0.897	0.813	0.822	0.816
13	291.5	1.000	0.977	0.884	0.901	0.891
14	335.8	0.981	0.961	0.866	0.880	0.868
15	379.5	0.938	0.920	0.832	0.857	0.850
16	418.1	0.971	0.969	0.870	0.926	0.892
17	440.1	0.978	0.975	0.872	0.934	0.894
18	470.9	0.995	1.000	0.893	0.970	0.919

Appendix Table C-9. Data for BTEX BTC 9 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	1.5	0.024	0.034	0.035	0.040	0.030
2	5.0	0.054	0.036	0.034	0.032	0.033
3	8.4	0.227	0.042	0.042	0.038	0.044
4	11.7	0.467	0.055	0.050	0.046	0.054
5	15.5	0.628	0.085	0.057	0.052	0.062
6	31.4	0.847	0.413	0.082	0.079	0.089
7	45.0	0.828	0.589	0.105	0.086	0.112
8	62.9	0.906	0.774	0.202	0.154	0.209
9	75.8	0.895	0.807	0.289	0.220	0.295
10	97.6	0.886	0.819	0.424	0.345	0.435
11	138.4	0.966	0.933	0.694	0.623	0.708
12	189.7	1.000	0.973	0.825	0.782	0.842
13	220.7	1.008	0.997	0.874	0.848	0.900
14	258.9	1.004	0.981	0.879	0.868	0.905
15	304.4	0.981	0.964	0.889	0.896	0.921
16	352.9	0.990	0.970	0.856	0.925	0.878
17	405.7	1.011	0.991	0.885	0.938	0.893
18	447.9	1.038	1.020	0.923	0.973	0.928

Appendix Table C-10. Data for BTEX BTC 10 from Column 10A.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.0	0.021	0.032	0.029	0.031	0.029
2	5.9	0.091	0.037	0.035	0.034	0.039
3	10.0	0.329	0.047	0.043	0.040	0.051
4	13.9	0.579	0.075	0.051	0.048	0.063
5	17.9	0.710	0.126	0.057	0.053	0.071
6	37.3	0.885	0.523	0.094	0.085	0.113
7	54.0	0.872	0.705	0.159	0.128	0.179
8	70.0	0.904	0.813	0.267	0.216	0.284
9	99.9	0.920	0.864	0.476	0.418	0.493
10	141.9	0.976	0.930	0.670	0.643	0.676
11	192.8	0.972	0.942	0.780	0.772	0.792
12	231.6	0.968	0.947	0.815	0.827	0.833
13	240.6	1.014	0.986	0.865	0.876	0.871

Appendix Table C-11. Data for BTEX BTC 1 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	5.9	0.047	0.032	0.009	0.021	0.045
2	9.0	0.382	0.010	0.008	0.018	0.040
3	12.4	0.659	0.020	0.007	0.016	0.038
4	18.7	0.801	0.114	0.007	0.014	0.034
5	22.5	0.889	0.242	0.006	0.014	0.034
6	29.8	0.900	0.506	0.009	0.018	0.037
7	39.9	0.911	0.700	0.021	0.020	0.049
8	51.2	0.945	0.788	0.103	0.065	0.143
9	62.0	0.935	0.841	0.195	0.127	0.231
10	73.1	0.970	0.906	0.355	0.261	0.388
11	149.0	0.963	0.918	0.726	0.692	0.733
12	200.3	1.047	1.033	0.883	0.861	0.887
13	264.5	0.879	0.866	0.774	0.766	0.786
14	308.4	0.969	0.969	0.905	0.891	0.894
15	352.1	0.867	0.861	0.817	0.806	0.818
16	438.7	0.877	0.874	0.825	0.825	0.829

Appendix Table C-12. Data for BTEX BTC 2 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	1.1	0.012	0.014	0.035	0.035	0.016
2	4.5	0.023	0.010	0.023	0.018	0.008
3	8.2	0.191	0.011	0.022	0.015	0.006
4	12.3	0.598	0.021	0.023	0.016	0.007
5	17.6	0.745	0.074	0.023	0.014	0.006
6	21.9	0.821	0.181	0.032	0.027	0.013
7	31.9	0.907	0.502	0.044	0.031	0.015
8	46.2	0.935	0.738	0.097	0.097	0.126
9	58.0	0.946	0.824	0.112	0.109	0.081
10	69.8	0.925	0.815	0.167	0.176	0.141
11	85.1	0.978	0.899	0.282	0.324	0.268
12	132.2	0.906	0.844	0.504	0.524	0.521
13	177.4	0.979	0.927	0.777	0.694	0.802
14	249.4	1.051	1.033	0.971	0.909	0.975
15	316.5	0.951	0.935	0.862	0.851	0.849
16	401.4	0.943	0.933	0.744	0.881	0.773
17	432.3	0.980	0.972	0.865	0.930	0.844

Appendix Table C-13. Data for BTEX BTC 3 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.3	0.028	0.010	0.024	0.019	0.023
2	6.0	0.077	0.012	0.026	0.017	0.030
3	9.9	0.371	0.022	0.035	0.022	0.042
4	13.9	0.613	0.043	0.035	0.021	0.043
5	17.7	0.732	0.091	0.041	0.023	0.049
6	21.5	0.786	0.176	0.061	0.042	0.073
7	36.1	0.739	0.449	0.079	0.045	0.094
8	51.7	0.853	0.700	0.128	0.085	0.145
9	67.8	0.845	0.745	0.159	0.149	0.174
10	83.4	0.952	0.889	0.246	0.279	0.260
11	133.9	0.951	0.898	0.326	0.580	0.336
12	186.7	0.956	0.912	0.584	0.712	0.592
13	225.8	0.993	0.966	0.707	0.800	0.711
14	274.0	0.995	0.945	0.767	0.811	0.761
15	317.2	0.980	0.941	0.828	0.827	0.825
16	362.6	0.996	0.963	0.878	0.865	0.872
17	408.4	0.981	0.969	0.818	0.885	0.828
18	458.8	1.001	0.998	0.914	0.931	0.925

Appendix Table C-14. Data for BTEX BTC 4 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.1	0.086	0.044	0.047	0.055	0.055
2	5.7	0.178	0.056	0.051	0.055	0.057
3	9.2	no data	no data	no data	no data	no data
4	12.9	no data	no data	no data	no data	no data
5	16.4	no data	no data	no data	no data	no data
6	31.7	0.916	0.514	0.122	0.114	0.132
7	42.1	0.845	0.612	0.144	0.120	0.154
8	56.6	0.877	0.737	0.225	0.178	0.241
9	71.8	0.878	0.780	0.310	0.246	0.333
10	93.9	0.900	0.841	0.458	0.374	0.483
11	138.3	0.936	0.912	0.706	0.652	0.728
12	179.4	0.947	0.947	0.835	0.809	0.850
13	222.3	0.978	0.968	0.905	0.893	0.923
14	276.0	0.933	0.920	0.886	0.854	0.894
15	317.9	0.934	0.923	0.806	0.850	0.821
16	362.1	0.947	0.928	0.833	0.874	0.847
17	408.9	0.938	0.918	0.841	0.863	0.847
18	451.3	0.942	0.928	0.862	0.885	0.871

Appendix Table C-15. Data for BTEX BTC 5 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	1.6	0.019	0.020	0.062	0.076	0.082
2	5.1	0.068	0.018	0.052	0.057	0.067
3	8.8	0.309	0.022	0.046	0.049	0.057
4	12.6	0.622	0.049	0.049	0.051	0.058
5	16.4	0.757	0.102	0.049	0.050	0.057
6	32.6	0.811	0.443	0.061	0.055	0.065
7	46.3	0.882	0.678	0.110	0.080	0.111
8	67.4	0.925	0.815	0.252	0.178	0.251
9	85.9	0.913	0.846	0.390	0.299	0.392
10	104.4	0.964	0.913	0.548	0.455	0.548
11	152.4	0.929	0.903	0.737	0.706	0.745
12	196.4	0.890	0.964	0.868	0.849	0.854
13	242.9	0.942	0.923	0.848	0.851	0.853
14	289.4	0.994	0.974	0.949	0.972	0.945
15	312.1	1.002	1.015	1.018	1.038	1.016
16	332.1	0.946	0.941	0.923	0.948	0.923
17	380.6	0.938	0.900	0.852	0.879	0.857
18	425.3	1.046	1.036	0.951	0.962	0.948
19	454.8	0.931	0.920	0.840	0.847	0.851

Appendix Table C-16. Data for BTEX BTC 6 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.9	0.036	0.021	0.036	0.042	0.037
2	5.6	0.096	0.019	0.033	0.035	0.036
3	10.0	0.440	0.029	0.031	0.033	0.037
4	12.6	0.614	0.051	0.034	0.035	0.041
5	16.3	0.808	0.118	0.043	0.044	0.052
6	32.8	0.909	0.542	0.070	0.065	0.082
7	54.8	0.885	0.760	0.180	0.130	0.196
8	70.7	0.924	0.840	0.324	0.238	0.340
9	84.9	0.987	0.939	0.501	0.393	0.521
10	133.6	0.898	0.875	0.710	0.646	0.724
11	181.7	0.955	0.927	0.851	0.841	0.862
12	226.0	0.911	0.885	0.792	0.803	0.805
13	239.5	0.999	1.002	0.919	0.936	0.930
14	274.9	0.955	0.935	0.860	0.908	0.864
15	317.2	0.977	0.965	0.869	0.928	0.881
16	360.2	1.039	1.035	0.916	0.991	0.922
17	406.0	0.931	0.920	0.845	0.875	0.856
18	450.5	0.943	0.936	0.866	0.903	0.869

Appendix Table C-17. Data for BTEX BTC 7 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	3.1	0.046	0.022	0.038	0.044	0.040
2	6.6	0.338	0.041	0.040	0.043	0.043
3	10.3	0.633	0.090	0.041	0.043	0.045
4	14.0	0.827	0.196	0.047	0.047	0.051
5	17.7	0.803	0.301	0.050	0.047	0.055
6	33.5	0.893	0.682	0.142	0.119	0.146
7	49.4	0.863	0.767	0.275	0.222	0.279
8	57.8	0.950	0.879	0.395	0.332	0.398
9	73.6	0.953	0.906	0.529	0.483	0.539
10	108.7	0.967	0.939	0.735	0.727	0.744
11	151.9	0.970	0.964	0.875	0.877	0.881
12	200.4	0.986	0.970	0.905	0.898	0.911
13	240.5	1.006	1.001	0.962	0.957	0.963
14	290.3	0.953	0.938	0.899	0.920	0.911
15	340.0	1.014	1.011	0.947	0.977	0.963
16	384.6	0.925	0.907	0.832	0.877	0.847
17	426.9	0.965	0.966	0.882	0.952	0.894
18	454.7	0.974	0.970	0.875	0.955	0.887

Appendix Table C-18. Data for BTEX BTC 8 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	3.0	0.061	0.038	0.084	0.087	0.085
2	6.4	0.426	0.065	0.079	0.080	0.080
3	10.0	0.694	0.131	0.071	0.069	0.071
4	13.6	0.793	0.233	0.069	0.065	0.070
5	17.2	0.857	0.356	0.078	0.069	0.079
6	30.1	0.893	0.686	0.170	0.143	0.171
7	50.8	0.957	0.891	0.433	0.358	0.428
8	67.3	1.014	0.966	0.618	0.541	0.611
9	92.0	0.952	0.929	0.740	0.683	0.739
10	128.5	0.940	0.942	0.843	0.819	0.851
11	175.4	0.984	0.969	0.896	0.909	0.897
12	221.7	0.994	0.986	0.938	0.938	0.940
13	258.2	1.024	1.013	0.993	1.001	0.981
14	302.4	1.027	1.024	0.978	0.987	0.978
15	346.8	1.045	1.044	0.987	1.012	0.991
16	391.5	0.959	0.959	0.926	0.944	0.943
17	429.0	0.991	0.999	0.955	0.993	0.960
18	452.1	0.987	0.989	0.906	0.983	0.930

Appendix Table C-19. Data for BTEX BTC 9 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.9	0.082	0.024	0.035	0.040	0.034
2	6.3	0.469	0.072	0.041	0.042	0.043
3	9.9	0.739	0.174	0.051	0.048	0.053
4	13.3	0.834	0.295	0.065	0.057	0.066
5	16.8	0.838	0.382	0.074	0.062	0.076
6	32.3	0.894	0.699	0.207	0.172	0.203
7	45.1	0.916	0.801	0.350	0.292	0.344
8	55.5	0.932	0.843	0.459	0.396	0.456
9	68.0	0.979	0.921	0.614	0.550	0.605
10	86.1	0.921	0.880	0.685	0.641	0.691
11	118.1	0.977	0.941	0.829	0.822	0.830
12	160.6	0.959	0.940	0.872	0.886	0.875
13	210.3	0.915	0.922	0.880	0.903	0.892
14	241.4	0.959	0.942	0.893	0.924	0.896
15	281.4	0.906	0.880	0.897	0.935	0.904
16	325.9	0.991	0.966	0.917	0.969	0.922
17	374.8	0.960	0.953	0.887	0.936	0.899
18	430.8	0.974	0.956	0.920	0.947	0.918
19	448.2	1.020	1.011	0.969	0.991	0.976

Appendix Table C-20. Data for BTEX BTC 10 from Column 10B.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	2.9	0.084	0.031	0.043	0.050	0.049
2	6.4	0.440	0.098	0.054	0.055	0.062
3	9.8	0.611	0.178	0.061	0.059	0.071
4	13.3	0.759	0.302	0.084	0.076	0.095
5	16.7	0.750	0.395	0.107	0.093	0.120
6	32.1	0.965	0.761	0.284	0.234	0.302
7	47.3	0.953	0.856	0.462	0.388	0.482
8	57.7	1.062	0.964	0.610	0.526	0.624
9	73.0	1.054	0.958	0.689	0.624	0.713
10	119.3	1.034	0.992	0.870	0.858	0.878
11	160.3	0.975	0.957	0.899	0.915	0.908
12	189.7	0.962	0.930	0.887	0.906	0.885
13	195.4	0.984	0.964	0.927	0.964	0.926

Appendix Table C-21. BTEX removal data from Column 10A during first sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	14.2	2.894	0.134	4.937	0.228	2.307	0.106	1.397	0.064	0.482	0.022
2	44.3	2.088	0.376	4.631	0.693	2.298	0.330	1.415	0.201	0.493	0.070
3	75.1	1.357	0.548	3.798	1.115	1.983	0.545	1.232	0.334	0.436	0.116
4	111.1	0.919	0.681	3.534	1.542	1.990	0.776	1.256	0.479	0.457	0.168
5	142.0	0.525	0.753	2.877	1.863	1.707	0.961	1.080	0.596	0.398	0.211
6	207.4	0.244	0.834	2.643	2.448	1.747	1.327	1.116	0.828	0.418	0.297
7	242.1	0.170	0.858	2.301	2.726	1.727	1.522	1.123	0.954	0.423	0.345
8	276.8	0.152	0.876	1.813	2.957	1.680	1.714	1.114	1.080	0.426	0.392
9	346.3	0.133	0.908	1.324	3.310	1.632	2.086	1.105	1.330	0.429	0.489
10	381.0	0.063	0.919	0.838	3.432	1.236	2.248	0.847	1.439	0.337	0.532
11	496.7	0.041	0.938	0.427	3.669	1.020	2.671	0.766	1.742	0.329	0.657
12	612.5	0.039	0.953	0.332	3.811	0.946	3.039	0.800	2.035	0.392	0.792
13	728.2	0.018	0.964	0.147	3.901	0.402	3.292	0.376	2.256	0.216	0.906
14	1075.4	0.009	0.979	0.064	4.020	0.114	3.582	0.111	2.530	0.084	1.075
15	1422.6	0.005	0.987	0.033	4.074	0.053	3.676	0.045	2.617	0.033	1.141
16	1793.0	0.006	0.993	0.045	4.121	0.068	3.749	0.057	2.678	0.036	1.182
17	2163.4	0.008	1.002	0.026	4.163	0.038	3.813	0.029	2.729	0.017	1.214
18	2533.8	0.002	1.008	0.016	4.189	0.022	3.848	0.017	2.757	0.009	1.229
19	2916.9	0.003	1.011	0.019	4.210	0.026	3.878	0.019	2.779	0.010	1.242
20	3044.6	0.002	1.012	0.019	4.218	0.028	3.889	0.019	2.787	0.012	1.246

Appendix Table C-22. BTEX removal data from Column 10A during second sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	17.9	2.116	0.123	3.639	0.211	1.638	0.095	1.174	0.068	1.555	0.090
2	62.6	1.531	0.387	3.821	0.752	1.752	0.341	1.261	0.245	1.662	0.323
3	100.9	1.260	0.560	4.267	1.254	1.972	0.572	1.446	0.413	1.897	0.544
4	142.4	0.523	0.680	2.708	1.723	1.328	0.794	0.987	0.576	1.293	0.759
5	213.4	0.287	0.773	2.984	2.377	1.782	1.151	1.379	0.848	1.862	1.122
6	250.5	0.164	0.800	2.121	2.683	1.496	1.348	1.185	1.002	1.637	1.331
7	287.5	0.134	0.818	1.809	2.919	1.365	1.520	1.084	1.138	1.486	1.519
8	338.6	0.101	0.838	1.369	3.182	1.297	1.740	1.057	1.315	1.458	1.762
9	383.3	0.085	0.851	1.062	3.358	1.253	1.925	1.050	1.468	1.473	1.975
10	466.3	0.070	0.872	0.687	3.594	1.147	2.247	1.025	1.747	1.511	2.376
11	517.4	0.057	0.882	0.507	3.692	0.993	2.424	0.937	1.910	1.427	2.619
12	594.0	0.046	0.895	0.361	3.800	0.786	2.645	0.801	2.125	1.345	2.963
13	638.7	0.040	0.901	0.291	3.847	0.631	2.748	0.672	2.232	1.198	3.147
14	906.9	0.024	0.929	0.153	4.041	0.247	3.130	0.301	2.655	0.748	3.993
15	1239.0	0.016	0.951	0.102	4.178	0.134	3.334	0.145	2.895	0.377	4.598
16	1649.0	0.012	0.970	0.081	4.299	0.102	3.490	0.100	3.057	0.220	4.995
17	2118.6	0.006	0.984	0.041	4.393	0.048	3.605	0.046	3.168	0.091	5.232
18	2575.0	0.005	0.993	0.036	4.450	0.040	3.670	0.036	3.229	0.069	5.350
19	2965.9	0.003	0.998	0.013	4.481	0.028	3.713	0.026	3.269	0.050	5.426
20	3281.4	0.003	1.002	0.022	4.500	0.027	3.741	0.024	3.295	0.045	5.474

Appendix Table C-23. BTEX removal data from Column 10A during third sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	9.6	3.139	0.097	4.828	0.150	2.482	0.077	1.561	0.048	2.229	0.069
2	47.9	1.922	0.412	4.163	0.708	2.236	0.370	1.417	0.233	2.012	0.332
3	84.9	1.269	0.603	3.536	1.170	1.959	0.622	1.236	0.392	1.778	0.560
4	122.0	0.818	0.728	3.579	1.597	2.145	0.868	1.375	0.549	2.023	0.788
5	159.0	0.553	0.810	3.839	2.042	2.570	1.151	1.664	0.731	2.502	1.059
6	197.3	0.193	0.857	1.871	2.396	1.308	1.391	0.842	0.887	1.264	1.293
7	277.6	0.076	0.892	1.161	2.791	1.262	1.726	0.858	1.108	1.410	1.641
8	314.6	0.103	0.903	1.530	2.952	1.870	1.914	1.266	1.236	2.049	1.848
9	388.7	0.034	0.919	0.463	3.191	0.813	2.235	0.568	1.456	0.951	2.208
10	512.1	0.040	0.934	0.379	3.360	0.944	2.587	0.706	1.710	1.250	2.649
11	639.8	0.037	0.950	0.229	3.485	0.674	2.922	0.577	1.976	1.219	3.160
12	742.0	0.034	0.961	0.226	3.561	0.604	3.133	0.556	2.163	1.282	3.574
13	1165.3	0.018	0.997	0.117	3.795	0.212	3.693	0.202	2.683	0.647	4.896
14	1548.9	0.013	1.016	0.077	3.916	0.109	3.893	0.093	2.867	0.249	5.453
15	1946.7	0.008	1.030	0.048	3.997	0.069	4.007	0.056	2.962	0.137	5.702
16	2391.1	0.008	1.041	0.050	4.068	0.078	4.113	0.064	3.049	0.154	5.912
17	2854.1	0.004	1.050	0.027	4.126	0.039	4.201	0.031	3.121	0.070	6.081
18	3347.9	0.009	1.061	0.028	4.171	0.039	4.263	0.031	3.170	0.072	6.194
19	3394.2	0.006	1.062	0.032	4.175	0.043	4.270	0.034	3.175	0.073	6.205

Appendix Table C-24. BTEX removal data from Column 10A during fourth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	10.9	3.048	0.108	5.519	0.195	3.098	0.109	2.109	0.074	2.705	0.095
2	49.7	1.725	0.408	4.683	0.836	3.043	0.496	2.126	0.341	2.819	0.443
3	89.8	1.551	0.621	5.197	1.479	3.277	0.906	2.269	0.626	3.029	0.823
4	133.1	0.866	0.790	4.648	2.168	3.081	1.351	2.137	0.935	2.848	1.234
5	219.5	0.266	0.948	3.274	3.277	2.813	2.177	1.983	1.512	2.711	2.013
6	264.2	0.206	0.983	2.873	3.722	2.824	2.585	1.994	1.800	2.714	2.406
7	308.9	0.152	1.009	2.150	4.086	2.600	2.978	1.877	2.080	2.598	2.790
8	391.9	0.099	1.042	1.280	4.547	2.240	3.628	1.716	2.563	2.525	3.479
9	462.1	0.075	1.062	0.865	4.791	1.986	4.109	1.591	2.939	2.442	4.044
10	577.1	0.068	1.089	0.606	5.065	1.716	4.799	1.520	3.519	2.659	4.994
11	698.4	0.048	1.111	0.372	5.257	1.074	5.347	1.047	4.023	2.090	5.928
12	804.2	0.039	1.126	0.278	5.369	0.736	5.657	0.773	4.336	1.761	6.588
13	1201.0	0.025	1.168	0.172	5.658	0.308	6.328	0.320	5.038	0.867	8.278
14	1545.0	0.017	1.191	0.121	5.822	0.195	6.608	0.185	5.319	0.450	9.012
15	2011.4	0.013	1.214	0.086	5.978	0.130	6.854	0.118	5.548	0.254	9.544
16	2346.1	0.009	1.226	0.058	6.057	0.086	6.971	0.077	5.653	0.161	9.769
17	2778.2	0.008	1.238	0.054	6.135	0.078	7.085	0.069	5.756	0.137	9.977
18	3302.9	0.007	1.250	0.041	6.215	0.057	7.199	0.050	5.857	0.098	10.177
19	3850.4	0.005	1.261	0.036	6.283	0.050	7.293	0.045	5.940	0.083	10.337

Appendix Table C-25. BTEX removal data from Column 10A during fifth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	14.7	3.030	0.145	5.959	0.284	3.070	0.147	2.318	0.111	2.993	0.143
2	42.5	2.286	0.384	5.632	0.806	3.055	0.422	2.365	0.321	3.152	0.419
3	79.5	1.591	0.616	5.444	1.471	3.139	0.794	2.478	0.612	3.350	0.810
4	119.7	1.023	0.786	5.309	2.170	3.213	1.207	2.539	0.938	3.469	1.253
5	206.1	0.350	0.979	4.115	3.489	3.008	2.078	2.402	1.630	3.302	2.201
6	249.3	0.235	1.020	3.286	4.007	2.814	2.485	2.262	1.956	3.121	2.650
7	304.9	0.164	1.055	2.196	4.500	2.411	2.955	1.993	2.339	2.828	3.186
8	400.6	0.112	1.098	1.435	5.064	2.348	3.694	2.037	2.965	2.966	4.085
9	496.4	0.083	1.129	0.885	5.424	1.913	4.355	1.778	3.557	2.802	4.980
10	643.3	0.060	1.162	0.528	5.760	1.328	5.126	1.410	4.316	2.613	6.268
11	764.6	0.055	1.185	0.446	5.951	1.077	5.599	1.244	4.837	2.700	7.312
12	1013.7	0.034	1.221	0.255	6.234	0.461	6.219	0.564	5.567	1.490	9.002
13	1384.0	0.022	1.255	0.158	6.482	0.220	6.628	0.241	6.050	0.638	10.279
14	1780.9	0.016	1.280	0.116	6.657	0.147	6.864	0.152	6.302	0.353	10.916
15	2233.5	0.011	1.300	0.081	6.802	0.101	7.046	0.101	6.488	0.215	11.332
16	2645.8	0.009	1.313	0.066	6.900	0.080	7.167	0.079	6.608	0.161	11.583
17	3101.7	0.008	1.326	0.056	6.991	0.069	7.277	0.068	6.717	0.132	11.800
18	3728.5	0.006	1.340	0.047	7.096	0.057	7.405	0.055	6.842	0.107	12.042

Appendix Table C-26. BTEX removal data from Column 10A during sixth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	10.6	2.566	0.088	4.908	0.168	2.379	0.082	1.779	0.061	2.017	0.069
2	61.4	1.949	0.460	5.602	1.034	3.021	0.526	2.423	0.407	3.023	0.484
3	120.7	0.995	0.742	4.931	2.045	2.835	1.088	2.289	0.860	2.886	1.051
4	172.5	0.506	0.869	4.079	2.802	2.630	1.548	2.141	1.232	2.694	1.520
5	285.9	0.192	0.997	2.403	3.992	2.494	2.489	2.142	2.018	2.741	2.518
6	346.4	0.141	1.029	1.727	4.397	2.197	2.948	1.949	2.419	2.543	3.036
7	406.8	0.113	1.054	1.282	4.692	2.001	3.359	1.860	2.792	2.544	3.534
8	527.8	0.080	1.092	0.741	5.088	1.505	4.046	1.550	3.460	2.403	4.504
9	626.0	0.065	1.115	0.537	5.292	1.148	4.469	1.279	3.910	2.192	5.235
10	762.1	0.051	1.141	0.379	5.494	0.766	4.891	0.915	4.394	1.795	6.114
11	877.8	0.042	1.158	0.296	5.620	0.531	5.134	0.650	4.687	1.387	6.710
12	1541.4	0.022	1.227	0.143	6.093	0.170	5.887	0.189	5.590	0.396	8.627
13	1904.1	0.016	1.249	0.107	6.240	0.117	6.056	0.123	5.773	0.233	8.996
14	2367.0	0.012	1.270	0.081	6.381	0.087	6.210	0.089	5.932	0.161	9.291
15	2914.5	0.009	1.289	0.062	6.508	0.067	6.347	0.068	6.071	0.118	9.539
16	3333.2	0.008	1.300	0.054	6.586	0.059	6.433	0.059	6.157	0.102	9.688
17	3776.1	0.007	1.310	0.047	6.658	0.051	6.511	0.052	6.237	0.087	9.823

Appendix Table C-27. BTEX removal data from Column 10A during seventh sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	11.6	2.742	0.103	5.271	0.198	2.615	0.098	1.678	0.063	1.913	0.072
2	59.5	1.965	0.468	5.238	1.013	2.980	0.532	1.982	0.347	2.614	0.423
3	110.6	1.124	0.724	5.070	1.866	3.160	1.040	2.192	0.692	3.060	0.893
4	158.4	0.615	0.859	4.402	2.601	2.978	1.517	2.086	1.024	2.946	1.359
5	360.5	0.137	1.105	1.610	4.569	2.208	3.214	1.721	2.270	2.568	3.163
6	403.7	0.143	1.124	1.453	4.783	2.211	3.523	1.772	2.515	2.725	3.534
7	455.1	0.112	1.145	1.154	5.000	2.193	3.890	1.881	2.819	3.020	4.012
8	595.7	0.078	1.189	0.688	5.420	1.521	4.736	1.432	3.574	2.694	5.314
9	728.5	0.059	1.218	0.474	5.669	1.073	5.294	1.080	4.114	2.311	6.391
10	861.3	0.046	1.241	0.352	5.847	0.754	5.687	0.787	4.516	1.846	7.285
11	1245.6	0.031	1.289	0.216	6.201	0.347	6.372	0.353	5.226	0.909	9.000
12	1765.6	0.017	1.330	0.116	6.481	0.171	6.809	0.150	5.649	0.382	10.088
13	2252.1	0.013	1.353	0.093	6.646	0.146	7.058	0.112	5.856	0.300	10.625
14	2767.7	0.010	1.372	0.072	6.784	0.093	7.258	0.087	6.022	0.174	11.021
15	3212.2	0.008	1.385	0.059	6.878	0.077	7.380	0.072	6.136	0.142	11.249
16	3671.4	0.006	1.395	0.050	6.959	0.064	7.486	0.061	6.235	0.115	11.440

Appendix Table C-28. BTEX removal data from Column 10A during eighth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	12.8	2.207	0.091	4.568	0.189	2.529	0.105	1.869	0.077	2.494	0.103
2	67.2	1.569	0.425	4.768	1.013	2.858	0.580	2.194	0.436	3.139	0.600
3	122.8	0.807	0.638	4.123	1.813	2.546	1.066	1.955	0.809	2.799	1.135
4	182.1	0.353	0.750	3.064	2.503	2.130	1.515	1.649	1.155	2.373	1.631
5	293.2	0.155	0.841	1.976	3.410	2.107	2.278	1.719	1.761	2.519	2.512
6	352.4	0.120	0.868	1.439	3.738	1.927	2.665	1.631	2.083	2.434	2.987
7	404.3	0.100	0.886	1.076	3.949	1.755	2.974	1.545	2.350	2.397	3.393
8	552.4	0.072	0.927	0.600	4.351	1.281	3.703	1.287	3.029	2.272	4.513
9	663.5	0.055	0.950	0.412	4.533	0.906	4.097	0.985	3.438	2.015	5.285
10	774.6	0.033	0.966	0.240	4.651	0.511	4.352	0.592	3.722	1.362	5.893
11	885.8	0.037	0.979	0.256	4.740	0.475	4.529	0.563	3.930	1.390	6.388
12	1345.0	0.022	1.023	0.149	5.042	0.205	5.035	0.222	4.513	0.566	7.844
13	1777.1	0.016	1.050	0.105	5.220	0.130	5.269	0.133	4.762	0.300	8.450
14	2289.3	0.011	1.073	0.077	5.371	0.092	5.453	0.091	4.948	0.191	8.857
15	2716.1	0.008	1.087	0.057	5.464	0.071	5.566	0.064	5.055	0.137	9.083
16	3328.0	0.007	1.102	0.049	5.570	0.060	5.696	0.059	5.177	0.119	9.336
17	3521.2	0.006	1.106	0.046	5.599	0.056	5.732	0.055	5.212	0.108	9.407

Appendix Table C-29. BTEX removal data from Column 10A during ninth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	16.5	2.283	0.122	4.893	0.262	2.458	0.132	1.860	0.100	2.407	0.129
2	70.0	1.489	0.449	4.428	1.069	2.328	0.546	1.771	0.414	2.320	0.538
3	123.4	0.682	0.637	3.404	1.746	1.933	0.915	1.506	0.698	2.082	0.919
4	177.8	0.405	0.733	3.663	2.370	2.593	1.314	2.088	1.015	2.926	1.361
5	288.9	0.156	0.833	1.892	3.370	1.864	2.116	1.526	1.665	2.137	2.272
6	340.8	0.120	0.857	1.410	3.647	1.693	2.415	1.427	1.913	2.021	2.621
7	392.7	0.102	0.875	1.097	3.858	1.590	2.691	1.389	2.150	2.051	2.963
8	570.4	0.061	0.922	0.488	4.314	0.968	3.428	0.981	2.832	1.722	4.050
9	714.9	0.046	0.947	0.329	4.505	0.613	3.798	0.684	3.222	1.391	4.779
10	800.1	0.040	0.959	0.278	4.589	0.499	3.951	0.571	3.395	1.279	5.147
11	926.0	0.034	0.974	0.231	4.693	0.370	4.128	0.433	3.600	1.053	5.623
12	1402.2	0.021	1.017	0.140	4.979	0.171	4.545	0.183	4.076	0.429	6.766
13	2027.2	0.013	1.051	0.087	5.208	0.097	4.817	0.099	4.360	0.201	7.405
14	2523.6	0.009	1.069	0.065	5.331	0.072	4.953	0.072	4.497	0.138	7.678
15	2950.4	0.008	1.081	0.055	5.414	0.061	5.046	0.060	4.588	0.114	7.852
16	3457.6	0.006	1.092	0.044	5.496	0.050	5.137	0.049	4.679	0.091	8.021
17	3658.9	0.005	1.095	0.040	5.523	0.045	5.168	0.044	4.709	0.081	8.077

Appendix Table C-30. BTEX removal data from Column 10A during tenth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	14.7	1.582	0.075	3.413	0.163	1.656	0.079	1.294	0.062	1.460	0.070
2	57.7	1.299	0.276	3.665	0.655	1.852	0.323	1.491	0.256	1.760	0.294
3	113.9	0.786	0.466	3.634	1.320	1.875	0.663	1.506	0.528	1.778	0.616
4	164.4	0.382	0.562	3.011	1.864	1.762	0.960	1.434	0.769	1.708	0.901
5	255.3	0.147	0.639	1.774	2.568	1.458	1.434	1.229	1.161	1.510	1.375
6	303.6	0.104	0.659	1.292	2.808	1.318	1.652	1.148	1.347	1.427	1.605
7	355.4	0.079	0.675	0.913	2.993	1.168	1.860	1.048	1.532	1.356	1.838
8	540.6	0.056	0.715	0.468	3.408	0.857	2.468	0.887	2.112	1.371	2.657
9	652.4	0.038	0.732	0.292	3.545	0.561	2.725	0.634	2.388	1.110	3.106
10	785.2	0.032	0.747	0.223	3.656	0.373	2.926	0.438	2.618	0.862	3.530
11	987.9	0.030	0.767	0.208	3.798	0.312	3.150	0.387	2.890	0.859	4.095
12	1441.8	0.015	0.801	0.109	4.030	0.132	3.477	0.144	3.280	0.303	4.950
13	1901.1	0.014	0.823	0.089	4.178	0.098	3.649	0.101	3.462	0.194	5.320
14	2628.3	0.009	0.849	0.062	4.356	0.070	3.847	0.069	3.663	0.127	5.698
15	3106.7	0.005	0.860	0.040	4.435	0.045	3.936	0.045	3.751	0.078	5.857
16	3353.6	0.006	0.864	0.044	4.468	0.049	3.973	0.049	3.788	0.085	5.922

Appendix Table C-31. BTEX removal data from Column 10B during first sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	11.3	3.204	0.124	5.655	0.219	2.888	0.112	1.816	0.070	0.657	0.025
2	44.1	2.241	0.430	5.108	0.824	2.593	0.420	1.606	0.263	0.557	0.094
3	72.3	1.578	0.615	4.598	1.294	2.453	0.664	1.533	0.415	0.536	0.147
4	106.2	1.000	0.765	4.264	1.808	2.402	0.946	1.518	0.592	0.542	0.209
5	140.0	0.595	0.857	3.780	2.276	2.343	1.222	1.483	0.766	0.538	0.272
6	173.9	0.342	0.912	3.069	2.673	2.063	1.477	1.305	0.928	0.476	0.331
7	219.0	0.189	0.953	2.312	3.090	1.860	1.781	1.193	1.121	0.442	0.402
8	271.5	0.115	0.980	1.721	3.453	1.788	2.110	1.181	1.335	0.448	0.482
9	329.8	0.077	0.999	1.174	3.742	1.588	2.447	1.086	1.562	0.430	0.570
10	546.9	0.026	1.038	0.304	4.293	0.726	3.309	0.604	2.191	0.304	0.843
11	686.9	0.017	1.048	0.262	4.429	0.492	3.601	0.428	2.438	0.241	0.974
12	791.8	0.013	1.054	0.165	4.506	0.400	3.762	0.366	2.581	0.226	1.058
13	1141.7	0.008	1.066	0.064	4.643	0.134	4.082	0.126	2.876	0.085	1.244
14	1491.6	0.004	1.074	0.027	4.698	0.048	4.192	0.043	2.977	0.028	1.312
15	1853.5	0.003	1.078	0.012	4.722	0.018	4.233	0.015	3.013	0.010	1.336
16	2215.4	0.002	1.082	0.022	4.743	0.036	4.267	0.028	3.040	0.016	1.352
17	2577.3	0.002	1.085	0.020	4.769	0.039	4.313	0.030	3.076	0.017	1.373
18	2966.0	0.002	1.087	0.014	4.792	0.026	4.357	0.019	3.109	0.010	1.391
19	3056.7	0.002	1.088	0.013	4.796	0.025	4.365	0.018	3.115	0.010	1.394

Appendix Table C-32. BTEX removal data from Column 10B during second sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	52.5	1.316	0.237	3.080	0.554	1.561	0.281	1.084	0.195	1.489	0.268
2	91.4	1.399	0.418	4.511	1.061	2.341	0.541	1.633	0.376	2.229	0.516
3	126.3	0.685	0.543	3.154	1.520	1.757	0.787	1.250	0.549	1.730	0.753
4	161.3	0.130	0.592	0.850	1.761	0.508	0.923	0.366	0.646	0.513	0.888
5	196.3	0.173	0.610	1.520	1.903	1.076	1.018	0.799	0.716	1.152	0.988
6	231.3	0.083	0.626	0.946	2.051	0.809	1.131	0.626	0.801	0.931	1.113
7	266.3	0.029	0.632	0.388	2.131	0.410	1.204	0.330	0.859	0.510	1.199
8	301.3	0.055	0.637	0.740	2.198	0.794	1.276	0.636	0.917	0.956	1.287
9	336.2	0.045	0.643	0.612	2.280	0.731	1.368	0.600	0.991	0.923	1.400
10	382.9	0.064	0.652	0.809	2.393	1.075	1.512	0.896	1.111	1.408	1.587
11	560.8	0.050	0.687	0.498	2.792	0.914	2.120	0.860	1.646	1.556	2.491
12	802.1	0.026	0.718	0.201	3.081	0.390	2.659	0.403	2.169	0.867	3.494
13	922.8	0.020	0.728	0.151	3.154	0.275	2.797	0.288	2.312	0.660	3.809
14	1296.7	0.012	0.748	0.087	3.307	0.133	3.059	0.134	2.582	0.320	4.438
15	1610.4	0.011	0.761	0.076	3.394	0.111	3.190	0.105	2.710	0.238	4.738
16	1991.5	0.008	0.774	0.059	3.482	0.079	3.313	0.071	2.825	0.152	4.992
17	2435.1	0.005	0.783	0.036	3.554	0.052	3.413	0.045	2.914	0.092	5.178
18	2872.4	0.004	0.789	0.023	3.599	0.037	3.479	0.033	2.972	0.066	5.297
19	3116.0	0.003	0.792	0.021	3.618	0.033	3.509	0.029	2.998	0.057	5.348

Appendix Table C-33. BTEX removal data from Column 10B during third sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	12.2	2.588	0.109	3.839	0.161	1.940	0.081	1.195	0.050	1.710	0.072
2	50.4	2.235	0.424	5.190	0.752	2.761	0.389	1.700	0.240	2.413	0.342
3	85.4	1.484	0.648	5.131	1.372	2.784	0.722	1.704	0.444	2.412	0.631
4	120.4	0.710	0.779	4.082	1.924	2.528	1.040	1.569	0.640	2.280	0.913
5	155.4	0.346	0.843	2.931	2.345	2.074	1.317	1.311	0.813	1.946	1.166
6	190.4	0.247	0.878	2.648	2.680	2.221	1.574	1.433	0.978	2.166	1.413
7	231.2	0.167	0.907	2.011	3.006	1.992	1.869	1.308	1.170	2.016	1.706
8	272.0	0.119	0.927	1.383	3.244	1.656	2.124	1.118	1.339	1.775	1.971
9	312.8	0.105	0.943	1.281	3.430	1.981	2.379	1.405	1.516	2.382	2.262
10	350.7	0.071	0.954	0.771	3.563	1.294	2.592	0.940	1.668	1.608	2.521
11	601.4	0.024	0.995	0.190	3.976	0.438	3.337	0.397	2.243	0.951	3.622
12	718.0	0.019	1.004	0.155	4.046	0.396	3.503	0.389	2.400	1.086	4.030
13	1044.6	0.020	1.025	0.102	4.190	0.165	3.817	0.150	2.703	0.408	4.867
14	1417.8	0.047	1.069	0.131	4.339	0.196	4.048	0.164	2.904	0.395	5.381
15	1767.6	0.018	1.108	0.063	4.456	0.092	4.221	0.076	3.048	0.173	5.722
16	2094.1	0.010	1.123	0.049	4.519	0.062	4.307	0.049	3.118	0.107	5.879
17	2444.0	0.008	1.133	0.042	4.573	0.056	4.378	0.045	3.174	0.100	6.003
18	2825.1	0.006	1.143	0.035	4.623	0.047	4.445	0.036	3.227	0.078	6.119
19	3233.3	0.004	1.150	0.024	4.665	0.033	4.501	0.026	3.270	0.055	6.212

Appendix Table C-34. BTEX removal data from Column 10B during fourth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	10.9	3.108	0.117	5.645	0.212	3.148	0.118	2.176	0.082	2.710	0.102
2	53.2	1.733	0.467	4.855	0.972	2.909	0.557	1.976	0.382	2.566	0.484
3	113.5	0.614	0.710	4.315	1.921	3.075	1.176	2.130	0.807	2.810	1.040
4	151.0	0.370	0.773	3.883	2.448	3.280	1.584	2.304	1.092	3.114	1.421
5	188.4	0.237	0.812	3.060	2.894	3.105	1.995	2.229	1.383	3.087	1.819
6	225.9	0.165	0.838	2.230	3.234	2.726	2.370	2.004	1.656	2.817	2.199
7	269.7	0.127	0.860	1.608	3.522	2.510	2.762	1.907	1.949	2.818	2.621
8	313.4	0.098	0.877	1.135	3.728	2.222	3.117	1.764	2.224	2.724	3.037
9	365.2	0.081	0.893	0.801	3.900	1.895	3.483	1.581	2.522	2.607	3.511
10	598.5	0.048	0.944	0.333	4.354	0.827	4.572	0.833	3.487	1.812	5.279
11	773.4	0.035	0.969	0.225	4.521	0.456	4.957	0.473	3.879	1.176	6.175
12	941.8	0.030	0.988	0.176	4.637	0.293	5.173	0.294	4.100	0.746	6.730
13	1175.1	0.026	1.011	0.141	4.764	0.202	5.372	0.189	4.294	0.445	7.206
14	1531.4	0.020	1.039	0.111	4.919	0.146	5.584	0.128	4.487	0.262	7.638
15	1894.2	0.016	1.061	0.094	5.046	0.119	5.749	0.102	4.631	0.198	7.925
16	2318.1	0.013	1.082	0.089	5.180	0.115	5.919	0.098	4.776	0.181	8.200
17	2674.7	0.010	1.096	0.077	5.281	0.108	6.056	0.090	4.891	0.163	8.410
18	3165.8	0.009	1.113	0.054	5.391	0.084	6.217	0.072	5.027	0.129	8.656
19	3536.6	0.011	1.126	0.055	5.460	0.081	6.323	0.071	5.118	0.132	8.822

Appendix Table C-35. BTEX removal data from Column 10B during fifth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	6.7	3.058	0.071	5.068	0.117	2.297	0.053	1.852	0.043	1.985	0.046
2	40.6	2.195	0.376	5.787	0.747	3.051	0.364	2.441	0.292	3.177	0.346
3	78.1	1.403	0.607	5.176	1.452	2.818	0.741	2.179	0.589	2.964	0.740
4	118.7	0.772	0.758	4.561	2.130	2.729	1.127	2.131	0.889	2.933	1.151
5	156.2	0.427	0.835	3.625	2.656	2.401	1.457	1.881	1.147	2.619	1.508
6	199.9	0.254	0.886	3.089	3.160	2.441	1.820	1.949	1.434	2.764	1.912
7	245.2	0.169	0.919	2.389	3.586	2.280	2.187	1.861	1.731	2.701	2.337
8	284.1	0.126	0.939	1.839	3.868	2.071	2.477	1.725	1.970	2.554	2.687
9	342.4	0.092	0.961	1.256	4.177	1.817	2.866	1.572	2.299	2.453	3.188
10	387.8	0.078	0.974	0.968	4.350	1.621	3.133	1.456	2.535	2.363	3.562
11	601.6	0.049	1.021	0.444	4.868	1.066	4.119	1.150	3.491	2.342	5.288
12	802.4	0.034	1.049	0.224	5.098	0.475	4.649	0.556	4.078	1.308	6.545
13	1058.1	0.021	1.074	0.157	5.265	0.274	4.978	0.315	4.460	0.806	7.472
14	1414.7	0.015	1.096	0.105	5.425	0.148	5.236	0.158	4.749	0.381	8.198
15	1859.3	0.011	1.116	0.077	5.564	0.102	5.426	0.105	4.949	0.224	8.659
16	2296.6	0.011	1.133	0.065	5.670	0.077	5.561	0.077	5.085	0.152	8.941
17	2806.2	0.010	1.151	0.061	5.780	0.071	5.690	0.068	5.212	0.125	9.183
18	3275.3	0.010	1.168	0.052	5.870	0.057	5.793	0.056	5.312	0.106	9.370
19	3796.0	0.009	1.185	0.050	5.961	0.052	5.890	0.051	5.408	0.091	9.546

Appendix Table C-36. BTEX removal data from Column 10B during sixth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	17.5	2.727	0.164	5.156	0.309	2.642	0.159	2.292	0.138	2.357	0.141
2	59.6	1.455	0.466	5.078	1.048	2.889	0.558	2.300	0.469	2.891	0.521
3	103.3	0.646	0.623	3.886	1.721	2.560	0.967	2.073	0.797	2.652	0.936
4	155.8	0.289	0.707	2.842	2.326	2.348	1.408	1.976	1.162	2.612	1.410
5	204.8	0.171	0.746	2.031	2.736	2.036	1.776	1.739	1.474	2.408	1.832
6	253.8	0.115	0.770	1.440	3.027	1.755	2.095	1.549	1.750	2.243	2.223
7	310.9	0.085	0.790	1.006	3.267	1.491	2.413	1.371	2.036	2.104	2.648
8	368.0	0.066	0.804	0.727	3.437	1.262	2.683	1.214	2.289	1.952	3.046
9	619.9	0.035	0.848	0.281	3.872	0.556	3.468	0.616	3.080	1.217	4.415
10	848.4	0.023	0.871	0.177	4.052	0.319	3.811	0.366	3.465	0.776	5.196
11	1190.9	0.016	0.894	0.107	4.218	0.162	4.094	0.184	3.788	0.389	5.881
12	1810.5	0.013	0.924	0.074	4.411	0.090	4.362	0.100	4.089	0.174	6.479
13	2167.8	0.009	0.938	0.055	4.490	0.065	4.458	0.068	4.191	0.119	6.659
14	2614.4	0.009	0.952	0.049	4.570	0.054	4.549	0.058	4.288	0.095	6.823
15	3131.6	0.009	0.968	0.045	4.653	0.046	4.638	0.047	4.381	0.076	6.975
16	3527.1	0.010	0.981	0.048	4.717	0.045	4.700	0.043	4.442	0.070	7.074

Appendix Table C-37. BTEX removal data from Column 10B during seventh sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	15.9	2.475	0.135	5.773	0.315	3.272	0.178	2.503	0.137	3.118	0.170
2	73.1	0.931	0.469	4.720	1.344	3.130	0.806	2.275	0.605	3.074	0.777
3	124.5	0.379	0.585	3.340	2.055	2.807	1.330	2.110	0.992	2.948	1.309
4	176.0	0.192	0.635	2.202	2.544	2.476	1.796	1.942	1.350	2.833	1.819
5	232.0	0.126	0.666	1.409	2.891	2.090	2.235	1.730	1.702	2.694	2.349
6	287.9	0.092	0.687	0.924	3.115	1.678	2.596	1.476	2.010	2.448	2.843
7	340.4	0.074	0.701	0.652	3.257	1.358	2.870	1.250	2.255	2.234	3.264
8	399.9	0.061	0.715	0.477	3.372	1.047	3.115	1.017	2.486	1.956	3.692
9	704.3	0.034	0.765	0.224	3.738	0.369	3.854	0.394	3.223	0.920	5.193
10	945.7	0.028	0.790	0.174	3.902	0.258	4.113	0.272	3.498	0.650	5.843
11	1365.5	0.017	0.822	0.100	4.100	0.131	4.393	0.119	3.780	0.271	6.506
12	1743.3	0.013	0.842	0.078	4.214	0.095	4.540	0.082	3.910	0.176	6.796
13	2282.7	0.011	0.864	0.067	4.348	0.086	4.707	0.067	4.048	0.147	7.095
14	2765.5	0.007	0.878	0.042	4.438	0.084	4.848	0.047	4.143	0.192	7.375
15	3248.3	0.008	0.891	0.048	4.512	0.055	4.963	0.049	4.223	0.087	7.606
16	3549.2	0.009	0.900	0.052	4.563	0.065	5.025	0.061	4.280	0.107	7.706

Appendix Table C-38. BTEX removal data from Column 10B during eighth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	21.0	1.893	0.136	4.754	0.342	2.643	0.190	2.020	0.145	2.783	0.200
2	70.0	0.726	0.356	3.804	1.061	2.602	0.631	2.087	0.490	3.131	0.697
3	122.4	0.294	0.448	2.764	1.652	2.449	1.085	2.007	0.859	2.960	1.245
4	167.9	0.171	0.484	1.933	2.019	2.195	1.448	1.861	1.161	2.893	1.702
5	223.9	0.100	0.511	1.095	2.309	1.655	1.817	1.492	1.482	2.489	2.219
6	281.0	0.073	0.527	0.720	2.487	1.343	2.111	1.289	1.755	2.319	2.690
7	331.0	0.058	0.539	0.505	2.592	1.046	2.316	1.055	1.956	2.040	3.063
8	388.1	0.055	0.550	0.435	2.684	0.938	2.510	0.996	2.157	2.137	3.472
9	666.6	0.027	0.589	0.171	2.974	0.271	3.087	0.298	2.775	0.728	4.840
10	873.6	0.020	0.605	0.127	3.080	0.179	3.247	0.195	2.950	0.457	5.261
11	1237.8	0.014	0.627	0.085	3.213	0.107	3.425	0.110	3.141	0.236	5.694
12	1673.3	0.011	0.645	0.062	3.322	0.071	3.558	0.071	3.276	0.138	5.974
13	2066.0	0.009	0.658	0.054	3.400	0.063	3.648	0.062	3.366	0.111	6.142
14	2547.0	0.009	0.672	0.044	3.482	0.052	3.743	0.052	3.461	0.101	6.316
15	2940.6	0.007	0.683	0.035	3.536	0.040	3.805	0.036	3.521	0.071	6.432
16	3487.3	0.008	0.696	0.037	3.603	0.043	3.883	0.042	3.594	0.085	6.579

Appendix Table C-39. BTEX removal data from Column 10B during ninth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	14.6	2.052	0.103	4.756	0.238	2.358	0.118	1.953	0.098	2.282	0.114
2	58.3	0.867	0.321	3.670	0.870	2.153	0.456	1.673	0.370	2.162	0.447
3	106.9	0.334	0.422	2.382	1.374	1.812	0.787	1.487	0.633	2.007	0.795
4	158.7	0.174	0.467	1.778	1.744	2.055	1.130	1.831	0.928	2.884	1.230
5	211.5	0.108	0.492	1.037	1.999	1.289	1.433	1.153	1.198	1.840	1.657
6	254.4	0.083	0.506	0.743	2.130	1.053	1.606	0.985	1.356	1.655	1.914
7	310.6	0.064	0.520	0.526	2.252	0.862	1.790	0.850	1.532	1.527	2.221
8	360.1	0.053	0.530	0.392	2.330	0.671	1.920	0.681	1.662	1.291	2.460
9	626.1	0.030	0.568	0.179	2.590	0.267	2.348	0.294	2.107	0.640	3.341
10	824.6	0.022	0.586	0.124	2.693	0.149	2.490	0.160	2.262	0.346	3.677
11	1201.4	0.017	0.611	0.090	2.832	0.100	2.650	0.101	2.431	0.204	4.032
12	1633.5	0.012	0.633	0.066	2.948	0.071	2.777	0.074	2.561	0.126	4.277
13	2200.3	0.009	0.653	0.049	3.059	0.052	2.896	0.051	2.683	0.089	4.486
14	2634.1	0.008	0.666	0.045	3.129	0.046	2.968	0.045	2.754	0.077	4.610
15	3005.0	0.008	0.676	0.039	3.182	0.041	3.024	0.040	2.809	0.069	4.703
16	3445.8	0.007	0.687	0.036	3.239	0.034	3.080	0.033	2.864	0.057	4.799

Appendix Table C-40. BTEX removal data from Column 10B during tenth sparging cycle.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (mg)	Toluene Conc. (mg/L)	Toluene Mass Removed (mg)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Removed (mg)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Removed (mg)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (mg)
1	16.197	1.769	0.098	4.445	0.247	2.026	0.113	1.625	0.090	1.843	0.102
2	59.929	0.674	0.282	3.080	0.811	1.733	0.395	1.444	0.321	1.686	0.367
3	107.024	0.283	0.359	2.080	1.228	1.504	0.656	1.310	0.543	1.622	0.634
4	158.474	0.140	0.396	1.310	1.527	1.239	0.898	1.135	0.759	1.501	0.910
5	206.872	0.087	0.415	0.861	1.707	1.020	1.086	0.983	0.934	1.386	1.150
6	255.852	0.063	0.428	0.583	1.829	0.805	1.239	0.810	1.085	1.213	1.368
7	360.808	0.046	0.447	0.358	1.998	0.633	1.498	0.693	1.356	1.282	1.817
8	504.249	0.029	0.465	0.175	2.129	0.263	1.718	0.298	1.599	0.553	2.268
9	765.229	0.017	0.486	0.098	2.252	0.115	1.888	0.128	1.790	0.250	2.628
10	1043.684	0.015	0.501	0.077	2.335	0.079	1.980	0.082	1.890	0.153	2.821
11	1433.198	0.011	0.518	0.059	2.426	0.054	2.069	0.055	1.981	0.090	2.983
12	1965.898	0.008	0.535	0.047	2.523	0.049	2.164	0.049	2.076	0.081	3.139
13	2421.286	0.007	0.547	0.039	2.590	0.039	2.232	0.039	2.145	0.063	3.251
14	3079.070	0.006	0.561	0.031	2.669	0.039	2.320	0.033	2.227	0.071	3.402
15	3353.749	0.006	0.567	0.031	2.698	0.029	2.352	0.029	2.256	0.049	3.459

Appendix Table C-41. K_d, Mass sorbed, mass removed, and cumulative mass remaining for BTEX compounds on Column 10A.

Compound	K _d (L/kg)	Mass sorbed (mg)	Mass removed (mg)	Cum. mass remaining (mg)
Benzene BTC 1	15.1	1.02	1.1	-0.08
Benzene BTC 2	20.8	1.45	1	0.37
Benzene BTC 3	20.2	1.65	1.06	0.96
Benzene BTC 4	16.4	1.09	1.26	0.79
Benzene BTC 5	16.4	1.12	1.34	0.57
Benzene BTC 6	17.6	1.19	1.31	0.45
Benzene BTC 7	11.3	0.78	1.4	-0.17
Benzene BTC 8	19.5	1.27	1.11	-0.01
Benzene BTC 9	14.5	0.97	1.1	-0.14
Benzene BTC 10	13.9	1.02	0.86	0.02
Toluene BTC 1	34.0	4.56	4.22	0.34
Toluene BTC 2	37.8	5.68	4.5	1.52
Toluene BTC 3	37.8	6.9	4.18	4.24
Toluene BTC 4	38.4	5.75	6.28	3.71
Toluene BTC 5	37.2	5.84	7.1	2.45
Toluene BTC 6	37.2	5.89	6.66	1.68
Toluene BTC 7	29.6	4.71	6.96	-0.57
Toluene BTC 8	41.6	6.23	5.6	0.06
Toluene BTC 9	32.1	5.04	5.52	-0.42
Toluene BTC 10	29.6	4.96	4.47	0.07
Ethylbenzene BTC 1	92.6	5.21	3.89	1.32
Ethylbenzene BTC 2	89.4	5.36	3.74	2.94
Ethylbenzene BTC 3	92.6	8.35	4.27	7.02
Ethylbenzene BTC 4	90.7	6.34	7.29	6.07
Ethylbenzene BTC 5	89.4	6.07	7.4	4.74
Ethylbenzene BTC 6	92.0	6.24	6.51	4.47
Ethylbenzene BTC 7	83.1	6.15	7.49	3.13
Ethylbenzene BTC 8	90.1	6.13	5.73	3.53
Ethylbenzene BTC 9	76.2	5.5	5.17	3.86
Ethylbenzene BTC 10	69.9	4.94	3.97	4.83
p-&m-xylene BTC 1	100.2	3.58	2.79	0.79
p-&m-xylene BTC 2	103.9	4.72	3.29	2.22
p-&m-xylene BTC 3	95.1	5.6	3.17	4.65
p-&m-xylene BTC 4	98.3	4.74	5.94	3.45
p-&m-xylene BTC 5	96.4	5.11	6.84	1.72
p-&m-xylene BTC 6	93.2	5.13	6.24	0.61
p-&m-xylene BTC 7	87.6	4.66	6.23	-0.96
p-&m-xylene BTC 8	98.3	5.22	5.21	-0.95
p-&m-xylene BTC 9	86.9	5.58	4.71	-0.08
p-&m-xylene BTC 10	76.2	4.47	3.79	0.6
o-xylene BTC 1	97.0	1.28	1.25	0.03
o-xylene BTC 2	93.9	6.61	5.47	1.17
o-xylene BTC 3	92.6	9.34	6.21	4.3
o-xylene BTC 4	88.8	6.66	10.34	0.62
o-xylene BTC 5	88.8	7.35	12.04	-4.07
o-xylene BTC 6	83.8	6.51	9.82	-7.38
o-xylene BTC 7	81.3	6.9	11.44	-11.92
o-xylene BTC 8	90.1	7.63	9.41	-13.7
o-xylene BTC 9	73.1	6.71	8.08	-15.07
o-xylene BTC 10	68.0	5.61	5.92	-15.38

Appendix Table C-42. K_d, Mass sorbed, mass removed, and cumulative mass remaining for BTEX compounds on Column 10B.

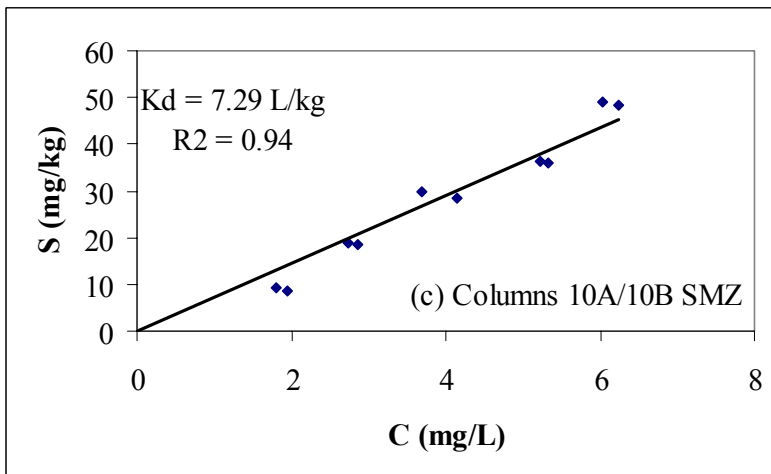
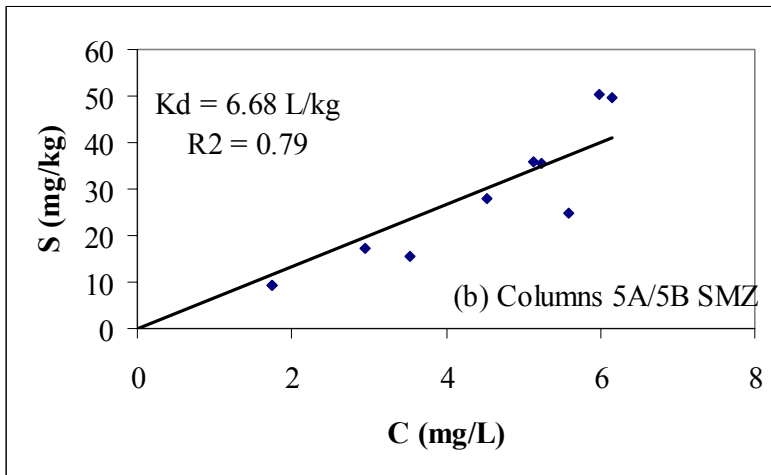
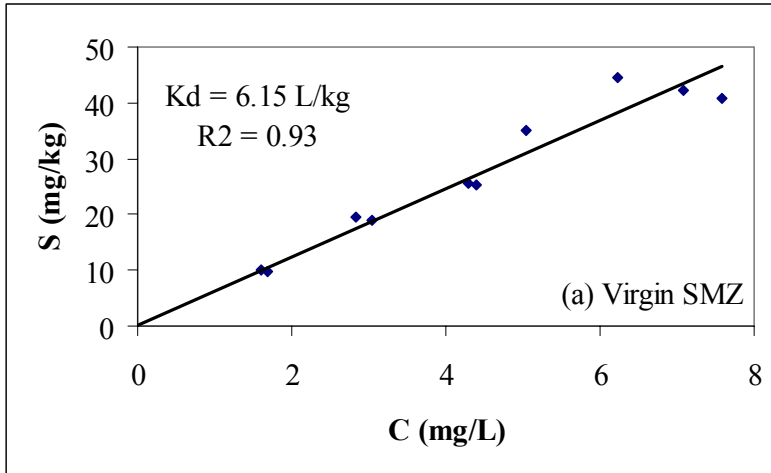
Compound	K _d (L/kg)	Mass sorbed (mg)	Mass removed (mg)	Cum. mass remaining (mg)
Benzene BTC 1	12.8	0.92	1.09	-0.17
Benzene BTC 2	16.1	1.07	0.79	0.11
Benzene BTC 3	18.8	1.39	1.15	0.35
Benzene BTC 4	26.2	1.66	1.13	0.88
Benzene BTC 5	24.9	1.54	1.18	1.24
Benzene BTC 6	22.8	1.31	0.98	1.57
Benzene BTC 7	19.5	1.02	0.9	1.69
Benzene BTC 8	10.1	0.51	0.7	1.5
Benzene BTC 9	25.5	1.18	0.69	1.99
Benzene BTC 10	6.0	0.29	0.57	1.71
Toluene BTC 1	39.0	4.98	4.8	0.18
Toluene BTC 2	37.0	5.4	3.62	1.96
Toluene BTC 3	41.0	6.6	4.66	3.9
Toluene BTC 4	43.7	6.23	5.46	4.67
Toluene BTC 5	41.0	5.94	5.96	4.65
Toluene BTC 6	43.0	5.68	4.72	5.61
Toluene BTC 7	35.6	4.34	4.56	5.39
Toluene BTC 8	23.5	2.74	3.6	4.53
Toluene BTC 9	45.0	4.93	3.24	6.22
Toluene BTC 10	22.8	2.53	2.7	6.05
Ethylbenzene BTC 1	106.2	6.1	4.36	1.74
Ethylbenzene BTC 2	98.1	5.5	3.51	3.73
Ethylbenzene BTC 3	102.8	7.85	4.5	7.08
Ethylbenzene BTC 4	88.7	6.07	6.32	6.83
Ethylbenzene BTC 5	89.4	5.41	5.89	6.35
Ethylbenzene BTC 6	90.0	5.44	4.7	7.09
Ethylbenzene BTC 7	74.6	4.55	5.02	6.62
Ethylbenzene BTC 8	58.5	3.23	3.88	5.97
Ethylbenzene BTC 9	79.3	4.01	3.08	6.9
Ethylbenzene BTC 10	55.8	2.68	2.35	7.23
p-&m-xylene BTC 1	113.6	4.17	3.12	1.05
p-&m-xylene BTC 2	106.2	4.64	3	2.69
p-&m-xylene BTC 3	108.2	5.5	3.27	4.92
p-&m-xylene BTC 4	97.4	4.52	5.12	4.32
p-&m-xylene BTC 5	98.1	4.63	5.41	3.54
p-&m-xylene BTC 6	98.1	4.62	4.44	3.72
p-&m-xylene BTC 7	82.6	3.58	4.28	3.02
p-&m-xylene BTC 8	65.8	2.82	3.59	2.25
p-&m-xylene BTC 9	79.3	3.65	2.86	3.04
p-&m-xylene BTC 10	68.5	2.53	2.26	3.31
o-xylene BTC 1	106.2	1.54	1.39	0.15
o-xylene BTC 2	101.5	6.71	5.35	1.51
o-xylene BTC 3	102.8	8.84	6.21	4.14
o-xylene BTC 4	86.0	6.27	8.82	1.59
o-xylene BTC 5	89.4	6.64	9.55	-1.32
o-xylene BTC 6	88.0	6.08	7.07	-2.31
o-xylene BTC 7	73.9	5.13	7.71	-4.89
o-xylene BTC 8	59.1	4.03	6.58	-7.44
o-xylene BTC 9	82.0	5.1	4.8	-7.14
o-xylene BTC 10	53.8	3.02	3.46	-7.58

Appendix Table C-43. CXTFIT 2.1 calculations used to create manuscript Figure 2.

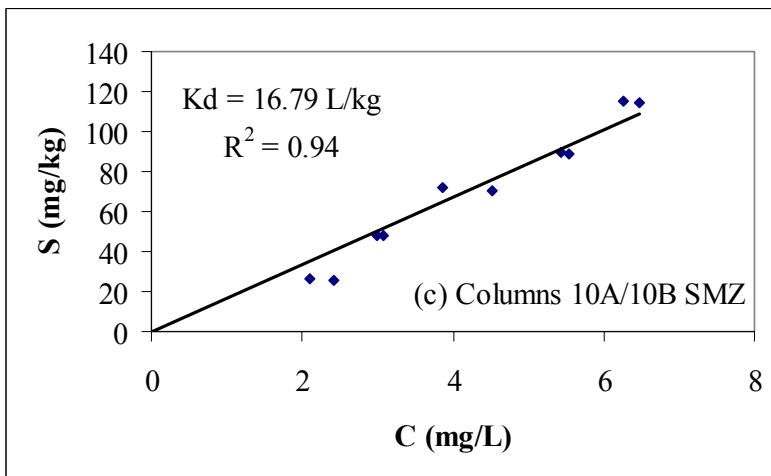
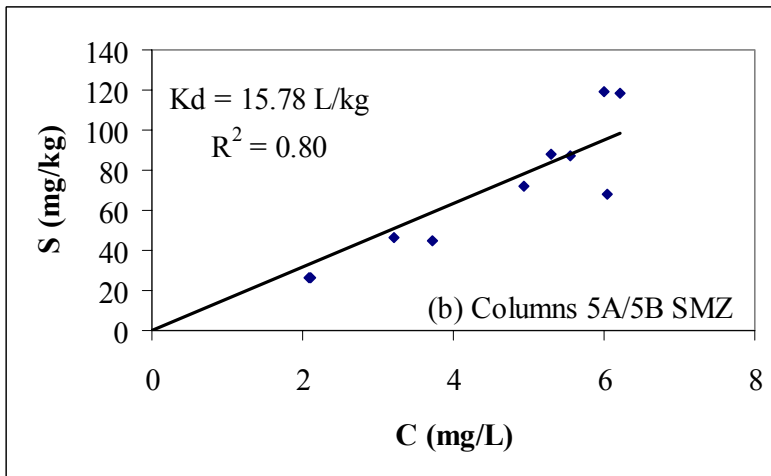
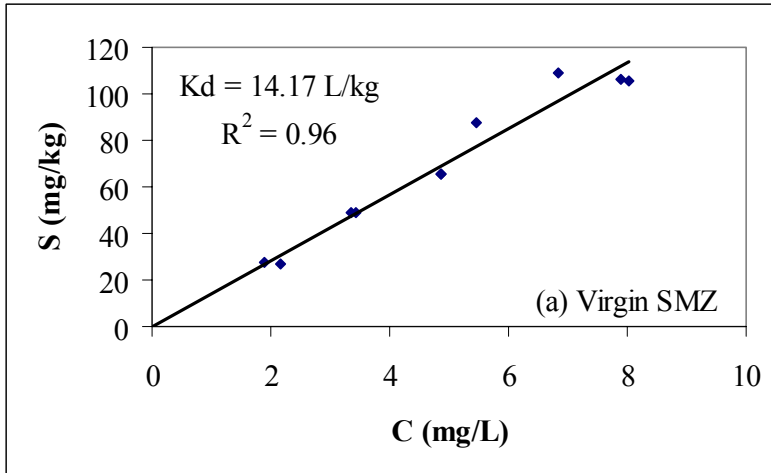
Sample	Pore Volumes	Fitted Benzene C/Co	Fitted Toluene C/Co	Fitted Ethylbenzene C/Co	Fitted p-&m-xylene C/Co	Fitted o-xylene C/Co
1	2.8	0.000	0.000	0.000	0.000	0.000
2	6.7	0.047	0.000	0.000	0.000	0.000
3	10.4	0.509	0.000	0.000	0.000	0.000
4	14.5	0.862	0.003	0.000	0.000	0.000
5	18.6	0.929	0.040	0.000	0.000	0.000
6	30.3	0.939	0.520	0.000	0.000	0.001
7	41.9	0.942	0.813	0.011	0.005	0.029
8	53.4	0.945	0.867	0.083	0.047	0.149
9	64.8	0.948	0.880	0.230	0.157	0.323
10	76.0	0.951	0.887	0.389	0.302	0.467
11	87.1	0.953	0.894	0.512	0.430	0.557
12	134.1	0.962	0.919	0.700	0.661	0.685
13	207.0	0.973	0.947	0.799	0.774	0.778
14	254.0	0.978	0.959	0.844	0.825	0.823
15	307.3	0.983	0.970	0.884	0.869	0.863
16	346.4	0.986	0.976	0.906	0.895	0.887
17	389.4	0.988	0.981	0.926	0.917	0.908
18	417.0	0.990	0.984	0.937	0.929	0.920

APPENDIX D. BATCH EXPERIMENT RESULTS

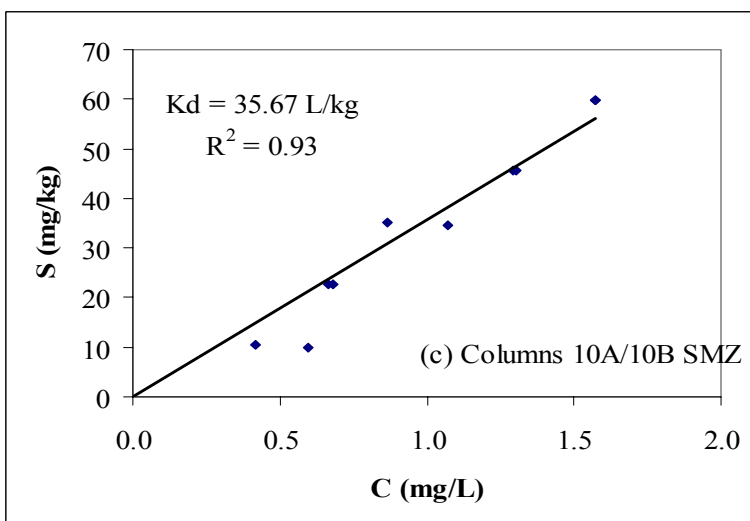
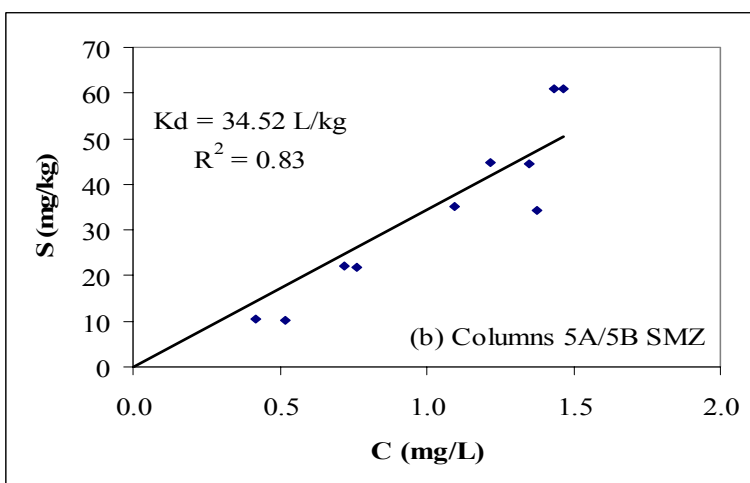
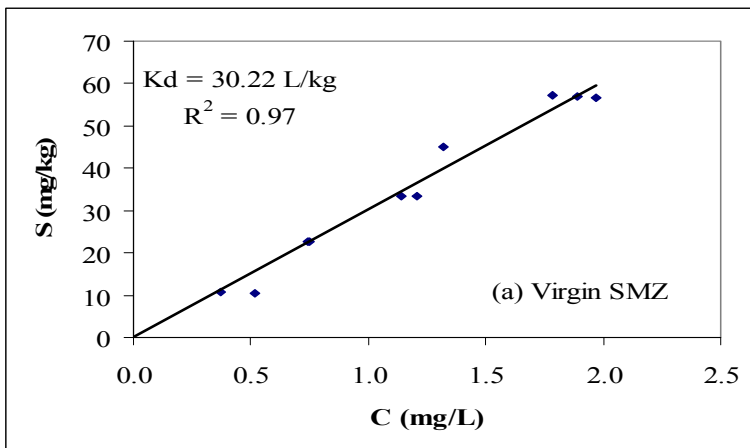
The methods used to perform the batch experiments were summarized in the manuscript. This section provides the results obtained from the experiments shown in Appendix Figures D-1 through D-5 and the data is compiled in Appendix Tables D-1 through D-15. The results from the two sets of blank samples (containing BTEX but no SMZ) show that very little volatilization loss occurs during shaking and centrifugation, but one-third to one-half of the BTEX escapes during the transfer of supernatant to a vial for analysis. The “% Solute Retained During Transfer” was determined by dividing the average concentration of the “Conc. Blank with Transfer” by the average concentration of the “Conc. Blank without Transfer” for each initial concentration level. The samples containing SMZ were corrected for volatilization loss during transfer by dividing the equilibrium concentration obtained from GC analysis by the average percent of solute retained during the transfer process. Thus, assuming that the BTEX in the supernatant in the SMZ-containing vials behaves similarly during transfer processes, the equilibrium concentration reported in the tables below is corrected for the loss of BTEX during the transfer prior to GC analysis. The initial solution concentration for each initial concentration level was taken as the average of two duplicate standards that were prepared and analyzed immediately when all other blank and SMZ-containing vials were prepared. The concentrations of these duplicates is shown in Appendix Tables D-1 through D-15 in the left-most column.



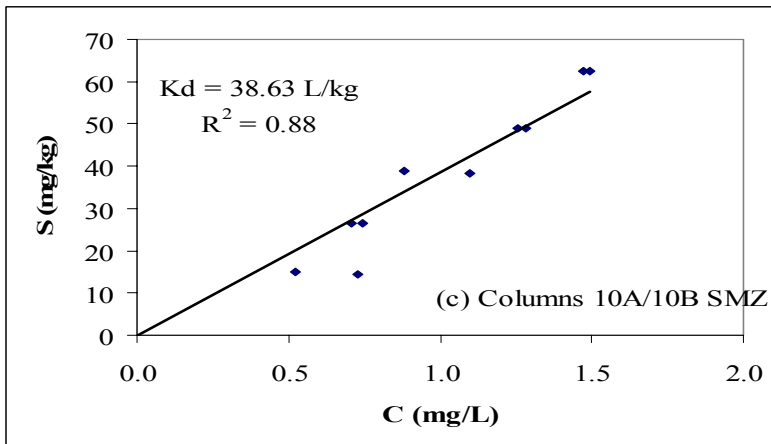
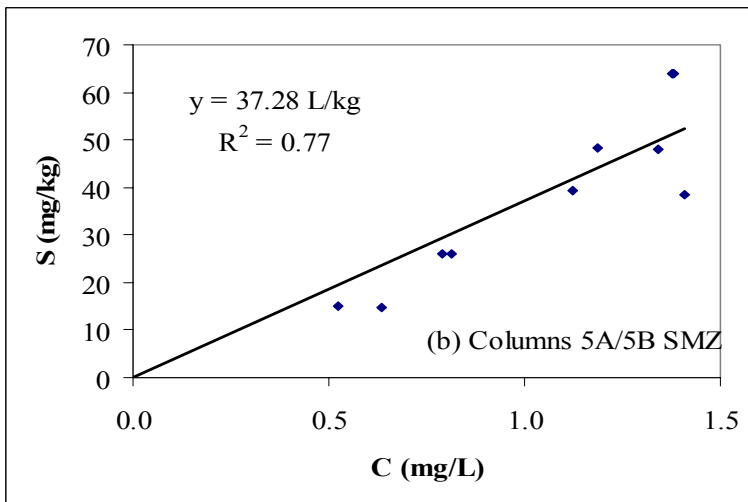
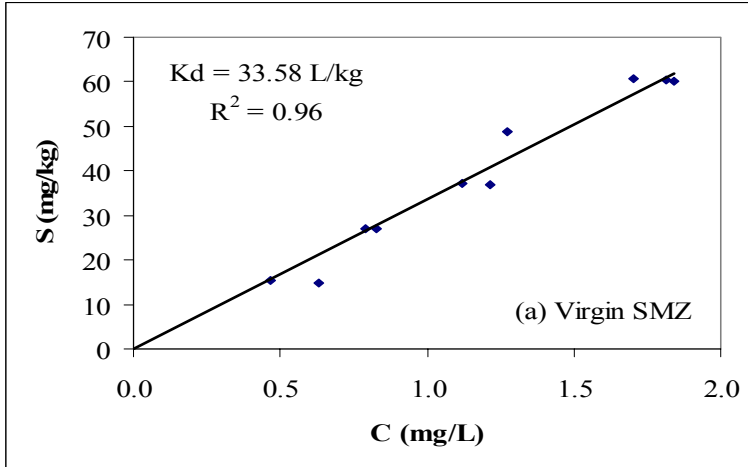
Appendix Figure D-1. Benzene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.



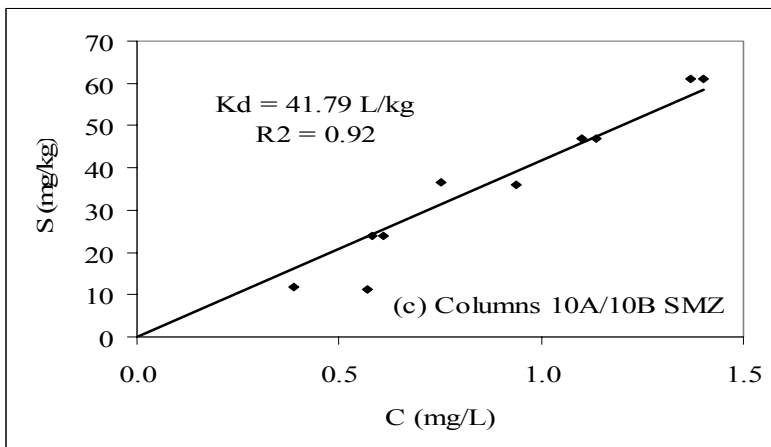
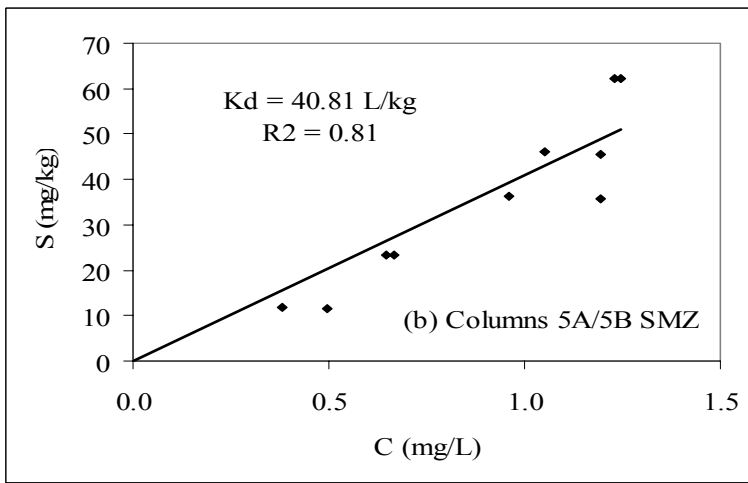
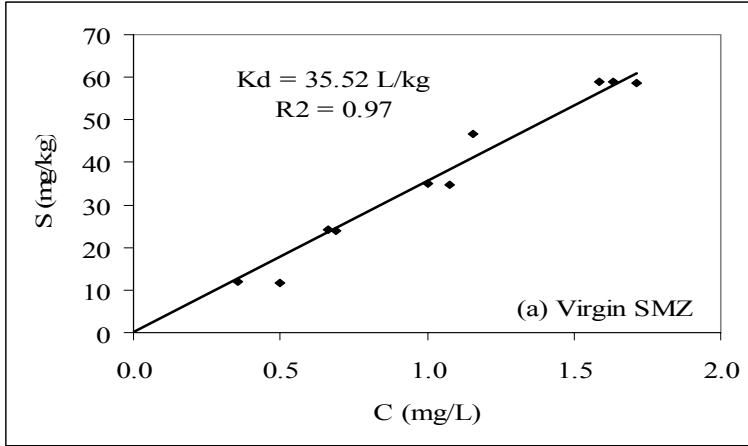
Appendix Figure D-2. Toluene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.



Appendix Figure D-3. Ethylbenzene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.



Appendix Figure D-4. p- & m-xylene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.



Appendix Figure D-5. *o*-xylene sorption isotherm for (a) virgin SMZ; (b) Columns 5A/5B SMZ; and (c) Columns 10A/10B SMZ.

Appendix Table D-1. Benzene sorption on virgin SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
3.54	1.70	9.87	2.33	3.73	0.60
3.88	1.61	10.13	2.47	4.32	
6.95	2.84	19.46	4.14	6.14	0.67
no data	3.04	18.89	4.27	6.41	
9.37	4.29	25.55	5.82	9.50	0.64
9.70	4.40	25.21	6.02	8.88	
12.34	7.57	40.69	7.69	11.62	0.64
12.63	5.04	35.16	7.17	11.62	
15.84	6.24	44.61	10.27	15.14	0.64
15.62	7.08	42.13	9.26	15.25	
				Average:	0.64

Appendix Table D-2. Benzene sorption on Column 5A/5B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
3.61	1.74	9.26	2.34	3.93	0.60
3.58	1.75	9.24	2.35	3.95	
6.51	2.95	17.11	4.20	6.84	0.62
6.37	3.53	15.40	4.35	7.01	
10.95	5.59	24.90	6.34	no data	0.65
9.70	4.54	28.00	5.95	9.42	
12.74	5.23	35.45	7.41	12.61	0.61
12.65	5.13	35.76	7.88	no data	
15.67	5.99	50.27	9.72	15.36	0.63
18.25	6.15	49.79	9.70	15.65	
				Average	0.62

Appendix Table D-3. Benzene sorption on Column 10A/10B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
3.35	1.94	8.72	2.51	3.94	0.62
3.86	1.81	9.11	2.43	4.02	
6.65	2.73	18.94	4.00	6.50	0.60
6.82	2.85	18.56	no data	6.79	
9.74	4.15	28.45	5.64	9.57	0.60
10.58	3.69	29.81	5.85	9.69	
12.95	5.22	36.29	7.77	13.04	0.62
12.85	5.32	36.00	7.71	12.09	
17.78	6.03	48.96	9.12	15.47	0.60
15.55	6.23	48.38	9.25	14.96	
				Average	0.61

Appendix Table D-4. Toluene sorption on virgin SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
8.10	2.15	27.16	4.84	8.27	0.57
8.63	1.89	27.91	5.12	9.16	
14.77	3.35	49.25	8.28	13.14	0.62
no data	3.42	49.04	8.39	13.71	
19.80	4.87	65.54	11.33	19.40	0.61
20.11	4.86	65.57	11.66	18.53	
25.50	8.01	105.64	14.87	23.87	0.60
26.16	5.47	87.26	13.74	24.10	
32.23	6.83	109.12	19.24	30.99	0.60
32.34	7.88	106.03	17.81	31.14	
				Average:	0.60

Appendix Table D-5. Toluene sorption on Column 5A/5B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
8.25	2.11	26.56	4.85	8.56	0.57
8.12	2.08	26.65	4.83	8.57	
14.08	3.22	46.08	8.30	14.19	0.59
13.68	3.72	44.61	8.68	14.73	
22.59	6.05	68.37	12.32	no data	0.60
20.46	4.94	71.61	11.43	19.74	
25.69	5.56	86.93	14.51	25.70	0.58
25.93	5.31	87.67	15.13	no data	
32.13	5.99	119.06	18.56	31.22	0.59
36.19	6.22	118.39	18.58	31.94	
				Average:	0.58

Appendix Table D-6. Toluene sorption on Column 10A/10B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
7.68	2.41	25.47	5.12	8.57	0.58
8.59	2.10	26.37	4.91	8.57	
14.06	2.98	48.22	7.89	13.79	0.57
14.42	3.07	47.96	no data	14.09	
19.99	4.52	70.25	10.67	19.82	0.55
21.76	3.86	72.18	11.20	19.92	
26.24	5.42	89.42	15.18	26.37	0.59
26.42	5.55	89.05	14.87	24.78	
34.96	6.27	115.30	17.53	31.44	0.57
31.89	6.48	114.68	17.76	30.27	
				Average:	0.57

Appendix Table D-7. Ethylbenzene sorption on virgin SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
2.92	0.52	10.34	1.54	2.91	0.52
3.01	0.37	10.77	1.62	3.12	
6.21	0.75	22.64	3.14	5.58	0.55
no data	0.74	22.66	3.08	5.79	
9.16	1.21	33.32	4.57	8.71	0.54
9.27	1.14	33.52	4.70	8.41	
12.09	1.89	57.01	6.20	11.06	0.53
12.38	1.32	45.08	5.67	11.22	
15.55	1.79	57.31	8.01	14.87	0.52
15.73	1.97	56.78	7.55	14.86	
				Average:	0.53

Appendix Table D-8. Ethylbenzene sorption on Column 5A/5B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
2.95	0.52	10.18	1.53	3.01	0.51
2.90	0.42	10.48	1.52	2.96	
6.17	0.72	22.03	3.15	5.91	0.53
5.90	0.76	21.89	3.32	6.23	
9.92	1.38	34.28	4.87	no data	0.53
9.24	1.10	35.10	4.50	8.81	
12.00	1.35	44.36	6.11	11.97	0.52
12.16	1.22	44.75	6.29	no data	
15.64	1.43	61.06	8.04	15.05	0.53
16.99	1.46	60.97	7.94	15.33	
				Average:	0.52

Appendix Table D-9. Ethylbenzene sorption on Column 10A/10B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
2.79	0.60	9.97	1.63	3.01	0.53
3.07	0.42	10.49	1.54	2.98	
6.07	0.68	22.62	3.02	5.90	0.51
6.24	0.66	22.68	no data	5.94	
9.07	1.07	34.68	4.19	8.89	0.49
9.84	0.87	35.28	4.47	8.95	
12.20	1.30	45.58	6.34	12.10	0.53
12.50	1.29	45.62	6.17	11.60	
16.44	1.57	59.93	7.63	15.13	0.51
15.84	1.57	59.93	7.71	14.67	
				Average:	0.51

Appendix Table D-10. p-&m-xylene sorption on virgin SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
4.08	0.63	14.79	2.17	4.05	0.54
4.24	0.47	15.28	2.30	4.28	
7.34	0.83	26.95	3.78	6.58	0.56
no data	0.79	27.06	3.73	6.82	
10.09	1.21	36.95	5.09	9.46	0.55
10.17	1.12	37.22	5.22	9.24	
12.97	1.81	60.34	6.81	11.80	0.55
13.26	1.27	48.72	6.18	12.00	
16.32	1.70	60.66	8.50	15.49	0.54
16.51	1.84	60.25	8.02	15.39	
				Average:	0.55

Appendix Table D-11. p-&m-xylene sorption on Column 5A/5B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
4.17	0.64	14.69	2.18	4.14	0.52
4.11	0.52	15.02	2.15	4.13	
7.21	0.79	25.97	3.74	6.83	0.55
6.94	0.81	25.90	3.94	7.21	
10.98	1.41	38.48	5.54	no data	0.54
10.32	1.12	39.32	5.05	9.85	
12.81	1.34	47.93	6.63	12.67	0.53
13.12	1.19	48.39	6.81	no data	
16.33	1.38	64.00	8.46	15.60	0.54
17.68	1.38	63.99	8.42	15.85	
				Average:	0.54

Appendix Table D-12. p-&m-xylene sorption on Column 10A/10B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
3.93	0.73	14.28	2.29	4.13	0.54
4.28	0.52	14.89	2.15	4.08	
7.10	0.74	26.47	3.55	6.86	0.52
7.22	0.71	26.57	no data	6.83	
9.97	1.10	38.28	4.71	9.79	0.50
10.78	0.88	38.92	5.01	9.73	
13.01	1.28	48.87	6.92	12.81	0.54
13.31	1.26	48.95	6.75	12.36	
17.01	1.49	62.57	7.96	15.60	0.52
16.46	1.47	62.63	8.10	15.14	
				Average:	0.52

Appendix Table D-13. o-xylene sorption on virgin SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
3.21	0.50	11.54	2.05	3.22	0.64
3.30	0.35	11.98	2.15	3.39	
6.51	0.69	24.00	4.00	5.92	0.66
no data	0.66	24.08	3.91	6.10	
9.43	1.08	34.69	5.75	8.98	0.66
9.49	1.00	34.92	5.89	8.78	
12.36	1.63	58.80	7.71	11.48	0.64
12.64	1.15	46.61	7.11	11.62	
15.83	1.59	58.94	9.84	15.13	0.63
15.96	1.71	58.56	9.36	15.22	
				Average:	0.64

Appendix Table D-14. o-xylene sorption on Column 5A/5B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
3.26	0.50	11.45	2.04	3.29	0.62
3.20	0.38	11.79	2.03	3.25	
6.47	0.65	23.41	4.00	6.19	0.65
6.18	0.67	23.35	4.23	6.49	
10.13	1.19	35.72	6.10	no data	0.64
9.48	0.96	36.40	5.63	9.21	
12.22	1.19	45.65	7.67	12.25	0.63
12.35	1.05	46.06	7.80	no data	
15.83	1.23	62.19	9.84	15.23	0.64
17.07	1.25	62.14	9.83	15.55	
				Average:	0.64

Appendix Table D-15. o-xylene sorption on Column 10A/10B SMZ.

Initial Conc. (mg/L)	Equil. Conc. (mg/L)	Amt. Solute Sorbed (mg/kg)	Conc. Blank with Transfer (mg/L)	Conc. Blank without Transfer (mg/L)	% Solute Retained During Transfer
3.08	0.57	11.22	2.15	3.27	0.64
3.37	0.39	11.76	2.05	3.25	
6.30	0.61	23.78	3.84	6.19	0.62
6.49	0.58	23.86	no data	6.22	
9.27	0.94	36.00	5.25	9.17	0.59
10.10	0.75	36.54	5.56	9.18	
12.37	1.13	46.93	7.99	12.53	0.64
12.76	1.10	47.04	7.86	12.13	
16.49	1.40	60.95	9.73	15.93	0.62
16.04	1.37	61.05	9.83	15.43	
				Average:	0.62

APPENDIX E. FIELD COLUMN METHODS AND RESULTS

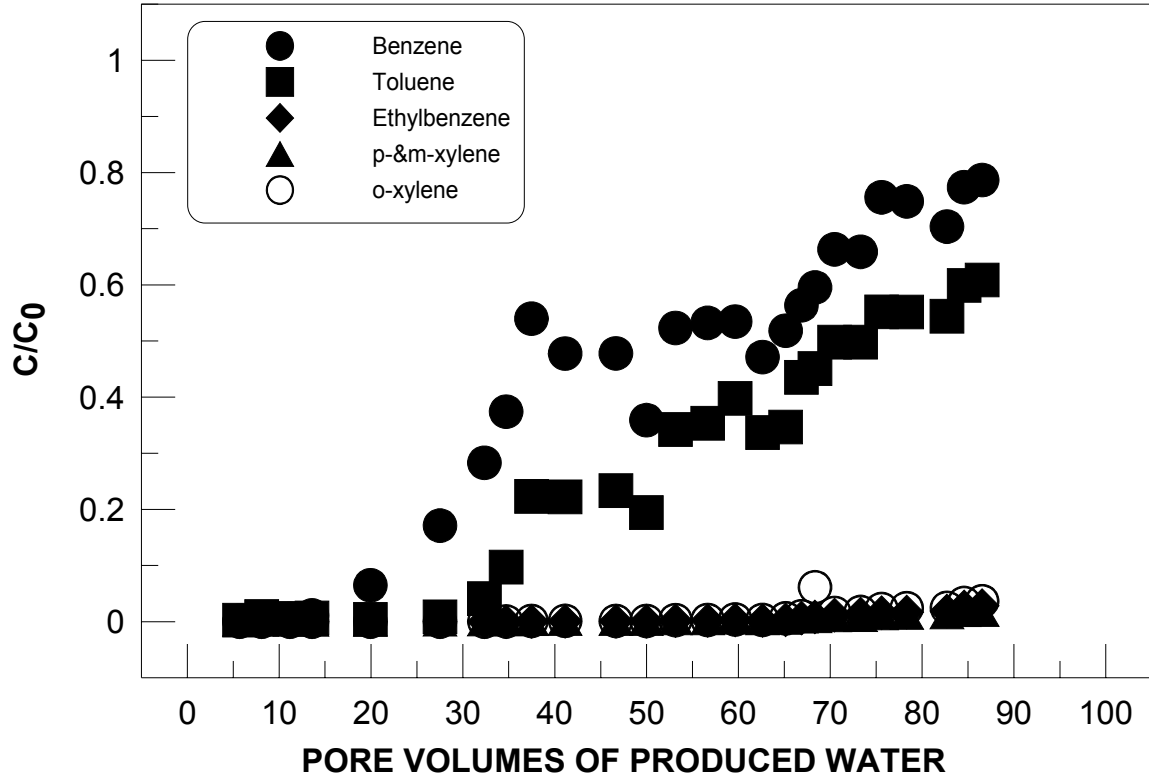
The methods used to perform the field experiments were summarized in the manuscript. This section provides a more thorough explanation of these methods, and the results obtained from the experiments.

In addition to the field-scale SMZ treatment system discussed in the manuscript, we operated a second field column while the primary column was undergoing regeneration. This second column was only operated with virgin SMZ and was not regenerated. The objective for the second column was to provide a means to continue to treat produced water while the primary field column was undergoing regeneration. The second field column was smaller than the primary column, with a radius of 305 mm and a length of 1120 mm. The available volume of this column was approximately 68 L. The system contained approximately 100 mm of headspace and held 60 kg of 14-40 mesh SMZ.

The smaller column was in operation for approximately 45 hours. The initial flow rate during this run was 95 L/hr (2.6 PV/hr). However, as with the larger column, there was a drop in flow rate as the trial progressed, dropping to 47 L/hr (1.3 PV/hr) at the end of the run. A large increase in BTEX influent concentrations occurred during the last 36 hours of operation. It is believed that these elevated measurements were caused by the discharge of one or more trucks carrying produced water with these high BTEX levels into the separation tanks. During this run, BTEX levels fluctuated within the following ranges: benzene 20-36 mg/L, toluene 32-61 mg/L, ethylbenzene 2-20 mg/L, p-&m-

xylene 17-79 mg/L, o-xylene 4-41 mg/L. The BTC for the smaller field column is shown in Appendix Figure E-1.

Appendix Table E-1 contains the BTC data on virgin SMZ in the larger field column, Appendix Table E-2 contains the BTC data on regenerated SMZ in the larger field column, Appendix Table E-3 contains the BTC data on virgin SMZ in the smaller field column, and Appendix Table E-4 provides the air-sparging data for the larger field column.



Appendix Figure E-1. Observed BTEX breakthrough on virgin SMZ in smaller field column.

Appendix Table E-1. Data for BTEX BTC on virgin SMZ in larger field column.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
1	0.4	0.000	0.000	0.000	0.000	0.000
2	1.7	0.000	0.000	0.000	0.000	0.000
3	2.6	0.000	0.001	0.000	0.000	0.000
6	4.9	0.001	0.000	0.000	0.000	0.000
7	5.7	0.003	0.000	0.000	0.000	0.000
8	6.5	0.007	0.000	0.000	0.000	0.000
9	8.2	0.011	0.001	0.000	0.000	0.000
11	11.9	0.173	0.023	0.000	0.000	0.000
12	13.8	0.204	0.023	0.000	0.000	0.000
14	17.6	0.616	0.170	0.000	0.001	0.000
15	19.5	0.675	0.206	0.000	0.001	0.000
16	21.5	0.709	0.256	0.000	0.001	0.000
19	27.4	0.788	0.339	0.000	0.002	0.003
20	29.3	0.800	0.369	0.000	0.002	0.003
22	33.3	0.775	0.402	0.000	0.018	0.003
24	37.2	0.792	0.445	0.002	0.002	0.005
25	39.1	0.831	0.498	0.003	0.003	0.006
26	41.4	0.704	0.414	0.002	0.003	0.005
28	45.5	0.632	0.389	0.003	0.003	0.005
29	47.6	0.872	0.546	0.005	0.004	0.008
30	49.6	0.808	0.551	0.005	0.004	0.008
31	51.7	0.814	0.568	0.006	0.004	0.010
32	53.7	0.774	0.548	0.005	0.004	0.009
35	59.5	0.793	0.566	0.007	0.005	0.011
36	62.8	0.820	0.593	0.009	0.006	0.015
37	64.9	0.829	0.611	0.011	0.007	0.017
38	66.8	0.835	0.617	0.011	0.007	0.018
39	68.5	0.803	0.599	0.011	0.007	0.018
41	72.8	0.733	0.578	0.012	0.008	0.019
43	78.9	0.806	0.592	0.012	0.008	0.021
44	81.5	0.783	0.574	0.012	0.008	0.020

Appendix Table E-2. Data for BTEX BTC on regenerated SMZ in larger field column.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
80	0.6	0.028	0.124	0.097	0.091	0.153
81	2.3	0.018	0.118	0.085	0.083	0.142
83	6.1	0.011	0.127	0.085	0.091	0.157
84	7.8	0.011	0.125	0.075	0.084	0.133
85	9.8	0.043	0.111	0.072	0.080	0.130
86	11.4	0.012	0.126	0.091	0.090	0.152
87	13.3	0.244	0.111	0.093	0.099	0.164
89	17.0	0.342	0.098	0.103	0.107	0.172
90	19.1	0.409	0.107	0.113	0.121	0.192
92	23.9	0.511	0.125	0.139	0.165	0.233
93	26.9	0.570	0.139	0.139	0.148	0.230
94	29.1	0.554	0.119	0.119	0.128	0.201
95	31.4	0.500	0.091	0.105	0.119	0.173
96	34.1	0.590	0.113	0.120	0.143	0.209
97	36.2	0.585	0.128	0.117	0.138	0.190
101	45.6	0.787	0.222	0.103	0.107	0.164
103	49.5	0.886	0.314	0.157	0.167	0.248
105	53.2	0.850	0.304	0.122	0.138	0.199
107	56.9	0.833	0.419	0.135	0.151	0.211
110	65.2	0.578	0.405	0.075	0.080	0.121

Appendix Table E-3. Data for BTEX BTC on virgin SMZ in smaller field column.

Sample	Pore Volumes	Benzene C/Co	Toluene C/Co	Ethyl-benzene C/Co	p-&m-xylene C/Co	o-xylene C/Co
45	0.2	0.000	0.000	0.000	0.000	0.000
47	5.7	0.002	0.003	0.000	0.000	0.000
48	8.1	0.007	0.009	0.000	0.000	0.000
49	11.2	0.005	0.006	0.000	0.000	0.000
50	13.6	0.011	0.007	0.000	0.000	0.000
52	19.9	0.065	0.004	0.000	0.000	0.000
55	27.5	0.171	0.009	0.000	0.000	0.000
57	32.3	0.283	0.041	0.000	0.000	0.000
58	34.7	0.374	0.097	0.000	0.001	0.000
59	37.5	0.540	0.223	0.001	0.001	0.001
60	41.1	0.478	0.222	0.001	0.001	0.001
62	46.7	0.478	0.233	0.001	0.001	0.001
63	50.0	0.359	0.194	0.001	0.001	0.001
64	53.2	0.523	0.342	0.002	0.003	0.003
65	56.6	0.532	0.353	0.002	0.003	0.003
66	59.6	0.535	0.398	0.003	0.004	0.004
67	62.6	0.471	0.337	0.002	0.003	0.003
68	65.1	0.518	0.347	0.003	0.003	0.006
69	66.9	0.564	0.435	0.006	0.006	0.010
70	68.3	0.595	0.451	0.008	0.006	0.061
71	70.5	0.663	0.498	0.011	0.008	0.016
72	73.3	0.659	0.498	0.013	0.008	0.017
73	75.6	0.756	0.552	0.016	0.011	0.022
74	78.3	0.749	0.552	0.017	0.012	0.024
76	82.7	0.704	0.544	0.019	0.013	0.024
77	84.6	0.774	0.599	0.026	0.017	0.033
78	86.5	0.787	0.608	0.028	0.017	0.036
79	88.3	0.762	0.592	0.029	0.017	0.035

Appendix Table E-4. BTEX removal data from 14-inch field column during air sparging.

Sample	Pore Volumes	Benzene Conc. (mg/L)	Benzene Mass Removed (g)	Toluene Conc. (mg/L)	Toluene Mass Removed (g)	Ethyl-benzene Conc. (mg/L)	Ethyl-benzene Mass Rem. (g)	p-&m-xylene Conc. (mg/L)	p-&m-xylene Mass Rem. (g)	o-xylene Conc. (mg/L)	o-xylene Mass Removed (g)
1	16.3	2.541	2.159	3.174	2.696	0.269	0.229	0.313	0.266	0.408	0.347
2	40.6	1.809	4.464	2.813	6.281	0.131	0.395	0.186	0.503	0.219	0.626
3	65.0	1.269	6.081	2.640	9.646	0.073	0.489	0.122	0.659	0.114	0.772
4	91.0	0.449	6.691	1.105	11.148	0.025	0.523	0.047	0.723	0.037	0.822
5	119.5	0.369	7.240	1.186	12.911	0.029	0.565	0.059	0.810	0.038	0.878
6	148.0	0.287	7.666	1.130	14.592	0.028	0.607	0.068	0.911	0.042	0.940
7	172.3	0.320	8.074	1.393	16.366	0.039	0.657	0.089	1.024	0.055	1.010
8	196.7	0.263	8.410	1.394	18.143	0.048	0.718	0.119	1.176	0.069	1.097
9	225.2	0.132	8.606	0.778	19.300	0.028	0.760	0.069	1.278	0.047	1.167
10	253.6	0.138	8.811	0.931	20.684	0.037	0.815	0.097	1.421	0.058	1.252
11	279.6	0.095	8.940	0.745	21.697	0.034	0.860	0.092	1.546	0.055	1.327
12	305.7	0.096	9.071	0.803	22.788	0.039	0.913	0.108	1.694	0.065	1.416
13	334.1	0.041	9.133	0.376	23.346	0.021	0.945	0.064	1.790	0.040	1.476
14	362.6	0.048	9.204	0.471	24.047	0.026	0.984	0.081	1.909	0.050	1.551
15	419.5	0.043	9.333	0.434	25.335	0.026	1.062	0.079	2.144	0.051	1.702
16	476.4	0.030	9.422	0.374	26.448	0.027	1.143	0.088	2.406	0.058	1.876
17	533.3	0.017	9.472	0.243	27.170	0.022	1.208	0.071	2.617	0.050	2.023
18	590.2	0.009	9.498	0.140	27.586	0.015	1.251	0.066	2.812	0.047	2.164
19	655.2	0.011	9.537	0.219	28.330	0.025	1.336	0.092	3.124	0.068	2.394
20	704.0	0.005	9.551	0.047	28.450	0.006	1.350	0.098	3.374	0.074	2.582
21	785.3	0.005	9.574	0.140	29.046	0.019	1.429	0.075	3.693	0.058	2.830
22	798.8	0.013	9.583	0.315	29.268	0.044	1.460	0.173	3.816	0.132	2.924
23	820.5	0.012	9.596	0.290	29.597	0.045	1.511	0.176	4.015	0.136	3.078

APPENDIX F. ADDITIONAL ORGANIC MATERIAL IN PRODUCED WATER

The produced water from the field site in Wyoming contained numerous organic compounds. Untreated water collected during the field test in July 2002 was analyzed by an independent lab (DHL Analytical, Round Rock, TX) for TOC with a result of 470 mg/L. The analysis of the produced water collected for the laboratory experiments was presented in the manuscript with a TOC result of 1000 mg/L. BTEX levels were approximately 80 mg/L, meaning a significant number of organic compounds in the water were not quantified during analysis. The untreated water sample collected during the field test was also analyzed by DHL Analytical for total petroleum hydrocarbons (TPH) and semi-volatile components. The results of this analysis are presented in Appendix Table F-1.

Appendix Table F-1. TPH and semi-volatile analysis of untreated produced water collected during field testing (only noting compounds present above detectable limits).

Analysis	Result (mg/L)
TPH Range: C6-C12	129
TPH Range: >C12-C28	8.24
2,4- Dimethylphenol	0.816
2-Methylnaphthalene	0.160
2-Methylphenol	1.35
4-Methylphenol	1.00
Dibenzofuran	0.0044
Fluorene	0.0046
Naphthalene	0.164
Phenanthrene	0.0038
Phenol	0.764

The identity of the remaining unaccounted organic compounds is difficult to determine. A list of organic components that may exist in the produced water used in this study can be constructed based on compounds identified from other produced waters. Witter and Jones (1999) reported the following organic components of produced water from seven samples at a California oil-processing facility: heterocyclic polysulfides, butanoic acids, pentanoic acids, hexanoic acids, heptanoic acids, phenols, benzene, toluene, xylenes, 3-thiophene carboxaldehyde, benzenemethanethiol, *N,N*-dimethylaninododecane, and other unknown compounds. The sum of all measured organic compounds ranged from 0.93 to 57.8 mg/L in the seven samples collected. McCormack et al. (2001) identified a range of polar organic compounds in produced water from the North Sea including imidazolines, alkylbenzene sulfonates, quaternary ammonium compounds, and ethoxylates. Specific compounds identified included linear alkylbenzenesulfonates, alkyldimethylbenzylammonium compounds, 2-alkyl-1-ethylamine-2-imidazolines, 2-alkyl-1-[*N*-ethylalkylamide]-2-imidazolines and a di-[alkyldimethylammonium-ethyl]ether.

Many of the compounds discussed above are polar, which are not attracted to SMZ like neutral compounds such as BTEX are. If many of the unidentified organic compounds are polar, a significant portion of the TOC in produced water will pass through the SMZ system without being removed. Effluent samples from the laboratory column experiments were analyzed for TOC to determine how much organic material was removed from the produced water. The samples for this test were collected following the completion of a sorption cycle from the reservoir containing all effluent water from the cycle. The results from this test are shown in Appendix Table F-2. These

results show that a significant portion of TOC passes through the column, and one effluent sample (9th effluent) has a higher TOC than the influent water. These results indicate that many organic compounds present in the produced water are polar compounds. This conclusion is supported by Jacobs et al. (1992), who determined that polar compounds represent 84% of total organic compounds in effluent produced water in the North Sea.

Appendix Table F-2. TOC analysis of produced water used in laboratory column experiments.

Sample	TOC (mg/L)
Influent	1000
Column 10A 3 rd sorption cycle effluent	950
Column 10A 6 th sorption cycle effluent	990
Column 10A 9 th sorption cycle effluent	1200

To determine which semi-volatile compounds were removed from SMZ during the field tests, a sample of effluent water was collected for semi-volatile analysis from the smaller field column at 2.4 PV. Appendix Table F-3 shows the results of the influent semi-volatile analysis (also shown in Appendix Table F-1) and the 2.4 PV effluent semi-volatile analysis. These results show that many semi-volatile compounds are completely retained by SMZ at early time while the concentration of other compounds is reduced by two orders of magnitude. One compound, benzyl alcohol, was present in the effluent concentration but not in the influent concentration. The reason for this is most likely because the influent sample was not collected at the same time as the effluent sample, and benzyl alcohol was not present at the time the influent sample was collected. Produced water from the region the field site is located in was constantly being delivered to the site and the produced water composition in the separation tanks could have been changing with each additional water delivery.

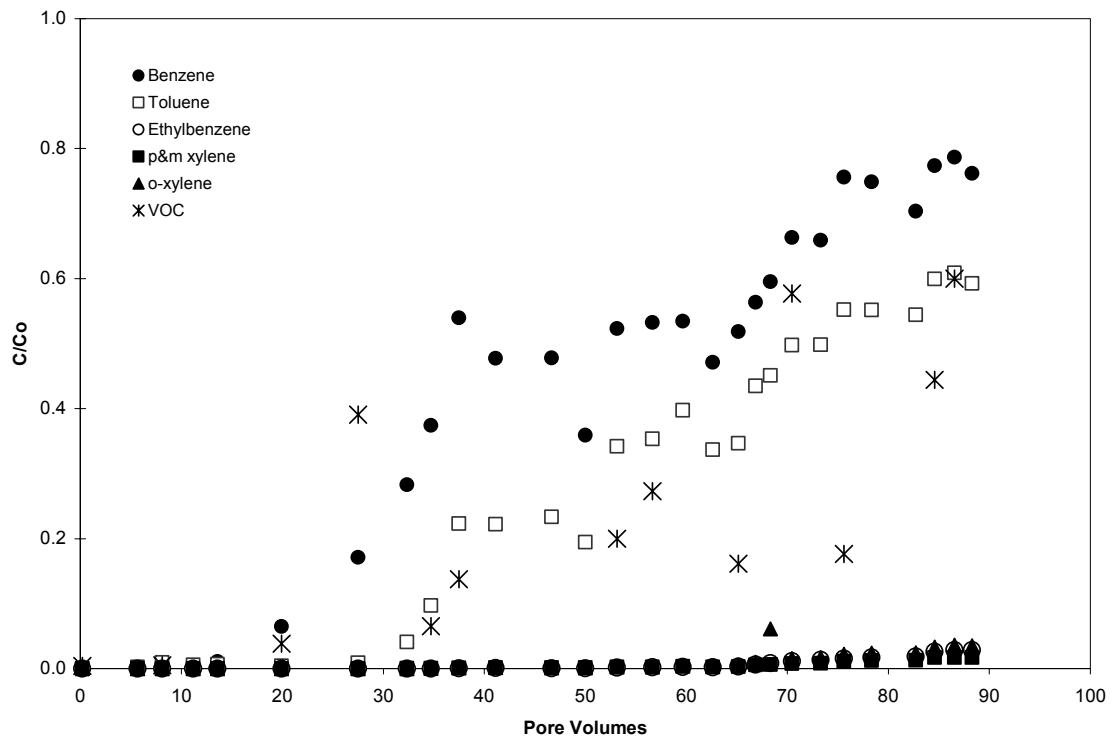
Appendix Table F-3. Semi-volatile breakthrough at 2.4 PV from smaller field column.

Analysis	Influent Conc. (mg/L)	Effluent Conc. (mg/L)
2,4- Dimethylphenol	0.816	Not Detected
2-Methylnaphthalene	0.160	0.0038
2-Methylphenol	1.35	0.0184
4-Methylphenol	1.00	Not Detected
Benzyl Alcohol	Not Detected	0.0086
Dibenzofuran	0.0044	Not Detected
Fluorene	0.0046	Not Detected
Naphthalene	0.164	Not Detected
Phenanthrene	0.0038	Not Detected
Phenol	0.764	Not Detected

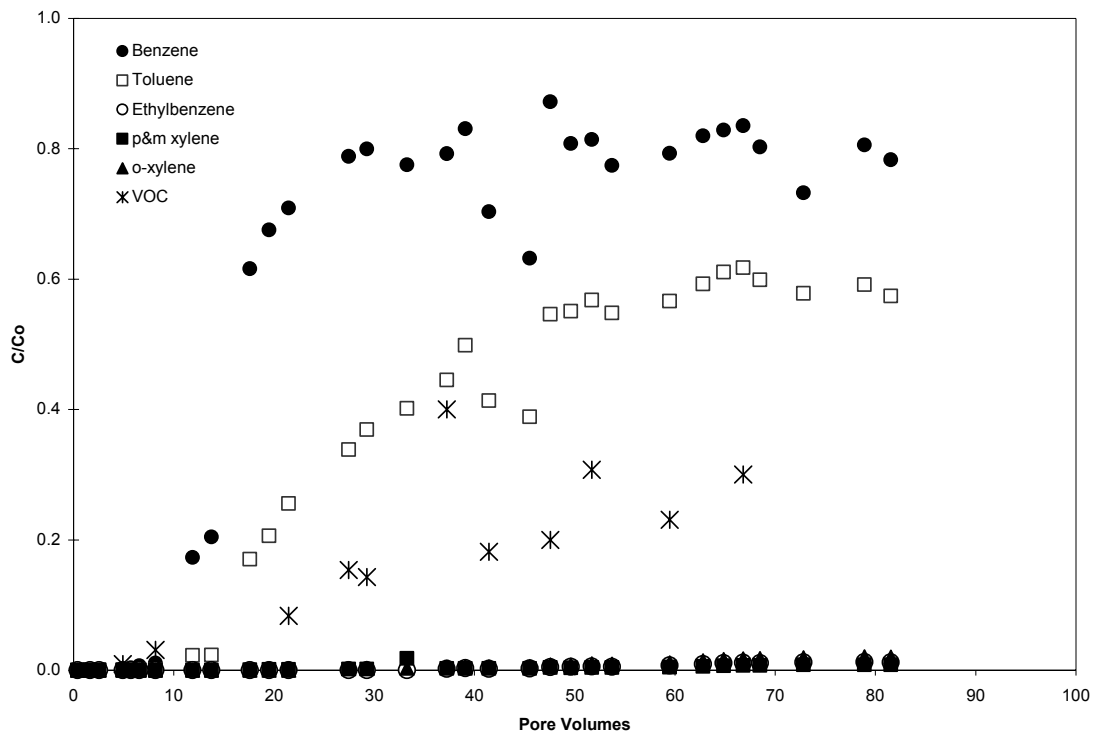
One additional method was utilized to monitor the organic compounds present in produced water during the field tests. A photoionization detector (described in the manuscript) was used to record the concentration of volatile organic compounds (VOC) in headspace above influent and effluent water samples. To collect samples for this analysis, 2.5 L glass bottles were filled to the same level (approximately 1/3 full) and the headspace in these bottles was sampled with the photoionization detector. The breakthrough curves for VOC are shown in Appendix Figures F-1, F-2, and F-3 for virgin SMZ in the smaller field column, virgin SMZ in the larger field column, and regenerated SMZ in the larger field column, respectively. The two plots containing virgin SMZ data (Appendix Figures F-1, F-2) show that the effluent VOC concentration increases rapidly shortly after toluene breakthrough. This can be explained because toluene composes a significant portion of the VOC in this produced water. The VOC breakthrough on regenerated SMZ occurs shortly before toluene breakthrough. This could be caused by the incomplete air-sparging of many VOC (including toluene), concentrating them at the effluent end of the column and releasing them in effluent water at earlier time. This is consistent with the observations of ethylbenzene and xylenes in early effluent water

samples on regenerated SMZ, even though no ethylbenzene or xylenes was present in the effluent water from virgin SMZ treatment. The data used to construct these figures are shown in Appendix Tables F-1, F-2, and F-3, respectively.

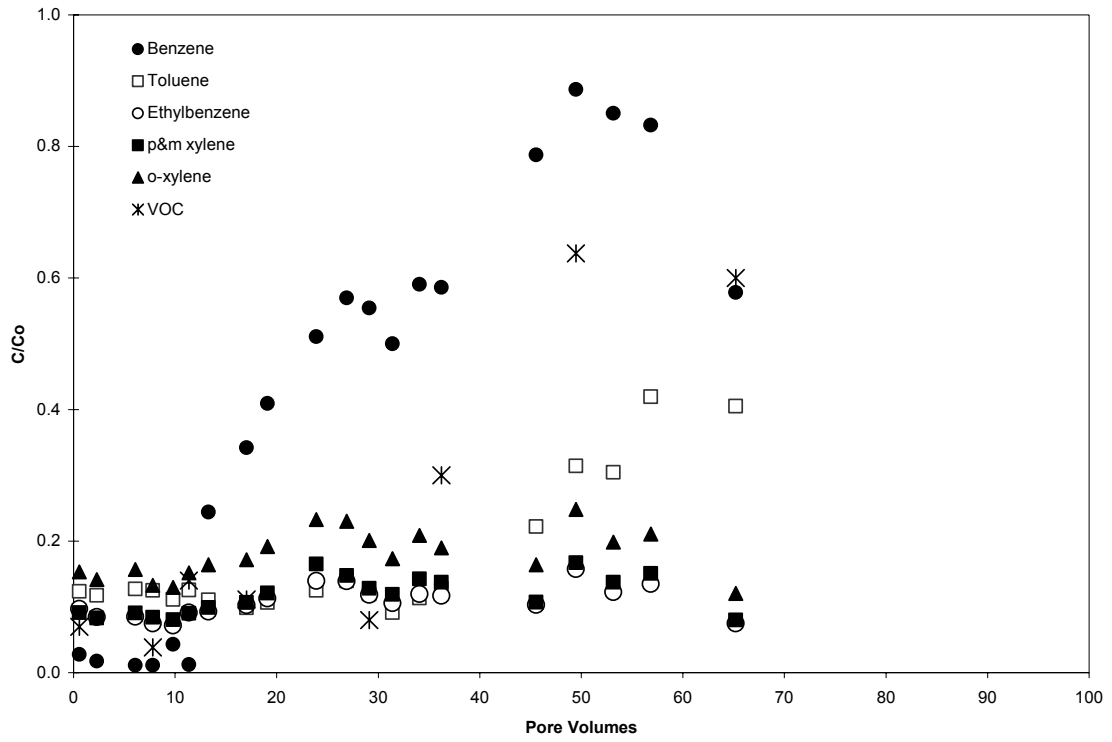
Future work should be performed to identify what hazardous components are present in produced water that are not removed by SMZ. The TOC results presented in this appendix show that many organic compounds do pass through the SMZ system, but that BTEX and many of the semi-volatiles are retained in the system.



Appendix Figure F-1. PID measurements with BTEX BTCs on virgin SMZ in smaller field column.



Appendix Figure F-2. PID measurements with BTEX BTCs on virgin SMZ in larger field column.



Appendix Figure F-3. PID measurements with BTEX BTCs on regenerated SMZ in larger field column.

Appendix Table F-4. PID measurements recorded on virgin SMZ in smaller field column.

VOC influent (ppm)	VOC effluent (ppm)	C/C₀	Pore Volumes
700	3	0.004	0.210
600	3	0.005	8.099
650	25	0.038	19.932
640	250	0.391	27.504
1300	85	0.065	34.709
800	110	0.138	37.470
1500	300	0.200	53.151
1100	300	0.273	56.648
990	160	0.162	65.150
520	300	0.577	70.470
850	150	0.176	75.589
900	400	0.444	84.569
500	300	0.600	86.541

Appendix Table F-5. PID measurements recorded on virgin SMZ in larger field column.

VOC influent (ppm)	VOC effluent (ppm)	C/C₀	Pore Volumes
390	3.7	0.009	4.917
480	15	0.031	8.178
600	50	0.083	21.472
650	100	0.154	27.449
700	100	0.143	29.275
500	200	0.400	37.244
550	100	0.182	41.437
600	120	0.200	47.559
650	200	0.308	51.689
650	150	0.231	59.465
750	225	0.300	66.800

Appendix Table F-6. PID measurements recorded on regenerated SMZ in larger field column.

VOC influent (ppm)	VOC effluent (ppm)	C/C₀	Pore Volumes
1000	70	0.070	0.580
1300	50	0.038	7.812
500	70	0.140	11.362
900	100	0.111	17.037
250	20	0.080	29.115
500	150	0.300	36.215
400	255	0.638	49.461
550	330	0.600	65.218

APPENDIX F REFERENCES

- Jacobs, R. P. W. M., Grant, R. O. H., Kwant, J., Marquenie, J. M., and Mentzer, E. (1992). "The composition of produced water from Shell operated oil and gas production in the North Sea." *Produced Water*, J. P. Ray and F. R. Engelhart, eds., Plenum Press, New York, 13-21.
- McCormack, P., Jones, P., Hetheridge, M. J., and Rowland, S. J. (2001). "Analysis of oilfield produced waters and production chemicals by electrospray ionization multi-stage mass spectrometry (ESI-MS)." *Wat. Res.*, 35(15) 3567-3578.
- Witter, A. E., and Jones, A. D. (1999). "Chemical characterization of organic constituents from sulfide-rich produced water using gas chromatography/mass spectrometry." *Environ. Tox. and Chem.*, 18(9) 1920-1926.

APPENDIX G. APPLICABLE PRODUCED WATERS FOR AN SMZ TREATMENT SYSTEM

The manuscript and appendices presented in this document have shown the applicability of surfactant-modified zeolite in a produced-water treatment system. SMZ successfully removes BTEX, semi-volatiles, and other VOC from produced water, but many other organic compounds and inorganic salts pass through the system. Therefore, the usefulness of SMZ in a standalone treatment system is best in locations where the influent water has a low salinity or in locations where the salinity of the effluent water is allowed to be high, such as at offshore locations. An SMZ-based treatment system could also be combined with other treatment systems, such as reverse-osmosis, that require the removal of some organic compounds before treatment. The use of SMZ for removal of organic contaminants may be limited by what additional organic compounds are present in the produced water. SMZ does not effectively remove polar organic compounds from water and may not lower overall TOC significantly, although it does remove BTEX and some other hazardous compounds. If these additional organic compounds are of regulatory concern, the use of SMZ for treatment may not be the best option.