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Lynn E. Katz

Project Manager

Abstract

Co-produced water from the oil and gas industry accounts for a significant waste stream in the United States. It is by some estimates the largest single waste stream in the country, aside from nonhazardous industrial wastes. Characteristics of produced water include high total dissolved solids content, dissolved organic constituents such as benzene and toluene, an oil and grease component, and chemicals added during the oil-production process. While most of the produced water is disposed via reinjection, some must be treated to remove organic constituents before the water is discharged. Current treatment options are successful in reducing the organic content; however, they cannot always meet the levels of current or proposed regulations for discharged water. Therefore, an efficient, cost-effective treatment technology is needed. Surfactant-modified zeolite (SMZ) has been used successfully to treat contaminated ground water for organic and inorganic constituents. In addition, the low cost of natural zeolites makes their use attractive in water-treatment applications.

This report summarizes the work and results of this four-year project. We tested the effectiveness of surfactant-modified zeolite (SMZ) for removal of BTEX with batch and column experiments using waters with BTEX concentrations that are comparable to those of produced waters. The data from our experimental investigations showed that BTEX sorption to SMZ can be described by a linear isotherm model, and competitive effects between compounds were not significant. The SMZ can be readily regenerated using air stripping. We field-tested a prototype SMZ-based water treatment system at produced water treatment facilities and found that the SMZ successfully removes BTEX from produced waters as predicted by laboratory studies. When compared to other existing treatment technologies, the cost of the SMZ system is very competitive. Furthermore, the SMZ system is relatively compact, does not require the storage of potentially hazardous chemicals, and could be readily adapted to an automated system.

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1. Introduction

1.1 Problem Statement

The United States oil and gas industry generates more than three billion tons of saline wastewater every year (API, 1987). This is by some estimates the single largest waste stream in the U.S., aside from non-hazardous industrial wastes (Allen and Rosselot, 1994). This so-called produced water contains many pollutants, including dispersed and dissolved hydrocarbons, salts, and metals. In addition to prevalent oil and grease, the presence of hazardous aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX) increases the toxicity of produced water (Fucik, 1992). Quality tends to be field-specific, and varies within and between reservoirs and types of fields such as oil, gas, and coal-bed methane.

Although most produced water generated by onshore oil and gas operations is disposed of through deep-well reinjection, a substantial percentage of it is discharged to the environment after minimal treatment to remove dispersed oil and suspended solids. Offshore and coastal facilities normally release their effluent to the ocean, and many small producers cannot afford the high price of deep-well reinjection. These small producers must release their effluent through surface discharge. Due to concerns regarding the harmful constituents in produced water, members of the industry feel that regulation of all types of produced water disposal will soon become more stringent (Lawrence *et al.*, 1995).

In addition, many of the areas used by the onshore oil and gas industry are arid, and in these regions, water is a valuable commodity. The ability to reuse produced water for beneficial purposes such as irrigation, livestock watering, and road maintenance would substantially benefit communities in water-scarce regions. Hence, produced water treatment that can yield an effluent that is environmentally innocuous or of sufficient quality to permit reuse would benefit producers, community members, and the environment.

Current treatment methods do not focus on the removal of BTEX compounds. Rather, the traditional oil/water separation tanks and hydrocyclones serve to recover oil that can be refined and marketed. Research has been conducted to evaluate various other methods to remove hazardous compounds in produced water, but much of this research has focused on expensive technologies that are not economically viable for small producers. Lawrence and others (1995) concluded that further research was needed to improve removal efficiencies for oil and grease and dissolved organic compounds.

Cost is a major consideration in the evaluation of treatment processes, especially for small scale producers. A stripper well that produces two barrels of oil per day at a price of \$12/bbl yields a profit in the cents to low dollar range. If 20 bbls/day of produced water result from this operation, then any treatment requirement must be low cost (cents/day, or a few cents/bbl). Because of larger volumes, total costs increase greatly if off-shore produced water cannot be directly discharged, or if the treatment process requires the well to be shut-in. The development of cost effective processes is therefore essential to the development of any treatment process for produced water.

Treatment through sorption onto materials such as surfactant-modified zeolite (SMZ) may be both effective and relatively inexpensive. Zeolites are naturally occurring

aluminosilicate minerals that have large capacities for cation exchange. By utilizing this property, natural zeolites can be modified by cationic surfactants, rendering them capable of sorbing anions, cations, and non-polar organic compounds such as BTEX. One study has shown that SMZ can reduce BTEX levels in contaminated water (Janks and Cadena, 1992). While the sorption capacity of SMZ for BTEX is low relative to other adsorbents, it is likely that the SMZ is readily regenerated based on proposed sorption mechanisms. Thus, feasibility analysis of an SMZ treatment process should include a study the potential for regeneration. In order to evaluate the cost-effectiveness of an SMZ treatment process, design criteria for an SMZ system for produced water must be established, and these design criteria should include a cost-effective method for regeneration.

1.2 Objectives and Approach

The overall goal of this research was to develop a cost-effective and practical method of treating co-produced waters from oil-field sources using a treatment scheme that includes surfactant-modified zeolite. Potential impediments to system performance and potential methods of system regeneration were also addressed. Existing data on SMZ use as a treatment method for contaminated ground water and an experimental program were used to support the development process. The experimental program included three components: laboratory scale batch experiments, laboratory scale column experiments, and a pilot test. The objectives of this work are as follows:

Objective 1: Verify sorptive properties of SMZ for BTEX in laboratory studies;

Objective 2: Design a practical, inexpensive, modular system for SMZ use in the field;

Objective 3: Verify the system at a field site;

Objective 4: Test regeneration methods for spent SMZ;

Objective 5: Develop a cost analysis for the process.

The first task required to accomplish these objectives was to conduct a review of literature pertaining to produced water composition and treatment. The literature review included:

- a description of the sources, characteristics and variability of produced waters with respect to salinity and BTEX concentrations to aid the site selection and composition of synthetic waters to be used in the laboratory studies;
- a discussion of the current and proposed regulations for BTEX in produced water to set the effluent objectives for the proposed treatment scheme;
- a description of various treatment alternatives to assess which processes should be considered during the cost analysis; and,

- a review of literature describing the characteristics of surfactant modified zeolite.

This literature review is presented in Chapter 2, Background.

Based on the literature review, it was determined that a number of parameters would impact sorption of BTEX compounds from produced water including the presence of multiple BTEX components, salinity, temperature and other hydrophobic or moderately hydrophobic compounds present in the produced water background matrix. For example, produced water contains salt concentrations that can vary from 100 ppm - 300,000 ppm. This high salinity may enhance the sorbability of BTEX on SMZ due to a “salting out” effect. The “salting out” effect is a commonly known phenomenon that reduces the solubility of organic compounds in water (Schwarzenbach *et al.*, 1993). As salt concentrations increase, water molecules become bound to the electrolyte ions which reduces the amount of water molecules available to dissolve organic molecules. Hence, these compounds are forced into a non-aqueous phase. Though the salting out effect usually acts to decrease the solubility of non-polar organic compounds, it has also been found to result in the increase of aqueous solubility for a few weakly polar compounds such as phenol (Hashimoto *et al.*, 1984).

As a result, laboratory scale experiments were designed to study the impact of each of these parameters on BTEX sorption as part of phase I of the experimental plan. The details of the research plan and experimental methods are presented in Chapter 3 and the experimental results are presented in Chapter 4. Batch experiments were conducted to evaluate multicomponent sorption phenomena in ultrapure water, saline water, and actual produced water, and to quantify the impact of salinity and temperature on the equilibrium sorption parameters. Selected conditions were also examined in laboratory scale column studies to confirm the sorption equilibrium parameters determined from the batch experiments, and to aid in the development of design criteria for the field scale column. The design of the laboratory and field columns was based on the RSSCT approach described by Hand *et al.* (1984). This method assumes that both internal and external diffusion may affect the rates of sorption. The goal of the method is to simulate sorption behavior in long-term pilot studies operation using a smaller scale setup that maintains dynamic similitude between the performance of the large scale and small scale adsorption columns (Sontheimer *et al.* 1988).

The literature review suggested that cost effective regeneration should be possible using an air stripping process. Laboratory column studies were conducted to test this method of regeneration as part of Objective 4 of the project. The methods and results for these experiments are also presented in Chapters 3 and 4, respectively.

The results from the laboratory studies associated with Objective 1, were used to develop the SMZ adsorption system outlined in Objective 2. Produced water characterization of several sites provided criteria for selection of the Wyoming Site for conducting field studies associated with Objective 3 and 4. A pilot scale adsorption/regeneration system was constructed based on the design criteria. The performance of the system was then tested at the field site. The results of the studies were then used to conduct a cost-analysis of the SMZ process. The analysis, presented in Chapter 4, included a comparison of the costs of the SMZ process to other potential treatment approaches.

2. Executive Summary

Co-produced water from the oil and gas industry accounts for a significant waste stream in the United States. It is by some estimates the largest single waste stream in the country, aside from nonhazardous industrial wastes. Characteristics of produced water include high total dissolved solids content, dissolved organic constituents such as benzene and toluene, an oil and grease component, and chemicals added during the oil-production process. While most produced water is disposed via reinjection, some facilities are required to remove organic constituents before the water is discharged. Current treatment options are successful in reducing oil and fewaw; however, they cannot always meet the levels of current or proposed regulations for discharged water. Therefore, an efficient, cost-effective treatment technology is needed for removal of dissolved constituents such as benzene, toluene, ethylbenzene and xylenes (BTEX).

Treatment through sorption onto materials such as surfactant-modified zeolite (SMZ) may be both effective and relatively inexpensive. Zeolites are naturally occurring aluminosilicate minerals that have large capacities for cation exchange. By utilizing this property, natural zeolites can be modified by cationic surfactants such as hexadecyltrimethylammonium (HDTMA). HDTMA is a tetrasubstituted ammonium cation with a permanently charged pentavalent nitrogen and a long, straight alkyl chain (C₁₆). The long hydrocarbon chain imparts a strong degree of hydrophobicity to the surfactant tail while the positively charged ammonium head remains hydrophilic. Counterions such as bromide or chloride serve to neutralize the cationic effect of the head group a rendering them capable of sorbing anions. Thus, thSMZ has some adsorption capacity for cations, anions, and non-polar organic compounds such as BTEX.

The overall goal of this research was to develop a cost-effective and practical method of treating co-produced waters from oil-field sources using a treatment scheme that includes surfactant-modified zeolite. Potential impediments to system performance and potential methods of system regeneration were also addressed. Existing data on SMZ use as a treatment method for contaminated ground water and an experimental program were used to support the development process. The experimental program included three components: laboratory scale batch experiments, laboratory scale column experiments, and a pilot test.

Batch sorption experiments were performed to characterize sorption of BTEX to SMZ as a function of salinity, temperature, and in the presence of produced water. The goals of the laboratory scale column tests were to evaluate process kinetics, verify the batch results, assess the feasibility of the process in a continuous flow system, and evaluate the potential for regeneration of the SMZ using an air sparging system. Several possible sites/sources of produced water were evaluated including a small producer in East Texas near Smithville, a gas well array near Houston, Texas, an offshore oil well, and a treatment facility owned by BC Technologies in Wamsutter, Wyoming. The facility owned by BC Technologies was chosen as the site for field study in this project because the salinity, BTEX concentrations, source quantity, and reproducibility of source volumes and chemistry were all appropriate for field tests.

Single-solute and multi-solute sorption tests showed that the partitioning of BTEX compounds remained linear through concentrations ranging over five orders of magnitude. The distribution coefficients for the BTEX compounds increased with increasing

compound hydrophobicity, and as proven through hypothesis testing, the distribution coefficients for benzene and toluene were not significantly changed by the addition of the remaining BTEX compounds. Furthermore, the distribution coefficients for benzene and toluene were underestimated by typical published correlations relating organic carbon normalized partition coefficients to either aqueous solubility or octanol- water partition coefficients. As a result, independent correlations between the distribution coefficient and either octanol-water partition coefficient or aqueous solubility were developed using data generated in this study. BTEX sorption isotherms on SMZ in saline solutions remained linear; however, statistically significant increases in the distribution coefficients for all of the BTEX were observed when the salt concentration in solution was increased to 100,000 ppm or greater. Empirical relationships were developed to correlate the increase in the distribution coefficient as a function of the salt concentration, but attempts to predict distribution coefficients with the Setchenow equation or regressions based on first-principles were unsuccessful. The BTEX distribution coefficients increased with increasing temperature. The data was used to estimate enthalpy values and an analysis of the enthalpy data was used to confirm that the process was endothermic and consistent with a partitioning mechanism for sorption.

Batch sorption isotherms were also developed in a produced water background using produced water obtained from the Wamsutter site owned by BC Technologies and operated by Crystal Solutions, LLC. The produced water used in the batch experiments contained 11,400 ppm total dissolved solids. In all cases, the produced water BTEX distribution coefficients were higher than those obtained in ultrapure water; however, the differences were only statistically significant for the benzene and m- & p- xylene.

Laboratory scale column experiments confirmed the sorption capacities and the effect of salinity and background produced water obtained in the batch studies. Laboratory scale regeneration tests showed that air sparging was effective in stripping all of the benzene and toluene from the column, but not all of the ethylbenzene and the xylenes were removed under the conditions employed. The breakthroughs of benzene and toluene for the regenerated SMZ were similar to their breakthroughs with virgin SMZ.

The field test conducted at the BC Technologies site in Wamsutter, WY successfully verified the laboratory findings. The SMZ treatment system removed BTEX using virgin SMZ and regenerated SMZ. Benzene breakthrough in the field column occurred after a greater number of pore volumes than observed in the laboratory columns, suggesting that the background produced water increased the sorption capacity of the SMZ for benzene.

Regeneration of a 14-inch column showed results similar to regeneration of the lab column. Benzene was the first compound to be removed from the spent SMZ, and was the only compound that fully stripped from the column. Comparison of breakthrough profiles from the regenerated SMZ to the virgin SMZ suggested that the regenerated SMZ had a greater capacity for benzene. This result was consistent with the results of the laboratory columns.

When compared to other existing treatment technologies, the cost of the SMZ system is very competitive. Furthermore, the SMZ system is relatively compact, does not require the storage of potentially hazardous chemicals, and could be readily adapted to an automated system. The analysis also demonstrated that the cost of the system would depend on the need for off-gas treatment and the replacement interval for the SMZ.

3. Background

This literature review describes the characteristics of produced water, identifies potential processes for treating produced water, describes the components used to manufacture surfactant modified zeolite, and reviews previous literature relevant to its use for produced water. The review also provides information necessary for determining the key parameters required for evaluating SMZ sorption of BTEX from produced water.

3.1 Produced Water

3.1.1 Sources of Produced Water

Oil and gas exploration and production processes require large volumes of water. The three industries that combine to form the oil and gas industry are oil, coalbed methane, and conventional non-associated gas producers. The aqueous effluent from these operations is the largest volume stream in the oil and gas operation and exploration processes (Janks and Cadena, 1992). For every barrel of oil that is generated, ten barrels of produced water result (API, 1987). Every 1000 cubic feet of coalbed methane and conventional non-associated gas results in 0.31 and 0.023 barrels of produced water, respectively (Lawrence *et al.*, 1995).

Produced water is generated throughout the oil and gas production process. Water that is naturally present in oil and gas reservoirs, referred to as formation water, is often pumped out with the crude oil and gas. In addition, water is pumped back into the reservoir to maintain reservoir pressure and force oil and gas into production wells. Smaller oily streams are also generated from oil storage facilities, and process and drainage water (Jacobs *et al.*, 1992). This produced water is normally recovered at the production wellhead. However, the effluent stream can also be recovered via pipeline drips and/or separators, processing/conditioning plants, and underground storage facilities (Fillo *et al.*, 1992). These sources annually generate more than three billion tons of produced water (API, 1987).

The constituents in produced water vary with reservoir and type of production, but usually include dissolved salts and metals, soluble and insoluble hydrocarbons, treating chemicals, radionuclides and dissolved gases (Caudle *et al.* 1995). The BTEX compounds are the major volatile components found in produced water, but the concentration of BTEX varies substantially among water samples (Fillo *et al.*, 1992). Polynuclear aromatic hydrocarbon concentrations in produced water are generally far below their toxic levels. Dissolved salt concentrations in produced water vary from about 100 ppm to 300,000 ppm (Fillo *et al.*, 1992). For example, total dissolved solids (TDS) concentrations range from 40,000 ppm to over 100,000 ppm. Oil and grease are often in the form of very small droplets as a mixture of oxygenated compounds and small amounts of hydrocarbons. Semi-volatile compounds exist mostly as C₁₀-C₃₀ straight-chain alkanes, but phenols, carboxylic acids, and naphthalene are all present in smaller concentrations (Fillo *et al.*, 1992). Metals, such as barium, strontium, arsenic, cadmium, lead, nickel and mercury etc. have been found in produced water samples. Treating chemicals added into the process, include scale inhibitors, corrosion inhibitors, biocides,

emulsion breakers etc. The presence and concentration of these chemicals vary depending on the specific requirement of the process. Not only are some of the volatile organics and hydrogen sulfide believed to be toxic to aquatic organisms, the high salinity associated with many produced waters is thought to be another source of aquatic toxicity.

The temperature of produced water varies with several geographical, geological and separation process factors. Some water is discharged barely near ambient temperatures while others are discharged at 200°F for offshore facilities (Stephenson *et al.* 1992).

3.1.2 Produced Water Characterization

The constituents found in produced water vary with geological setting and type of production, but usually include dissolved salts and metals, soluble and insoluble hydrocarbons, and hydrogen sulfides (Lawrence *et al.*, 1995). In general, *offshore oil* production generates effluent that is higher in total dissolved solids (TDS) but lower in BTEX concentrations than *onshore gas* production. *Onshore oil* production usually results in a water with BTEX and TDS concentrations between those of offshore oil and onshore gas production (Lawrence *et al.*, 1995; Smith *et al.*, 1996; Fillo *et al.*, 1992). The BTEX compounds are the most prevalent volatile compounds found in produced water, but levels of BTEX contamination vary substantially among water samples (Fillo *et al.*, 1992). Fillo *et al.* found that BTEX compounds were detected in 75-80% of production samples and in all storage samples. Total dissolved solids (TDS) concentrations vary even more than BTEX concentrations. These salt and metal concentrations can range from lower than 100 parts per million (ppm) to greater than 300,000 ppm (Fillo *et al.*, 1992). The USEPA Maximum Contaminant Levels (MCLs) for BTEX in drinking water and representative concentration ranges of BTEX and TDS are presented in Table 3.1.

Table 3.1 Representative BTEX and TDS Concentrations for Produced Water

Measured Constituents	Concentration Range (µg/L unless otherwise noted)	Maximum Contaminant Levels (µg/L)
Benzene	70 – 4400	5
Toluene	90 – 5800	1000
Ethylbenzene	29 – 110	700
m-Xylene^a	70 – 460	10000
o-Xylene^a	12 – 110	10000
p-Xylene^a	35 – 290	10000
Total Dissolved Solids (TDS)	100 – 300000 ppm	Variable

^a Xylene concentrations are normally reported and regulated as combined xylene.

Combined xylene concentrations can range up to 5000 µg/L.

References: Smith *et al.*, 1996; Lawrence *et al.*, 1995; Fillo *et al.*, 1992

In addition to mineral salts and volatile organic compounds, oil and grease, semi-volatile compounds, and metals are also present in produced water. Oil and grease are generally present in small droplets that escape the oil/water separation unit. Semi-volatile compounds exist mostly as C₁₀-C₃₀ straight-chain alkanes, but phenols, carboxylic acids, and naphthalene are all present in smaller concentrations (Fillo *et al.*, 1992). Trace and heavy metals such as barium, strontium, arsenic, cadmium, lead, and mercury have been found in produced water samples, but the heavy metals have been detected at lower levels than other metals.

In certain geological formations, produced water also contains substantial amounts of hydrogen sulfide which can contribute to aquatic toxicity (Fucik, 1992). Mount *et al.*, (1992) determined that salinity also plays an important role in aquatic toxicity. These findings are consistent with other research suggesting that volatile organics, hydrogen sulfide, and salinity in varying combinations are the causes of toxicity (Schiff *et al.*, 1992; Sauer *et al.*, 1992). As a result, it is generally agreed that produced water is harmful to marine-life.

Thus, in addition to the known and potential carcinogenic and neurotoxic properties of BTEX compounds, other compounds in produced water are also of concern. As such, various regulations regarding produced water disposal exist.

3.1.3 Regulation of Produced Water Disposal

Produced water is normally disposed of via three options: deep-well injection, surface discharge, and recycle/reuse. Regulation of water that is injected into saline aquifers is conducted through the Underground Injection Control program of the Safe Drinking Water Act (SDWA). This water is exempt from Subtitle C of the Resource Conservation and Recovery Act (RCRA) and can be injected into non-drinking water aquifers through Class II wells (RCRA: Section 3001 (b) (2) (A)). Despite the exemption from Subtitle C, Subtitle D of RCRA continues to apply, and handling and disposal of produced water must still be conducted in compliance with these regulations. In addition, states can also have restrictions on deep-well injection and applicable state regulations must be followed.

Discharge to onshore, coastal, and offshore waters is primarily governed through the Clean Water Act and issuance of National Pollutant Discharge Elimination System (NPDES) permits (Fillo *et al.*, 1992). Only those onshore producers who generate a maximum of 10 barrels of oil or associated gas per day, or those who generate effluent of sufficiently high quality for beneficial reuse can be granted NPDES permits for onshore surface discharge (Lawrence *et al.*, 1995). In addition to limiting the volume of effluent wasted, these permits also state maximum allowable oil and grease concentrations, metal concentrations, toxicity, and a variety of other parameters. Although most coastal and offshore waters are classified as federal territories, some waters off the states of Florida and Texas remain within state boundaries. In these states, as well as several others, the state environmental agencies are responsible for issuing NPDES permits and overseeing compliance with other federal and state regulations.

State regulations are also the primary method of control over recycling and reuse of produced water. Many western states experience arid conditions which limit the amount of water available for irrigation, livestock watering, and wetting of unpaved dirt roads. Some waters generated through oil and gas production are of sufficient quality for these uses and are therefore utilized. Application of produced water for these purposes is usually governed by state agencies on a case-by-case basis (Fillo *et al.*, 1992). Treatment of the produced water that does not currently meet standards for beneficial reuse would allow this wastewater to become a commodity for both producers and residents of water-scarce areas. Lawrence *et al.* (1995) state that future regulations for produced water would require additional treatment for the removal of organic compounds and minerals. Thus, removal of BTEX would be an important step in treatment of produced water.

3.2 Potential Treatment Options

3.2.1 Current Treatment Methods

Current methods for treatment of produced water have focused on removal of oil and grease and suspended solids. Those producers who are required to treat their effluent mostly rely on oil/water separation, hydrocyclones, and gas flotation (Santos and Wiesner, 1997). These common treatment methods share the characteristic that they allow viable oil to be extracted. Thus, they prove economically beneficial to producers, and so the industry continues to use and refine them. For example, Casaday (1993) conducted a study on how to improve gas flotation methods for oil recovery and suspended solids removal. However, these methods do not remove dissolved hydrocarbons, metals, or salts (Bilstad and Espedal, 1996). As previously stated, regulations for produced water disposal may become stricter in the future and these constituents may have to be removed to meet these standards (Santos and Wiesner, 1997). In addition, for reuse of produced water in arid areas, treatment methods must improve water quality to levels acceptable for reuse. Because current treatment appears to be ineffective for hydrocarbons, metals and dissolved salts, several studies have been conducted to test other removal methods.

Produced Water Treatment through Filtration

Physical methods of salt and oil/grease removal have been investigated by several researchers. Tao *et al.* (1993) utilized the San Ardo water treatment pilot plant in California to convert oil field produced water into an effluent that satisfied California's drinking water standards. The pilot plant included chemical clarification, softening, filtration, and reverse osmosis (RO). Extensive fouling of the RO unit was encountered so this problem had to be solved before further treatment could occur. The authors stated that after the plant was optimized, water containing 7,000 mg/L total dissolved solids, 250 mg/L silica, and 170 mg/L soluble oil was successfully handled by the treatment system. Although the study included information about BTEX removal, the method for that removal was not explained and volatilization could have occurred throughout the treatment process. Additionally, the use of RO can be very expensive. Capital costs

were estimated to be \$7-9 million for a 50,000 barrels/day (b/d) plant and operating expenses were stated to be up to \$0.08/bbl.

A less expensive treatment option that has been considered is membrane filtration. Bilstad and Espedal (1996) conducted a pilot scale study aboard an offshore drilling platform. The authors stated that as the amount of produced water in the North Sea increases, European effluent standards for the disposal of the water are also expected to become more stringent. Hence, they chose to study membrane filtration for the removal of dispersed and dissolved hydrocarbons and metals. Through their study, it was found that while microfiltration (MF) did not perform to standards, ultrafiltration (UF) generated effluent that would meet more stringent standards for total hydrocarbons, suspended solids, and dissolved constituents. Reduction of benzene, toluene, and xylenes reached 54% while reduction of total hydrocarbons was 95%. Heavy metals, including copper and zinc, were also reduced by 95%. The authors further declared that no irreversible fouling was experienced during the study and included in their conclusion the necessary design criteria for large-scale UF plants. Although costs are reported in 1996 British pounds rather than in U.S. dollars, the cost for a plant that would treat 50,000 m³/day remained at least \$2 million dollars less than the RO unit described in the previous study.

In contrast to the study conducted by Bilstad and Espedal (1996), Santos and Wiesner (1997) stated that ultrafiltration membranes do not typically remove dissolved materials such as salts and small organic compounds. The results from their research showed that with the exception of iron, inorganic species were not removed and only larger hydrocarbons, such as dispersed oil, were rejected by the UF membrane. The authors suggested that pronounced iron removal was the result of oxidation and subsequent precipitation. Indeed, fouling due to iron precipitation became a problem during the study. However, oil and grease were successfully removed from the four different produced waters tested and effluent levels for these constituents were well below foreseen U.S. standards. Chemical cleaning of the membranes had mixed results for the various waters tested. In certain circumstances, the authors stated that fouling worsened after chemical cleaning. Variability of the results of different water sample led the authors to conclude that the economic feasibility of this treatment method depends on the characteristics of the specific water to be treated. As a result, the blanket use of UF technology as a Best Available Technology (BAT) standard is unadvisable at this time.

3.2.2 Innovative Treatment Methods

3.2.2.1 Bubble Separation of Hydrocarbons

Thoma *et al.* (1999) tested the microbubble-based separation of dissolved aliphatic and aromatic hydrocarbons from synthetic produced water into a floating immiscible layer on top of a water column. By changing the gas flow rate of the microbubbles, different removal efficiencies for test organic compounds were attained. With a gas flow rate of 100 mL/min, octane and decane were reduced 95% and 75% in 25 and 30 minutes, respectively. However, even after 360 minutes at a gas flow rate of 60 mL/min, only 40% of the dissolved ethylbenzene and toluene was removed. Raising the gas flow rate to 200 mL/min increased the removal of the aromatic hydrocarbons to 70%. Although

benzene was reported to be a test compound, no further results for this compound were included in the paper. The removal of other dissolved compounds, such as salts, metals, or other hydrocarbons, was not tested in this study and costs for the process were not reported.

3.2.2.2 Oxidation of Organic Compounds

Bessa *et al.* (2001) researched photocatalytic treatment and oxidation with hydrogen peroxide of four different produced waters. The authors explained that the unique nature of semiconductors allows them to be powerful oxidants in the presence of high-energy photons. Using a titanium oxide semiconductor, the authors studied how phenols would undergo chemical oxidation in the presence of a high-pressure mercury lamp. Prior to the oxidation, the produced waters had to undergo clarification to remove particulate matter. During the subsequent photocatalysis, air was continuously bubbled into a stirred water column. Although the authors stated that no volatilization of low-molecular weight organics, such as BTEX, was observed, they offered no experimental data to corroborate that statement. Bubbles were reported to remove organic compounds from solution in the previous study so it seems unlikely that no organic compounds partitioned into the air phase while the water column was bubbled with air.

Nevertheless, the authors further reported results for the oxidation of phenol through photocatalysis and through contact with hydrogen peroxide. These results were presented as total reduction in peaks obtained through gas chromatography/mass spectroscopy (GC/MS). The peaks for compounds that initially eluted late were shown to decrease substantially with time of photocatalysis. However, the size of peaks for compounds with smaller retention times increased because, presumably, the larger compounds were transformed into these smaller compounds through oxidation. These results also showed that one brand of semiconductor performed substantially better and did not degrade whereas the other brand corroded. Lastly, the authors stated that the use of hydrogen peroxide is inadvisable because of the increased corrosion on the semiconductor plates. This treatment technique, though innovative, would likely prove uneconomical for the small oil and gas producer because of the expense associated with semiconductors.

3.2.2.3 Phytoremediation of Produced Water

Researchers at Argonne National Laboratory studied the use of halophilic plants to reduce produced water volume, enhance contaminant degradation, and immobilize pollutants in the root/rhizosphere zone (Negri and Hinchman, 1997). The optimal plants were chosen after extensive greenhouse testing, and results from an engineered plant ecosystem showed a 75% reduction of saline wastewater in 8 days. The salt concentrations tested ranged up to 6%, which the authors stated is twice the salinity of seawater. However the study did not specifically address the removal of compounds such as BTEX and metals. Because the effectiveness of this method would decrease in seasons other than the growing season, the authors suggested that phytoremediation be used in conjunction with another method. Nevertheless, for producers who are located in remote regions, this treatment method could prove to be low cost and low maintenance.

3.2.2.4 Sorption of Produced Water by Commercially Available Sorbents

Sorption studies have focused mainly on the removal of BTEX compounds. Both activated carbon and ion exchange resins have been investigated. Powdered and granular activated carbon have been used for sorption in water treatment for many decades. Industrial scale production of activated carbon began in the 1920s when it was used primarily for the removal of chemicals that caused odors and bad taste in drinking water. Activated carbon (AC) was later found to remove non-polar organic pollutants from water and has been used for this purpose in many remediation sites and water treatment plants (Sontheimer *et al.*, 1988).

Activated carbon is produced from raw carbon sources such as peat, coconut shells, wood, and bituminous coal. After an initial pyrolysis step, the raw material is chemically activated and sieved into different sizes. The activation process produces a highly porous material containing surface areas typically ranging from 500 to 1400 m²/g. Because the surface of activated carbon is primarily hydrophobic, it is an excellent sorbent for organic compounds. (Sontheimer *et al.*, 1988).

Powdered activated carbon (PAC) consists of particles less than 0.05 mm in diameter. This material is primarily added as a suspension in rapid mix and flocculation basins to remove odor and bad-taste causing compounds from drinking water. After a contact time of 10-15 minutes, the PAC is removed through flocculation and filtration and then regenerated. Because of the small size of this material, PAC is not normally used as filter media. In addition to large head losses due to back pressure, PAC also promotes excessive bacterial growth which leads to additional head losses (Sontheimer *et al.*, 1988).

Granular activated carbon (GAC) ranges in particle size from 0.3 to 3 mm and is the primary sorbent used in most remediation projects because of its excellent sorption properties (Sontheimer *et al.*, 1988). However, activated carbon has some drawbacks when used for sorption of organic chemicals. Sorption of most organic carbons onto activated carbon is typically described using a non-linear isotherm model (e.g. Freundlich isotherm) and the sorption process is often controlled by surface and/or pore diffusion processes. Competitive sorption often limits the sorption capacity for mixtures of organic compounds because only a finite number of adsorption sites exist on the surface. If one compound has much greater affinity for the AC, it can effectively take up the majority of available sites in an AC column. This allows the remaining compounds to stay in solution and can even cause higher effluent concentrations of some pollutants than the influent concentrations depending on the relative rates of diffusion. This latter phenomenon occurs when the rates of sorption are faster for the compound that has a lower affinity for the surface. In these cases, the compound with higher affinity for the AC exchanges with the lower affinity compound that has adsorbed more rapidly. In this manner, the effluent concentration for that first compound can be higher than the initial influent concentration (Sontheimer *et al.*, 1988).

Another drawback to using activated carbon for treatment of water with multiple types of contaminants is its inability to effectively remove metals and other polar constituents from solution. Many wastewaters contain trace amounts of heavy metals and hydrophilic

pollutants in addition to organic compounds. Most activated carbons cannot be used for the removal of all of these constituents because the hydrophobicity of the surface prevents the sorption of polar compounds.

Though the chemical properties stated above limit the attractiveness of AC as an all-purpose sorbent, the most significant deterrent for using AC is economic. Activated carbon is expensive to produce and to regenerate. The purchasing price for granular activated carbon can range from \$1.50 - \$2.50 per pound. Regeneration costs for activated carbon are also quite high because of the large amount of energy required. Based on these high costs and because of its limited potential in wastewaters containing constituents other than organics, activated carbon may not be the most suitable sorbent for small scale oil producers.

Gallup *et al.* (1996) used commercially manufactured carbonaceous sorbents, Ambersorb, to reduce BTEX concentrations in oil-field produced water. These compounds are created from the partial pyrolysis of macroporous polymer beads. The pyrolysis process causes the materials to lose their ionic functional groups and retain non-polar surfaces (Weber and van Vliet, 1981). The resulting compounds exhibit hydrophobic properties that allow non-polar organic compounds to be effectively removed from water. Ambersorb® 572 and 563 (Rohm and Haas Company; Spring House, PA) carbonaceous sorbents are formed through the partial pyrolysis of macroporous sulfonated styrene-divinylbenzene ion exchange resin (Parker, 1992). They tend to be hard black spherical beads with average diameters between 0.085-0.3 mm (Rohm and Hass, 1992-1999; Isacoff *et al.*, 1992).

The research conducted by Gallup *et al.* used column studies to compare the Ambersorb® 572 to Hydrodarco GAC (American Norit Co., Inc.; Atlanta, GA) and organically-modified clays EC-100 and EC-199 (Biomin Inc.; Huntington Woods, MI). Each 5 cm glass column contained 50 cm³ of the sorbents being tested. Aqueous solutions containing 50-150 mg/L of dissolved BTEX compounds were allowed to flow at a rate of 1.1 mL per minute per cm³ of sorbent. After solving extensive clogging problems due to oil and grease, the authors stated that the Ambersorb® outperformed both the GAC and the modified clays tested and was less expensive than the GAC. After treatment of 1200 bed volumes, Ambersorb® 572 was reported to remove 93% of benzene and toluene while Hydrodarco GAC provided only a 23% removal. Additionally, the authors stated that the modified clays used in the study removed between 21-23% of benzene and toluene in the produced water. Although neither the commercial sorbents nor the GAC removed the emulsified oil, modified clays reduced the emulsified oil from 25 mg/L to 12 mg/L.

Isotherms and isotherm parameters were not included in the study. However, it was possible to estimate the sorption density through the information obtained from The California MTBE Research Partnership (1999) and the information presented in the Gallup *et al.* study about the column, influent BTEX concentrations, and percent removal of benzene and toluene. The estimated sorption density for Ambersorb® 572 at the end of the study was between 125 – 376 mg/g for an influent concentration of 25-130 mg/L BTEX.

Solvent regeneration of the carbonaceous sorbents was reported by Gallup *et al.* (1992) to be effective, but GAC could not be efficiently regenerated due to substantial oil fouling. Further demonstrations resulted in BTEX breakthrough as more strongly sorbing

species replaced BTEX compounds on the Amborsorb® 572. However, because the analytical HPLC techniques and the sorbent itself were proprietary, little methodological information was presented to fully evaluate these results.

Various methods of oil removal were tested in the Gallup *et al.* study because of the extensive fouling problems encountered in the field. Bench scale tests showed that modified clays could reduce the oil concentration by a factor of two but fouling continued to occur. Thus, a coalescer was tested and found to be very site- and water-dependent. However, a demonstration of compounds classified as emulsion breakers showed that Magnifloc 494C (Cytec Industries; West Patterson, NJ) was very successful at causing oil to float. The oil was then easily skimmed off and the remaining water was treated sufficiently by Amborsorb® 572, even after regeneration. The authors concluded that with the use of an effective oil and grease removal system, Amborsorb® carbonaceous sorbent was a better BTEX remover than either GAC or modified clays.

One substantial disadvantage of using a carbonaceous sorbent rather than modified clays or zeolite is the inability to remove hydrophilic compounds such as salts and metals. This study did not delve into this topic. In addition, although the authors stated that the expense of the commercial sorbent compared favorably to the cost of using GAC, no specific information was given about the capital costs or operating expenses. It was suggested that the regeneration of GAC would result in an annual increased cost 4 to 7 times that of Amborsorb® 572.

3.2.3 Surfactant Modified Zeolite

Janks and Cadena (1992) investigated BTEX and barium sorption capacities of zeolites modified with several different surfactants. The water used for this study was produced water from an oil field and contained 1% insoluble long chain hydrocarbons, 860 mg/L soluble hydrocarbons of which 70 mg/L consisted of BTEX compounds, and 10,300 mg/L total dissolved solids. Nine different surfactants and two types of zeolite, chabazite and clinoptilolite, were used in this study. The authors reported the CEC values for the two zeolites to be 72 meq/100 g for chabazite and 80 meq/100 g for clinoptilolite. The authors noted that the actual makeup of the zeolites included not only the zeolites themselves, but also compounds such as cristobalite, smectite, quartz, calcite, and dolomite. The nine surfactants included diethylenetriamine (DETA), ethylenediamine (EDA), monoethanolamine (MEA), piperazine (PIP), tetramethylammonium chloride (TMA), triethylamine (TEA), tetraethylenepentamine (TEPA), triethylenetetramine (TETA), and HDTMA-Cl. In contrast to the studies on BTX sorption (ethylbenzene not included) conducted by Bowman *et al.* (1993), the zeolites in the study performed by Janks and Cadena were treated only to 100% of their reported CEC values rather than 200%.

The batch tests were performed on dried modified zeolite. Initial spiking of the SMZ with produced water was followed by four hours of tumbling on a roller over at 25°C. The water was then analyzed by purge and trap gas chromatography. There was no mention of any centrifugation after the tumbling or what types of vials were used in the study. Benzene and toluene removal from laboratory solutions was tested and reported for HDTMA along with TMA and TEA, but the actual batch studies with produced water were conducted only with TMA, EDA, PIP, TETA, TEPA, and MEA. No explanation

was given regarding the exclusion of three surfactants, including HDTMA, from the batch tests. This missing information and the unique nature of zeolites from specific locations makes it difficult to compare results from this and other studies.

The authors cited several general observations regarding the results from their batch tests. For the ethyleneamine group, those surfactants with higher molecular weights tended to be less efficient at BTEX removal than lower molecular weight surfactants. Total BTEX removal ranged from 9.4% (MEA) to 85.2% (EDA) but the surfactants showed preference for specific compounds. Xylenes were removed most effectively by EDA while PIP seemed to exclude them. Even though TMA showed affinity for benzene ($K_D > 0.9$ L/g for chabazite and $K_D > 0.7$ L/g for clinoptilolite), it was almost as ineffective at toluene removal as natural zeolite. The hydroxyl group on the MEA served to generally exclude BTEX sorption. Interestingly, in this study, it was found that maximum distribution coefficients for benzene removal on TMA-modified chabazite and clinoptilolite occurred between 40-60% of the CEC. This is in contrast to results presented by Li *et al.* (2000) who found the maximum distribution coefficient (K_d) for HDTMA-modified zeolite at the CEC. However, comparisons between these studies may not be valid because of differences in surfactant, zeolite type, and zeolite size.

The authors also report the contents of their zeolite samples as analyzed through XRD. Smectite fractions ranged from 10-50% while cristobalite formed 7-24% and clinoptilolite 20-60% of the zeolites studied. Though the high variability of zeolite content in samples from different sources was noted, the sources of the zeolites used in this study were not discussed. Nevertheless, it was suggested that smectite fractions play an important role in BTEX removal. The authors stated that BTEX sorption may have actually occurred on the smectite and that the removal efficiency increased with smectite percentage. These assertions were supported by a correlation between BTEX removal and d-spacing of the smectite basal reflection. To explain the preference for specific BTEX compounds, it was hypothesized that the orientation of specific BTEX compounds may have allowed them to or excluded them from sorbing to smectite. The size and configuration of the surfactant tails also played a part in this theory.

Lastly, the authors reported that barium, which was used as a representative metal ion, was not substantially removed by five of the six surfactants tested. The sole exception was PIP, which reduced the initial barium concentration from 28 mg/L to 17.3 mg/L. Although this specific metal was not removed by the modified zeolites, Bowman *et al.* (1997) demonstrated that metals such as lead are sorbed by zeolite while others like strontium lose their affinity for the compound once it is modified. Because only one metal was used in this study, it is difficult to make a general statement about the affinity of heavy metals for SMZ.

Janks and Cadena concluded by stating that modified zeolites would be effective at BTEX removal in the field, especially because the presence of other organic and inorganic constituents did not seem to affect the removal capacity of the SMZ. It was implied that increased smectite percentage and the use of surfactants with small molecular sizes would result in the greatest sorption capacity for BTEX compounds. They also went on to suggest future research topics, including the determination of salt effects on BTEX removal and investigations on regeneration options.

3.2.3.1 Zeolite Properties

Natural zeolites are hydrated aluminosilicate minerals with cage-like structures. They have very high internal and external surfaces areas and high internal and external cation exchange capacities (CEC). According to Haggerty and Bowman (1994) forty-one naturally occurring zeolites have been found and several others have been synthesized, of which the most popular natural zeolite is clinoptilolite as shown in Figure 3.1. Its dry unit cell formula is $(Ca,Na_2,K_2)_3[Al_6Si_{30}O_{72}].24H_2O$. The largest cavity dimension within clinoptilolite was found by Newsom (1986) to be 4.4 x 7.2 Angstroms. The BET external surface area for zeolite from the St. Cloud mine in Winston, New Mexico was determined by Sullivan *et al.* (1997) to be 15.7 m²/g. The total cation exchange capacity (CEC) for clinoptilolite obtained from St. Cloud Mine, New Mexico is 230 meq/kg (Li, *et al.* Natural zeolites have low organic carbon contents (<0.5%) and do not favor sorption of organic compounds. However, natural zeolites have been found to effectively remove several types of metals, such as lead and strontium, from aqueous solutions (Bowman *et al.*, 1993).

Zeolites are similar to smectite clays in their surface chemistry properties, but these materials do not exhibit the shrink/swell behavior of clays in water. The measured cation exchange capacities of natural zeolite have been found to be as much as 50% greater than those of clays (Janks and Cadena, 1992). In addition, zeolite particles usually occur in millimeter or greater particle sizes. This larger particle size allows zeolites to be well suited for use as permeable barriers.

Surfaces of both clays and natural zeolites are negatively charged, making them hydrophilic. Positively charged counterions neutralize the zeolite's negative charge. Large cationic surfactant molecules can also neutralize the surface charge and they have greater affinity for the zeolitic surface.

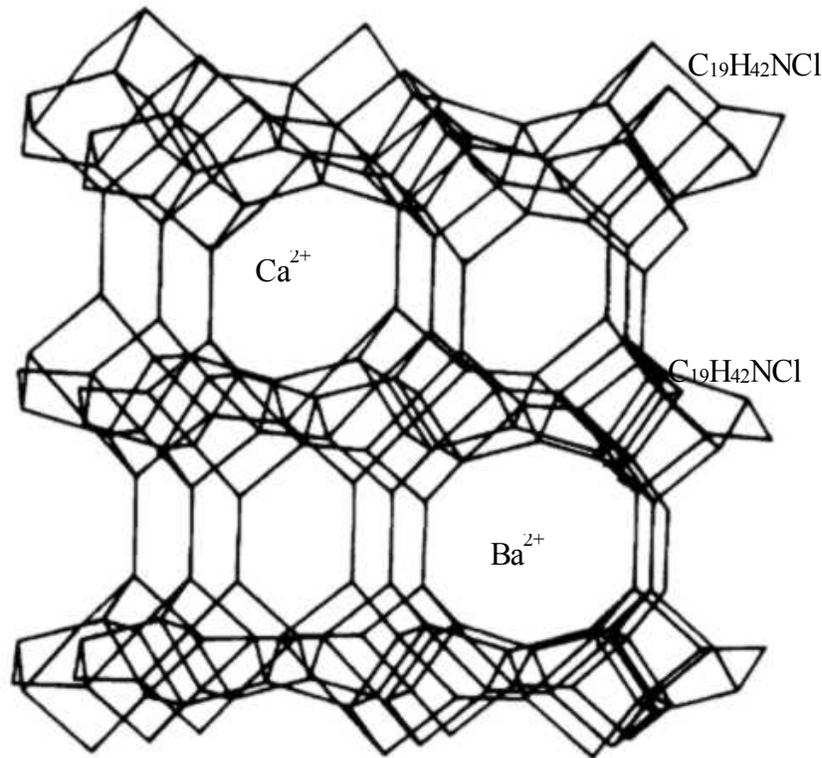


Figure 3-1 Crystal Structure for Clinoptilolite (adapted from Manley and Holmes, 1989, Minerals with Natural Advantage, *New Scientist*, March 25, 1989, pp. 39-43)

3.2.3.2 HDTMA

Surfactants are surface active agents that exhibit both hydrophobic and hydrophilic properties. The hydrophobic portions are commonly called tails and consist of hydrocarbon alkyl chains or aromatic rings. The opposing head groups can be charged or neutral, but tend to exhibit hydrophilic properties. These surfactants can be anionic, cationic, or non-ionic, depending on the charge of the head group. When in aqueous solutions, surfactant monomers form spherical micelles in which the head groups extend into the aqueous phase while the tail groups remain close to one another inside the micelles. This phenomenon occurs once the concentration of surfactant is high enough to exceed the critical micelle concentration (CMC). Many different surfactants exist and the phenomena described above apply to most of them, but only the surfactant most relevant to this research is described below.

Hexadecyltrimethylammonium (HDTMA) is a tetrasubstituted ammonium cation with a permanently charged pentavalent nitrogen and a long, straight alkyl chain (C_{16}) (Haggerty and Bowman, 1994). The long hydrocarbon chain imparts a strong degree of hydrophobicity to the surfactant tail while the positively charged ammonium head remains hydrophilic. Counterions such as bromide or chloride serve to neutralize the cationic effect of the head group.

This surfactant is commonly used in products such as hair conditioner, mouthwash, and fabric softener so it is assumed that the chemical is not hazardous (Li *et al.*, 1998). Furthermore, HDTMA is easily accessible and has been found to have excellent chemical properties for sorption-related water treatment.

3.2.3.3 SMZ

Saturation of natural zeolite with a surfactant such as HDTMA yields a surfactant-modified zeolite. As mentioned above, the cationic surfactant head exchanges with the naturally occurring cations on the surface of the zeolite. Due to the large size of HDTMA monomers, only external pore spaces are subject to this cation exchange. The surfactant is unable to enter the small internal pores and therefore, leaves the internal surface chemistry of the zeolite unchanged and potentially available for cation exchange (Barrer *et al.*, 1967; Li and Bowman, 1997).

Sorption of HDTMA has been described by the non-linear Langmuir isotherm (Figure 3.2) which assumes that monolayer adsorption occurs to a finite number of homogeneous sites. The equation for the Langmuir isotherm is shown below:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (3.1)$$

where Q_{\max} is the maximum sorption capacity (mmol/kg), b is the sorption intensity (L/mmol), and C_e is the aqueous phase equilibrium concentration (mmol/L).

The maximum sorption capacity can be obtained from a plot of the equilibrium sorbed phase concentration versus the equilibrium aqueous phase concentration of a solute as shown in Figure 3.2. This maximum sorption capacity is often used as an estimate of the exchange capacity (EC) and indicates that the maximum sorption capacity for HDTMA-Br- and HDTMA-Cl- are 208 and 151 mmol/kg, respectively. During the sorption process, the head group of the surfactant remains sorbed to the surface of the zeolite while the tail group floats in solution. To balance the positive charge of the head groups, counterions such as chloride and bromide form electrostatic bonds with the head groups. Due to the larger hydrated radius of chloride, Li and Bowman state that this counterion is less able to deeply penetrate the Stern layer and neutralize the head group's positive charge than the smaller hydrated bromide ion. Thus, the repulsion among head groups prevents surfactant sorption and reduces the exchange capacity for HDTMA-Cl. As a point of comparison, using a modified method developed by Ming and Dixon (1987), the external exchange capacity of zeolite has been found by Li and Bowman (1997) to be between 90 - 110 meq/kg, suggesting that the surfactant is forming a bilayer on the surface of the zeolite.

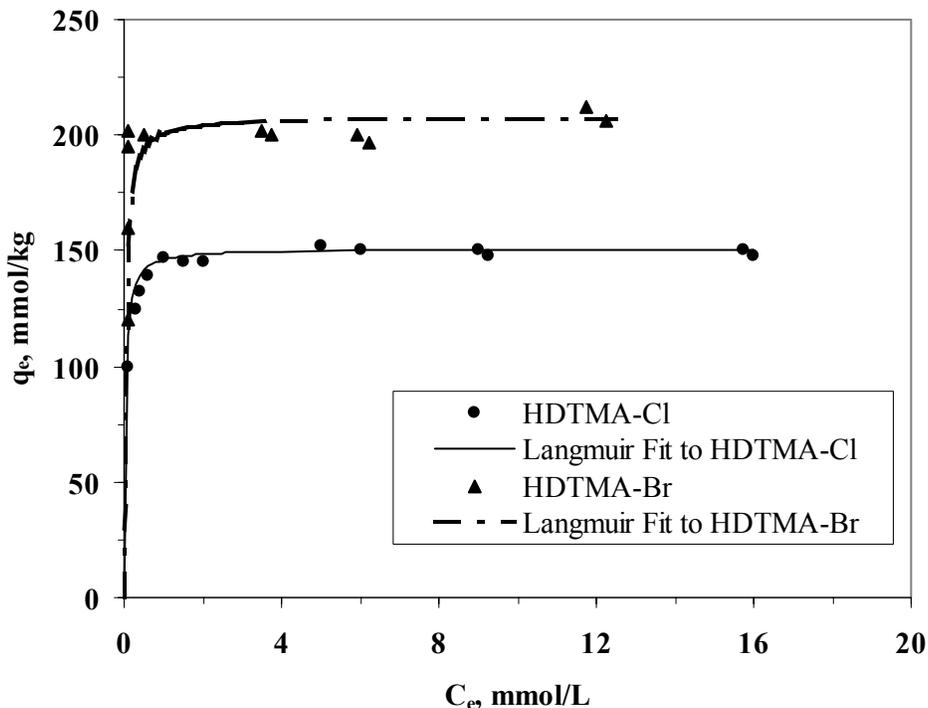


Figure 3.2 HDTMA Sorption to Zeolite

While the head groups sorb onto the zeolite surface, the hydrophobicity of the tail groups forces tail-tail interactions to occur and hemimicelles to form in order to minimize association with water molecules. In the past, it was believed that while the concentration of HDTMA remained below the critical micelle concentration (CMC), monolayer coverage would continue and surfactant monomers would attach to the surface as hemimicelles. As the concentration surpassed the CMC, monolayer coverage of the zeolite would be completed and patches of a second layer or admicelles would begin to develop above the bottom layer (Haggerty and Bowman, 1994). However, a more recent study conducted by Sullivan *et al.* in 1997 showed with Tapping Mode™ atomic force microscopy and high-resolution thermogravimetric analysis that the buildup of the HDTMA bilayer begins prior to completion of monolayer coverage. Chen *et al.* (1994) suggest that once the CMC is surpassed, previously formed micelles sorb onto negatively charged surfaces to create an admicelle or bilayer. These results were supported by Li and Bowman (1998) who determined that organic contaminants are sorbed at low HDTMA concentrations. If complete monolayer coverage were necessary prior to the formation of a patchy bilayer, these organic contaminants would not be strongly sorbed by the SMZ.

The formation of bilayers or hemimicelles creates a hydrophobic region inside the bilayer with positively charged outer head groups extending out into solution. Thus, the original negative charge of the natural zeolite is reversed by surfactant modification. Through ion exchange with these positively charged head groups, anionic contaminants can be removed from aqueous solutions. Several studies have shown that oxyanions such as arsenate, chromate, and selenate are very effectively removed from water by SMZ but not by untreated zeolite (Li and Bowman, 1997; Bowman *et al.*, 1997; Haggerty and

Bowman, 1994). It has also been shown that better sorption of oxyanions occurs when the counterions are weakly bonded (Li and Bowman, 1997). This intuitive trend was shown to increase in strength for hydrogen sulfate, chloride, and bromide, in that order. Although the sorption isotherms for these oxyanions all resembled Langmuir isotherms, the authors in each study were quick to point out that the sorption of the anions does not meet the assumed criteria for the Langmuir isotherm. Thus, the sorption can be described by the Langmuir parameters K_L and q_{\max} , but these parameters do not have true chemical significance.

The natural ability of zeolite to remove metallic cations from solution is somewhat altered by surfactant modification. The sorption of metals such as lead that originally sorbed to the internal pores of zeolite has been shown to remain unchanged (Haggerty and Bowman, 1994; Bowman *et al.*, 1997). Thus, the presence of HDTMA seems to have little effect on the sorption of metals onto internal pore sites within zeolite. However, those cations that were removed by cation exchange with the external surface of the natural zeolite cannot be removed from solution by treated zeolite (Bowman *et al.*, 1997). This inability to remove cations such as strontium is due to the strong sorption of the surfactant to the surface and to the repulsion between the metallic cations and the surfactant head groups.

3.2.3.3 Sorption Mechanisms and Predictive Models

The mechanism for non-polar organic sorption onto SMZ has been described as partitioning into the hydrophobic pseudophase formed by the tail groups of the HDTMA bilayer (Li and Bowman, 1998; Bowman *et al.*, 1993; Bowman *et al.*, 1997). Hydrophobic compounds have extremely large activity coefficients in water. A great deal of energy is required to break the hydrogen bonds linking water molecules to create cavities suitable for hydrophobic compounds (Schwarzenbach *et al.*, 1993). Additional energy is required to reconfigure water molecules into ice-like formations around non-polar organics. However, much less energy is required for non-polar organics to dissolve into a hydrophobic phase. Thus, thermodynamics drive this partitioning process and cause organic compounds such as benzene to leave the aqueous phase. The magnitude of the thermodynamic driving force is based on the water solubility of the various organic compounds. Because benzene has a higher water solubility than the other BTEX compounds, it is less likely to leave the aqueous phase (Schwarzenbach *et al.*, 1993). The relationship between water solubility and driving force to leave the aqueous phase also yields a corresponding relationship between the molecular weight of organic compounds and sorption. Increasing numbers of carbons on organic compounds increases the hydrophobicity and decreases the water solubility. Hence, xylenes are more hydrophobic than toluene, which is more hydrophobic than benzene (Schwarzenbach *et al.*, 1993).

At equilibrium, non-polar organic compounds distribute themselves between the hydrocarbon and water through a linear isotherm in which the aqueous phase concentration, C_e , is directly related to the sorbed phase concentration, q_e , by a single parameter defined as the distribution coefficient, K_d as shown:

$$q_e = K_d C_e \quad (3-2)$$

As a result, the distribution coefficient for sorption of hydrophobic compounds to organic matter is expected to increase with increasing solute hydrophobicity.

A study conducted by Bowman *et al.* (1993) demonstrated that removal of benzene, toluene, and para-xylene increased substantially with surface alteration of natural zeolite. In fact, the sorption of benzene increased 20-fold with SMZ as opposed to natural zeolite. The sorption isotherms for all of these three compounds were linear throughout the concentration ranges tested (0, 10, 50, 100, 150 and 250 mg/L for benzene and toluene and 0, 10, 50, 100, 150, and 198 mg/L for p-xylene). The distribution coefficient values determined in the study conducted by Neel and Bowman (1991) are shown in Table 3.2.

Table 3.2 Distribution Coefficients Determined by Neel and Bowman (1991)

<i>Chemicals</i>	Distribution Coefficient (K_d), L/kg
Benzene	8.59
Benzene with Toluene	8.44
Benzene with para-Xylene	9.40
Toluene	19.2
Toluene with Benzene	19.1
Para-Xylene	70.4
Para-Xylene with Benzene	56.6

During this same study, the effects of co-solutes were tested to see how the SMZ would respond to multiple organic contaminants. Single solutes were initially tested, followed by pairs of benzene/toluene, and benzene/p-xylene. It was determined that removal of these compounds did not significantly change when present in pairs. These results were consistent with earlier findings from Neel and Bowman (1991). The isotherm linearity combined with the lack of competitive effects support the proposed sorption mechanism involving absorption into the surfactant bilayer.

For soils, the magnitude of the distribution coefficient is related to the amount of organic matter present. For many neutral hydrophobic organics, sorption is directly proportional to the quantity of organic matter content in the solid (Chiou *et al.*, 1979; Karickhoff, 1981). Thus, the distribution coefficients can be normalized to the fractional organic matter content which generates organic matter partitioning coefficients, K_{om} (or organic carbon, K_{oc}) and these normalized coefficients are considered as a unique property of the organic chemical being sorbed K_{oc}/K_{om} , (Schwarzenbach *et al.* 1993).

$$K_d = K_{oc} f_{oc} \quad (3.3)$$

$$K_d = K_{om} f_{om} \quad (3.4)$$

where,

- K_{oc} : the organic carbon normalized sorption coefficient,
 K_d : the linear sorption coefficients specific to a particular sorbent and chemical combination,
 K_{om} : natural organic matter–water partition coefficient with a unit of L/kg om for soil.
 f_{oc} : the organic carbon content of that sorbent g oc/g dry soil
 f_{om} : the fractional organic matter content on a soil, which is a constant for a particular soil;

For soil, $K_{om}=1.724K_{oc}$ (Boethling and Mackay 2000); however, for SMZ the relationship between K_{om} and K_{oc} is

$$K_{om}=1.248K_{oc} \quad (3.5)$$

Differences in K_{om} from chemical to chemical primarily arise from corresponding differences in γ_w , and

$$K_{om} = \frac{\gamma_w * \bar{V}_w}{\gamma_{om} * \bar{V}_{om} * \rho_{om}} \quad (3.6)$$

where

- γ_{om} : activity coefficient reflecting the incompatibility of the sorbate associated with the natural organic matter as compared to in solution of its own liquid;
 γ_w : activity coefficient of solute in water, independent of aqueous concentration for neutral nonpolar compounds;
 \bar{V}_w : molar volumes of the water (L water mol⁻¹ water);
 \bar{V}_{om} : molar volumes of natural organic matter (L mol⁻¹ om);
 ρ_{om} : the organic matter density (kg om L⁻¹ om)

Schwarzenbach *et al.* 1993 also support the contention that temperature changes only affect γ_w , not much of γ_{om} .

In applying these relationships, the assumption is that sorption process is happened exclusively to the organic component of the SMZ, all organic carbon has same sorption capacity per unit mass. In this manner, Li and Bowman (1998) showed that Equation 2.3 only holds true when HDTMA loading is less than 100% of the external cation exchange capacity. It has also been found that Equation 3.3 is valid primarily when $f_{oc} > 0.001$ (McCarty *et al.*, 1981). For soils, it is possible to relate aqueous solubility (S) and octanol-water partitioning coefficients (K_{ow}) to partitioning into organic carbon (K_{oc}). In fact, several investigations have found empirical relationships that relate K_{oc} in soils of differing fractional organic matter contents (f_{om}) to K_{ow} and aqueous solubility (S).

These linear free-energy equations all take log linear forms:

$$\log(K_{oc}) = a * \log(K_{ow}) + b \quad (3.7)$$

$$\log(K_{oc}) = c * \log(S) + d \quad (3.8)$$

where a, b, c , and d are regression parameters. These relationships are presented in Table 3.3 along with their applicable organic compounds, organic carbon contents, and corresponding correlation coefficients (R^2). The values for K_{oc} and K_{om} were expressed as L/kg organic carbon and L/kg organic matter, respectively. The octanol-water partition coefficient was expressed as L water/L octanol and in most of the regressions, S was expressed in mol/L. However, in the regressions developed by Abdul *et al.* (1987), the solubility was expressed in mg/L.

Table 3.3 Published Correlations Relating K_{oc} , K_{om} , K_{ow} , and S

Source	Regression	Applicable Compounds	Applicable f_{oc} , %	R^2
Schwarzenbach <i>et al.</i> , 1993	$\log K_{om} = -0.93 \log S - 0.17$	Aromatic Hydrocarbons	Unreported	0.92
Schwarzenbach <i>et al.</i> , 1993	$\log K_{om} = 1.01 \log K_{ow} - 0.72$	Aromatic Hydrocarbons	Unreported	0.99
Karickhoff <i>et al.</i> , 1979	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	Benzene	0.13-3.29	1.00
Karickhoff, 1981	$\log K_{oc} = 0.989 \log K_{ow} - 0.346$	Benzene	0.11-2.38	0.997
Schwarzenbach and Westall, 1981	$\log K_{oc} = 0.72 \log K_{ow} + 0.49$	Toluene, Xylenes	1-33	0.95
Chiou <i>et al.</i> , 1983	$\log K_{om} = -0.729 \log S + 0.001$	Benzene, Ethylbenzene	$f_{om} = 1.9$	0.996
Chiou <i>et al.</i> , 1983	$\log K_{om} = 0.904 \log K_{ow} - 0.779$	Benzene, Ethylbenzene	$f_{om} = 1.9$	0.989
Abdul <i>et al.</i> , 1987	$\log K_{oc} = 1.04 \log K_{ow} - 0.84$	Benzene, Toluene, Xylenes	0.4-2	0.98
Abdul <i>et al.</i> , 1987	$\log K_{oc} = -0.74 \log S + 4.0$	Benzene, Toluene, Xylenes	0.4-2	0.99
Vowles and Mantoura, 1987	$\log K_{oc} = 1.20 \log K_{ow} - 1.13$	Benzene, Ethylbenzene, o- & p-Xylenes	4.02	0.998
Pussemier <i>et al.</i> , 1990	$\log K_{oc} = -0.531 + 1.009 \log K_{ow}$	BTEX	Unreported	0.92

All of these relationships were developed for sorption to natural soils, so their applicability to SMZ is unknown. If these published correlations can be used to predict the distribution coefficients for BTEX sorption to SMZ, this process can be easily modeled and the predictions can be used in future studies.

In their study, Li and Bowman (1998) tested the sorption of perchloroethylene (PCE) by SMZ and found that PCE sorption was dependent on both bound surfactant monomer

configuration and fractional organic carbon. The authors primarily studied the sorption of PCE as a function of surfactant loading and results showed that sorption occurred even for zeolite treated with small concentrations of HDTMA. Through manipulation of the initial and final concentrations of surfactant in solution, they found that PCE was most efficiently removed for surfactant concentrations at or below the external EC ($f_{oc} \approx 0.02$). This optimal efficiency may be accounted for by the finding that the point of zero charge (ZPC) was reached at a surfactant-loading of 80 – 90 mmol/kg, which is in agreement with the external EC of 90 – 110 meq/kg (Li and Bowman, 1998). The ZPC is also the point at which the surface exhibits the maximum hydrophobicity. Thus, theoretically, hydrophobic compounds such as PCE would have a greater attraction for the SMZ near the ZPC. As the surfactant concentration increased beyond the external EC up to the maximum amount of 200 mmol HDTMA/kg zeolite ($0.02 > f_{oc} > 0.04$), no further increase in distribution coefficient was reported. The authors state that this lack of increase in K_d values suggests the importance of both fractional organic carbon content and surfactant configuration to sorption onto SMZ. As a result, the above correlations may not be applicable to SMZ.

Recently, Li *et al.* (2000) researched the sorption of ionizable organic solutes by SMZ. The solutes tested included benzene and its ionizable counterparts phenol and aniline. Testing involved determining the effects of pH and surfactant loading on the sorption of pH-dependent compounds. Benzene was included in the study for comparative purposes. At neutral pH, all three compounds included in the study showed increasing distribution coefficients with increasing surfactant concentrations until monolayer coverage was achieved at 100 mmol/kg. Beyond this surfactant concentration, no increases in distribution coefficient were reported and the distribution coefficient for aniline actually decreased because of the electrostatic repulsion between the positively-charged head groups of the surfactant and the positively charged amine group of aniline. Results also showed that sorption of phenol increased as pH surpassed 7 whereas aniline demonstrated less affinity for the SMZ at low pH values. These results were consistent with the known acid-base characteristics of phenol and aniline whose pK_a values are 9.95 and 4.62, respectively.

As described above, SMZ has been shown to remove a wide variety of contaminants from aqueous systems. In fact, research shows that waters polluted simultaneously with several types of compounds can be effectively treated with SMZ. Bowman *et al.* (1993) found that water contaminated with benzene, toluene, p-xylene, lead, chromate, selenate, and sulfate could be treated with SMZ. While lead was effectively removed both prior to and after treatment of zeolite, all the other compounds were only removed after the material was modified with HDTMA. No evidence of competition among benzene, toluene, and p-xylene were found in this study. The competitive effects of multiple oxyanions in solution were not studied because only single inorganic compound solutions were exposed to SMZ. Nevertheless, the authors suggest that the use of this compound for *in situ* reactive barriers can result in relatively inexpensive remediation techniques for many sites. However, prior to using the material, its long term stability and the effects of various chemical conditions on its sorptive properties should be known.

Ionic Strength Effects on Sorption of Organics

Though studies specifically focusing on ionic strength effects on the sorption of organic compounds on SMZ have not been reported, general behavior of hydrophobic compounds in the presence of aqueous salts has been observed. The “salting out” effect is a well-known phenomenon in which water molecules bind to charged entities and prevent uncharged entities from developing necessary cavities in which to dissolve (Schwarzenbach *et al.*, 1993). The polar nature of water molecules causes them to have greater affinity for charged compounds, and once such electrolytes are in solution, water molecules almost immediately hydrate them. These tightly bound hydration shells reduce the amount of water available for dissolution of non-polar organic compounds, and these compounds cannot break the hydration shells to increase the number of available water molecules. The hydrogen bonding and van der Waals forces that connect hydrophobic compounds with water molecules are much weaker than the electrostatic bonds water molecules form with electrolytes. Hence, the water solubility of non-polar compounds decreases in the presence of salts and these organic compounds preferentially dissolve into another phase.

Setchenow (1889) developed an empirical relationship between aqueous solubility and salt concentration:

$$\log \left[\frac{C_w^{sat}}{C_{w,salt}^{sat}} \right] = K^s [salt]_t \quad (3.9)$$

where:

C_w^{sat} = solubility of compound in pure water (mass compound/volume of solution)

$C_{w,salt}^{sat}$ = solubility of compound in saline water (mass of compound/volume of solution)

K^s = salting constant (volume of solution/moles of salt)

$[salt]_t$ = total molar salt concentration (moles of salt/volume of solution)

Values for salting constants have been reported for a few organic compounds and for different salts. When used for compounds such as benzene and naphthalene, Equation 5 is valid over a wide range of salt concentrations (Schwarzenbach *et al.*, 1993). For non-polar organic compounds, the effects of several types of salts are additive and the salting constant can be expressed as:

$$K^s = \sum_i K_i^s x_i \quad (3.10)$$

where:

K_i^s = salting constant of salt i

x_i = mole fraction of salt i

In seawater, which consists of many types of salts, aqueous solubilities for several organic compounds decreased 10-50% as compared to pure water due to the presence of 0.5M salts (Schwarzenbach *et al.*, 1993). On the other hand, the presence of electrolytes decreases the salting out effect for polar organic compounds because the presence of a polar group decreases the hydrophobic surface area of the compound. The polar group

can also contribute to thermodynamically favorable interactions with the ions in solution (Schwarzenbach *et al.*, 1993). Though not much data for this phenomenon exist, the few that are available seem to support the assertion that the salting out effect is decreased (Hashimoto *et al.*, 1984).

Based on this knowledge, it is presumed that decreasing the aqueous solubility of a non-polar organic compound will increase the sorption of that compound onto a sorbent such as SMZ. This presumption can be tested by determining the distribution coefficients for several non-polar organic compounds. As larger magnitudes for distribution coefficients are found with increasing ionic strength, the compounds should be gaining affinity for the sorbent. However, to date, these tests have yet to be conducted for SMZ.

Temperature Effects on Sorption of Organics

Temperature has been known an important factor in affecting sorption process and the temperature of produced water varies from field to field. Previous studies of sorption to soils have reported increases, decreases or negligible effects of increasing temperature. Ten and co-workers (1996) reviewed most of the data on the temperature dependence of the sorption of organic compounds on soil, sediment and phenyl coated silica. However most of the data is based on pesticides, chlorinated benzenes and a number of polycyclic aromatic hydrocarbons. Piatt *et al.* (1996) reported that equilibrium distribution coefficients for naphthalene, phenanthrene, and pyrene to low organic carbon ($f_{oc} = 0.00019 \pm 0.00008$) aquifer sediments increases 1.1-1.6 times for a decrease in temperature from 26°C to 4°C, while solubility decreased by 2-3 times with over this temperature range. The increase in K_d with decreasing temperature was predicted assuming that the aqueous phase activity coefficient was the driving force for sorption of the PAHs. Dewulf *et al.* (1999) conducted a study on sorption of 12 VOCs to a Belgian riverine sediment ($f_{oc}=0.041$) as a function of temperature (2-25°C) by means of a modified equilibrium partitioning in a closed system (EPICS) technique. Chloroform, 1,1-dichloroethylene, tetrachloethylene, trichloroethylene, tetrachloroethylene, tetrachloromethane, benzene, toluene, ethylbenzene, o- and p-xylene were studied. It was found that the distribution coefficient K_d increased with increasing temperature for BTEX sorbed onto the sediment. The results are shown in Table 3.4.

Table 3.4 Effect of Temperature on Sediment/Water Linear Partitioning Coefficients

Compounds	T=2.3 ¹	T=3.8	T=6.2	T=8.0	T=13.5	T=18.6	T=25.0
Benzene	2.8±0.07	3.0±0.04	3.05±0.11	3.1±0.03	3.3±0.01	3.1±0.07	3.3±0.09
Toluene	7.04±0.2	8.5±0.36	8.9±0.17	8.9±0.26	10.3±0.1	8.5±0.35	9.1±0.4
Ethylbenzene	12.6±0.3	21.9±1.0	18.2±0.9	22.1±2.9	24.4±2.3	21.9±1.4	22.8±1.7
p-Xylene	12.7±0.4	23.1±0.5	18.3±1.4	23.5±3.9	25.3±2.9	24±1.3	24.7±2.2
o-Xylene	10.4±0.3	20.8±0.5	15.5±1.3	19.8±4.3	21.9±3.6	20.4±1.3	19.8±2.6

Reference: Dewulf et al. 1999

¹Temperature in degrees centigrade

Based on these results, it is expected that the distribution coefficients for BTEX sorbed onto SMZ will increase with increasing temperature over typical field temperatures.

3.2.3.4 Long Term Stability of SMZ

Li *et al.* (1998) performed a study on the stability of surfactant-modified zeolite under several chemical and biological conditions, including varying ionic strength, pH, and microbial activity. The findings from this study showed that SMZ is very stable in conditions involving high ionic strength (1 M CaCl₂), low pH, and high pH. Even after washing with 100 pore volumes, more than 90% of the HDTMA remained bound to the surface under these conditions. However, results also showed that HDTMA was subject to substantial desorption under conditions of low ionic strength and in high concentrations (1.0 mM) of cesium. Up to 50% of the surfactant washed off in the presence of 1.0 mM cesium while 20% desorbed in solutions of low ionic strength. The authors suggest that desorption in the presence of such high concentrations of cesium should not present a substantial problem as these concentrations are not commonly found even in highly contaminated systems. Li *et al.* also explain desorption in solutions of low ionic strength by stating that the electric double layer expands under such conditions and the interactions between the surfactant head groups and counterions are then weakened. This causes a destabilization of the admicelle and allows HDTMA monomers to desorb from the bilayer. These low ionic strength studies were conducted with Type I water which is not normally found at contaminated sites. Natural water systems and wastewaters generally include mineral salts, so SMZ should be stable when used at most sites. Additionally, the surfactant concentration required for monolayer coverage of the zeolite remained sorbed in all circumstances. As stated above, monolayer coverage has been found to be sufficient to efficiently remove organic contaminants from solution. Thus, even with desorption of some of the monomers forming the bilayer, SMZ can remain a viable sorbent for non-polar organics.

While several surfactants have been found to be biocidal, some bacteria can still degrade them (Gilbert and Al-taae, 1985). Thus, in order to use SMZ in natural systems, it is important that it resist microbial degradation. *Pseudomonas* sp. extracted from activated sludge has been found to metabolize aqueous HDTMA-Cl completely in 70 h (van Ginkel *et al.*, 1992). However, no studies on biodegradation of sorbed HDTMA had been completed prior to the research conducted by Li *et al.* (1998). These authors found that even after 12-17 weeks of incubation under aerobic and anaerobic conditions, more than 98% of the HDTMA remained sorbed to the zeolite. The counterion did not seem to have a substantial impact on biodegradation and both HDTMA-Br and HDTMA-Cl remained stable throughout the study. In addition, sorbed HDTMA did not inhibit microbial growth although aqueous HDTMA solutions were found to do so. Thus, although SMZ was not prone to degradation by microorganisms, neither was it biocidal to activated sludge bacteria. With these results, the authors state that the use of SMZ should not harm organisms found in the natural environment and can even be used to enhance biodegradation of pollutants.

3.2.3.5 Regeneration of SMZ

Sorbents for use in water treatment processes must be cost effective and therefore, the ability to reuse a sorbent is highly desired. All sorbents become saturated and must be regenerated prior to further use. A recent study conducted by Li and Bowman (2001) focused on this issue for SMZ saturated with chromate and PCE. Extraction of chromate was attempted using a carbonate solution, chemical reduction of chromate was tested with sodium dithionite, and PCE was removed through air sparging. Regeneration of chromate-saturated SMZ through extraction by carbonate proved successful when the pH decreased to 5 (110% regeneration efficiency), but the material only resulted in 75% and 63% regeneration efficiencies at pH 8 and 11, respectively. In addition, further tests showed that hydraulic conductivity was severely hampered as carbon dioxide filled the pore spaces of the SMZ. This gas formed as a result of carbonate reacting with protons at low pH values. Thus, due to the impracticality of this regeneration method, the reduction of chromate was attempted. In these tests, it was found that 85% of the residual chromate was reduced *in situ*, but breakthrough was detected earlier with the regenerated SMZ than with the virgin material. The authors suggest that a decrease in chromate sorption affinity or changes in the hydraulic properties of the system may have caused an increase in hydrodynamic dispersion and earlier breakthrough.

The tests conducted on PCE-saturated SMZ demonstrated that both the carbonate solution and air sparging fully regenerated the sorbent. Thus, it was shown that SMZ can be chemically regenerated, although decreased hydraulic conductivity or earlier breakthrough may occur when saturated with chromate. The authors also suggested that these regeneration methods can be utilized for both *ex situ* and *in situ* sorbent systems once the systems are modified with appropriate recirculation apparatus.

3.3 Literature Review Summary

Produced water contains many constituents that are considered harmful to humans and the environment. Regulations for the disposal of this wastewater may become increasingly stringent in the future and treatment methods will have to include removal of benzene, toluene, ethylbenzene, and xylenes (BTEX) among other components. In addition, deep-well reinjection is not economically feasible for many small producers, and reuse of produced water can benefit both producers and communities in arid areas. Thus, a low-cost method for produced water treatment that can remove BTEX compounds will benefit the oil and gas industry as well as the environment.

Traditional produced water treatment methods such as oil/water separation and hydrocyclones do not remove dissolved constituents from produced water. More sophisticated techniques like reverse osmosis, ultrafiltration, and photocatalytic oxidation are expensive and would probably not be viable for small producers. Although it requires large amounts of area, phytoremediation is low-cost and effective at volume reduction, but BTEX removal efficiency has not been reported. Sorption to GAC and commercial carbonaceous sorbents has been demonstrated to remove non-polar organics, but these

sorbents tend to be cost- and maintenance-intensive and do not remove heavy metals from solution. Surfactant-modified zeolite has been shown to be a versatile sorbent that can remove anions, cations, and non-polar organic compounds from water.

The use of surfactant-modified zeolite for produced water treatment in one study demonstrated its effectiveness at reducing the concentration of BTEX compounds in oil-field water. However, results from this study did not include batch tests conducted with the commonly found surfactant, HDTMA and a predictive model relating the hydrophobicity of a compound to the linear partitioning coefficient were not developed. Additionally, ionic strength and temperature effects were not explored although the authors did cite investigation of ionic strength effects as a field deserving future study. Indeed, the salting out effect is known to substantially decrease the aqueous solubility of hydrophobic compounds, and because produced water is classified as a brine, the presence of salts can act to increase partitioning of non-polar organics to non-aqueous phases.

Produced water temperatures at field scale sites also vary among sites and temporally at a particular site. It is assumed that higher temperatures will increase the sorption of BTEX onto SMZ because the aqueous activity coefficient of BTEX increases with temperatures above 20°C; however, the magnitude of the change in the sorption capacity as measured by a linear partitioning coefficient (K_d) is not expected to be very significant.

4. Experimental Plan and Methodology

4.1 Approach

The experimental program included three components: laboratory scale batch experiments, laboratory scale column experiments, and a field test. A brief description of the experiments conducted for each of these components is described below.

4.1.1 Batch Studies

Batch sorption experiments were performed to characterize sorption of BTEX to SMZ as a function of salinity, temperature, and in the presence of produced water. This relationship could then be used for predicting the sorption capacity of SMZ under different field-scale conditions. The goal of the batch study conducted in the presence of produced water was to compare the distribution coefficients of BTEX sorbed onto SMZ in ultrapure water, saline water and produced water.

4.1.2 Column Studies

The goals of the laboratory scale column tests were to evaluate process kinetics, verify the batch results, and assess the feasibility of the process in a continuous flow system. Various approaches can be used to evaluate kinetics in column reactions, including the rapid small-scale column test (RSSCT) developed by Crittenden and co-workers. This method assumes that both internal and external diffusion may affect the rates of sorption. The principle of this method is to simulate sorption behavior in pilot and field scale systems using a smaller scale setup that maintains perfect similarity between the performance of the large scale and small scale adsorbers (Sontheimer *et al.* 1988). The RSSCT approach uses a set of scaling parameters to reduce the size and flowrates in field scale columns to laboratory scale columns. The adsorbent particle size, hydraulic loading and EBCT of the RSSCT are determined by using scaling equations described by Hand *et al.* (1984). Thus, RSSCT columns should mimic the breakthrough curves of the full-scale columns as long as the assumptions inherent in the scaling equations are valid.

Regeneration studies were also conducted in laboratory scale columns as well as the pilot scale field test columns. The spent SMZ was regenerated by air-sparging using compressed air tank and a flowmeter to control flowrate through the column. Samples were taken periodically by withdrawing gas through a sampling port at the effluent end of the column. The air-sparging experiment was continued until the BTEX mass coming off of the column was negligible. The regenerated SMZ was again saturated with the aqueous BTEX solution. The input BTEX concentration and flow rate were the same as for the original saturation.

4.1.3 Field Studies

Several possible sites/sources of produced water were evaluated including a small producer in East Texas near Smithville, a gas well array near Houston, Texas, an offshore

oil well, and a treatment facility of BC Technologies in Wamsutter, Wyoming. The facility of BC Technologies was chosen as the site for field study in this project. The site is operated by Crystal Solutions, LLC., and is located in an oil producing region just outside of Wamsutter, WY. The facility is set up to receive produced water from the region by tanker trucks. Two columns were used in the field to test the capability of SMZ treatment of BTEX in this facility. The columns were provided by a local Culligan distributor in Austin, TX, and were readily adapted to the needs of this study by substituting the ion exchange resin with SMZ.

4.2 Materials

4.2.1 BTEX compounds

Benzene, ortho-xylene, and para-xylene were obtained from J. T. Baker (Phillipsburg, NJ). Toluene was obtained from EM Science (Gibbstown, NJ), ethylbenzene from Mallinckrodt Chemical Inc. (Paris, KY), and meta-xylene from Aldrich (Milwaukee, WI). All of these chemicals were 99% purity. Their chemical formulas, molecular weight and water solubilities (25°C, 1 atm) are reported in Table 4.1.

Table 4.1 Chemical and Physical Properties of BTEX Compounds

	Benzene	Toluene	m-Xylene	o-Xylene	p-Xylene	Ethylbenzene
Chemical formula	C ₆ H ₆	C ₇ H ₈	C ₈ H ₁₀			
Molecular Weight (g/mol)	78	92	106	106	106	106
Log Water Solubility at 25°C (mol/L)	-1.64	-2.25	_____	-2.76	-2.77	-2.80

Reference: Schwarzenbach *et al.* 1993

4.2.2 α,α,α -Trifluorotoluene (TFT)

An internal standard was used during gas chromatography analyses of BTEX compounds. The internal standard was α,α,α -trifluorotoluene (TFT) purchased from Restek Corption at an initial concentration of 2500 $\mu\text{g/mL}$. The solution was initially diluted to 25mg/L in methanol and stored at -18°C .

4.2.3 Electrolytes for Saline Water Preparation

A number of the experiments conducted in this research used synthetically prepared background water. The dissolved solids were added to the synthetic water using reagent grade calcium chloride (CaCl₂), magnesium sulfate (MgSO₄), sodium chloride (NaCl), and potassium chloride (KCl). The sodium chloride and calcium chloride were obtained from EM Science (Gibbstown, NJ), magnesium sulfate was obtained from J. T. Baker

(Phillipsburg, NJ), and the potassium chloride was obtained from Fisher Scientific (Fairlawn, NJ). All of these chemicals were dried at 105°C for 24 hours prior to use.

4.2.4 Natural Zeolite

The zeolite used in this study was a clinoptilolite from the St. Cloud mine in Winston, New Mexico. Clinoptilolite has an approximate chemical formula of $(Ca, Na, K)_6Al_6Si_{30}O_{72} \cdot 24H_2O$ and the dimensions of the open channels in are $0.89 \times 0.35 \text{ nm}^2$ for the 10-member ring and $0.44 \times 0.30 \text{ nm}^2$ for the 8-member ring. These dimensions are large enough for diffusion of a small cation but too small for a surfactant the size of hexadecyltrimethylammonium (HDTMA) head groups. An XRD analysis conducted by Sullivan *et al.* (1997), found it to be comprised of 74% clinoptilolite, 5% smectite, 10% quartz cristobalite, 10% feldspar, and 1% illite. Potassium and calcium were determined to be the major exchangeable cations and the external cation exchange capacity was calculated to be between 90-110 meq/kg (Li and Bowman, 1997). The internal, or zeolitic, cation exchange capacity was 800 meq/kg. Sullivan *et al.* (1997) also found that the BET external surface area for the material was $15.7 \text{ m}^2/\text{g}$.

The zeolite was ground and screened to two different grain sizes: 14 x 40 mesh (1.4 to 0.4 mm) for the field columns and 18 x 100 mesh (0.18 to 0.15 mm) for the laboratory columns. Batch experiments were conducted with both particles sizes depending on the experiments.

4.2.5 Hexadecyltrimethylammonium Surfactant

Hexadecyltrimethylammonium chloride (HDTMA, or cetyltrimethylammonium chloride, CTAC) obtained from Aldrich (Milwaukee, WI) was selected for use in this research for surfactant modification based on previous research by P.I. Bowman and co-workers. HDTMA has a molecular weight of 320 g/mole, a critical micelle concentration of 0.9 mM, and is a bulk production surfactant used in shampoo, mouthwash, and other products.

4.2.6 Hexadecyltrimethylammonium Surfactant Modification of Zeolite

HDTMA sorption to zeolite creates an organic coating over the surface of the zeolite, which allows partitioning of the organic molecules into the organic coating. The procedure to coat the SMZ with the surfactant involves mixing the surfactant and zeolite for several hours followed by several stages of washing with ultrapure water.

Specifically, a solution containing 3000 mL of 0.1 M HDTMA-Cl solution was prepared and mixed with 1000 g of zeolite. The mixture was placed into ten 500 mL polyethylene centrifuge bottles and equilibrated on a shaker at 150 rpm and 25°C for 8 hour, which was sufficient to achieve sorption equilibrium (Bowman *et al.*, 1997). Experiments conducted at New Mexico Tech (Bowman *et al.*, 1997) have shown that HDTMA does not sorb to plastic labware including polyethylene.

After equilibrium, the mixture was centrifuged to yield a clear supernatant solution (7250 G for 50 min) and the supernatant was removed and saved for later HDTMA analysis. The HDTMA-zeolite was washed with two 180 mL portions of ultrapure water (water treated using a Milli-Q system, ultrapure Corp., Bedford, MA). For each wash,

the bottles were shaken at 150 rpm for 15 min and centrifuged at 7250 g for 50 min. The samples were air-dried following the final washing.

Supernatant analysis showed that the HDTMA loading rate was 180 mmol/kg for 14×40 SMZ compared to 157 mmol/kg for the 80×100 SMZ. The amount of HDTMA sorbed was calculated from the difference between the initial and final concentrations. After drying, the SMZ was sieved again to remove fines.

The organic carbon content, which is primarily responsible for sorption of non-polar organic compounds to soils (Chiou 1989), was increased by HDTMA modification. The 14×40-mesh size SMZ had an organic carbon content of 0.041 and the 80×100 mesh size had an organic carbon content of 0.036.

4.2.7 Produced Water

4.2.7.1 Sources

Many company representatives were hesitant to participate in this research. Four possible sites/sources of produced water were evaluated. The first was a small producer in East Texas near Smithville. The water from the tested sources was quite fresh and is in current use for agricultural purposes (irrigation and stock watering). BTEX concentrations were too low for experimental use, however. The second source was from a gas well array near Houston, Texas. This water was moderately saline with useful concentrations of BTEX. The third was a source of water from an offshore oil well, again, moderately to highly saline with appropriate BTEX concentrations. The available volumes of water were not sufficient for field testing (volumes quite variable and chemistry variable). The final, selected source was from the treatment facility of BC Technologies in Wamsutter, Wyoming. BC Technologies provides produced water treatment and disposal options for small oil and gas producers in Wyoming. As previously stated, produced water differs with location and type of operation. Thus, the sample obtained from this facility contained a mixture of many different effluents and should be generally representative of produced water generated by the onshore gas industry in the Northern Rocky Mountains. The produced water at the site tended to be high in BTEX concentrations and of moderate salinity (10,000 ppm – 30,000 ppm).

4.2.7.2 Sample Collection

Samples for analysis of BTEX and semi-volatile compounds were collected in 40 mL volatile organics analysis (VOA) vials with screw cap and PTFE/silicone septa. The samples for each site were placed in plastic bags to prevent cross-contamination and then stored in the dark in an ice chest. All of these vials and their caps were rinsed three times with the produced water before taking samples. Care was taken not to introduce air bubbles into the vials when screwing the caps onto the vials.

Collection of produced water for use in laboratory experiments required larger volume containers. Zero-Headspace Extraction (ZHE) vessels are commonly used for the Toxicity Characteristic Leaching Procedure (TCLP) endorsed by the EPA for testing the leaching ability of hazardous wastes. However, these containers also provide a headspace-free environment in which to store samples of water that contain volatile

compounds. Using the spigot on the holding tank, four stainless steel ZHE vessels (Ultrapure, Inc.) were rinsed three times with produced water prior to being completely filled (~250 mL) and pressurized to 20 psi by an air compressor.

4.2.7.3 Characterization of Field Samples

All three water samples that were acquired were analyzed to determine their initial characterization. The Phillips Petroleum samples were analyzed at UT for BTEX and by an outside laboratory (DHL Analytical, Round Rock, Texas) for total petroleum hydrocarbons (TPH), anions, and cations. The MCA Petroleum samples were analyzed only by DHL Analytical for TPH, BTEX, semi-volatile organics, ammonia, anions, and cations. The Wamsutter site samples were provided by John Harju and were analyzed for BTEX and TDS at UT and DHL Analytical and for metals by DHL Analytical.

4.3 Analytical Methods

4.3.1 Analysis for BTEX

Laboratory and field samples and BTEX standards were analyzed at either the University of Texas or New Mexico Tech through headspace analysis and gas chromatography. Preliminary experiments using gas chromatography/mass spectroscopy showed that all of the BTEX compounds could be uniquely identified and quantified in the presence of the produced waters used in this research with the exception of ethylbenzene. Ethylbenzene eluted close to or at the same time as a chemical that was most likely 2-methyl octane and that o-xylene was also found to elute near nonane. However, both of these non-BTEX chemicals showed small peaks and the remaining BTEX compounds were not found to co-elute with other chemicals. In addition, selected field samples were also analyzed by DHL Analytical Laboratories to provide verification of our results.

The GC/Headspace method used for BTEX analysis was capable of analyzing BTEX concentrations to the ppb range. Samples and standards were placed in headspace vials were crimped shut with aluminum crimp caps fitted with PTFE/black butyl rubber septa (Agilent Technologies, HP9301-0976). After all of the samples and standards were prepared, an internal standard was injected through the septa into the aqueous solutions. The internal standard, α,α,α -trifluorotoluene (TFT), eluted from the GC between the benzene and toluene peaks. Because the TFT (Restek) was purchased at a concentration of 2,500 $\mu\text{g/mL}$, it was diluted to 25 mg/L in methanol prior to use. A constant volume of 200 μL was then injected into the headspace vials to yield an internal standard concentration of 1000 $\mu\text{g/L}$. The standards and samples were then placed in a Tekmar 7000 Headspace Autosampler (HSA). The headspace autosampler was heated to increase partitioning of BTEX compounds into the headspace above the aqueous solution. The HSA working conditions are listed in Table 4.2. A 1 mL sample of that headspace was then transferred into a Hewlett-Packard (HP) 5890 gas chromatograph (GC) equipped with a 30 m Restek capillary column (RTX-624; ID0.53 mm; DF3.0) and flame ionization detector (FID) detector. Compressed air and hydrogen were burned in the FID with nitrogen as an auxiliary gas. Helium was used as an inert carrier gas at a flowrate of

36 mL/min. The GC operating conditions and ramping program in this study are listed in Table 4.3.

Table 4.2 Headspace Operating Conditions for BTEX Analysis

Zone Temperatures		°C
	Water bath	80
	Loop	170
	Transfer Line	170
Event Times		Minutes
	Vial Equilibration	15
	Mixing	10
	Pressurization	1
	Pressure Equilibration	0.25
	Loop filling	1
	Loop Equilibration	0.25
	Loop Injection	1
Helium Flowrate		
	mL/min	1

Table 4.3 GC Operating Conditions for BTEX Analysis

Ramping Program		
	Initial Oven Temp	40 °C
	Initial Time	1 min
	Rate	20 °C min ⁻¹
	Final Oven Temp	85 °C
	Final Time	0 min
	Rate A	0.5 °C min ⁻¹
	Final Oven Temp	90 °C
	A Final Time A	1 min
Other Settings		
	Injector Temp	250 °C
	FID Detector Temp	275 °C
	Col. Head Press.	11 psi
	Base Signal	0.1

Data from the gas chromatograph were analyzed with EZChrom Chromatography Data System (Scientific Software, Inc., San Ramon, CA; (510) 244-6622), version 6.5 software. An internal standard (TFT) was used to define the area ratios of the amount of each BTEX compound detected to the amount of TFT detected were used to prepare calibration curves. The elution times for the BTEX compounds and TFT are shown in Table 4.4.

Table 4.4 GC Detection Times for BTEX Compounds and TFT

Compound	Peak Detection Times (± 0.01)
	minutes
Benzene	2.84
α,α,α-Trifluorotoluene	3.40
Toluene	4.11
Ethylbenzene	5.90
p- & m-Xylenes	6.11
o-Xylene	6.84

The method detection limit (MDL) was calculated according to Method 1030E of Standard Methods for the Examination of Water and Wastewater (1989). For this process, seven samples containing 9 µg/L of BTEX were analyzed. The standard deviation of these results was calculated and multiplied by the Student's one-tailed t-value for 99% confidence and six degrees of freedom ($t = 3.14$). The final results from this process are presented in Table 4.5.

Table 4.5 Method Detection Limits for BTEX Compounds

	Benzene	Toluene	Ethylbenzene	m- & p-Xylenes	o-Xylene
MDL (µg/L)	1.0	0.94	1.2	1.1	1.1

Several steps were taken to assure the quality of the data collected. Standard curves, which served to calibrate the instruments, were run prior to every analysis. The instruments used in the investigations were not turned off between analysis of standard solutions and batch samples because prior experience showed that data become slightly skewed if the machines are not left on throughout an analytical run. These standard curves were for the most part run with triplicates to ensure statistical significance. If the correlation coefficient (R^2) for the standard curves was below 0.995, these tests were redone until sufficient R^2 values were obtained.

The single-solute studies were conducted in triplicate to allow the calculation of standard deviation. Replicates for the multi-solute studies were constrained by the maximum number of headspace vials allowed on the autosampler. However, duplicates were used to compare results among samples.

Checks were included within the sample runs to ascertain whether the standard curve remained valid for the samples. If the results for these checks did not agree within 5% of the known concentration, the analysis was rejected and the entire batch test was rerun. These checks were prepared identically to the solutions for the standard curve.

One concern that arose during the course of the project involved the impact of the background produced water matrix on the headspace method. To evaluate the impact of the produced water background, an experiment was conducted for which standard curves were prepared for both ultrapure water and produced water to determine whether the presence of produced water had an impact on BTEX analyses. In a column test, the effluent from the column changes over the course of the experiment. These two matrices, ultrapure water and produced water represent the extremes in variability. If there is little difference between BTEX concentrations obtained from these two matrices, then it is unlikely that the presence of produced water in the samples would affect the BTEX analyses for all of the column effluent samples. As shown in Table 4.6, there is a slight increase in the calibration curve slope in the produced water matrix. However, the percent increase in the slope is well within the analysis error of the gas chromatography method. In the column experiment with produced water, calibration curves were prepared using a produced water background. Because the variability between calibration curves was so small, no corrections were made when using this calibration curves for laboratory and field samples; however, analysis of the produced water from the Wyoming field site were evaluated using a standard addition technique to account for the produced water matrix.

Table 4.6 Calibration Curve Slopes Obtained from Matrices of Ultrapure Water and Produced Water

Compound	Calibration Curve Slope from Ultrapure Water	Calibration Curve Slope from Produced Water
Benzene	783.79	793.87
Toluene	763.65	772.79
Ethyl benzene	739.27	746.81
m-&p-Xylene	373.98	378.15
o-Xylene	805.59	816.5

4.3.2 Preparation of Standards for BTEX Analysis

It was found that working with methanol solutions reduced BTEX losses due to volatilization during transfer processes. Thus, stock solutions of high concentrations of BTEX in methanol were used for both standard curve preparation and batch tests. To avoid co-solvency effects, the amount of methanol in aqueous solutions was kept below 1% by volume (Pinal *et al.*, 1990). Stock solutions of 10 g/L, 1 g/L, 0.2 g/L, and 0.03 g/L in methanol were made for all of the BTEX compounds combined and for benzene and toluene, individually. These individual stock solutions were used to test the effects of multiple solutes in solution.

Stock solutions were prepared in serial dilutions. However, the initial solution was prepared by first calculating the correct volume of neat BTEX compounds required to generate a 10 g/L solution in methanol. This volume was found through the following formula:

$$C = \frac{\rho * 10^3 * X}{10^3 * V * P} \quad (4.1)$$

where:

C = desired concentration (g/L)

R = density of pure BTEX compound (g/mL)

10³ in numerator = conversion from mL to L

X = volume of BTEX compound required to reach desired concentration (μL)

10³ in denominator = conversion from μL to mL

V = volume of methanol for dilution (mL)

P = purity of BTEX compounds in decimal form

Further dilutions were prepared with volumetric pipettes to generate the three remaining concentrations. Because the solutions were made in methanol, it was assumed that negligible volatilization of BTEX compounds would occur during the transfer phase. Pasteur pipettes were used to transfer each of the four solutions to 2 mL GC vials that were immediately crimped shut, labeled, and stored in a -18°C freezer. According to the manufacturers of the septa (Agilent Technologies, Wilmington, DE; HP5182-0837), the vials should have remained leak-free for 4 months, but during this study, vials older than 2 months were discarded.

Standard curve solutions were in general generated in triplicate for a range of concentrations (0-10 mg/L). After many curves were produced, it became clear that the GC became saturated after approximately 1,500 μg/L of a single BTEX compound. Hence, the standard curves prepared after reaching this conclusion included only the concentrations shown in Table 4.7.

Table 4.7 Standard Curve Solution Concentrations

Desired Standard Solution Concentration
μg/L
0
9
15
30
60
120
200
500
800
1000
1500

These aqueous solutions were prepared in 22 mL headspace vials (Agilent Technologies; HP5182-0837) by initially using a 5 mL volumetric pipette to fill each vial with 5 mL of water. The vials were then loosely capped to minimize evaporation until BTEX stock solutions were injected into them. To determine the volume required for injection, the following formula was used:

$$V_1C_1 = V_2C_2 \quad (4.2)$$

where:

V_1 = volume of stock solution required (μL)

C_1 = concentration of stock solution (g/L)

V_2 = volume of standard solution (mL)

C_2 = desired concentration ($\mu\text{g/L}$)

In order to account for the complex chemistry of the samples obtained from the Wamsutter site by Crystal Solutions, LLC., the standard curves used for their analysis were generated with diluted sample waters using a standard addition technique (Skoog and West, 1998). The standard curve solutions were prepared with 5 mL ultrapure water followed by injecting 50 μL of produced water through the septa in consideration of the complex chemistry. The produced water was actually diluted by a factor of 100. The vials were then sealed with crimp caps fitted with PTFE/black butyl rubber septa. The varying volumes of BTEX stock solutions required to generate a range of standard concentrations were then injected with gastight syringes through the septa. Following these injections, the internal standard was also added to the vials through the septa. It was assumed that the absolute value of the intercepts of the linear standard addition calibration curves for the BTEX compounds was the BTEX concentration in the produced water sample. Figure 4.1 shows a representative linear curve for the benzene concentration analysis of the produced water obtained from the Wamsutter site by Crystal Solutions, LLC. As shown in the standard curve, the vertical axis reflects the initial benzene concentration that is represented by the negative of the y-intercept. Because the initial produced water was diluted 100-fold, the value for the initial benzene concentration was found by multiplying the magnitude of the intercept by 100.

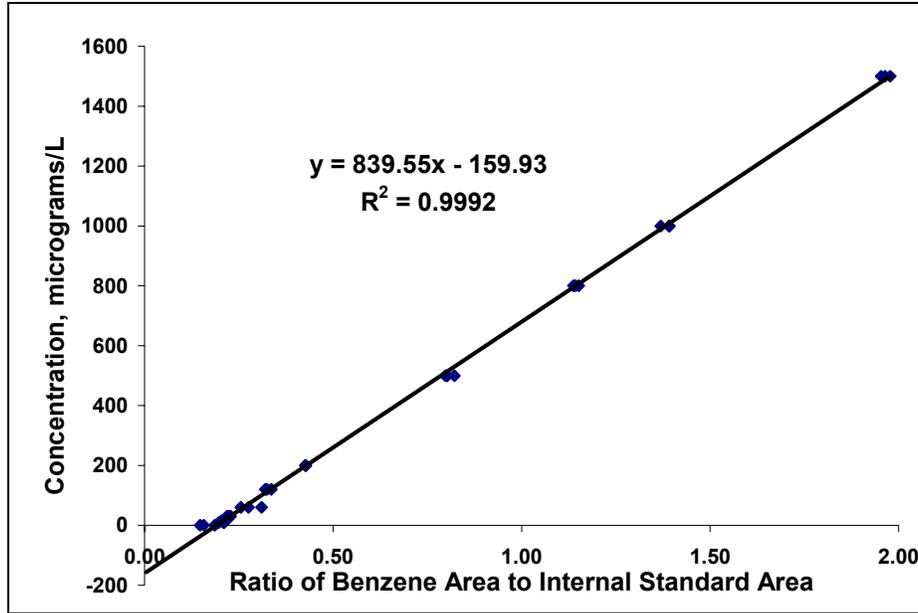


Figure 4.1 Standard Curve for Benzene in Wamsutter Site Holding Pond Produced Water

4.3.3 Analysis for Metals and Semi-Volatiles

DHL Analytical laboratories were used to analyze all produced water samples for metals, total petroleum hydrocarbons, and semi-volatiles. The samples provided by Crystal Solutions LLC, underwent testing for cations, anions and arsenic, barium, lead, and cadmium as well as semi-volatile compounds. For the other produced water limited metal analyses were conducted. The analytical techniques used and reporting limits for the methods are presented in Tables 4.8 to 4.10. Method TX1005 is a state-approved analytical technique in Texas while the remaining methods listed are all endorsed by the EPA.

Table 4.8 Metals Analysis Methods Used by DHL Analytical

Analysis	Method	Units	Reporting Limit
Metals: ICP-MS	SW6020		
Arsenic		µg/L	10.0
Barium		µg/L	100
Cadmium		µg/L	1.00
Lead		µg/L	3.00

Table 4.9 Ion Analysis Methods Used by DHL Analytical

Analysis	Method	Units	Reporting Limit
Anions	SW9056 or E300		
Chloride		mg/L	200
Nitrate-N		mg/L	0.500
Sulfate		mg/L	3.00
Metals	SW6020		
Calcium		µg/L	5000
Magnesium		µg/L	1000
Potassium		µg/L	1000
Sodium		µg/L	50000
Alkalinity	E310.1	mg/L	10

Table 4.10 Results from Analyses of MCA Petroleum Corp. Samples

Analysis	Method	Units	Reporting Limit
TPH	TX1005	mg/L	5.0
TOC	E415.1	µg/L	400
PAHS	SW827		
2,4-Dimethylphenol		µg/L	80
2-Methylnaphthalene		µg/L	80
2-Methylphenol		µg/L	80
4-Methylphenol		µg/L	80
Dibenzofuran		µg/L	4
Fluorene		µg/L	4
Naphthalene		µg/L	8.25
Phenanthrene		µg/L	4
Pyrene		µg/L	4
Phenol		µg/L	80

4.4 Batch Adsorption Studies

Once the produced water samples had been characterized, batch tests were conducted to study the adsorption of BTEX compounds onto SMZ. These batch tests had several foci:

- compare adsorption of single BTEX compounds versus multiple BTEX compounds in ultrapure water
- study the effects of ionic strength on single- and multi-solute BTEX adsorption in ultrapure water
- study the differences in adsorption caused by the complex chemistry of produced water

Hence, several different types of batch test methods were developed.

4.4.1 Single- and Multi-Solute Batch Experiments

Single and multi-solute batch isotherm experiments were conducted over a range of initial BTEX concentrations. Because the aqueous solubilities of benzene and toluene are higher than all of the other compounds and the octanol-water partitioning coefficients (K_{ow}) are lower (Table 4.11), it was felt that these two compounds would be the least absorbable and future design of treatment columns would have to be based on these solutes. Hence, the competitive effects of the other BTEX compounds on the sorption of benzene and toluene were of primary interest in the multi-solute experiments.

Table 4.11 Octanol/Water Partition Coefficients and Aqueous Solubilities of BTEX Compounds

Compound	log K_{ow} at 20°C (L octanol/L water)	-log S at 20°C (mol/L)
Benzene	2.13	1.66
Toluene	2.69	2.25
Ethylbenzene	3.15	2.84
m-Xylene	3.20	2.73
p-Xylene	3.15	2.73
o-Xylene	3.12	2.78

Reference – Schwarzenbach *et al.* (1993)

To obtain data throughout several orders of magnitude, the following initial BTEX concentrations were used in the single-solute studies: 0, 0.005, 0.01, 0.1, 1, 10, 40, and 75 mg/L. Each single-solute batch study was conducted in either duplicate or triplicate, depending on the test. The remaining batch tests were limited by the number of vials allowed on the headspace autosampler, so duplicates could not be used for some tests. Blanks (vials excluding SMZ but including BTEX) were used to determine the effects of SMZ.

The initial step of these batch tests was to saturate the SMZ with ultrapure water to replicate the physical scenario of a potential treatment column. Ultrapure water is produced by the Milli-Q UV Plus water purification system with reverse osmosis and ultraviolet radiation disinfection. A resin mixture polisher in the Milli-Q system also removed trace organics and inorganics. Preliminary tests showed that centrifuge tubes (Corex, Corning) with PTFE lined screw caps allowed substantial losses to occur. Thus, the same 22 mL headspace vials used in the preparation of standard curves were used throughout these tests so as to minimize volatilization. All vials were first weighed with their crimp caps and septa loosely capping them. Once the vials were separated into those that would contain SMZ (samples) and those that would not (blanks), the appropriate vials were filled with 2.5 g of SMZ. Prior to crimping the vials, approximately 20 mL of ultrapure water were added to each vial. All of the vials were then placed in a 20°C room for 24 hours of tumbling at 11 rpm.

After 24 hours of mixing, the vials were removed from the tumbler and uncrimped. Each vial was then completely filled with ultrapure water to eliminate headspace in the system, loosely capped, and weighed. After measuring the water temperature, the density and mass of water were used to calculate the volume of water in each vial. Then the correct volumes of stock solution required to obtain the initial concentrations listed above were calculated. These volumes were injected with gastight syringes near the bottom of each vial to minimize opportunity for the BTEX compounds to volatilize and escape the system. Each vial was sealed immediately after injection and once all of the vials were sealed, they were again placed in the 20°C room for 24 hours of tumbling at 11 rpm. Past studies showed that this period of time would be adequate for equilibration (Neel and Bowman, 1991).

Following tumbling, all vials were centrifuged at 4000 rpm for 30 minutes with a Beckman Model J2-21 centrifuge fitted with a JA-20 rotor at 20°C. Rubber sleeve adapters (Corning 8446-A0) were required to minimize breakage of the small 22 mL headspace vials. Nevertheless, a few vials did break during spinning.

Sample extraction was conducted once the vials had been centrifuged. This step was most susceptible to losses due to volatilization because some of the vials had to be unsealed. Those vials that initially contained BTEX concentrations greater than 1.5 mg/L were diluted to prevent saturation of the GC column. The extent of dilution depended on the initial concentration, but involved either a factor of 10 or a factor of 100. Diluted samples were prepared by initially adding the appropriate water volume to clean 22 mL headspace vials, which held a total of 5 mL of fluid. Then, the proper volume of sample supernatant was extracted and injected into the dilution water. These vials were immediately sealed and stored until all other samples had been transferred to clean vials for analysis.

Those samples that did not require dilution were directly transferred to clean headspace vials. However, because of the back pressure generated in these vials, it was not possible to extract 5 mL of sample without venting. Hence, part of the crimp caps on these vials was removed, leaving a small space between the septa and vial lip exposed. A 10 mL glass barrel syringe was quickly forced into this space and 5 mL of the fluid in the middle of the vial were extracted. This volume was immediately transferred to clean headspace vials which were then sealed. Contamination with either BTEX or SMZ was an issue during this process. Thus, each syringe was rinsed seven times with ultrapure water prior to reuse. A glass barrel syringe was used in this transfer because large volume gastight syringes required too much time to fill. Throughout the time that the gastight syringe was extracting fluid, volatilization was occurring through the opening created previously. Glass barrel syringes were used to prevent this occurrence.

After all of the samples had been transferred to clean headspace vials for analysis, the internal standard was injected through the septa into each vial. Care was taken not to allow the needle to touch any liquid which could cause contamination of other vials. The vials were then immediately placed on the HSA carousel and analyzed. All of the HSA and GC settings remained the same as for the standard curves that were run immediately prior to the batch test analyses.

The only difference between batch tests conducted with single or multiple solutes was the type of stock solution used for BTEX injection. Stocks containing only one compound were used for the single-solute studies, whereas stocks containing all of the BTEX compounds were injected into vials for multi-solute tests.

Characterization of Losses from Batch Experiments

The initial concentrations for the batch tests included 0, 0.005, 0.01, 0.1, 1.0, 10, 100, and 250 mg/L BTEX. However, results from the blanks used in the study (vials including BTEX but not SMZ) showed that losses between 20-86% occurred in the vials containing solutions of the last two concentrations listed above. The presence of SMZ changed the volatility characteristics of the compounds so it was not possible to correlate losses from blanks with those in the vials containing SMZ. Hence, the data for the 100 and 250 mg/L BTEX vials were not used in the final analysis.

It is likely that most of the losses that occurred for these high BTEX concentrations were during the initial BTEX injection into the headspace vials prior to tumbling. The vials were filled completely with water prior to injection so as to minimize headspace. The volumes of stock solution required to attain the high concentrations were large enough to cause the loss of some solution. Although injections were made into the middle of the vials rather than the top, the loss of solution could have also caused the loss of BTEX compounds. This theory is supported by the lack of substantial losses for the lower concentrations which did not require large volumes of stock solution compared to the 100 mg/L and 250 mg/L BTEX samples. Table 4.12 presents the losses that occurred in the blanks for each of the initial BTEX concentrations used in the multi-solute sorption study.

Table 4.12 BTEX Percent Losses Observed in Multi-Solute Sorption Study in Ultrapure Water

Initial Concentration, mg/L	Benzene	Toluene	Ethylbenzene	m- & p-Xylenes	o-Xylene
0.005	4	7	14	8	13
0.01	7	8	10	7	11
0.1	3	4	3.2	2.7	3.6
1	18	10	6	6	8
10	7	10	10	10	10
100	20	41	67	68	65
250	36	66	86	86	85

4.4.2 Ionic Strength Effects Batch Experiments

The water used in batch tests conducted with solutions of differing salinities included not only ultrapure water, but also moderate and high salinity solutions. As previously stated, produced water salinity can range from 100 ppm – 300,000 ppm with moderate waters falling between 10,000 and 30,000 ppm. Solutions containing 30,000 ppm salts and 300,000 ppm were attempted for a single-solute study, but the latter solution exceeded the salt solubility at a 20°C. Thus, this water was diluted to 231,000 ppm. Later multi-solute tests involved the preparation of 100,000 ppm and 200,000 ppm solutions rather than the 231,000 ppm solution.

The salts used in the generation of saline solutions included NaCl, CaCl₂, MgSO₄, and KCl. The specific salts and the percentages of each salt dissolved in solution were determined on the basis of common occurrence in produced waters. The percentages for each salt in solution are reported in Table 4.13.

Table 4.13 Composition of Saline Solutions

Salt	Percentage in Solution
NaCl	94
CaCl₂	5
MgSO₄	0.5
KCl	0.5

Solutions were prepared with salts that had been dried for 24 hours in an 105°C oven. Drying was used to prevent the miscalculation of salt masses due to hydration. Each salt was weighed out and added to 500 mL of ultrapure water to generate the appropriate salinity. Because such large amounts of salts were added to water, the density of that water was recalculated for use in batch tests. This calculation was conducted through gravimetric analysis of a 50 mL volumetric flask filled with saline solution. The densities of the 30,000 ppm, 100,000 ppm, 200,000 ppm, and 231,000 ppm solutions are reported in Table 4.14.

Once the salt solutions were prepared, they were substituted for ultrapure water during the batch studies. Batch tests were conducted with ultrapure water and multiple saline

solutions. The vials containing ultrapure water were treated in the same manner as described in the previous section. The vials used for the saline solutions were infused with the appropriate salt solution rather than ultrapure water throughout the procedure. Hence, SMZ saturation as well as dilution occurred with saline solutions.

Table 4.14 Saline Solution Densities

Solution Salinity	Density
ppm	g/mL
30,000	1.022
100,000	1.084
200,000	1.168
231,000	1.173

The single-solute study was conducted in saline solutions with benzene concentrations of 0, 0.01, 0.1, 1, 10, 40, and 75 mg/L. The losses generated in the blanks used in this study were within acceptable levels for both 30,000 ppm and 231,000 ppm salt solutions. These percent losses are reported in Table 4.15. In contrast to the single-solute study, the blanks used in the multi-solute study exhibited substantial losses for higher BTEX concentrations and salinities. The initial concentrations used in this study were 0, 0.015, 1, 10, and 75 mg/L. Large losses occurred in the blanks for all of the BTEX compounds when the initial BTEX concentration was 75 mg/L. Thus, the samples that contained this same initial BTEX concentration could not be used to generate sorption isotherms. In addition, as salinity increased to 200,000 ppm, the losses for all of the BTEX compounds became unacceptable when initial BTEX concentrations were 10 mg/L or greater. Hence, data generated for BTEX sorption at initial BTEX concentrations of 10 mg/L or greater could not be used to generate isotherms for the 200,000 ppm salt solution. The percent lost of each BTEX compound in the three salt solutions used in this study are reported in Table 4.16. Because of the losses in the 200,000 ppm salt solution, only the data gathered for the 0, 0.015, and 1 mg/L initial BTEX concentrations are presented in Chapter 5. These data were not used to generate a sorption isotherm at this salinity. Rather, the distribution coefficients for individual data points were calculated and reported. If these distribution coefficients were similar, they would theoretically describe a single sorption isotherm.

Table 4.15 Benzene Compound Losses in Blanks for Single-Solute Study in Saline Solutions

Initial Concentration (mg/L)	30,000 ppm Solution (% lost)	231,000 ppm Solution (% lost)
0.01	6	13
0.1	12	13
1	2	3
10	5	5
40	3	4
75	2	5

Table 4.16 BTEX Compound Losses in Blanks for Multi-Solute Study in Saline Solutions

Compound	Initial Concentration (mg/L)	30,000 ppm Solution (% lost)	100,000 ppm Solution (% lost)	200,000 ppm Solution (% lost)
Benzene	0.015	-10	-10	-8
	1	-2	-1	-1
	10	-5	-3	14
	75	6	22	52
Toluene	0.015	-5	-15	-10
	1	-2	0	3
	10	-3	-1	39
	75	30	59	85
Ethylbenzene	0.015	1	2	14
	1	-2	1	9
	10	-1	3	69
	75	63	86	97
m- & p-Xylenes	0.015	-1	0	14
	1	-1	2	13
	10	0	5	72
	75	64	86	97
o-Xylene	0.015	2	0	8
	1	-3	-1	5
	10	-4	1	65
	75	59	83	96

4.4.3 Temperature Effect Batch Studies

Batch isotherms were conducted in 22 mL headspace vials with crimp caps, and the initial concentrations for the batch isotherm test ranged from 100 to 40,000 $\mu\text{g/L}$ BTEX. The temperature study was prepared in ultrapure water. Teflon-faced butyl rubber septa, vials and caps were weighed prior to use. To each isotherm vial, 2.5 g SMZ was added. Blank samples that did not contain SMZ for each concentration were used to quantify the extent of volatilization of BTEX compounds during the experimental process. For each concentration, triplicate samples were prepared. All vials were filled with ultrapure water almost full and crimped shut. All vials were then placed in 4 °C, 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, or 36 °C constant temperature rooms for 24 hours and mixed at 11 rpm for the purpose of water saturating the SMZ. The ultrapure water to be used to fill the remaining headspace was stored in the corresponding temperature controlled room for one day. After 24 hours, all vials were removed from the tumbler, uncrimped and completely filled with ultrapure water leaving no headspace, and loosely capped. The vials were then reweighed, so that the mass of water added could be obtained from the

difference between the final and initial weights and the weight of SMZ. The densities of water at 4 °C, 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, and 36 °C were measured to calculate the volume of water in each vial, respectively. Then the required volumes of stock solutions were calculated and injected using gas-tight syringes near the bottom of each vial (minimizing volatilization) to obtain the desired initial concentration of BTEX (0, 100, 10000, 10000, 40000 µg/L) in each vial. Each vial was sealed immediately after injection to avoid loss of BTEX compounds from solution. All of the vials were then placed in a tumbler (11 rpm) in the corresponding temperature controlled rooms for another 24 hours. Previous studies showed that 24 hours was sufficient time for sorption equilibrium to occur. In fact, for toluene one hour was shown to be sufficient. After tumbling, all vials were centrifuged at 4000 rpm for 30 minutes in a centrifuge equipped with a JA-20 rotor (Beckman Model J2-21). Rubber sleeve adaptors (Corning 8446-A0) were used to avoid breakage of the 22 mL vials during centrifugation. Even so some vials did break during the centrifuge process.

Five mL of supernatant containing initial BTEX concentrations of 0, 100, 1000, 10000 µg/L to 22 mL were used for the sample analysis. Due to the backpressure within the vials, it was not possible to extract 5 mL of supernatant without venting. As a result, the vials were partially opened with only a small space between the septa and vial lip exposed to the atmosphere. For the vials containing the highest initial BTEX concentration (40,000 µg/L), 50 µL of supernatant was extracted from each vial and added to a 22 mL headspace vial containing 5 mL of ultrapure water, yielding a dilution factor of 100. The vials were crimped immediately. Contamination with either SMZ or BTEX could occur in the transferring process, thus, each syringe was rinsed seven times with ultrapure water prior to extraction of the next vial. After all of the samples had been transferred to headspace vials, a 200 µL internal standard (25 mg/L) was injected through the septa into each vial before analysis. Then the vials were immediately placed on the HSA for analysis. Calibration curves were run prior to each batch test and the HSA and GC were not shut down while waiting for the batch vials to be ready. Results from the blanks used in the study (vials including BTEX but not SMZ) showed that losses did occur but were within acceptable ranges as shown in Table 4.17. Sorption to SMZ affected the amount of BTEX volatilized from solution so it was not possible to correlate losses from blanks with those vials containing SMZ.

Table 4.17 BTEX Compound Losses in Batch Temperature Tests

Compound	Initial Concentration (µg/L)	Batch Test at 4°C (%)	Batch Test at 10°C (%)	Batch Test at 15°C (%)	Batch Test at 20°C (%)	Batch Test at 25°C (%)	Batch Test at 36°C (%)
Benzene	100	1	-1	-2	2	3	4
	1000	1	1	4	1	2	-1
	10000	-4	-7	-11	0	-7	-7
	40000	1	1	0	7	7	-2
Toluene	100	1	-1	-2	1	4	5
	1000	0	1	4	0	2	0
	10000	-4	-8	-5	1	-8	-7
	40000	2	3	1	2	2	0
Ethylbenzene	100	1	-1	-2	2	5	6
	1000	0	1	5	0	2	0
	10000	-4	-8	0	3	-9	-6
	40000	4	5	6	2	0	3
m,p-Xylene	100	1	-1	-2	2	5	6
	1000	-1	1	5	1	2	1
	10000	-4	-7	0	3	-8	-5
	40000	4	5	7	8	13	3
o-Xylene	100	0	-1	-2	2	4	5
	1000	0	0	4	1	2	0
	10000	-4	-7	-2	3	-8	-6
	40000	3	4	-5	1	1	2

4.4.4 Batch Studies with Produced Water

Rather than testing the removal of BTEX compounds already in produced water, researchers used the produced water as a matrix. The complex chemistry of this wastewater was assumed to change the adsorption behavior of BTEX onto SMZ. Therefore, additional amounts of BTEX stock solutions were injected into the produced water to magnify the effects of produced water chemistry. A single batch study was conducted with produced water that was spiked with BTEX concentrations of 0, 0.01, 0.1, 1, and 10 mg/L. One blank and two samples were included for each of these concentrations. In order to keep the adsorption time for both the initial and injected BTEX the same, saturation of the SMZ with produced water was not attempted. Rather, previously weighed blank vials containing no SMZ and sample vials containing 2.5 g of SMZ were completely filled with produced water and loosely capped immediately prior to weighing. Transfer of the produced water from the VOA vials to the headspace vials was conducted with a 30 mL glass-barrel syringe that was rinsed seven times with ultrapure water between subsequent transfers. The VOA vials were vented during water extraction through the insertion of a needle into the septa. This needle was removed after each extraction process.

Evaluation of the produced water density and the total mass of the sample in the vials allowed the calculation of the volume of water in each vial. These volumes were calculated through a spreadsheet immediately after each vial was weighed. The spreadsheet was set up to allow the calculation of the volume of BTEX stock solution required to obtain the desired additional BTEX concentration in each vial. The calculated volume of stock solution was then transferred into the headspace vials by removing the cap and injecting the solution into the middle of the vial. Each vial was crimp sealed immediately after injection. Every vial was prepared in this manner, and tumbling and centrifugation for these vials were conducted in the same way as described for the other types of batch tests.

Analysis for this batch test posed a few problems because of the unknown initial BTEX concentration already in the produced water prior to spiking due to losses during sample preparation. It is probable that most of these losses occurred during weighing and injection of BTEX because the vials had to be left unsealed until injection was completed. This assertion is supported by the presence of greater BTEX concentrations in the produced water blanks not injected with additional BTEX than in the blanks injected with small volumes of additional BTEX. The blanks that did not require additional BTEX were immediately sealed after filling, but the vials requiring injections had to remain uncovered for a time during injection.

Due to these losses, an assumption for baseline BTEX concentrations had to be made to proceed with data analysis and development of isotherms. The assumption agreed upon was that the blanks for each additional BTEX concentration actually represented the baseline concentration for that set of vials. For example, it was assumed that the set of vials that had an additional 1 mg/L BTEX injected into them contained a baseline BTEX concentration from the produced water equal to the concentrations found in the vial that had no SMZ but was also injected with the additional compounds. This assumption did not allow the determination of losses for the blanks, but prior batch tests showed that the methods used had minimized these losses in the past. Hence, it was also assumed that any losses that occurred after the injection were negligible because the same methods were used for sample tumbling, centrifugation, and transfer into headspace vials for analysis.

4.4.5 Statistical Analyses for Batch Experiments

Hypothesis testing was used to determine whether various isotherms were statistically parallel. By proving the parallelism of these isotherms, it can be said they are statistically equivalent because all of these isotherms were forced to pass through the origin ($q_e = 0$ and $C_e = 0$) during analysis. The hypothesis testing consisted of proving or disproving a null hypothesis by testing all other possible hypotheses. The null hypothesis for all comparisons was that the isotherms being compared were parallel. By proving that the slopes of the isotherms were not greater than, less than, or unequal to each other, the null hypothesis was proven. A full explanation of the method can be found in Kleinbaum *et al.* (1988), but a synopsis is provided below.

The null hypothesis (H_o) is symbolized as:

$$H_o : \beta_{1A} = \beta_{1B} \quad (4.3)$$

where β_{1A} is the slope of isotherm A and β_{1B} is the slope of isotherm B. The alternative hypotheses that can be tested to disprove the null hypothesis (H_A) are:

$$H_A : \begin{cases} \beta_{1A} > \beta_{1B} & \text{(one sided)} & (4.4) \\ \beta_{1A} < \beta_{1B} & \text{(one sided)} & (4.5) \\ \beta_{1A} \neq \beta_{1B} & \text{(two sided)} & (4.6) \end{cases}$$

The test statistic (T) used to test each of these alternative hypotheses is defined as:

$$T = \frac{\beta_{1A} - \beta_{1B}}{S_{\beta_{1A} - \beta_{1B}}} \quad (4.7)$$

where $S_{\beta_{1A} - \beta_{1B}}$ is an approximation of the standard deviation of the estimated difference between the slopes for isotherms A and B. This estimated standard deviation is the square root of the sample variance which is defined as:

$$S_{\beta_{1A} - \beta_{1B}}^2 = S_{P,Y|X}^2 \left[\frac{1}{(n_A - 1)S_{X_A}^2} + \frac{1}{(n_B - 1)S_{X_B}^2} \right] \quad (4.8)$$

where:

$S_{P,Y|X}^2$ = a pooled estimate of σ^2 based on residual mean-square errors for the slopes of isotherms A and B

n_i = number of samples used to generate isotherms i

$S_{X_A}^2$ = variance of x-values used to generate isotherm A

$S_{X_B}^2$ = variance of x-values used to generate isotherm B

The value for $S_{P,Y|X}^2$ can be found through:

$$S_{P,Y|X}^2 = \frac{(n_A - 2)S_{Y|X_A}^2 + (n_B - 2)S_{Y|X_B}^2}{n_A + n_B - 4} \quad (4.9)$$

where $S_{Y|X_A}^2$ and $S_{Y|X_B}^2$ are the residual mean-square errors for isotherms A and B. Once all of these values are calculated, the test statistic (T) can be compared with Student's t with $n_A + n_B - 4$ degrees of freedom and a significance level of α . Whether the one sided Student's t value or the two sided value is used depends on the hypothesis being tested. The critical regions for the alternative hypotheses are:

$$\begin{cases} T \geq t_{n_A+n_B-4, 1-\alpha} & \text{for } H_A: \beta_{1A} > \beta_{1B} & \text{(one sided)} & (4.10) \\ T \leq -t_{n_A+n_B-4, 1-\alpha} & \text{for } H_A: \beta_{1A} < \beta_{1B} & \text{(one sided)} & (4.11) \\ |T| > t_{n_A+n_B-4, 1-\alpha} & \text{for } H_A: \beta_{1A} \neq \beta_{1B} & \text{(two sided)} & (4.12) \end{cases}$$

If any of these hypotheses is proven, the null hypothesis is invalid and the slopes for the isotherms are not statistically equal. If none of the alternative hypotheses is proven, the null hypothesis remains valid and the isotherms are found to be parallel.

These hypotheses were tested for isotherms generated in the single-solute and multi-solute studies conducted in ultrapure water to determine whether competitive effects significantly changed the distribution coefficients of benzene and toluene. The single- and multi-solute isotherms generated in the salinity studies were also compared to ensure that the presence of salts did not allow competitive effects between BTEX compounds to become significant. The isotherms generated in the multi-solute studies conducted in both ultrapure water and salt solutions were compared to demonstrate the effects of salinity on BTEX sorption. Lastly, the BTEX sorption isotherms found for produced water were compared to both the ultrapure and salt solution studies to determine whether these isotherms were changed by the chemistry of the produced water.

The confidence level at which these hypothesis tests were performed was determined through a comparison of replicate isotherms generated for benzene in ultrapure water. These isotherms represent the variation that can occur when replication of isotherms is attempted. The largest confidence level at which the null hypothesis was valid for these isotherms was 99.95%. Hence, all other comparisons were conducted with this confidence level.

4.5 Column Adsorption Studies

In order to design an RSSCT, several field-scale design parameters must be specified. Therefore, a number of assumptions were made regarding the operation of the pilot scale testing to be conducted for the field tests. First, the volume of water to be treated each day was assumed to be 3,000 liters (approximately 20 bbl/day). A hydraulic loading rate of 2 gpm/ft² was assumed for the pilot scale column. A porosity of 0.6 and bulk density of 1 g/cm³ was assumed based on previous studies by Bowman *et. al* (2001). One day of service time was estimated. The adsorption capacity of 14x40 SMZ for benzene was estimated to be 8.24 µg/g. Benzene was used for the design basis, because it was the least hydrophobic BTEX compound and the compound of greatest health concern at low concentrations.

The service time, flow rate and influent concentration (a C_{in} of 835 µg/L was assumed) determined the mass of contaminant (benzene) passing through the column during that period. The mass of SMZ required to treat the contaminant was obtained by dividing the mass of contaminant passing through the column by the adsorption capacity for benzene. The column volume was obtained by dividing the mass of SMZ required by the bulk density of packed SMZ. The diameter of the column was derived from the column sectional area, which was obtained by dividing the flow rate Q by the hydraulic loading rate. The length of the column was obtained by dividing the volume of the column by the column cross sectional area. The pilot-scale column dimensions were determined assuming that the produced water could contain significant salinity. Thus, an adsorption capacity of 32.96 µg of benzene/g of SMZ was used for the initial design. The assumed dimensions of the prospective pilot scale column and the lab scale column parameters are reported in Tables 4.18 and 4.19 respectively. It was expected that 14x40

mesh size of SMZ would be used in the pilot scale column test. The particle diameter corresponding to 14x40 mesh size is 2.4 -1.4 mm with an average diameter of 1.9mm. Scaling using this particle size and the RSSCT design equations yields a particle size for the laboratory scale columns corresponding to 80x100 mesh size.

Table 4.18 Prospective Pilot Scale Column Dimensions

Flowrate (L/day)	q_e ($\mu\text{g/g}$)	Bulk Density (g/cm^3)	Service life (days)	Benzene adsorbed (mg)	Column Volume (L)	Column Diameter (cm)	Column Length (cm)	Hydraulic loading (gpm/ft^2)
3000	32.96	1	1	2505	76	18	297	2

Table 4.19 Dimensions of the Lab Scale Column

Internal Diameter (ID)	0.80 cm
Length	27 cm
Volume	50.3 cm ³
Cross-Sectional Area	2.01 cm ²
Volumetric Flux	22.5 mL/min
Porosity Estimate	0.6
Hydraulic loading rate	10.98 gpm/ft ²
Flowrate	22.5 mL/min

Lab-scale column studies were conducted to verify the batch adsorption capacities determined previously and to evaluate how accurately we can predict BTEX breakthrough in the SMZ columns. This data was used for the design of the pilot-scale column-testing phase of this project. The approach was to collect and analyze data from laboratory scale columns packed with SMZ. In each experiment, a Tedlar bag was filled with the influent water containing BTEX. Flow was initiated through the column and influent and effluent samples were collected as a function of time. The influent concentration was chosen based on analysis of field produced water samples. The influent concentrations of BTEX were sampled less frequently than the effluent concentrations because preliminary results suggested that the influent concentration was constant over the course of the experiment. Effluent BTEX concentration data was used to develop breakthrough curves for each compound. In some cases, these data were compared to predictions derived from batch experiments, and in other cases the data was used to determine sorption capacities for the BTEX compounds.

Breakthrough Profile Analysis

The CXTFIT Code for Estimating Transport Parameters from Laboratory or Field Tracer Experiments Version 2.0 (US Salinity Laboratory, Toride et al, 1995) was used to calibrate and predict breakthrough profiles from the experiments. Specifically, CXTFIT2 was used to solve the direct problem of using transport parameters and batch isotherm parameters to predict contaminant (BTEX) breakthrough curves, and to solve the inverse problem to estimate distribution coefficients based on column effluent data. For the direct problem, CXTFIT2 predicts solute concentrations at a given location (column

outlet) as a function of time. For the inverse problem, CXTFIT2 uses a nonlinear least-squares algorithm to optimize unknown parameters by best fitting the observed data points with predicted ones.

The assumptions inherent in the model used in CXTFIT2 were a constant flux or velocity, homogeneous packing of sorbent in the columns (with homogeneous properties of the medium, including porosity), and saturated conditions. No production or decay of contaminant was assumed. The boundary condition at the column inlet was assumed to be a constant concentration input of BTEX. Inputs included boundary and initial values conditions, column length (since data was collected at the column outlet), and average linear velocity (which is dependent on porosity). The initial condition for the column inlet is $C(0,T)=C_0(T)$. The top (column outlet) boundary condition is a flux-averaged concentration (MODC=2). The modeling approach used in the initial studies assumed local linear local equilibrium sorption using a retardation factor as shown in

$$R=1+(\rho_b * K_d / \theta) \quad (4.13)$$

where,

R is the retardation factor, which quantifies retardation of reactive solute compared to a non-reactive one,

θ is the porosity or volumetric moisture content,

ρ_b is the bulk density (g/cm^3), and

K_d is the linear sorption distribution coefficient,

Hydrodynamic dispersion was not measured in the initial experiments; however, it was estimated by (EPA, 1986):

$$D=0.1X_{\max}v \quad (4.14)$$

where v is the linear velocity through the column, D is the hydrodynamic dispersion coefficient, and X_{\max} is the column length.

In the direct problem, the projected time and flux averaged concentration were derived for all BTEX species based on the K_d values from batch studies. Thus, the model results are truly predictive in this case. In the inverse problem, the retardation factor, and hence K_d values, were derived for all BTEX species based on the collected breakthrough data from the column study. In this case, the breakthrough data served to calibrate the model.

4.5.1 Single- and Multi-Solute Column Experiments

A schematic of the column set up is shown in Figure 4.2. The entire column apparatus (including end fitting, ferrule, screens, and three-way valves) was weighed while empty. The column was then packed with SMZ (80 x 100 mesh) by adding small amounts of SMZ to the column which was attached onto a shaking rack with unbalanced motors. This step was repeated until the column was completely filled with SMZ. At least four hours was needed to ensure good packing. Both ends of the column were sealed with the end fittings and ferrules and the column was weighed again to determine the amount of dry SMZ within the column. The weights were used to calculate a dry bulk density

which is equal to the mass of SMZ per filled volume of the column. Empty and filled column, endfitting weights and other important parameters are provided in Table 4.20.

The column was secured vertically using a ring stand with the inlet at the bottom and the outlet at the top (Figure 4.2). Stainless steel tubing (1/8") was secured to both ends of the column via 3-way Swagelok stainless steel valves. The influent tubing was attached to a high-pressure pump to ensure a constant flow rate through the column. The SMZ-filled column was saturated with ultrapure water (that had been vacuum-filtered to remove any air bubbles) at a flow rate of 2 mL min^{-1} for approximately 24 hr. Once the column was saturated, it was sealed by closing the 3-way valves, and the column was weighed once more to determine the column pore volume.

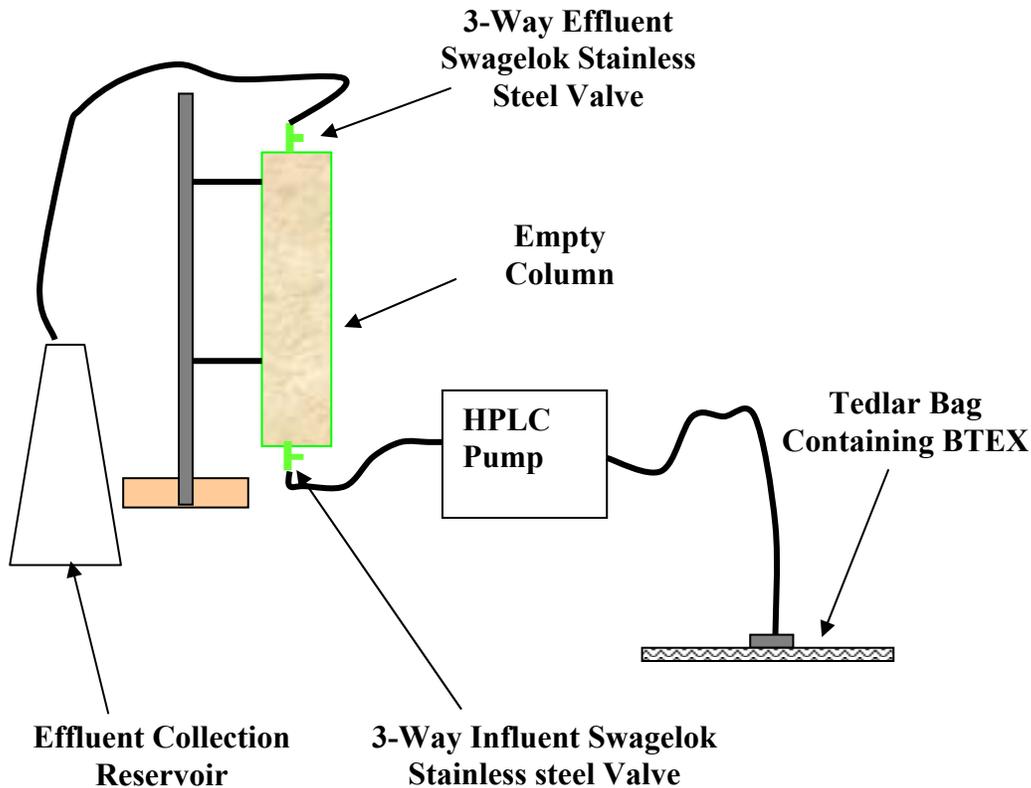


Figure 4.2 Diagram of Laboratory Column Adsorption System

Table 4.20 Lab-Scale Column Parameters

Column No.	Empty Mass (g)	Filled Mass (g)	Endfitting Mass (g)	Water (g)	Bulk Density (g/cm^3)	Porosity
1*	59.64	73.09	30.25	6.96	0.99	0.52
2**	59.64	73.22	30.25	6.85	1.0	0.56
3***	59.64	73.52	30.25	6.80	1.067	0.50

*Column 1 was conducted with ultrapure water background.

** Column 2 was conducted with 100,000 saline water

***Column 3 was conducted with produced water from the Wamsutter site.

The influent BTEX solution was prepared in a collapsible 5-L Tedlar® Gas Sampling Bag (SKC, item no. 231-08A) with a barbed on/off valve. First, the volume of solution was estimated and injected into the Tedlar bag. Approximately 2 liters of solution was injected into the bag through the on/off valve using a jumbo gas-tight glass syringe. Any air bubbles in the bag were extracted through the on/off valve after filling up the reservoir with ultrapure water. Then 200 μL of BTEX stock solution (10 g L^{-1}) were transferred into the bag through the on/off valve using a gas-tight glass syringe yielding a 1000 $\mu\text{g/L}$ concentration of BTEX. The solution was well mixed using manual agitation.

The on/off valve was then connected to the HPLC pump using 1/8" stainless steel tubing. Another piece of stainless steel tubing (1/8") connected the pump to the three-way valve at the bottom of the column. Teflon tubing was attached to the three-way valve at the top of the column with the other end staying in a 2-L glass flask as an effluent collection container.

The BTEX solution was introduced into the column at a flow rate of 22 ml min^{-1} . Effluent samples (5 mL) were taken every 2 to 3 minutes by attaching 10-ml gas-tight glass syringes (Hamilton), which was replaced by a 5-mL non gas-tight glass syringe to the outlet of the three-way valve at the end of the column. Samples were collected until the SMZ column was exhausted. Influent samples (5 mL) were taken every 10 or 15 minutes to ensure that the influent concentration was constant during each run. The samples were immediately transferred to glass headspace free vials and sealed with aluminum crimp caps (fitted with Teflon-faced Butyl rubber septa). They were then analyzed using gas chromatography after all samples were collected.

4.5.2 Column Study in Saline Water Background

The salts (and the percentage of each salt) used in the preparation of the 100,000 ppm TDS salt solution used in this research were the same as those used in the batch experiments. All salts were dried for 24 hours in a 105°C oven to remove any moisture before use. Each salt was weighed accordingly and added to ultrapure water to prepare the 100,000 ppm saline water. The target concentration for the saline water column test was approximately 1000 $\mu\text{g/L}$. The same procedure was followed as described in 4.4.1 for the column operation.

4.5.3 Column Study in Produced Water Background

The influent reservoir was filled with produced water from a ZHE filled with produced water obtained from the Wamsutter, WY site by Crystal Solutions, LLC and stored at 4C in our laboratory. The samples were allowed to equilibrate in the influent reservoir for one day to allow the temperature to be as close to 20°C before running the column. The column operation followed the procedure described in Sections 4.4.1.

4.5.4 Regeneration Tests

The regeneration tests were conducted at New Mexico Tech using the same approach used in the experiments at the University of Austin for the adsorption phase. A glass column 270-mm long with a 4-mm radius was selected for the laboratory tests and was packed with SMZ (80x100 mesh). The column was purged with CO₂ for 24 hr in order to flush out any air remaining in the column, followed by saturation with purified water (reverse osmosis).

The influent BTEX solution (with a concentration of 16 mg L⁻¹ for each of the six compounds) was prepared in a collapsible 10-L (12" x 19") Tedlar® Gas Sampling Bag (Alltech) with a barbed on/off valve. The BTEX solution was introduced into the saturated column at a flow rate of 1.19 cm min⁻¹. Influent and effluent samples were taken to monitor the BTEX concentrations flowing into and out of the column. Flow was terminated when the BTEX effluent concentrations were equal to the influent concentrations; the column was then sealed prior to regeneration.

The spent SMZ was regenerated by air-sparging as shown in the schematic in Figure 4.3. A 65-mm, single-float flowmeter (Cole Parmer) and compressed gas tank (air) were attached to the influent end of the column for the regeneration step. The compressed air tank was set to 20 psi and the flowmeter was used to control flowrate through the column. Flowrate was set at 2.3 mL min⁻¹. Using a 1.0-mL glass gas-tight syringe, samples periodically were taken by withdrawing gas through a sampling port at the effluent end of the column. The air-sparging experiment was continued until the BTEX mass coming off of the column was negligible.

The regenerated SMZ was again saturated with the aqueous BTEX solution. The input BTEX concentration and flow rate were the same as for the original saturation. However, for this experiment the SMZ-filled column was not purged with CO₂ or saturated with pure water prior to introducing the BTEX solution.

Aqueous BTEX concentrations from the laboratory columns were measured using a Hewlett-Packard (HP) Model 7694 headspace sampler attached to a HP Model 5890A gas chromatograph (GC) with a 30 m 0.53-mm ID Megabore® high resolution column (J&W, model GS-Q) and flame ionization detector (FID) with helium as the carrier gas. The GC was calibrated during each run with five BTEX standards of varying concentrations over the linear response range. *p*-Xylene and *m*-xylene were not resolved by this method and were treated as a single compound.

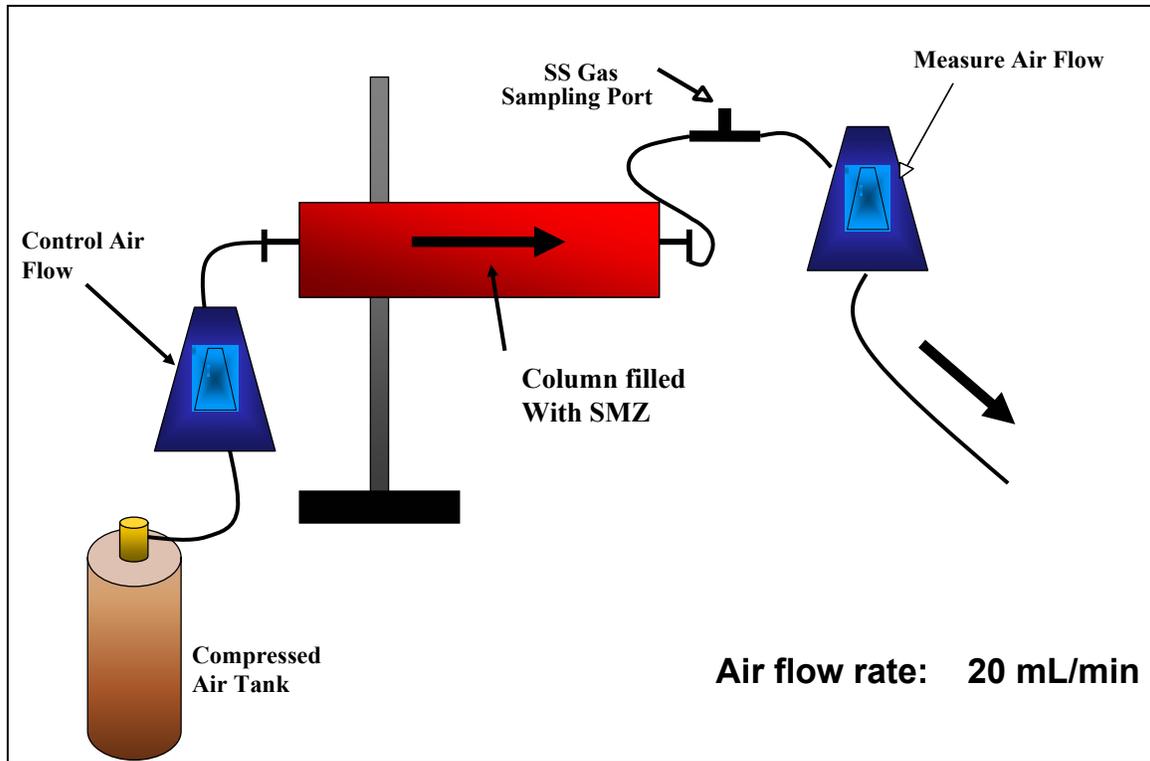


Figure 4.3 Diagram of Laboratory Column Regeneration System

4.6 Field Tests

4.6.1 Site Selection

As stated above, four possible sites/sources of produced water were evaluated. Based on the characterization studies and the availability of the site, the treatment facility of BC Technologies in Wamsutter, Wyoming was selected. The salinity, BTEX concentrations, source quantity, and reproducibility of source volumes and chemistry were all appropriate for field tests.

4.6.2 System Design

The columns selected for use in the field trials were provided by a local Culligan distributor in Austin, TX. Originally designed for use in ion exchange systems, the columns were readily adapted to the needs of this study by substituting the ion exchange resin with SMZ. The columns were constructed from fiberglass and PVC and were designed to operate with the influent stream dispersing at the top of the resin and flowing down to the bottom. Inside the column, the influent port contained a coarse filter to prevent large debris from fouling the column. At the bottom of the column, a perforated collector plate funneled the water up a 1" PVC pipe through the middle of the column to the effluent port.

Two of these columns were used in the field. The first column was 14" in diameter and 48" in height, while the second had a diameter of 12" and was 44" in height. The

available volumes of these columns were approximately 3.6 ft³ and 2.4 ft³ respectively. The 14" column was completely filled with 192.0 lbs. of 14x40 mesh SMZ, while the 12" column contained approximately 4" of headspace and held 132.25 lbs of 14x40 SMZ.

4.6.3 Field Experiments

The site chosen for the field study is operated by Crystal Solutions, LLC., and is located in an oil producing region just outside of Wamsutter, WY. The facility is set up to receive produced water from the region by tanker truck. The water is unloaded from the trucks into an oil/water separation tank. Overflow from this tank flows into a second separation tank. Both tanks are identical, and measure approximately 20' in height and 10' in diameter. Oil is sent into an oil condensate tank for later processing. As the second separation tank fills with water, it flows into a lined separation pond. From the separation pond, water is pumped through a series of lined evaporation ponds.

The field columns were connected to the second separation tank at a 4" valve located about 2' from the bottom. This connection point provided approximately 15' of head, driving water flow through the SMZ system. Just downstream of the tank valve was a strainer to prevent large debris from entering the system. The 4" line was reduced to a 1" PVC pipe that ran to a flow meter, sample port, and influent port of the column. The effluent pipe from the column consisted entirely of 1" PVC, contained a sample port for effluent sample collection, and led into the lined separation pond. Regeneration was attempted in the field using a portable air compressor provided by the field operators. The same setup was used, except the influent water connection was replaced with an air connection, and an air flow meter was used. The effluent line remained in place until the column was drained. The effluent pipe was then replaced with tygon tubing so air samples could be collected easily.

Influent and effluent water samples were collected from the sample ports periodically. A portable photoionization detector (PID) 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 placing the tygon tubing of the effluent air into the bottom of the vial and filling until all the original air in the vial had been displaced. The vial was then quickly closed and sealed as the tygon tubing was being removed.

The 14" column was the first column connected and run from the separation tank (Figure 4.4). This column was operated for about 46 hours with a few minutes downtime to repair a minor leak. During the operation, the flow rate averaged 25 gph but was dropping throughout the course of the run to 17.5 gph. It is believed this drop in flow rate was caused by clogging of the SMZ pores inside the column by particles in the water. BTEX concentrations were constant throughout the trial at levels similar to those of the previous analysis.

The 12" column was put into service next and was in operation for approximately 45 hours, with 1 hour of stoppage for repairs. The average flow rate during this run was 19 gph. However, once again there was a drop in flow rate as the trial progressed, reaching as low as 12.5 gph. A large increase in BTEX influent concentrations occurred during the last 36 hours of operation, when BTEX concentrations jumped to the highest concentrations observed during the testing. Toward the end of the run with the 12"

column, most BTEX concentrations had fallen from these peaks, but were still high. 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.

Regeneration was intended to occur for approximately 12 hours, or until the PID gave insignificant readings from the effluent air. However, due to compressor failure, regeneration had to take place sporadically with active regeneration taking place for about 8.5 hours at air flow rates between 3.0 and 3.5 scfm.

Although the regeneration was not complete, the 14-inch column was run a second time for nearly 48 hours, with an average flow rate of 20 gph. Once again, flow rate dropped with time, reaching as low as 16.5 gph. The BTEX concentrations were consistent during this operation, at levels slightly higher than the 14-inch column trial with virgin SMZ. The concentrations averaged: benzene- 20 mg/L, toluene- 40 mg/L, ethylbenzene- 30 mg/L, m-&p-xylene- 30 mg/L, and o-xylene-5 mg/L.

Aqueous BTEX concentrations from the field columns were measured using a Tekmar 7000 headspace sampler attached to an HP 5890 GC equipped with a 30 m 0.53-mm ID Restek capillary column (RTX-624) and FID. Nitrogen was an auxiliary gas, and helium was the carrier gas.



Figure 4.4 Testing of a prototype SMZ-based water treatment column at a water treatment facility near Wamsutter, WY.: (a) a SMZ column connected to waste water storage tanks at the treatment site; (b) an enlarged view of the SMZ column with sampling valves.

5. Results

5.1 Produced Water Characterization

Produced waters from three different oil fields were characterized during the initial phase of this project. The first water was obtained from an offshore platform operated by Phillips Petroleum in the Gulf of Mexico. This sample was observed to be quite salty and had a distinct odor. In contrast, the second water sample, obtained from onshore oil-producing fields operated by MCA Petroleum Corporation in Flatonia, Texas, was neither salty nor odorous. The third water was from the treatment facility of BC Technologies in Wamsutter, Wyoming. BC Technologies provides produced water treatment and disposal options for small oil and gas producers in Wyoming.

5.1.1 Phillips Petroleum Offshore Sample

The analysis conducted at the University of Texas at Austin for this sample consisted of identifying the amount of BTEX dissolved in the produced water. With respect to BTEX concentrations (Table 5.1), the Phillips Petroleum water had the desired characteristics, but samples are not easily acquired because the samples must be obtained directly from the offshore platform in the Gulf of Mexico.

DHL Analytical laboratories in Round Rock, Texas, conducted further analyses of the concentrations of Total Petroleum Hydrocarbons (TPH), cations, and anions. The DHL results shown in Table 5.2 suggest that the water is moderately to highly saline. The TPH testing proved inconclusive for any hydrocarbons present below the detection limit of 5 mg/L. No petroleum hydrocarbons present at concentrations above this detection limit were detected.

Table 5.1 BTEX Concentrations in Phillips Petroleum Water Samples

Compound	Average	Standard Deviation
	µg/L	µg/L
Benzene	835	43
Toluene	227	15
Ethylbenzene	19	1
p- & m-Xylenes	42	1
o-Xylene	48	1

Table 5.2 TPH, Anions and Cations in Phillips Petroleum Water Samples

Analyses	Method	Result	Units	Reporting Limit
TPH	TX1005	ND	mg/L	5.0
Anions	SW9056			
Chloride		58700	mg/L	200
Nitrate-N		ND	mg/L	0.500
Sulfate		ND	mg/L	3.00
Metals	SW6020			
Calcium		1690000	µg/L	5000
Magnesium		263000	µg/L	1000
Potassium		151000	µg/L	1000
Sodium		33200000	µg/L	50000

Note: ND – not detected

5.1.2 MCA Petroleum Corporation Onshore Samples

Samples were taken both upstream and downstream of the detention ponds at the MCA Burleson oil field. The upstream samples were taken directly from an outfall from the tank used to separate oil and water. The downstream samples were taken from the discharge outfall from the last detention pond. This discharge was being applied directly to the land around it, in effect creating an artificial wetland. DHL Analytical laboratories analyzed these samples for a number of parameters

The parameters that were tested for by DHL included the following: TPH, semivolatile organics, anions, aqueous ammonia, metals, and BTEX. The results from these analyses and the methods used by DHL are included in Table 5.3. The semivolatile organics analysis included 67 different chemicals. However, none of these compounds were detected above the detection limits so all of the 67 unique chemicals are not included in Table 4.3.

As seen in the Table 5.3, the MCA Petroleum water samples have very low concentrations of salt and non-detectable amounts of BTEX both upstream and downstream of the detention ponds. Although the low salt concentrations may be a natural tendency for the water in the Flatonia, Texas area, the lack of BTEX compounds may be linked with the site's water discharge processes. As shown in Figure 5.1, the water from the separation tank is directly discharged into a pond via an open pipe. This allows substantial volatilization to occur both in the pipe and during the time when the water flow is exposed to the atmosphere. Thus, as these characteristics would not have allowed us to determine the efficacy of the proposed treatment process and was not selected for further study.

Table 5.3 Results from Analyses of MCA Petroleum Corp. Samples

Sample Location	Analyses	Method	Result	Units	Reporting Limit
Up Stream	TPH	TX1005			
	C ₆ -C ₁₀		ND	mg/L	4.72
	C ₁₀ -C ₂₈		7.45	mg/L	4.72
	Semivol. Organics	SW8270C	ND	µg/L	Varies
	Anions	SW9056			
	Chloride		20.9	mg/L	1
	Nitrate-N		ND	mg/L	0.500
	Sulfate		11.1	mg/L	3.00
	Ammonia (as N)	M4500-	0.716	mg/L	0.250
	Metals	SW6020			
	Calcium		2090	µg/L	100
	Magnesium		547	µg/L	100
	Potassium		1940	µg/L	100
	Sodium		211000	µg/L	5000
	Aq. BTEX	SW8021B			
	Benzene		ND	µg/L	5.0
	Toluene		ND	µg/L	5.0
	Ethylbenzene		ND	µg/L	5.0
Xylenes, Total		ND	µg/L	5.0	
Down Stream	TPH	TX1005			
	C ₆ -C ₁₀		ND	mg/L	5.81
	C ₁₀ -C ₂₈		ND	mg/L	5.81
	Semivol. Organics	SW8270C	ND	µg/L	Varies
	Anions	SW9056			
	Chloride		20.1	mg/L	1
	Nitrate-N		ND	mg/L	0.500
	Sulfate		10.1	mg/L	3.00
	Ammonia (as N)	M4500-	ND	mg/L	0.250
	Metals	SW6020			
	Calcium		2120	µg/L	100
	Magnesium		538	µg/L	100
	Potassium		1810	µg/L	100
	Sodium		189000	µg/L	5000
	Aq. BTEX	SW8021B			
	Benzene		ND	µg/L	5.0
	Toluene		ND	µg/L	5.0
	Ethylbenzene		ND	µg/L	5.0
Xylenes, Total		ND	µg/L	5.0	

Note: ND – not detected



Figure 5.1 Produced Water Outfall for MCA Petroleum Corp.

5.1.3 Produced Water from BC Technologies Wamsutter Treatment Facility

The site, located in an oil producing region just outside of Wamsutter, WY is operated by Crystal Solutions, LLC. It receives produced water from the region by tanker truck. The water is unloaded from the trucks into an oil/water separation tank. Overflow from this tank flows into a second separation (or holding) tank. Both tanks are identical, and measure approximately 20’ in height and 10’ in diameter. The results from the initial analysis of samples from this facility were limited to selected metals, BTEX and TDS. Results for both the oil/water separation tank and holding tank, and the TDS results for the holding tank are reported in Table 5.4 The water from the oil/water separation tank was not tested for TDS because this water would not be used for subsequent batch tests.

Table 5.4 Initial Metals Analysis for Wamsutter Site Samples

Analyses	Method	Result	Units	Reporting Limit
Metals: ICP-MS	SW6020			
Arsenic		24.4	µg/L	10.0
Barium		8650	µg/L	100
Cadmium		None Detected	µg/L	1.00
Lead		6.58	µg/L	3.00

Table 5.5 Initial BTEX Concentrations and Total Dissolved Solids in Wamsutter Site Samples

Compound	Oil/Water Separation Tank	Holding Tank
Benzene (µg/L)	13.0	2.6
Toluene (µg/L)	30.6	6.1
Ethylbenzene (µg/L)	1.4	0.2
m- & p-Xylenes (µg/L)	7.1	1.9
o-Xylene (µg/L)	3.8	0.7
TDS (mg/L)	-	11,280

Based on the results of the analyses from the three water sources and the potential for conducting a field study at the site, this site was selected for further study. The salinity, BTEX concentrations, source quantity, and reproducibility of source volumes and chemistry were all appropriate for field tests. Furthermore, the site personnel were eager to participate in our study.

As a result, two subsequent analyses of the water were conducted at the time of the field test (July, 2002) and approximately one year later. These results are presented in Table 5.6 which also provides a comparison of the values to reported literature ranges. The differences in contaminant levels in these produced waters confirms the reported variability of water quality for this type of waste stream (Smith *et al.*, 1996; Lawrence *et al.*, 1995; Fillo *et al.*, 1992). It also suggests that the selected site has low to moderate levels of salinity, high BTEX concentrations, and low to moderate phenol levels.

Table 5.6 Comparison of Produced Water Characteristics from the Wamsutter Site to Reported Literature Values

Analysis	Parameter	units	Literature ¹	Summer 2002	Summer 2003
Total Petrol. Hydrocarbons	C6-C12	mg/L	-	128.5	43.5
	C12-C28	mg/L	-	7.3	ND
	C28-C35	mg/L	-	ND	ND
	total	mg/L	2-565	135.8	43.5
Total Dissolved Solids		mg/L	-	11400	10230
Total Organic Carbon		mg/L	0-1500	470	2983
Anions	Bromide	mg/L	-	ND	22
	Chloride	mg/L	80-200000	4510	4400
	Flouride	mg/L	-	10	57
	Sulfate	mg/L	2-1650	56.6	13
Cations	Calcium	mg/L	13-25800	38.1	30
	Magnesium	mg/L	8-6000	9.47	6.4
	Potassium	mg/L	24-4300	1530	44
	Sodium	mg/L	132-97000	4050	4100
Alkalinity (CaCO ₃)	Bicarbonate	mg/L	77-3990	2860	3120
	Carbonate	mg/L	-	ND	60
	Hydroxide	mg/L	-	ND	ND
	Total	mg/L	-	2860	3180
Metals	Mercury	ug/L	1-2	ND	---
	Arsenic	ug/L	5-300	ND	---
	Barium	ug/L	1300-650000	9920	---
	Cadmium	ug/L	5-200	ND	---
	Chromium	ug/L	20-1100	ND	---
	Lead	ug/L	2-8800	ND	---
	Selenium	ug/L	<0.001	25.2	---
	Silver	ug/L	1-150	ND	---
Semivolatiles	2,4-Dimethylphenol	ug/L	¹	816	802
	2-Methylnaphthalen	ug/L	¹	160	717
	2-Methylphenol	ug/L	¹	1350	1440
	4-Methylphenol	ug/L	¹	1000	672
	Dibenzofuran	ug/L	-	4.4	ND
	Fluorene	ug/L	-	4.6	ND
	Naphthalene	ug/L	-	164	419.2
	Phenanthrene	ug/L	-	3.8	ND
	Phenol	ug/L	9-23000 ²	764	2383
BTEX	Benzene	ug/L	77-44000	21300	15800
	Tolulene	ug/L	90-5800	33200	36700
	Ethylbenzene	ug/L	29-110	22800	1400
	m&p-Xylene	ug/L	47-400	9800	6400
	o-Xylene	ug/L	70-460	4900	3400

¹ Literarure data from Tibbetts *et al.* (1992)

² Phenol data given as sum of all phenols

Note: ND - Not Detected

5.2 Batch Adsorption Studies

There were three primary objectives of the batch sorption studies. The first was to evaluate the sorption behavior of BTEX compounds on SMZ in ultrapure water. The second goal involved the study of BTEX removal efficiency by SMZ in the presence of various salt concentrations. Lastly, the effects of produced water chemistry on BTEX sorption were investigated through the determination of distribution coefficients in this matrix. Hypothesis testing was used to determine whether isotherms developed under these different solution conditions were statistically identical. The distribution coefficients determined from the single-solute batch tests were compared to values predicted by various types of correlations published in literature. If these correlations compare favorably to observed data, then they could be used in future studies to predict sorption of BTEX in other produced waters.

5.2.1 Single-Solute Batch Isotherms

Many adsorbents in natural and engineered systems exhibit lower removal efficiencies in complex systems due to competitive sorption. Prior to building an SMZ treatment system for streams contaminated with BTEX, data quantifying these competitive effects need to be gathered. Hence, the first objective of this research was met through tests conducted with both specific BTEX compounds and combinations of all six chemicals. These tests demonstrated how sorption to SMZ was affected as more chemicals were added to solution. Effects were quantified through the determination of distribution coefficients in both single-solute and multi-solute cases. The distribution coefficients determined from the isotherms were statistically compared to determine whether differences in adsorption capacity were evident in the presence of additional sorbates. Thus, the first task was to quantify sorption in single-solute systems for toluene and benzene, the two least hydrophobic compounds.

Single-solute sorption studies included initial concentrations of 0, 0.005, 0.01, 0.1, 1, 10, 40, and 75 mg/L. Results from the single-solute studies conducted with benzene and toluene are presented in Figures 5.2 and 5.3. Figure 5.2(b) and Figure 5.3 (b) include the 95% confidence limits on the results obtained in this study. Distribution coefficients (K_d) were calculated for all of the isotherms using the LINEST linear regression tool built into Microsoft Excel 2000. Each isotherm was based on the model:

$$q_e = K_d C_e \quad (5.1)$$

where q_e is the sorption density, K_d is the distribution coefficient, and C_e is the equilibrium concentration. As shown in these isotherms, sorption was linear throughout a wide range of concentrations, and the 95% confidence limits on K_d were calculated. A comparison of distribution coefficients demonstrates that toluene has a greater affinity for SMZ than benzene. This result is supported both by benzene's aqueous solubility which is higher than that of toluene and the K_{ow} which is lower.

The linear model fit the data for both benzene and toluene well, as demonstrated by the coefficients of determination (R^2). This strong linear trend was apparent throughout the wide range of BTEX concentrations tested. Triplicates were used throughout the single-solute studies so that statistical analyses could be conducted on the results. Tables 5.7 and 5.8 present the averages and standard deviations for the sorption density and equilibrium concentrations measured for the benzene and toluene single-solute studies, respectively.

Table 5.7 Benzene Sorption Capacities for Sorption to SMZ in Ultrapure Water

Initial Concentration ($\mu\text{g/L}$)	Final Concentration ($\mu\text{g/L}$)		Sorption Density ($\mu\text{g/g}$)	
	Average	Std. Dev.	Average	Std. Dev.
0	0	0	0	0
5	2.2	0.093	0.023	0.00079
10	4.5	0.17	0.045	0.0013
100	48.4	2.0	0.41	0.014
1000	515	16	4.0	0.10
10000	5427	858	38	6.3
40000	18162	883	176	4.8
75000	34153	745	324	5.3

Table 5.8 Toluene Sorption Capacities for Sorption to SMZ in Ultrapure Water

Initial Concentration ($\mu\text{g/L}$)	Final Concentration ($\mu\text{g/L}$)		Sorption Density ($\mu\text{g/g}$)	
	Average	Std. Dev.	Average	Std. Dev.
0	0	0	0	0
5	1.1	0.054	0.032	0.00047
10	2.2	0.07	0.063	0.0019
100	22	0.8	0.62	0.005
1000	229	5	6.4	0.03
10000	2234	26	62	1.3
40000	8975	246	249	2.2
75000	15922	260	471	2.3

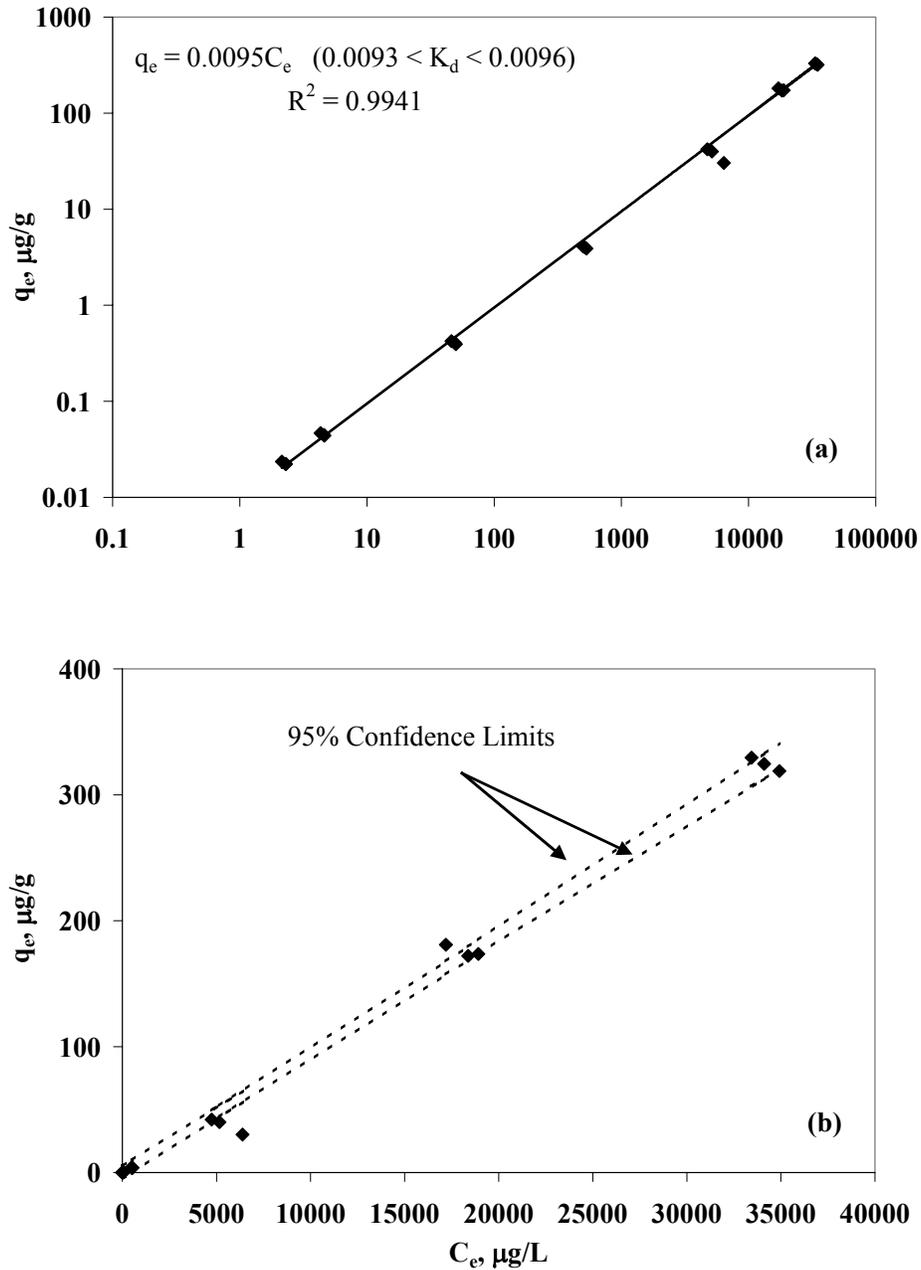


Figure 5.2 Single-Solute Sorption Isotherm for Benzene on SMZ in Ultrapure Water (a) Logarithmic ($q_e = K_d C_e$ with 95% Confidence Limits for K_d (L/g SMZ) in Parentheses); (b) Linear (95% Confidence Limits for Data Shown by Dashed Lines)

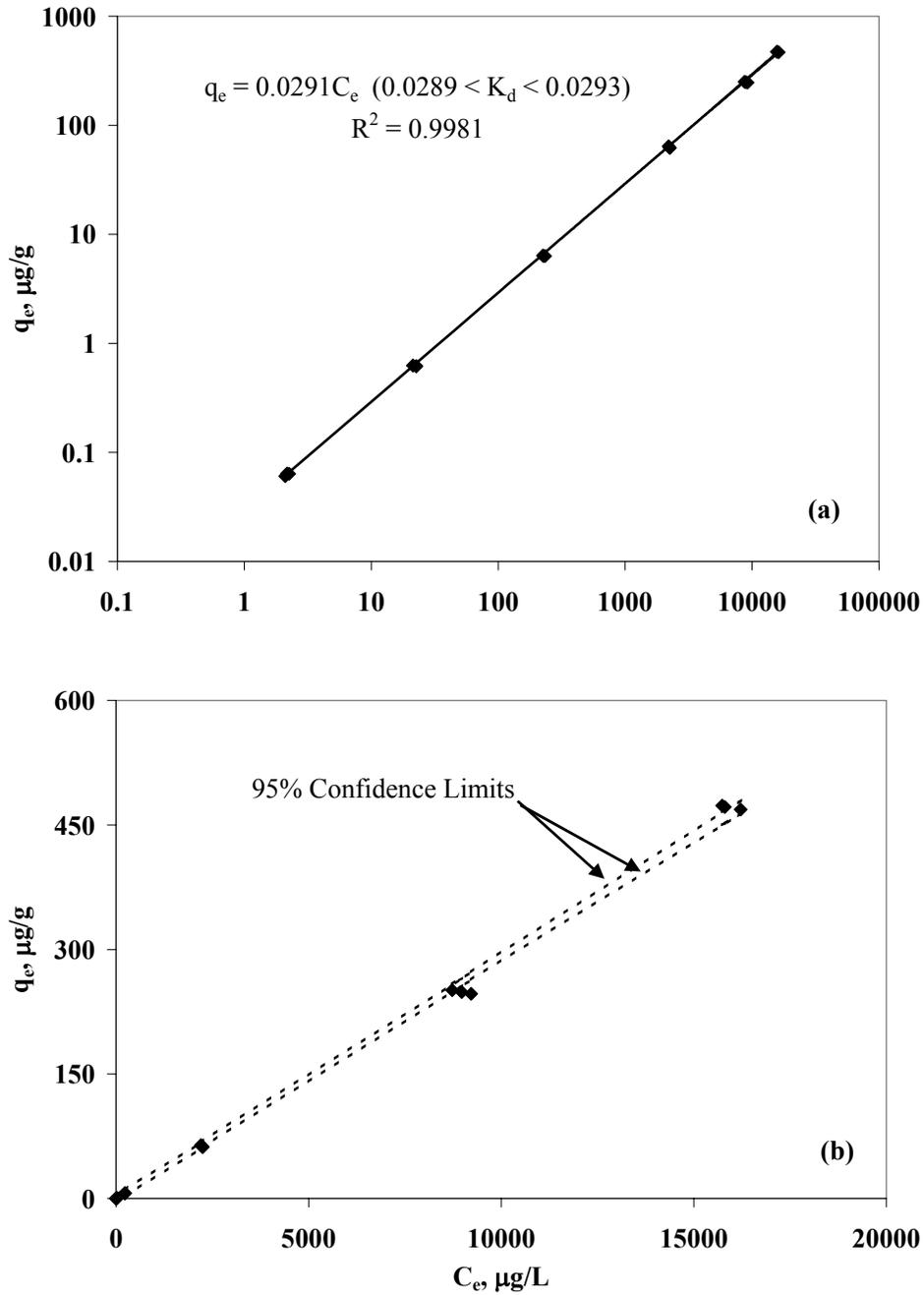


Figure 5.3 Single-Solute Sorption Isotherm for Toluene on SMZ in Ultrapure Water (a) Logarithmic ($q_e = K_d C_e$ with 95% Confidence Limits for K_d (L/g SMZ) in Parentheses); (b) Linear (95% Confidence Limits for Data Shown by Dashed Lines)

The percent of each compound removed was calculated for benzene and toluene. The average removal of benzene was 52% while that of toluene was 78%. As expected for a linear isotherm, the removal for each compound was relatively constant and increased removal at lower concentrations was not observed. These removals were consistent with the values of the distribution coefficients in that the numerical value for benzene was smaller than for toluene. This was expected because toluene has a lower aqueous solubility than benzene, and therefore, a greater preference for the hydrophobic phase present in SMZ.

Comparison of Single-Solute Results with Published Correlations

As stated in Chapter 2, numerous correlations relating either the octanol-water partitioning coefficient (K_{ow}) or aqueous solubility (S) to the partitioning coefficient onto organic carbon (K_{oc}) have been reported in literature. Schwarzenbach *et al.* (1993) also stated that a relationship between the distribution coefficient and the organic matter partitioning coefficient (K_{om}) exists. This relationship is

$$K_d = K_{om} f_{om} \quad (5.2)$$

where f_{om} is the fractional organic matter content on a soil. The SMZ used in this study had an f_{om} of 0.051 as calculated by the HDTMA loading of 180 mmol/kg.

With this equation and values for K_{ow} and S found in literature, it was possible to compare the observed distribution coefficients to those that would be predicted by the published correlations. These correlations were conducted with specific soils and for certain compounds. While most of the correlations involved benzene, only six included toluene. Hence, distribution coefficients for benzene and toluene were calculated with only the correlations that were developed with the appropriate chemicals. The results for these comparisons for benzene and toluene are presented in Tables 5.9 and 5.10, respectively.

The distribution coefficients found in this study for benzene and toluene were 9.5 L/kg and 29.1 L/kg, respectively. A comparison between these values and those predicted by the published correlations shows that the correlations dramatically underestimated the K_d values for both benzene and toluene. Thus, the use of these correlations would not be accurate for the prediction of benzene and toluene sorption on SMZ. As mentioned earlier, the published correlations were found through studies conducted on soils with various organic carbon contents. These results suggest that HDTMA is a much better sorbent than soil organic matter for moderately hydrophobic contaminants.

Because none of the published correlations proved to accurately predict observed distribution coefficient values, regressions were conducted between the K_d values found in this study and the K_{ow} and S values found in literature for the BTEX compounds.

Table 5.9 Benzene Distribution Coefficients Predicted Using Published Correlations

Source	Correlation	Calculated K_d (L/kg)
Schwarzenbach <i>et al.</i> (1993)	$\log K_{om} = -0.93 \log S - 0.17$	0.97
Schwarzenbach <i>et al.</i> (1993)	$\log K_{om} = 1.01 \log K_{ow} - 0.72$	1.11
Karickhoff <i>et al.</i> (1979)	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	1.98
Karickhoff (1981)	$\log K_{oc} = 0.989 \log K_{ow} - 0.346$	1.37
Chiou <i>et al.</i> (1983)	$\log K_{om} = -0.729 \log S + 0.001$	0.67
Chiou <i>et al.</i> (1983)	$\log K_{om} = 0.904 \log K_{ow} - 0.779$	0.57
Abdul <i>et al.</i> (1987)	$\log K_{oc} = 1.04 \log K_{ow} - 0.84$	0.56
Abdul <i>et al.</i> (1987)	$\log K_{oc} = -0.74 \log S + 4.0$	0.97
Vowles and Mantoura (1987)	$\log K_{oc} = 1.20 \log K_{ow} - 1.13$	0.63
Pussemier <i>et al.</i> (1990)	$\log K_{oc} = 1.009 \log K_{ow} - 0.531$	0.99
Results of This Study	-	9.5

Table 5.10 Toluene Distribution Coefficients Predicted Using Published Correlations

Source	Correlation	Calculated K_d (L/kg)
Schwarzenbach <i>et al.</i> (1993)	$\log K_{om} = -0.93 \log S - 0.17$	3.43
Schwarzenbach <i>et al.</i> (1993)	$\log K_{om} = 1.01 \log K_{ow} - 0.72$	4.07
Schwarzenbach and Westall (1981)	$\log K_{oc} = 0.72 \log K_{ow} + 0.49$	6.35
Abdul <i>et al.</i> (1987)	$\log K_{oc} = 1.04 \log K_{ow} - 0.84$	2.16
Abdul <i>et al.</i> (1987)	$\log K_{oc} = -0.74 \log S + 4.0$	2.34
Pussemier <i>et al.</i> (1990)	$\log K_{oc} = 1.009 \log K_{ow} - 0.531$	3.63
Results of This Study	-	29.1

These regressions are shown in Figures 5.4 and 5.5 along with several of the published correlations that were developed for combined BTEX compounds. The predicted values for K_{om} and K_{oc} from these correlations were converted to predicted K_d values with the relationships $K_d = K_{om}f_{om}$ and $K_d = K_{oc}f_{oc}$ where $f_{om} = 0.051$ and $f_{oc} = 0.041$ for SMZ.

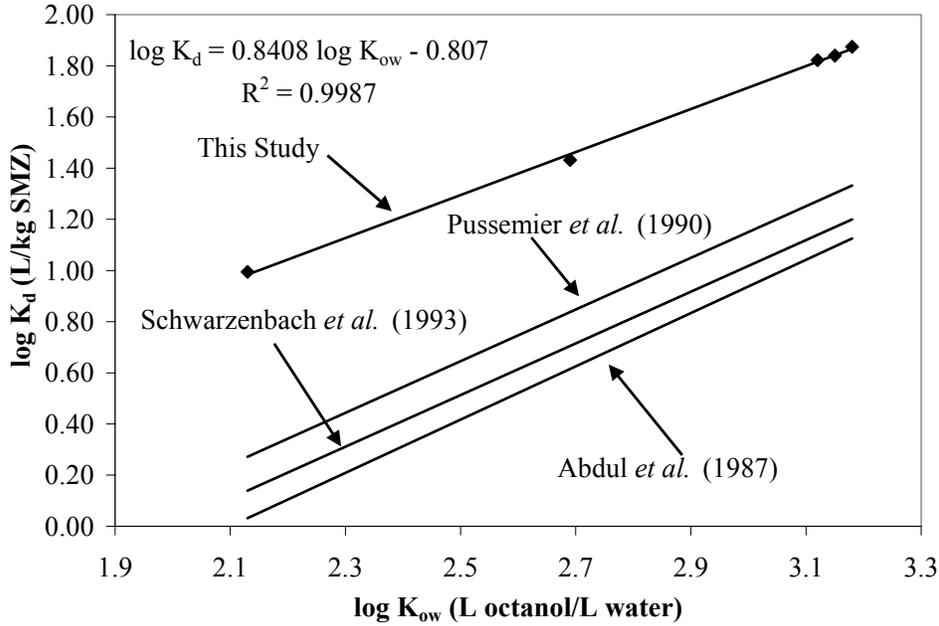


Figure 5.4 Relationships Between K_d and K_{ow}

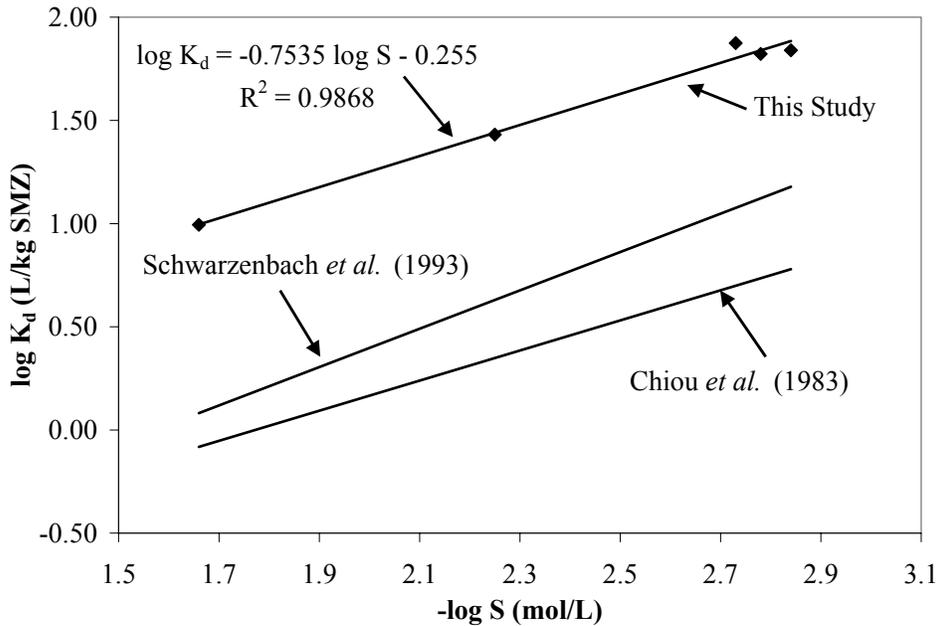


Figure 5.5 Relationships Between K_d and S

As shown in both Figures 5.4 and 5.5, the regressions developed from this study result in much higher K_d values than previously published correlations developed for soil organic matter. In addition, the correlation developed with K_{ow} provides a better fit to the data than the correlation developed with solubility.

5.2.2 Multi-Solute Batch Isotherms

If competitive effects were to impact the sorption of BTEX compounds by SMZ, the distribution coefficients for benzene and toluene would significantly differ from those found in single-solute studies. The Ideal Adsorbed Solution Theory (IAST) indicates that sorption for compounds that have linear single-solute sorption isotherms will not change in the presence of multiple solutes (Weber and DiGiano, 1996). Multi-solute sorption studies in ultrapure water were conducted to determine whether this theory holds for SMZ.

Figure 5.6 shows the sorption isotherm data for all of the BTEX compounds in the multi-solute study. Linear regressions and distribution coefficients are not included in Figure 5.6 to minimize clutter. Rather, the coefficients of determination (R^2), distribution coefficients, and 95% confidence limits on K_d are reported in Table 5.7. As shown in Figure 5.6, the data for ethylbenzene and the xylenes lie very close to one another. The similarity of the data may be explained because the solubilities of ethylbenzene and all of the xylenes are relatively close in value. Thus, each exhibits approximately the same affinity for SMZ. The R^2 values for each isotherm show the goodness of fit for all of the data gathered during this test. The K_d values presented in Table 5.11 represent the slope of each isotherm when the y-intercept for the model

$$q_e = K_d C_e + y_{\text{intercept}} \quad (5.3)$$

was forced to equal zero. However, determination of the 95% confidence limits for the data used to develop the isotherms showed that none of the y-intercept values were statistically different from zero, even when they were not forced to this value. This is represented in Figure 5.7 for a benzene isotherm plotted on a linear scale with 95% confidence limits on the y-intercept. Hence, as widely accepted, Equation 5.1 describes the linear sorption of these non-polar organic compounds quite well. Though data are not presented here, similar results were found for all remaining isotherms.

Table 5.11 Multi-Solute Isotherm Distribution Coefficients for BTEX in Ultrapure Water

Compound	R^2	K_d (L/g SMZ)	95% Confidence Limits on K_d
Benzene	0.9993	0.00982	0.00968, 0.00101
Toluene	1.000	0.0270	0.02699, 0.0271
Ethylbenzene	0.9999	0.0692	0.0687, 0.0692
m- & p-Xylenes	0.9999	0.0749	0.0745, 0.0752
o-Xylene	1.000	0.0664	0.0659, 0.0669

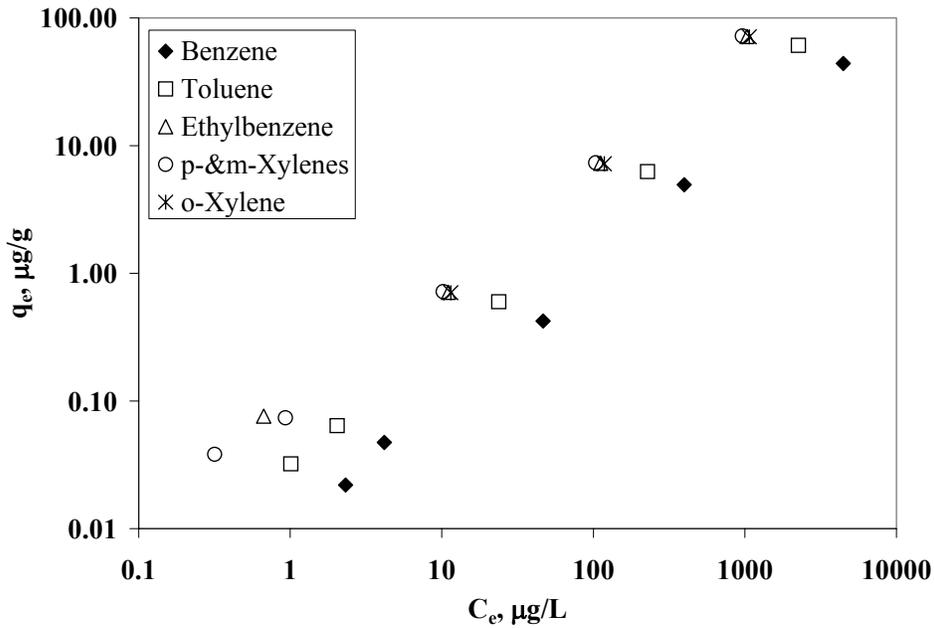


Figure 5.6 Multi-Solute Sorption Isotherms for BTEX on SMZ in ultrapure Water

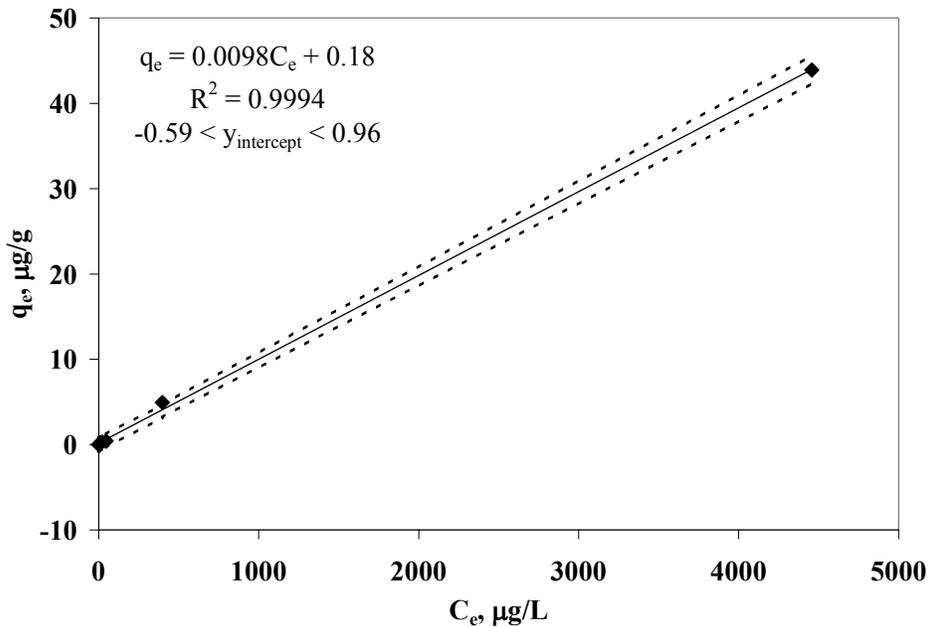


Figure 5.7 Benzene Sorption Isotherm in Presence of Other BTEX Compounds with 95% Confidence Limits on Data (shown in dashed lines) and y-Intercept

The average removal efficiencies for all of the BTEX compounds in a combined system are presented in Table 5.12. Again, the percent removed for each compound remained relatively constant as expected for a linear isotherm. The removal of ethylbenzene and the xylenes was substantially greater than that of benzene or toluene. This result supports the use of benzene and toluene as design compounds for treatment systems because they will most likely be the compounds that will require the largest volume of SMZ to meet design criteria. In addition to showing the least affinity for SMZ, benzene and toluene are also typically found in higher concentrations in produced water than other BTEX compounds.

Table 5.12 BTEX Removal Efficiencies for SMZ in Multi-Solute Sorption Study

Compound	Removal Efficiency (%)
Benzene	56
Toluene	78
Ethylbenzene	92
m- & p-Xylenes	91
o-Xylene	93

Statistical Comparisons of Single-Solute and Multi-Solute Sorption Isotherms

As stated in Chapter 4, statistical comparison of the isotherms between single-solute and multi-solute studies was examined through the use of hypothesis testing. Separate regression fits were conducted to compare benzene and toluene single-solute isotherms with their corresponding multi-solute isotherms. The null hypothesis for these tests was that the slopes (distribution coefficients) for each isotherm were equal. By proving that the slope for the single-solute isotherm was not greater than, less than, or unequal to the slope for the multi-solute isotherm, the null hypothesis could be confirmed. Were a slope found to be significantly different from another, the null hypothesis was rejected and these slopes were determined to be unequal.

Table 5.13 includes the results from these statistical tests. With a 99.95% confidence level, the single-solute and multi-solute isotherms for both benzene and toluene were found to be statistically equal. No competitive effects could be distinguished in the multi-solute sorption test. This is in contrast to results found by other researchers who cited significant multi-solute effects in aqueous systems (Stuart *et al.*, 1991). Stuart *et al.* studied the effects of competition between benzene, toluene, and the xylenes (BTX). Toluene and the xylenes were shown to experience less sorption in the presence of the other BTX compounds while benzene sorption increased in the presence of these compounds. However, the Stuart *et al.* study was conducted with a natural sandy loam soil. The discrepancy in the results found in the present research and those found by Stuart *et al.* may be due to the differences in chemical and physical characteristics between SMZ and natural soils.

Because competitive effects were not apparent during this study, the published correlations that were used to compare the observed and predicted K_d values for benzene

and toluene in the single-solute studies would still result in erroneous sorption predictions for solutions containing multiple solutes. However, the regressions with the data collected in this research show good correlation between K_{ow} and K_d as well as between S and K_d . Again, these regressions are shown above in Figures 5.4 and 5.5.

Table 5.13 Results from Hypothesis Testing for Single-Solute and Multi-Solute Sorption Studies in Ultrapure Water

Compound	K_d from Single-Solute (L/kg)	K_d from Multi-Solute (L/kg)	T-Value	Validity of Null Hypothesis for Equal Slopes between Single and Multi-solute Isotherms
Benzene	9.5	9.82	-0.19	Valid
Toluene	29.1	27.0	0.64	Valid

Conclusions for Single-Solute and Multi-Solute Sorption Studies in ultrapure Water

Benzene and toluene sorption to SMZ can be described with linear isotherms in both single-solute and multi-solute systems. A multi-solute study demonstrated that the remaining BTEX compounds also follow strong linear trends throughout a large range of concentrations and sorption densities. Statistical regressions showed that the presence of ethylbenzene and the xylenes does not significantly change the distribution coefficients for benzene or toluene. In addition, the magnitude of distribution coefficients are inversely related to the aqueous solubilities of the BTEX compounds as shown in Figure 5.5. The most soluble chemicals, benzene and toluene, show the least removal by SMZ. Therefore, the removal of these compounds should be used as design criteria for systems that incorporate SMZ for the treatment of BTEX-contaminated waste streams.

Predicted distribution coefficients found through published correlations should not be used to describe the sorption of BTEX compounds to SMZ. These relationships dramatically underestimate the distribution coefficients found in this research. A possible reason for this may be that SMZ has sufficiently different chemical properties from soil to preclude the use of published correlations for sorption to this material. However, the regressions that were developed in this research show good correlation between the octanol-water partition coefficient and distribution coefficient as well as between aqueous solubility and distribution coefficient. Hence, these regressions may describe the sorption to SMZ better than previously published correlations developed for natural soil and sediment.

5.2.3 Batch Studies in High Salinity Background Water

Produced water can range in salinity from 100 ppm – 300,000 ppm (Fillo *et al.*, 1992), and many researchers have shown that increasing ionic strength tends to decrease the aqueous solubility of non-polar organic compounds (Schwarzenbach *et al.*, 1993). Both of these facts support the hypothesis of this research that increased solution salinity will enhance the removal of BTEX compounds from produced water through sorption onto SMZ. This hypothesis was tested through sorption studies conducted with BTEX compounds in solutions of varying salinities for both single-solute benzene experiments

and multi-solute BTEX experiments. The solutions were made with different amounts of NaCl, CaCl₂, KCl, and MgSO₄ dissolved in ultrapure water. Results from the single-solute and multi-solute studies were compared through hypothesis testing.

As mentioned in Chapter 3, Setchenow developed an equation in 1889, relating changes in aqueous solubility to the total salt concentration present in solution (Setchenow, 1889). This equation is presented below:

$$\log \left[\frac{C_w^{sat}}{C_{w,salt}^{sat}} \right] = K^s [\text{salt}]_t \quad (5.4)$$

where the numerator and denominator in the logarithm represent the solubility of a compound in pure water and a saline solution, respectively, K_s is the salting coefficient, and $[\text{salt}]_t$ is the total molar salt concentration present in solution. Through the use of this correlation and the following correlation from Schwarzenbach *et al.* (1993), distribution coefficients for different salt concentrations were predicted using $K_d = K_{om}f_{om}$.

$$\log K_{om} = -0.93 \log S - 0.17 \quad (5.5)$$

In Equation 5.5, K_{om} represents the partitioning coefficient onto organic matter and S is the aqueous solubility of a certain compound. This relationship does not take salt effects into account until Equation 5.4 is substituted into it, as explained below.

If the predicted distribution coefficients were to match those that were observed in the sorption studies, future design work for BTEX removal could be conducted with only the knowledge of salt concentration in the waste stream rather than through lab-scale batch tests.

5.2.3.1 Benzene Sorption onto SMZ in the Presence of Different Salt Concentrations

The sorption isotherms for benzene in ultrapure water and saline water with salt concentrations of 30,000 ppm, and 231,000 ppm are shown in Figure 5.8. The correlation coefficients, distribution coefficients, and 95% confidence limits on K_d are presented in Table 5.14. The data for benzene sorption in ultrapure water in Figure 5.8 encompass all of the data gathered for benzene in a single-solute system. However, in Table 5.14 the distribution coefficients and corresponding parameters are differentiated between the data gathered in the previous single-solute experiments with ultrapure water and the data gathered in control samples analyzed during the saline solution experimental phase. This differentiation was necessary because the isotherm developed for ultrapure water during the salinity studies was different from the previously developed isotherm (although, not statistically). Indeed, hypothesis testing used to determine the statistical difference between these two isotherms using a confidence level of 99.95% based on preliminary experiments indicated that the two isotherms were equivalent as shown in Table 5.15.

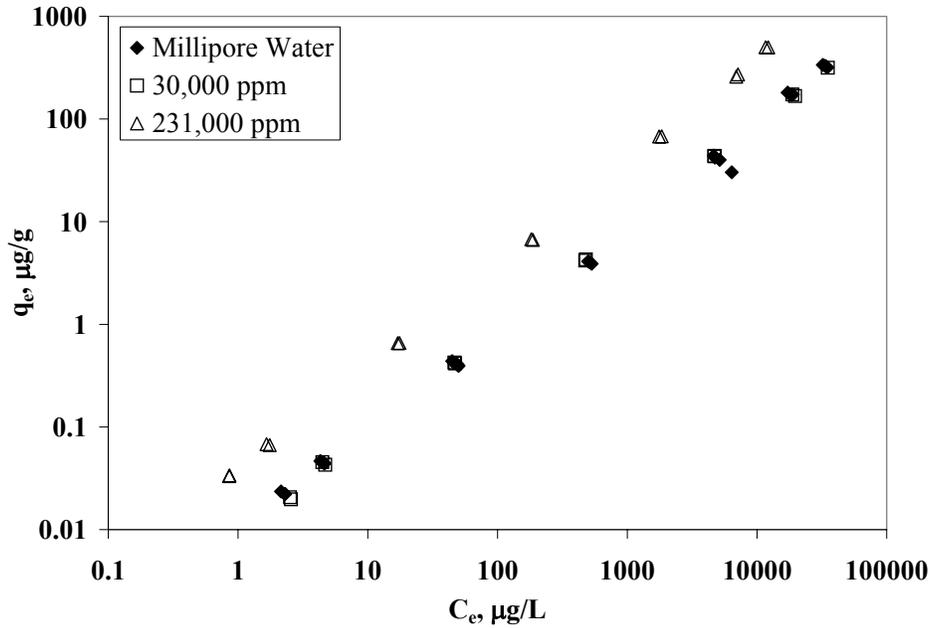


Figure 5.8 Benzene Sorption Isotherms at Differing Solution Salinities

Table 5.14 Distribution Coefficients for Benzene Isotherms in Ultrapure and Saline Water

Salinity (ppm)	R ²	K _d (L/g SMZ)	95% Confidence Limits on K _d
ultrapure (previously)	0.9941	0.00947	0.00934, 0.00960
ultrapure (saline study)	0.9997	0.0105	0.0103, 0.0107
30,000	0.9991	0.00895	0.00887, 0.00903
231,000	0.9966	0.0407	0.0402, 0.0412

Comparisons between the isotherm generated in a 30,000 ppm salt solution suggested that the distribution coefficient in the saline solution was slightly lower than the value determined from experiments in ultrapure water; however, only one of the ultrapure K_d values was statistically different than the 30,000 ppm K_d value. In contrast, hypothesis testing showed that the isotherm generated for benzene in a 231,000 ppm salt solution had a significantly greater slope than the two ultrapure isotherms and the 30,000 ppm salt solution isotherm.

Table 5.15 Results for Hypothesis Testing of Isotherms Generated in Single-Solute (Benzene) Studies in Ultrapure Water and Salt Solutions

Isotherms Being Compared	T-Value	Validity of Null Hypothesis for Equal Slopes between Ultrapure and Saline Water Isotherms
ultrapure (previous), ultrapure	-2.93	Valid
ultrapure (previous), 30,000 ppm	2.36	Valid
ultrapure, 30,000 ppm	11.67	Invalid
ultrapure (previously), 231,000 ppm	-53.3	Invalid
ultrapure, 231,000 ppm	-40.1	Invalid
30,000 ppm, 231,000 ppm	-63.0	Invalid

5.2.3.2 Multi-Solute BTEX Sorption onto SMZ in Salt Solutions

As in the studies conducted in ultrapure water, the effects of multiple organic solutes on sorption were investigated through multi-solute batch tests. Because all of the BTEX compounds and three different salt solutions were tested, a great deal of data were generated. Representative data are presented in this chapter, but most are included in Appendix B. The test results for benzene and toluene are shown in Figures 5.9 and 5.10. The basic patterns found in the data for these two chemicals were representative of the remaining BTEX compounds. This batch test was conducted with duplicates rather than triplicates because of the space constraint for the headspace autosampler. However, as seen in Figures 5.9 and 5.10, data from replicates were close to one another for both benzene and toluene. Similar results were also observed for the remaining BTEX compounds.

Although graphical results for ethylbenzene and the xylenes are not shown here, the correlation coefficients, distribution coefficients, and 95% confidence limits on K_d values for all of the BTEX compounds in 30,000 ppm and 100,000 ppm salt solutions are included in Table 5.16. Graphs of the isotherms for the remaining BTEX compounds in these same salt solutions and the data used to generate those isotherms are included in Appendix B. Because of the losses mentioned in Chapter 4, the data gathered for the 200,000 ppm salt solution are presented only as points in Figures 5.9 and 5.10 as well as in Appendix B. However, Table 5.17 includes the distribution coefficients calculated for each duplicate at this salt concentration.

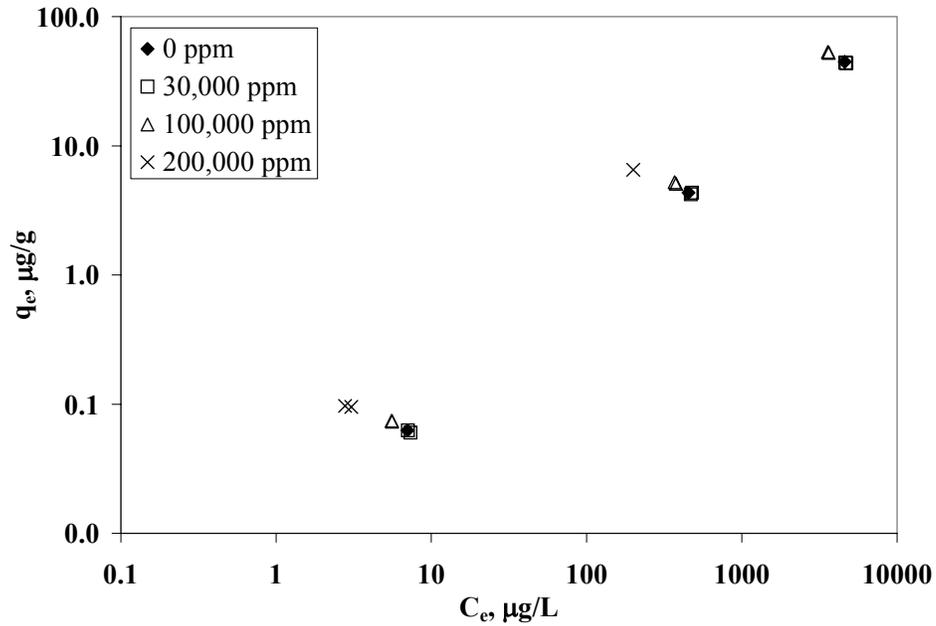


Figure 5.9 Benzene Sorption Isotherms at Differing Solution Salinities and in the Presence of the Remaining BTEX Compounds

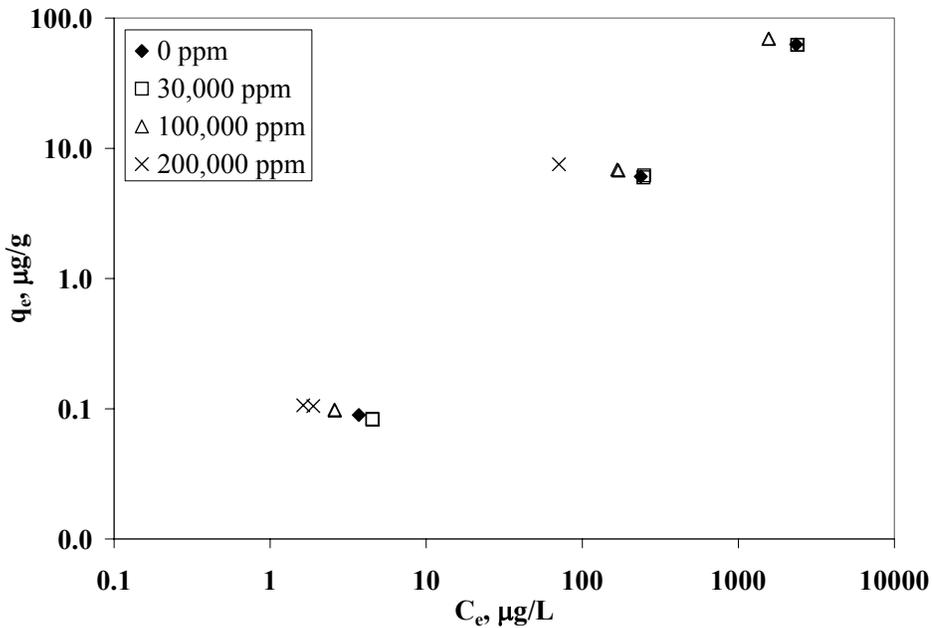


Figure 5.10 Toluene Sorption Isotherms at Differing Solution Salinities and in the Presence of the Remaining BTEX Compounds

Table 5.16 Distribution Coefficients for BTEX Sorption Isotherms in Ultrapure and Saline Background Water

Compound	Salinity (ppm)	R ²	K _d (L/g SMZ)	95% Confidence Limits on K _d
Benzene	ultrapure	1.000	0.00970	0.00968, 0.00972
	30,000	0.9997	0.00934	0.00929, 0.00939
	100,000	0.9997	0.0146	0.0145, 0.0147
Toluene	ultrapure	0.9998	0.0267	0.0266, 0.0268
	30,000	0.9998	0.0261	0.02607, 0.02613
	100,000	0.9997	0.0444	0.0442, 0.0446
Ethylbenzene	ultrapure	0.9998	0.0659	0.0655, 0.0663
	30,000	0.9996	0.0676	0.06759, 0.06761
	100,000	0.9996	0.124	0.1233, 0.1245
m- & p-Xylenes	ultrapure	0.9998	0.0735	0.0731, 0.0739
	30,000	0.9997	0.0762	0.07619, 0.07621
	100,000	0.9997	0.143	0.1420, 0.1434
o-Xylene	ultrapure	0.9998	0.0642	0.0638, 0.0646
	30,000	0.9995	0.0658	0.06578, 0.06582
	100,000	0.9997	0.119	0.1180, 0.1190

Table 5.17 Distribution Coefficients Calculated for Individual Data Points in 200,000 ppm Salt Solution

Initial BTEX Concentration (mg/L)	Benzene	Toluene	Ethylbenzene	m- & p-Xylenes	o-Xylene
0.015	0.0349	0.0653	ND	ND	ND
0.015	0.0312	0.0554	ND	ND	ND
1	0.0326	0.107	0.331	0.385	0.318

Note: ND – not detected

Because of the affinities of ethylbenzene and the xylenes for SMZ, the final concentrations of these compounds were below detection limits for the gas chromatograph. As a result, distribution coefficients could not be calculated for these compounds at the initial concentration of 0.015 mg/L. In addition, the duplicate values for the sample containing an initial BTEX concentration of 1 mg/L could not be presented in Table 5.17 because one of the duplicates broke during centrifugation. However, the values that were obtained for the distribution coefficients do yield some interesting information. The values for benzene are relatively close and can probably be used to generate an isotherm. Distribution coefficients for toluene did not correspond well between the lower and higher initial concentrations. Hence, these values probably do not accurately describe an isotherm at 200,000 ppm salinity. The magnitude of the values for ethylbenzene and the xylenes is substantially greater than K_d values for benzene or toluene. This is in keeping with the trend apparent throughout the other batch tests. These compounds have greater affinity for the hydrophobic phase and therefore, they are removed more effectively by SMZ. In addition, all of the values presented in Table 5.17 are greater than the distribution coefficients in solutions of lower salinity. Hence, a general conclusion that can be made about these data is that the 200,000 ppm salt solution creates an environment that allows the BTEX compounds to more easily leave the aqueous phase for the more hydrophobic phase in SMZ.

Figure 5.11 shows the increase in distribution coefficient with increasing salinity. Again, no statistically significant increase was found between the K_d values in ultrapure water and 30,000 ppm, but large increases were found for the 100,000 ppm salt concentration. This trend is more apparent for the least soluble of the BTEX compounds than for benzene or toluene, but Table 5.16 shows that the K_d values for these compounds also show increases at the higher salinities.

Statistical analysis also verified the hypothesis that the presence of multiple organic solutes did not significantly alter the sorption of benzene at 30,000 ppm. The null hypothesis was that the distribution coefficients found in the saline single-solute benzene and multi-solute benzene were equal at similar salinities. This null hypothesis was tested by determining whether the distribution coefficients were statistically greater than, less than, or unequal to each other. By proving that none of these scenarios hold for the isotherms being compared, it can be said that the null hypothesis is valid and that the distribution coefficients for each isotherm are statistically equal.

Comparisons were also made between the distribution coefficients found in the previous ultrapure water multi-solute study and those determined at the various salinities and in ultrapure water used in the controls for the present multi-solute study. Table 5.18 summarizes the results from these hypothesis tests. The results for the Millipore water compared to the Millipore water during the saline study show the ability to replicate multi-solute isotherms in Millipore water. As shown in Table 5.18, the isotherms for all of the BTEX compounds were found to be statistically the same in both tests involving only Millipore water. The major conclusion to be drawn from these results is that the distribution coefficient increased for the higher salt concentration of 100,000 ppm. This result is supported by the data collected at 200,000 ppm and the single-solute benzene data collected at 231,000 ppm.

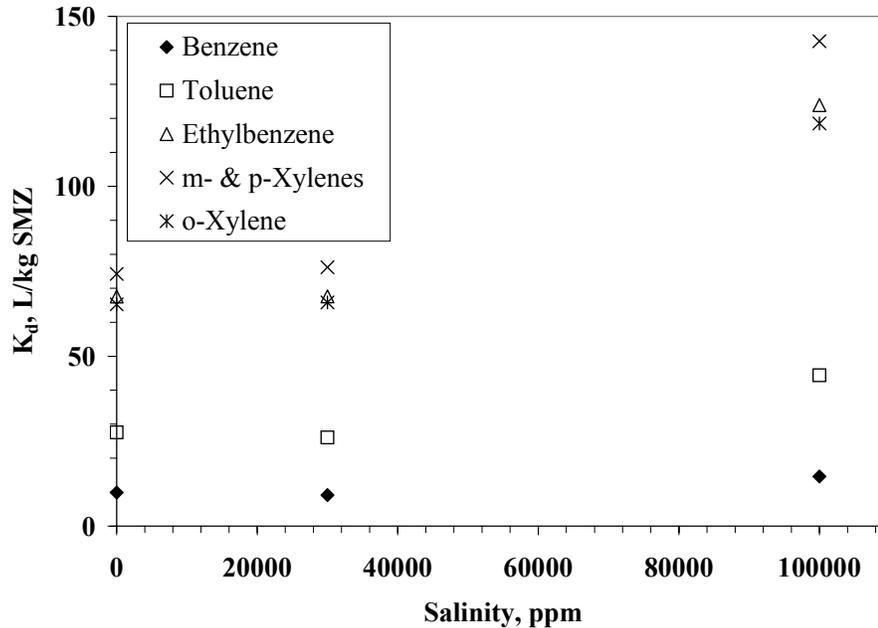


Figure 5.11 Distribution Coefficient as a Function of Salinity for BTEX Compounds Sorbed to SMZ

5.2.3.3 Predictive and Empirical Descriptions of BTEX Sorption in Saline Water

The ability to predict how sorption will change in the presence of various salinities would prove valuable for industries that generate saline waste streams that vary in salinity with time or temperature. Hence, Equations 5.4 and 5.5 were used to determine whether observed distribution coefficients could be accurately predicted for benzene and toluene. Other BTEX compounds were not addressed in this analysis because salting coefficients were found only for NaCl solutions containing benzene ($K^s = 0.196$) and toluene ($K^s = 0.240$) (Schwarzenbach *et al.*, 1993; Peng and Wan, 1998).

Combining Equations 4.4 and 4.5 yields the following equation (Schwarzenbach *et al.*, 1993):

$$\log K_{om,salt} = \log K_{om} + aK^s[salt] \quad (5.6)$$

where $K_{om,salt}$ is the partitioning coefficient for organic matter in the presence of salt, a is 0.93 for aromatic hydrocarbons, and the other variables were previously defined (Schwarzenbach *et al.*, 1993). Values for K_{om} were calculated with Equation 5.2 where K_d values were averages of the values found for the batch studies conducted in ultrapure water and f_{om} was 0.051 for SMZ. Because NaCl was the primary salt used to generate saline solutions, salting coefficients for the other salts were not used in the analysis (Schwarzenbach *et al.*, 1993). The molar NaCl concentrations were determined for each of the single-solute and multi-solute saline solutions, and Equation 5.6 was used to determine $K_{om,salt}$. This value was then converted back into $K_{d,salt}$ with Equation 5.2. Results from this analysis for benzene and toluene are presented in Table 5.19.

Table 5.18 Statistical Comparison Between Multi-Solute Studies Conducted in Ultrapure Water and Saline Solutions

Compound	Salinity (ppm)	T-Value	Result for Null Hypothesis	Description of Result
Benzene	Ultrapure	0.897	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	30,000	5.24	Invalid	$K_d \text{ Millipore} > K_d \text{ Salt}$
	100,000	-28.0	Invalid	$K_d \text{ Millipore} < K_d \text{ Salt}$
Toluene	Ultrapure	3.51	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	30,000	7.80	Invalid	$K_d \text{ Millipore} > K_d \text{ Salt}$
	100,000	-70.2	Invalid	$K_d \text{ Millipore} < K_d \text{ Salt}$
Ethylbenzene	Ultrapure	6.90	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	30,000	2.42	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	100,000	-61.6	Invalid	$K_d \text{ Millipore} < K_d \text{ Salt}$
m- & p-Xylenes	Ultrapure	2.79	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	30,000	-2.00	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	100,000	.71.7	Invalid	$K_d \text{ Millipore} < K_d \text{ Salt}$
o-Xylene	Ultrapure	4.00	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	30,000	0.887	Valid	$K_d \text{ Millipore} = K_d \text{ Salt}$
	100,000	-22.6	Invalid	$K_d \text{ Millipore} < K_d \text{ Salt}$

Table 5.19 Comparison of Observed and Predicted Distribution Coefficients for Benzene and Toluene in Saline Solutions

Salinity (ppm)	Benzene		Toluene	
	Predicted K_d (L/kg)	Observed K_d (L/kg)	Predicted K_d (L/kg)	Observed K_d (L/kg)
30,000	11.75	9.92 ^a	36.2	26.1
100,000	21.4	14.6	75.4	44.4
231,000	102	40.7	-	-

^a Value was averaged between single-solute and multi-solute tests at 30,000 ppm.

Because the observed and predicted K_d values did not agree for this comparison, another comparison was performed between the observed values for K_d and values that are predicted by:

$$\log K_{d,salt} = \log K_{d,Millipore} + 0.7535K^s[salt]_{total} \quad (5.7)$$

where $K_{d,salt}$ is the predicted value for the distribution coefficient in saline solutions and $K_{d,Millipore}$ is the observed distribution coefficient in Millipore water. This equation was generated by combining Equation 5.4 and the regression relating K_d to S found in this study. Results for this comparison are shown in Figures 5.12 and 5.13. Figure 5.12 includes predicted and observed values for the distribution coefficient for benzene while Figure 5.13 includes these values for toluene.

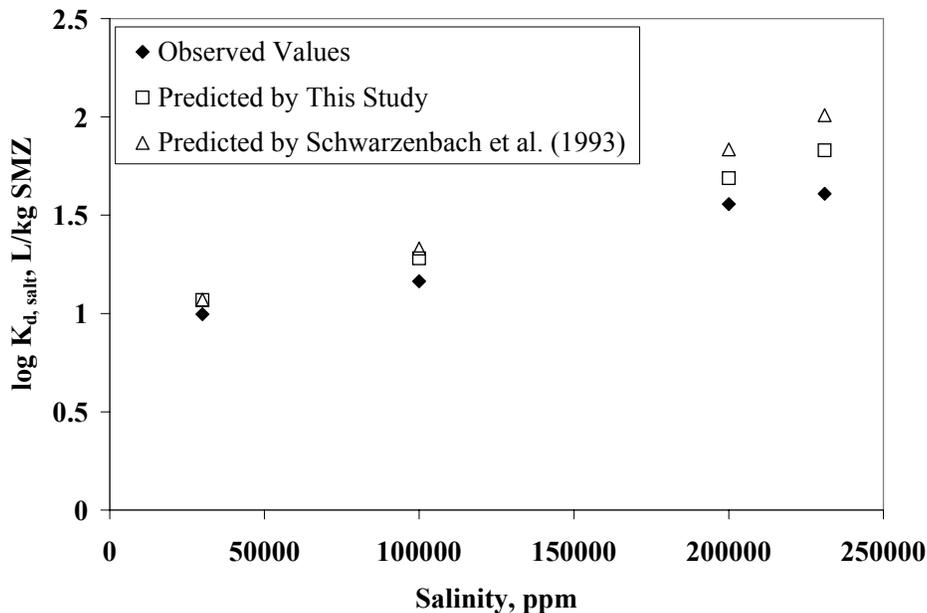


Figure 5.12 Observed and Predicted Distribution Coefficient Values for Benzene in Multi-Solute Saline Solutions

The values observed for benzene distribution coefficients in the 200,000 ppm salt solution were averaged and are included in Figure 5.12. Although the toluene distribution coefficient values at this salinity were not similar for various BTEX concentrations, the value found for 1 mg/L BTEX was used strictly for comparative purposes in Figure 5.13.

As shown in Figures 5.12 and 5.13, Equation 5.7 did not accurately predict the observed K_d values. However, values predicted by Equation 5.7 were closer to observed distribution coefficients than those predicted by Equation 5.6. Hence, if rough estimates of distribution coefficients are required, Equation 5.7 may predict these values to within an order of magnitude. Nevertheless, accurate predictions of K_d cannot be made with Equation 5.7.

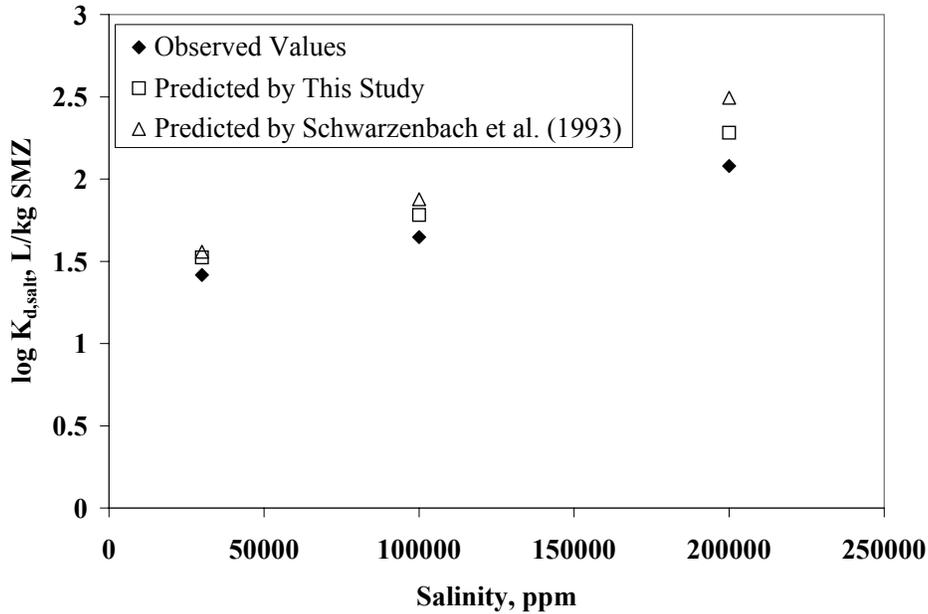


Figure 5.13 Observed and Predicted Distribution Coefficient Values for Toluene in Multi-Solute Saline Solutions

Also demonstrated in Figures 5.13 and 5.14 is that as salinity increases, the differences between predicted and observed values also increase for both the correlation developed during this study and the correlation developed by Schwarzenbach *et al.* (1993).

As a final step empirical relationships were developed to describe the variations in observed K_d values and salt concentrations for all of the BTEX compounds. These regressions all took the basic form:

$$\log K_{d,salt,observed} = a[salt]_M + b \quad (5.8)$$

where $K_{d,salt,observed}$ represents observed distribution coefficients, $[salt]_M$ is the total molar salt concentration, a is the empirically determined salting coefficient (K^s) multiplied by the magnitude of the slope of the $\log K_d$ - $\log S$ regression (Figure 5.4), and b is the logarithm of the distribution coefficient in pure water. The data used for these regressions are shown in Figure 5.14 and the calculated values for R^2 , a , b , and K^s are included in Table 5.20.

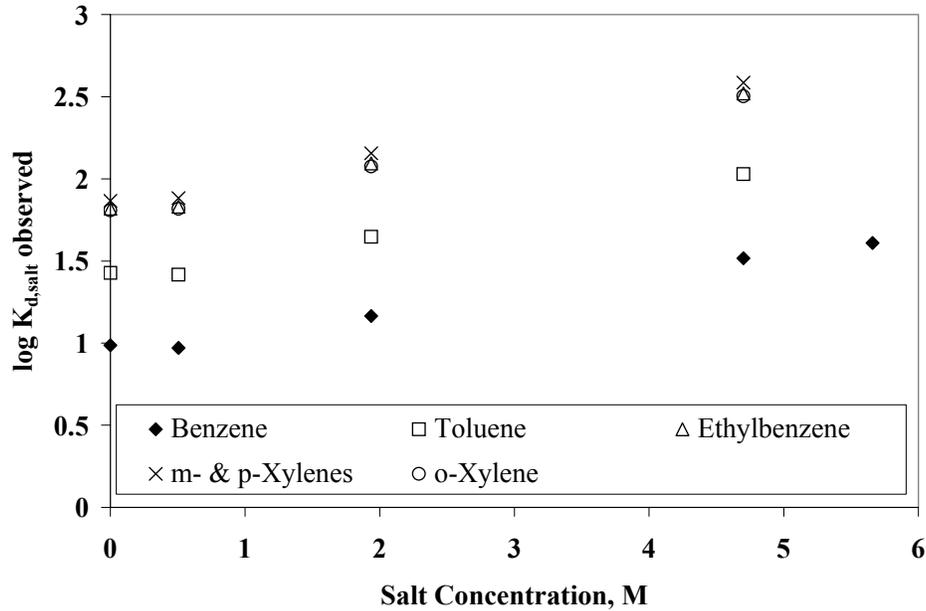


Figure 5.14 Data Used in $\log K_{d,salt} - [\text{salt}]_M$ Regressions

Table 5.20 Regression Parameters for $\log K_{d,salt} - [\text{salt}]_M$ Empirical Relationships

Compound	R ²	a (M ⁻¹)	b	K ^s (M ⁻¹)
Benzene	0.9907	0.118	0.948	0.156
Toluene	0.9874	0.135	1.39	0.179
Ethylbenzene	0.9928	0.155	1.79	0.206
m- & p-Xylenes	0.9935	0.159	1.83	0.211
o-Xylene	0.9928	0.154	1.78	0.204

The goodness of fit of these regressions is represented by the R² values in Table 5.17. These values are sufficient to estimate distribution coefficients for BTEX sorption onto SMZ in solutions of various salinities. Hence, the regressions can be used to quickly estimate the salt concentration required to reduce initial BTEX concentrations in solution to allowable effluent concentrations. Analysis of the salting coefficients calculated through these regressions shows that the values for benzene and toluene compare relatively well to values found in literature, 0.196 and 0.240, respectively (Schwarzenbach *et al.*, 1993; Peng and Wan, 1998).

5.2.3.4 Conclusions for Sorption of BTEX in Saline Solutions

As in the batch tests for the single-solute and multi-solute tests conducted in ultrapure water, there were no significant competitive sorption effects between the BTEX compounds in the saline solutions. Increases in K_d values for the BTEX compounds with increasing salinity were apparent for 100,000 ppm and higher salt concentrations, but could not be statistically proven for salt solutions of 30,000 ppm. Distribution coefficients for the compounds that initially had the lowest aqueous solubilities showed the most obvious increases, but sorption of benzene and toluene was also substantially enhanced by the presence of high concentrations of salt.

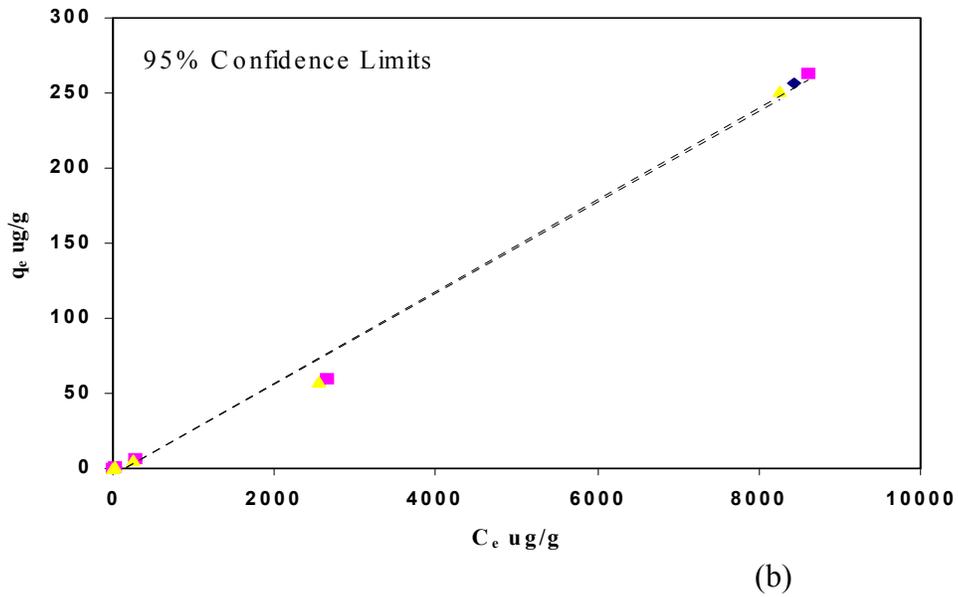
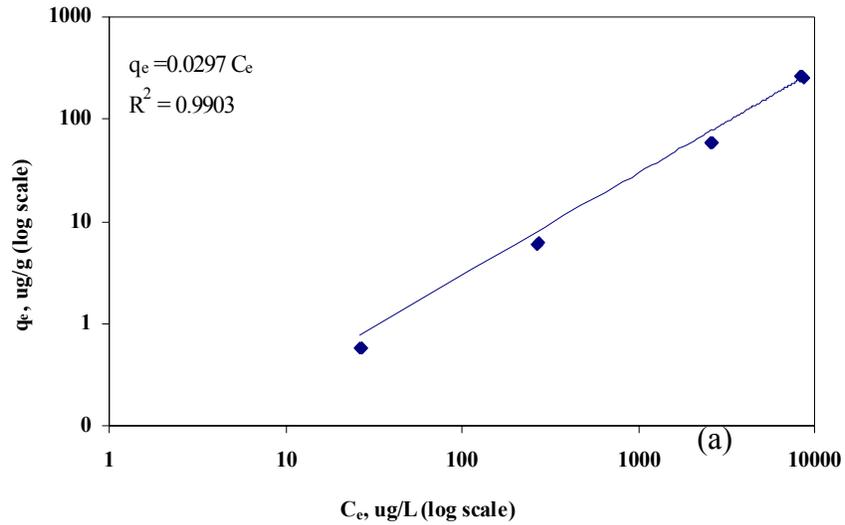
The prediction of K_d values through Equations 5.2 to 5.7 showed that these predictions were significantly greater than observed values. As a result, empirically based regressions having the same form as the prediction equations were developed. Regressions performed using observed distribution coefficients and known salt concentrations for the BTEX compounds in saline solutions yielded correlations which could be used for estimating distribution coefficients during SMZ treatment system design.

5.2.4 Effect of Temperature on BTEX Sorption to SMZ

Temperature has been recognized as an important factor to define the sorption characteristics of different solutes and sorbents. Schwarzenbach *et al.* (1993) stated that the temperature effect on the change of organic phase activity coefficients was negligible for NOM in soil, and the aqueous phase activity coefficients would be the sole factor affecting sorption enthalpy for hydrophobic and moderately hydrophobic solutes. He also stated that below 15°C the solubility of benzene decreases with increasing temperature and above 20°C the solubility of benzene increases with increasing temperature. Bohon and Claussen (1951) also found that benzene, toluene, ethylbenzene and m,p-xylene exhibited a solubility minimum near 18°C. As a result, it was initially assumed that the distribution coefficients for BTEX sorption onto SMZ would reach a maximum around 15-20°C. However, Dewulf *et al.* (1999) observed increasing sorption capacity with increasing temperature (2-25°C) in their study on sorption of BTEX to a Belgian riverine sediment. Due to the difference between SMZ and sediment and the limited temperature range considered by Dewulf and co-workers, examination of the impact of temperature was warranted in this study. The temperature range of 4-36°C was chosen in order to encompass the minimum solubility temperatures for BTEX and the environmental temperature range found in many field scale applications.

The initial concentration of BTEX used in the batch isotherm studies included 0, 100, 1000, 10000, and 40000 µg/L. Sorption was evaluated on 14x40 mesh size SMZ. Distribution coefficients (K_d) were calculated for all of the isotherms using the LINEST linear regression function in Microsoft Excel. The linear isotherm model presented in equation 5.1 was employed. As shown in Figure 5.15 for toluene, sorption was linear through a wide range of concentrations. This result held true for all of the BTEX compounds at all temperatures. Based on the values of the distribution coefficients (shown in Table 5.21), a much greater affinity of ethylbenzene and xylenes for SMZ was observed compared to toluene and benzene for all temperatures tested. These results are

consistent with the results of the experiments conducted for the ionic strength and multi-solute studies.



**Figure 5.15 Sorption Isotherm for Toluene on SMZ in Ultrapure Water at 20oC–
 (a) Linear scale showing data and regression equation (b) Logarithmic scale
 showing data and 95% confidence limits on the regression line.**

Table 5.21 Linear Isotherm Parameters for BTEX Multi-Solute Sorption to SMZ in ultrapure Water at Different Temperatures

Compound	Temp. (K)	R²	Kd (L/g SMZ)
Benzene	277.15	0.9899	0.0085
	283.15	0.9899	0.0094
	288.15	0.9924	0.0094
	293.15	0.9886	0.0109
	298.15	0.9931	0.0117
	309.15	0.995	0.012
Toluene	277.15	0.9883	0.0219
	283.15	0.9892	0.025
	288.15	0.9909	0.0263
	293.15	0.9903	0.0297
	298.15	0.9941	0.0319
	309.15	0.996	0.0329
Ethylbenzene	277.15	0.9829	0.0534
	283.15	0.9851	0.0628
	288.15	0.988	0.0671
	293.15	0.9896	0.0742
	298.15	0.9933	0.0794
	309.15	0.9946	0.0842
m,p-Xylene	277.15	0.9846	0.0601
	283.15	0.9869	0.0699
	288.15	0.9881	0.0755
	293.15	0.9895	0.0829
	298.15	0.9934	0.0886
	309.15	0.9957	0.0915
o-Xylene	277.15	0.9838	0.0549
	283.15	0.9856	0.0634
	288.15	0.9883	0.0665
	293.15	0.9887	0.0736
	298.15	0.9932	0.0786
	309.15	0.9951	0.0813

Note: The SMZ mesh size used in all experiments was 14×40

5.2.4.1 Comparison of Sorption Enthalpy Change with Published Data

One of the goals of this project was to provide a means to predict sorption capacity as a function of temperature. The effect of temperature on equilibrium constants is generally described using the van't Hoff equation:

$$\frac{d \ln K_d}{dT} = \frac{\Delta H_s^{net}}{R * T^2} \quad (\text{Vemulapalli, 1993}) \quad (5.9)$$

where ΔH_s^{net} represents the net sorption enthalpy (J/mol), T is the temperature in (°K), and R is the ideal gas constant (8.314 J/mol-°K). The higher the sorption enthalpy (ΔH_s^{net}), the greater effect of temperature on sorption capacity.

Based on the assumption that the change of enthalpy is constant over the considered temperature range, equation 5.9 can be integrated to yield a linear relationship between $\ln K_d$ and $1/T$,

$$\ln K_d = -\frac{\Delta H_s^{net}}{R * T} + const. \quad (5.10)$$

Data presented in Table 5.21 were used to determine the value of ΔH_s^{net} for SMZ sorption of each of the BTEX compounds. In order to calculate the sorption enthalpies for BTEX sorption to SMZ, $\ln K_d$ values were plotted vs. $1/T$ (van't Hoff plots) and the data was linearly regressed. These plots are presented in Figures 5.16 and 5.17. From Figures 5.16 and Figure 5.17 it can be seen that K_d increases with increasing temperature for each BTEX compound sorbed onto SMZ within the temperature range of 4-36°C. This finding is consistent with results for BTEX sorption onto sediment by Dewulf *et al.* (1999). Sorption enthalpies were obtained from the slopes of the regression equations using Equation 5.10. The enthalpy values are presented in Table 5.22 along with the 95% confidence limits for the enthalpy and correlation coefficients for the data. As shown in Table 5.22, all of the values of enthalpy are positive and relatively similar. A positive value of enthalpy suggests that it requires energy to extract BTEX from the aqueous phase and dissolve it into the organic carbon associated with the surfactant sorbed to the zeolite.

Dewulf *et al.* (1999) obtained very similar sorption enthalpies for benzene, toluene, ethylbenzene, and o- & p-xylene (m-xylene was not studied) sorbed onto a riverine sediment as shown in Table 5.23. However the 95% confidence limits for their enthalpies were much larger and the correlation coefficients were much weaker.

It is generally expected that the value of the sorption enthalpy will change with both the solute and sorbent. As shown in Table 5.24, previous studies examining sorption of aromatic hydrocarbons support this expectation. The sorption enthalpy changes with different sorbates for a specific sorbent. Note that in most of these studies, the enthalpy values for these contaminants were negative indicating that sorption will increase with decreasing temperature.

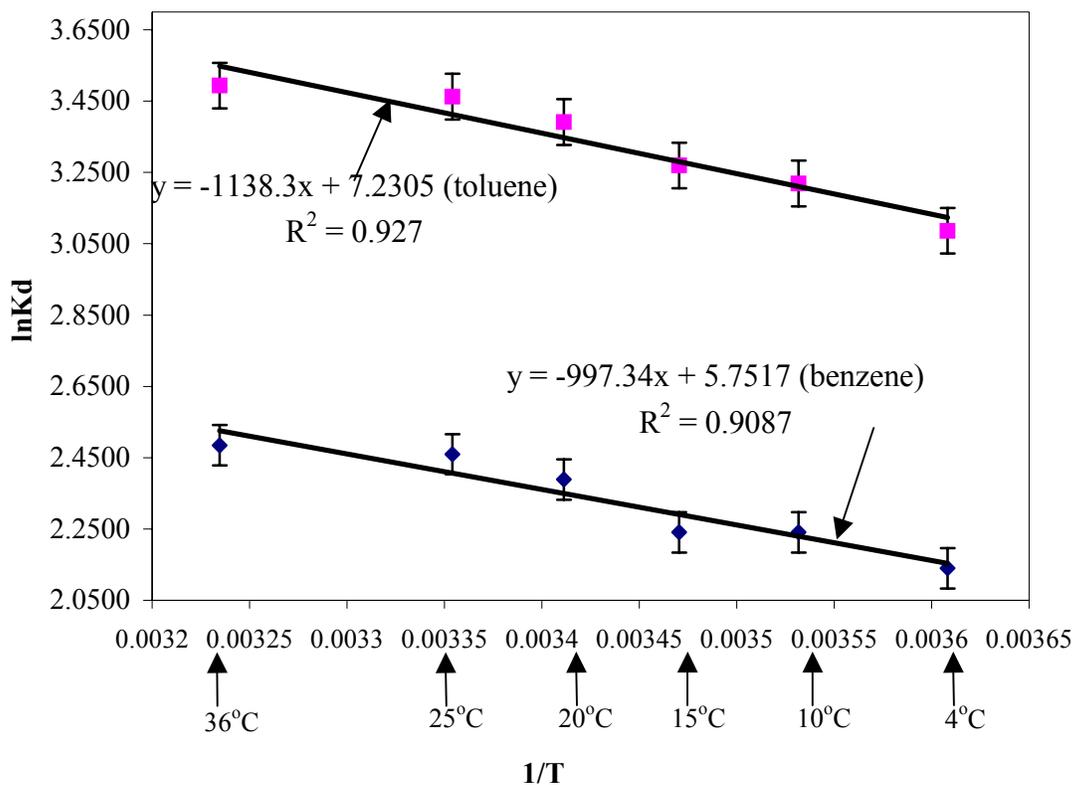


Figure 5.16 Van't Hoff Plots of SMZ Equilibrium Partitioning for Benzene and Toluene. Solid lines are regression lines. Bars indicate standard error bars.

Table 5.22 Sorption Enthalpies (ΔH_s^{net}) for Sorption of BTEX Compounds onto SMZ in Ultrapure Water

Compounds	ΔH_s^{net} (kJ/mol)	R^2
Benzene	8.26 (8.15, 8.37)	0.9087
Toluene	9.46 (9.33, 9.59)	0.927
Ethylbenzene	10.17 (10.04, 10.3)	0.9404
m&p-Xylene	8.9 (8.77, 9.03)	0.9153
o-Xylene	9.53 (9.41, 9.65)	0.9248

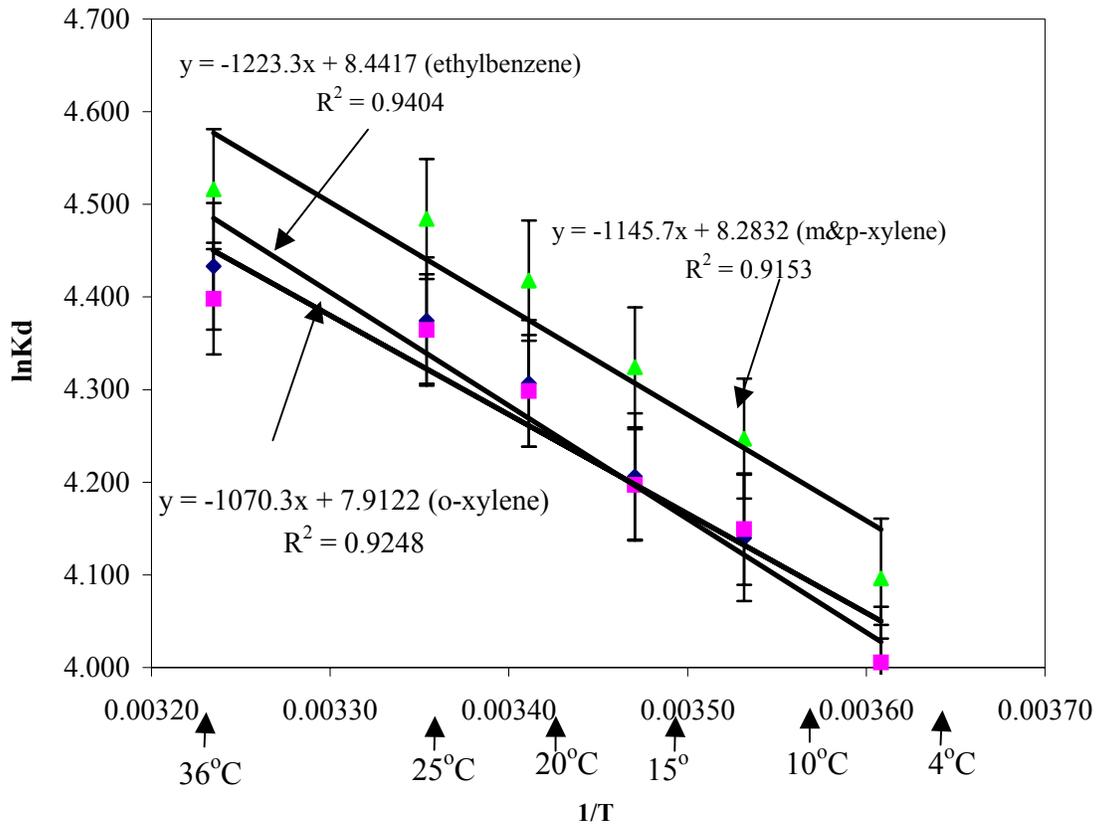


Figure 5.17 Van't Hoff Plots of SMZ Equilibrium Partitioning for Ethylbenzene, m, p-Xylene, and o-Xylene. Solid Lines are Regression Lines. Bars Indicate Standard Errors.

Table 5.23 Sorption Enthalpies for Sorption of BTEX Compounds onto Sediment (Dewulf et al.1999)

Compounds	ΔH_s^{net} (kJ/mol)	R^2
Benzene	3.5 (0.0, 6.9)	0.75
Toluene	4.4 (-4.9, 13.7)	0.48
Ethylbenzene	10.8 (-6.4, 27.9)	0.59
p-Xylene	12.8 (-5.4, 31)	0.63
o-Xylene	11.5 (-9.2, 32.2)	0.54

Table 5.24 Results from Previous Studies Examining the Influence of Temperature on Sorption Equilibrium

Compound	ΔH_s^{net} (kJ/mol)	Temperature range (°C)	Type of adsorbent ¹	Ref. ²
Naphthalene	-6.2 ± 3.1	6.5-37	Silt loam, 1% oc	1
Fluoranthene	-18.3	16-45	Sediment, 5.1% oc	2
Benzo[b]fluoranthene	-36.24	16-45	Sediment, 5.1% oc	2
Benzo[k]fluoranthene	-25.6	16-45	Sediment, 5.1% oc	2
Benzo[a]pyrene	-31.28	16-45	Sediment 5.1% oc	2
Benzo[ghi]perylene	-40.6	16-45	Sediment 5.1% oc	2
1,4-dichlorobenzene	-12 to -16	3-48	Phenyl-modified silica, 1.6% oc	3
1,2,4-trichlorobenzene	-13 to 17	3-48, 5-20	Phenyl-modified silica, 1.6% oc	3

¹oc = % organic carbon; om = % organic matter (= 1.7 oc)

²References: 1 = Wauchope *et al.* (1983); 2 = F. Lüers and Th. E. M. ten Hulscher (1996); 3 = Szecsody and Bales (1991)

5.2.4.2 Hypothesized Mechanism of Sorption

Not only can knowledge of the enthalpy be used to predict sorption distribution coefficients, but the impact of temperature on sorption capacity can also give insight into the sorption mechanism. The mechanism of BTEX sorption onto SMZ has been attributed to a partitioning of the organic contaminant into the organic “layer” on the solid surface (Chiou, 1989). The organic contaminant is more soluble in the organic surfactant layer than it is in the aqueous phase. Chiou *et al.* (1979) asserted that sorption enthalpy may be used to differentiate between adsorption processes and a partitioning mechanism. Adsorption refers to condensation of solutes (referred to as adsorbates) on surfaces or interior pores of a solid (adsorbent) by physical or chemical bonding forces. Partitioning refers to the organic chemical permeating into an organic medium by forces common to solution (e. g., by van der Waals forces). Chiou (1979) states that adsorption is generally exothermic in nature, while partitioning is thought to be only weakly exothermic or even endothermic. This supposition suggests that sorption enthalpies of organic solutes to soil organic matter (SOM) may be positive as shown in this study. Borisover *et al.* (1998) argued that when sorption enthalpies of organic solutes to SOM are more positive than the corresponding dissolution enthalpies from water, the sorption process can be considered as partitioning of those solutes into SOM.

To examine these contentions, it is necessary to understand the factors contributing to the net sorption enthalpy. The net enthalpy change for sorption (ΔH_s^{net}) of a compound to the organic matter in SMZ or any other soil organic matter is the result of two processes (Dewulf *et al.* 1999). According to Dewulf, the first step in the sorption process is to extract the solute (BTEX) from the aqueous phase. This is a reversible process and the reverse of this extraction process is commonly referred to as the excess enthalpy of solution (ΔH_{aq}). The second step in the sorption process is the dissolution of BTEX into organic matter associated with the SMZ (ΔH_{oc}). So ΔH_s^{net} can be expressed as:

$$\Delta H_s^{net} = \Delta H_{oc} - \Delta H_{aq} \quad (5.11)$$

where,

ΔH_{oc} : the change of enthalpy associated with dissolution of the solute into the organic phase (J/mol), and,

ΔH_{aq} : the change of enthalpy associated with dissolution of the solute into the aqueous phase (J/mol).

Distribution coefficients (K_d 's) determined from sorption experiments conducted at different temperatures can be used to determine the value of ΔH_s^{net} for a particular sorbate/sorbent system. As stated before, the net sorption enthalpy ΔH_s^{net} is a combination of ΔH_{oc} and ΔH_{aq} .

The temperature dependence of both components may influence the net sorption enthalpy. ΔH_{aq} can be calculated from

$$\ln \gamma_w = \frac{\Delta H_{aq}}{R * T} + const. \quad (5.12)$$

where γ_w is the (dimensionless) aqueous activity coefficient of the solute and can be calculated from,

$$\gamma_w = \frac{H''}{P_i} \quad (\text{Stumm and Morgan, 1981}) \quad (5.13)$$

$$H'' = \frac{H * R * T}{18 * 10^{-6}} * \exp\left(\frac{a}{T} + b\right) \quad (5.14)$$

$$P_i = \exp\left(\frac{c}{T} + d\right) \quad (5.15)$$

and where,

H is the dimensionless Henry's law coefficient,

H'' is the Henry's law coefficient (Pa/mole),

P_i is the saturated vapor pressure (Pa),

a, b are coefficients for calculation of Henry's law constant H'' , and

c, d are coefficients for calculation of vapor pressure.

The coefficients a, b, c and d are solute specific and have been determined by Dewulf *et al.* (1999) for BTEX as shown in Table 5.25. The activity coefficients γ_w were calculated using equation 5.13, 5.14 and 5.15 for temperatures of 4°C, 10°C, 15°C, 20°C, 25°C, and 36°C as shown in Table 5.26. The calculated values of γ_w were used to

estimate aqueous enthalpy values (ΔH_{aq}) for each of the BTEX compounds using linear regression of a plot of $\ln \gamma_w$ vs. $1/T$ and equation 5.12. These enthalpy values are also presented in Table 5.26 along with the correlation coefficient obtained from the regression analysis. The regressions provide good correlations even though the coefficients a and b were only determined for a temperature range of 2-25°C by Dewulf *et al.* (1995). The enthalpies ΔH_{aq} are positive values for all BTEX compounds. According to Dewulf *et al.* 1999, the enthalpies (ΔH_{aq}) account for the temperature dependence of both the aqueous solubility and vapor pressure.

Table 5.25 Values of Coefficients a, b, c and d for Calculation of Aqueous Activity Coefficients (Dewulf *et al.* 1999)

Compounds	a	b	c	d
Benzene	-3640	10.577	-4693	25.017
Toluene	-4064	12.150	-4567	23.495
Ethylbenzene	-4567	14.001	-4902	23.564
p-Xylene	-4479	13.597	-4939	23.596
o-Xylene	-4232	12.400	-5032	23.645

Table 5.26 Theoretical Aqueous Activities and Aqueous Enthalpy Values for BTEX Sorption

	Benzene	Toluene	Ethylbenzene	p-Xylene	o-Xylene
γ_w at 277.15°K	3063	9298	30133	30589	30026
γ_w at 283.15°K	2887	9141	30007	30171	28837
γ_w at 288.15°K	2754	9020	29916	29850	27942
γ_w at 293.15°K	2633	8907	29838	29953	27112
γ_w at 298.15°K	2521	8802	29770	29276	26341
γ_w at 309.15°K	2305	8595	29659	28735	24826
Calculated ΔH_{aq} (kJ/mol)	6.32±0.08	1.75±0.22	0.35±0.005	1.39±0.017	4.22±0.054
R ²	1	0.9994	0.9853	0.9999	0.999

From the values of ΔH_{aq} and ΔH_s^{net} , the enthalpy of dissolution of the compounds into the SMZ (organic carbon) ΔH_{oc} can be calculated using equation 5.11. In addition, 95% confidence intervals for ΔH_{oc} can be calculated via the standard deviations through the following relationship described by Dewulf *et al.* (1999),

$$[\text{SD}(\Delta H_{oc})]^2 = [\text{SD}(\Delta H_{aq})]^2 + [\text{SD}(\Delta H_s^{net})]^2 \quad (5.16)$$

where $\text{SD}(\Delta H_{oc})$, $\text{SD}(\Delta H_{aq})$, and $\text{SD}(\Delta H_s^{net})$ are the relative standard deviations of ΔH_{oc} , ΔH_{aq} , and ΔH_s^{net} respectively. ΔH_{oc} values obtained using equation 5.11 are presented in Table 5.27 with their 95% confidence limits. ΔH_{oc} values were positive for all BTEX compounds, which means it requires energy to dissolve BTEX into the organic carbon fraction of SMZ. The dissolution of BTEX into the organic matter of the solid phase (SMZ) requires more energy than extraction of BTEX out of aqueous phase ($|\Delta H_{oc}| > |-\Delta H_{aq}|$). The sorption process for all BTEX partitioning into SMZ is endothermic so that sorption is favored at higher temperature. Indeed, the results showed that the highest distribution coefficients were achieved at the temperature of 36°C within the range of 4-36°C. These results would suggest that a partitioning mechanism controls the sorption process.

Table 5.27 Calculated ΔH_{oc} Data with 95% Confidence Limits (kJ/mol) for Sorption of BTEX onto SMZ

Compounds	ΔH_{oc} (kJ/mol)
Benzene	14.58 (14.44, 14.72)
Toluene	11.21 (11.09, 11.34)
Ethylbenzene	10.52 (10.39, 10.66)
p-Xylene	10.29 (10.16, 10.42)
o-Xylene	13.74 (13.61, 13.87)

Chiou *et al.* (1979) concluded that the temperature dependence of K_d is related to the change in enthalpy of the dissolution of the solute in water, ΔH_{aq} , which is correlated to the temperature dependence of the solubility. Schwarzenbach *et al.* (1993) also argued that the enthalpy of dissolution (ΔH_{oc}) into natural organic matter (NOM) in soil should be quite small, and can be neglected. As shown in Table 5.27, values of ΔH_{oc} are not zero and there is a temperature impact on dissolution of BTEX into the organic phase. This contradicts Schwarzenbach and co-workers' (1993) hypothesis that there is no temperature impact on dissolution of BTEX into the organic phase. Furthermore, according to their hypothesis, the trend of the effects of temperature on K_d would follow the inverse of solubility trends. These trends are shown in Figure 5.16 for sorption data determined in this work and solubility data taken from the literature. As seen, for almost all of the BTEX compounds there is a minimum in solubility within the temperature range of the K_d data. If ΔH_{aq} was the only factor contributing to ΔH_s^{net} , these ΔH_s^{net} should follow the inverse trend of solubility. This trend was not apparent in our data or in Dewulf and coworker data (1999). If Schwarzenbach *et al.*'s (1993) hypothesis holds true, BTEX would have a maximum sorption capacity between 15 and 20°C and the plots of $\ln K_d$ vs. $1/T$ should not be linear as shown in Figure 5.16.

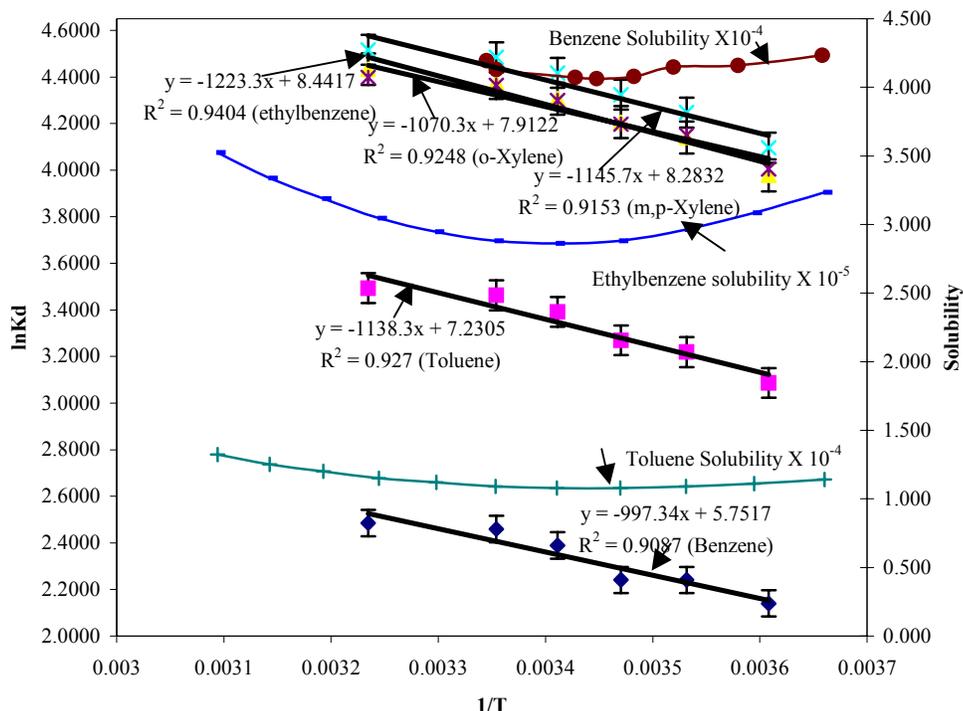


Figure 5.18 Comparison of BTEX sorption onto SMZ vs. BTEX solubility (Benzene solubility data are from May *et al.* (1983) and toluene and ethylbenzene solubility data are from Sawamura *et al.* 2001)

5.2.4.3 Conclusions Derived from the BTEX Sorption Temperature Study

The distribution coefficients found for all of the BTEX compounds sorbed onto SMZ increased with increasing temperatures from 4 °C to 36 °C. Regressions performed on the observed distribution coefficients for the BTEX compounds at all temperatures resulted in excellent correlations. Therefore, this relationship can be used to estimate distribution coefficients at field-scale. The sorption enthalpies were positive and ranged from 8.26 for benzene to 10.17 kJ/mol for ethylbenzene. The sorption process is endothermic which means the sorption capacities increase with increasing temperature. The magnitude of the change in the distribution coefficients as a function of temperature was smallest for benzene. Changes in the BTEX distribution coefficients as a function of temperature cannot be explained by examining the BTEX solubilities because ΔH_{oc} were not insignificant. A partitioning sorption mechanism was confirmed based on the sorption enthalpies.

5.2.5 Studies with Produced Water

Preliminary batch tests using produced water obtained by Crystal Solutions, LLC. from the Wamsutter, WY site holding tank suggested that a fraction of TDS, Barium and BTEX could be removed from solution using SMZ. Formal studies confirmed the BTEX results using produced water from the Wamsutter site with initial BTEX concentrations shown in Table 5.28. Produced water BTEX concentrations from the oil/water separation tank reported in Table 5.28 were determined at the University of Texas at Austin. Room temperature batch isotherms conducted using this produced water and 14x40 SMZ produced linear isotherms that followed the same trends as the ultrapure water isotherms.

Table 5.28 BTEX Concentrations in Produced Water from the Wamsutter, WY Site

Compound	Oil/Water Separation Tank (mg/L)
Benzene	15.4
Toluene	27.5
Ethylbenzene	1.4
m- & p-Xylene	9.0
o-Xylene	3.0

Note: These analyses were conducted at the University of Texas.

As shown in Figure 5.19, the isotherms remain linear for the isotherm range considered. Distribution coefficients for each isotherm are presented in Table 5.29.

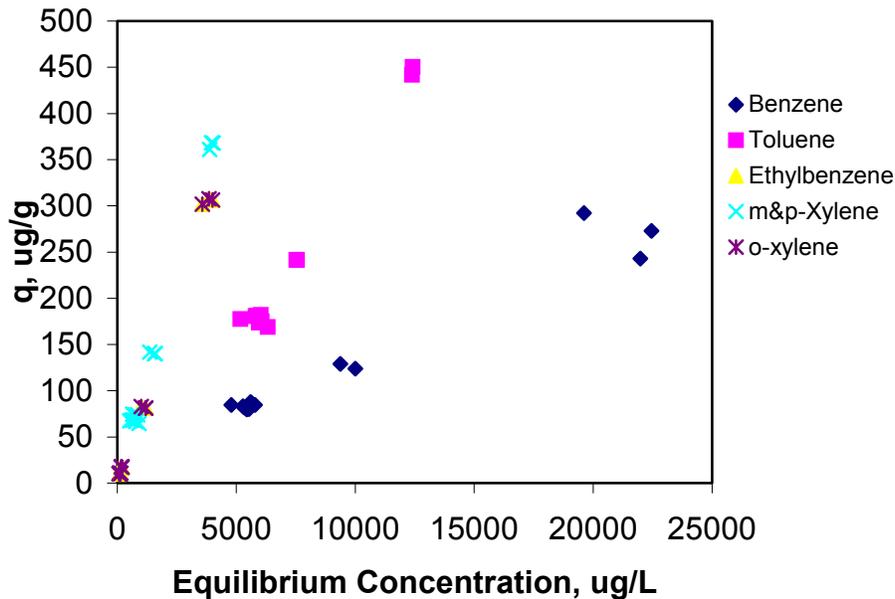


Figure 5.19 Sorption Isotherms for BTEX Compounds in a Produced Water Matrix

Table 5.29 Comparison of K_d values from Batch Isotherm Studies using Ultrapure and Produced Water Background using Hypothesis Testing

Compound	K_d (L/Kg SMZ) Ultrapure Water	R^2	K_d (L/Kg SMZ) Produced Water	R^2	T-Value	Result for Null Hypothesis
Benzene	10.9	0.988	13	0.93	2.20	Reject
Toluene	29.7	6	32.7	34	1.08	Retain
Ethylbenzene	74.2	0.990	79.4	0.93	1.82	Retain
m, p-Xylene	82.9	3	92.6	95	2.70	Reject
o-Xylene	73.6	0.989	77.4	0.99	1.34	Retain
		6		52		
		0.989		0.99		
		5		19		
		0.988		0.99		
		7		62		

Note: the experiments were conducted at 20°C.

The SMZ mesh size is 14×40.

The null hypothesis is that the distribution coefficients are equal.

Comparison of the K_d values from produced water and ultrapure water suggest that produced water increases BTEX sorption to SMZ. However, hypothesis testing for the null hypothesis that the K_d values are equal generated mixed results. The isotherms developed in produced water for benzene and m- & p- xylene were found to have greater slopes than the isotherms generated in ultrapure water. However, the null hypothesis was valid for the remaining BTEX compounds.

5.2.6 Batch Studies with Different Size SMZ Particles

Two particle sizes of SMZ were used in this research. Particles in the 14×40 mesh size range were used for field column studies. Particles in the 80×100 mesh size range were used in the lab scale column study. The K_d values for both mesh sizes were obtained from batch studies and the results are shown in Table 5.30.

Table 5.30 Comparison of K_d Values for Different Sizes of SMZ

Compounds	K_d (L/Kg) for 80×100 Mesh Size SMZ	K_d (L/Kg) for 14×40 Mesh Size SMZ
Benzene	5.7	9.7
Toluene	16.1	26.7
Ethylbenzene	40.9	65.9
m- & p- Xylene	46.5	73.5
o-Xylene	38.2	64.2

The 14×40 SMZ exhibited higher sorption capacities for all of the BTEX compounds compared to the 80×100 SMZ. While this result is not intuitive, it can be understood if the HDTMA loading onto each mesh size is compared. Results obtained from

measurements of the supernatant obtained during SMZ preparation indicate that more surfactant was adsorbed to the 14×40 mesh size SMZ. The loading rate of HDTMA was 180 mmol/kg for 14×40 SMZ compared to 157 mmol/kg for the 80×100 SMZ. The higher loading rate of HDTMA is likely responsible for the increase in sorption capacity for the larger particle size SMZ. Thus, particle size is less important than the amount of HDTMA sorbed.

5.3 Column Adsorption Studies

A lab scale column study was conducted to confirm the validity of K_d values for BTEX obtained in the batch studies and to evaluate whether mass transfer limitations were significant. This latter objective was addressed by comparing the data from the column studies to a one-dimensional model that assumes local equilibrium. The assumption used for this analysis is that a reasonable fit to the data using a model that assumes local equilibrium would support the contention that mass transfer limitations are negligible for this system.

5.3.1 Column Study in Ultrapure Water Background

A column study was performed using ultrapure water as a background solution to determine the basic breakthrough behavior of BTEX compounds in water. The results of this experiment are shown in Figure 5.20. As expected based on the batch isotherm K_d values, benzene was the first solute to appear in the column effluent (breakthrough) and m- & p- xylene were the last.

The initial assumption made in modeling BTEX sorption in the laboratory scale columns was that BTEX sorption follows local equilibrium behavior with minimal mass transfer limitations. Using CXTFIT2, the predicted breakthrough curves using the batch isotherm parameters for 80×100 mesh size SMZ are shown in Figure 5.21. The distribution coefficients for BTEX sorption used in predicting the breakthrough curves in ultrapure water are listed in Table 5.30. The input parameters for predicting the breakthrough curves using CXTFIT2 are shown in Table 5.31. As shown on Figure 5.21, the projected breakthrough curves based on the K_d values from batch study correlate well with the actual data. These results suggest that the initial assumption regarding the lack of mass transfer limitations in this process is valid.

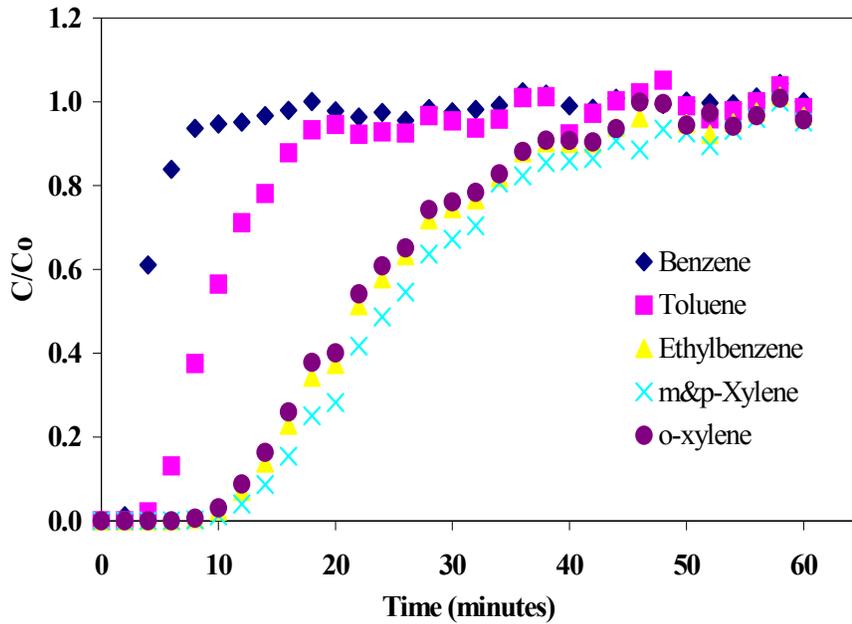


Figure 5.20 Breakthrough Curves for BTEX Sorbed onto SMZ in Ultrapure Water (The column flowrate was 22 mL/min, the porosity was 0.52, and the bulk density of the SMZ was 1g/cm³)

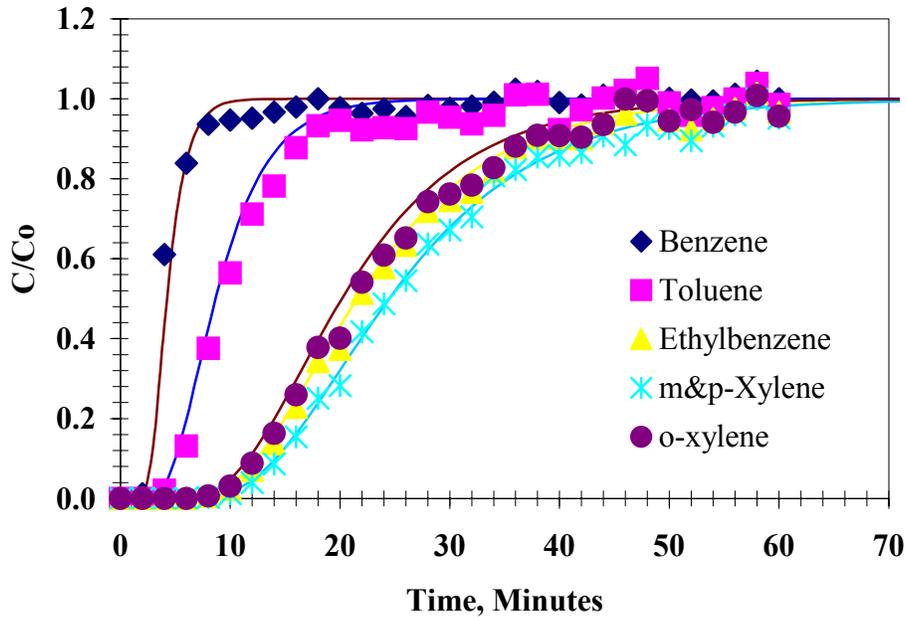


Figure 5.21 Comparison of Breakthrough Curves from Column Data and CXTFIT2 Predictions. Solid lines are from CXTFIT2 Predictions.

Table 5.31 Parameters Applied in CXTFIT2 for Predicting BTEX Breakthrough Curves in Ultrapure Water

	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Seepage Velocity (cm ³ /min)	84	84	84	84	84
Dispersion Coefficient	210	210	210	210	210
Retardation Factor	11.9	32	74.1	82.9	73.2

5.3.2 Column Study in Saline Water Background

Batch experiments suggested that salinity increases sorption capacity for salt concentrations exceeding 100,000 ppm. A second column study was conducted to confirm the batch findings. A solution containing 100,000 ppm total dissolved solids was chosen for this experiment. The column parameters used in this experiment are shown in Table 5.32 and the column effluent data are presented in Figure 5.22 along with CXTFIT2 calibration results.

Table 5.32 Parameters Used in CXTFIT2 to Calibrate K_d Values in Saline Water Column Study

	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Seepage Velocity (cm ³ /min)	84	84	84	84	84
Dispersion Coefficient	210	210	210	210	210

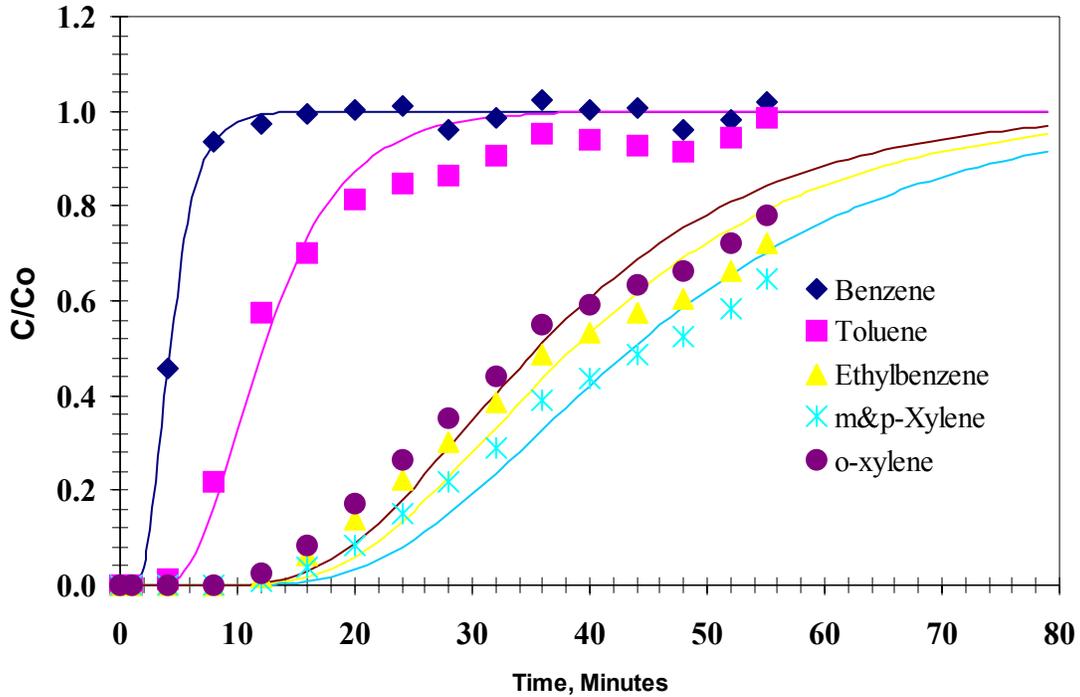


Figure 5.22 Breakthrough Curves for BTEX Sorbed onto SMZ in 100,000 Saline Water

Batch K_d values for sorption of BTEX to 80×100 SMZ in 100,000 saline water were not available. Therefore, CXTFIT2 was used to calculate K_d values for the column breakthrough data (Table 5.33). The K_d values for 100,000 ppm saline water and ultrapure water were compared with the data from the batch study using 14×40 SMZ in 100,000 ppm salinity water.

Table 5.33 Calculated Retardation Factors and Distribution Coefficients Determined using CXTFIT2 for BTEX Column Studies in Saline Water

Compound	Retardation Factor R from CXTFIT2	Calculated K_d by CXTFIT2 (L/kg)	R^2
Benzene	15.5 (15.45, 15.53)	8.7	0.997
Toluene	44.9 (44.71, 44.99)	26.4	0.970
Ethylbenzene	142.6 (142.5, 142.7)	84.9	0.956
m,p-Xylene	161.1 (161.0, 161.2)	96.4	0.962
o-Xylene	131.3 (131.1, 131.4)	78.2	0.964

As shown in Table 5.34, increases in sorption capacities with increasing ionic strength were on the same order of magnitude for batch and column studies and for the two particle sizes.

Table 5.34 Comparison of BTEX K_d Values for Ultrapure Water and 100,000 ppm Saline Water

Compounds	Mesh size	K_d (L/Kg) Values in ultrapure Water Background ¹	K_d (L/Kg) Values from 100,000 ppm Saline Water Background	Percentage Increase
Benzene	80×100	5.7	8.7 ³	152%
	14×40	9.7	14.6 ²	150%
Toluene	80×100	16.1	26.4 ³	164%
	14×40	26.7	44.4 ²	166%
Ethylbenzene	80×100	40.9	84.9 ³	207%
	14×40	65.9	124 ²	188%
m,p-Xylene	80×100	46.5	96.4 ³	207%
	14×40	73.5	143 ²	194%
o-Xylene	80×100	38.2	78.2 ³	204%
	14×40	64.2	119 ¹	185%

¹ K_d values obtained from batch isotherm data

² K_d values obtained from batch isotherm data in saline water

³ K_d values obtained from column data

5.3.3 Column Study in Produced Water Background

The final lab scale column test for the research involved evaluation of BTEX sorption with produced water from the Wamsutter Site owned by BC Technologies and operated by Crystal Solutions, LLC. The produced water was first extracted from Zero Headspace Extractor (ZHE) to a one-liter Tedlar bag. Bubbles were extracted from the valve on the Tedlar bag. The column study was then conducted using the same flowrate as used in the other column experiments. The BTEX breakthrough curves with produced water are shown on Figure 5.23.

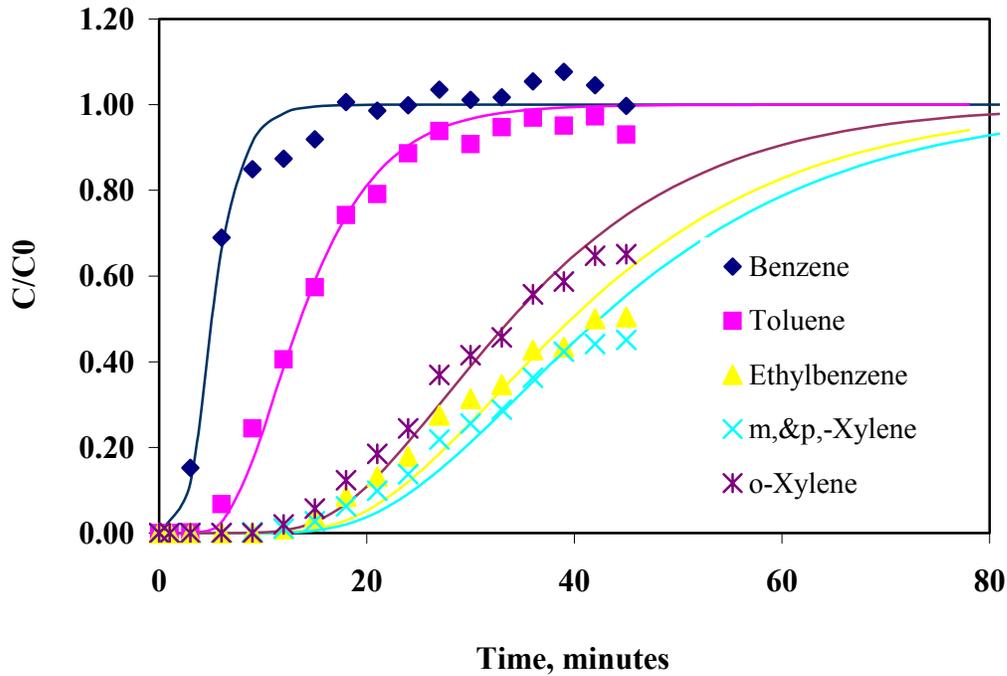


Figure 5.23 Breakthrough Curves for BTEX sorbed onto SMZ in Produced Water

CXTFIT2 was used to calculate the K_d values based on the column effluent data. Table 5.35 lists the input parameters for CXTFIT2 to calculate the retardation factors. See appendix B for the CXTFIT2 input file to calculate the distribution coefficients of BTEX in produced water. The resultant retardation factors, distribution coefficients, correlation coefficients and 95% confidence limits are shown in Table 5.36.

Table 5.35 Parameters Used in CXTFIT2 Calculating Retardation Factor (K_d Values) in Produced Water in Column Study

	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Seepage Velocity (cm ³ /min)	84	84	84	84	84
Dispersion Coefficient	210	210	210	210	210

Table 5.36 Calculated Retardation Factors and Distribution Coefficients, for CXTFIT2 for Produced Water Column Studies.

Compound	Retardation Factor, R, from CXTFIT2	Calculated K_d (L/kg)	R^2	Batch K_d (L/Kg) in Ultrapure Water
Benzene	18.46	8.2	0.9841	5.7
Toluene	50.21	23.1	0.9909	16.1
Ethylbenzene	146.7	68.3	0.9338	40.9
m,p-Xylene	156.5	72.9	0.9420	46.5
o-Xylene	125.1	58.2	0.9755	38.2

Note: bulk density $\rho_b = 1.067 \text{ g/cm}^3$ in this column study

Porosity $\theta = 0.5$

Flow rate = 22 mL/min

$R = 1 + \rho_b * K_d / \theta$

Distribution coefficients using produced water were greater than those obtained using ultrapure water for the same mesh size SMZ. However, the data were not statistically compared. The salt effect was thought to be one factor for the increase in sorption capacity observed in the presence of produced water. However, the TDS concentration for produced water the Wamsutter site was only 11,400 ppm which is lower than the threshold value observed in the saline water batch experiments. While the salt composition may be different for produced water, it is unlikely that the salt effect is responsible for the increase in sorption observed for produced water. It is possible that the increase in sorption may result from sorption of other produced water components into the SMZ organic matter which provides a more favorable sorption environment for BTEX.

Summary of Column Adsorption Results

Column studies confirmed that the distribution coefficients of BTEX sorption onto SMZ increased with increasing compound hydrophobicity. The column study with 100,000 ppm saline water also confirmed previous research suggesting that higher ionic strength increases BTEX sorption distribution coefficients. The magnitude of increase for the 100,000 ppm salt concentration in the column study was comparable to the batch results for ultrapure water and the same salt concentration for 14x40 mesh SMZ.

Produced water may have enhanced the sorption capacity of SMZ toward BTEX as compared with ultrapure water. Batch isotherm tests showed a significant increase in BTEX sorption, but the increase in sorption for several of the other components was not statistically significant. The column study with produced water provided greater distribution coefficients for BTEX sorption onto SMZ as compared with ultrapure water.

Finally, the ability of CXTFIT2 to provide reasonable predictions of BTEX sorption in ultrapure water and excellent calibration fits to breakthrough data obtained in the presence of saline and produced water suggests that mass transfer limitations were relatively low for the system studied.

5.3.4 Regeneration Tests

Figure 5.24 shows the results of the breakthrough of BTEX on virgin SMZ. Because of its low octanol-water partition coefficient (K_{ow}) and high solubility in water, benzene breakthrough occurs first, while compounds with higher K_{ow} and lower water solubility breakthrough later. The estimated amount of BTEX mass sorbed to the SMZ and estimated distribution coefficient (K_d) values are shown in Table 5.37. The K_d values determined in this experiment are similar and in some cases higher than those determined from batch experiments. A higher K_d indicates enhanced sorption of the compound.

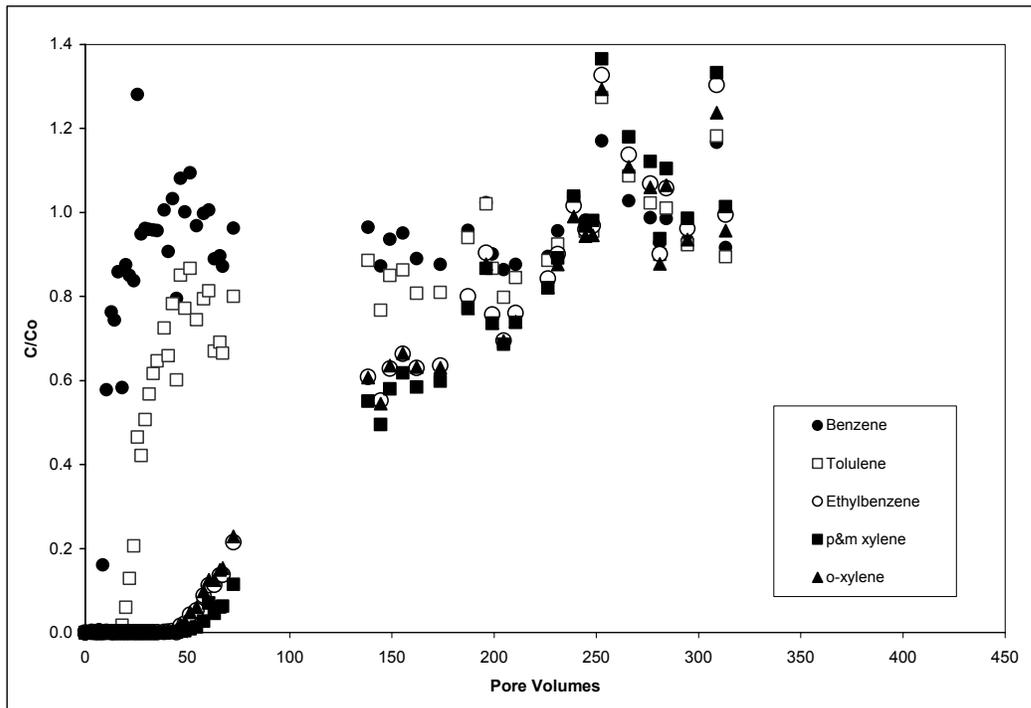


Figure 5.24 BTEX Breakthrough in a Laboratory Column Packed with Virgin SMZ

Figure 5.25 shows the cumulative masses of BTEX removed by air-sparging after the first column experiment. The compounds with the lowest K_{ow} were the most readily removed. While air sparging was effective in stripping all of the benzene and toluene from the column, not all of the ethylbenzene and the xylenes were removed under these conditions (data not shown).

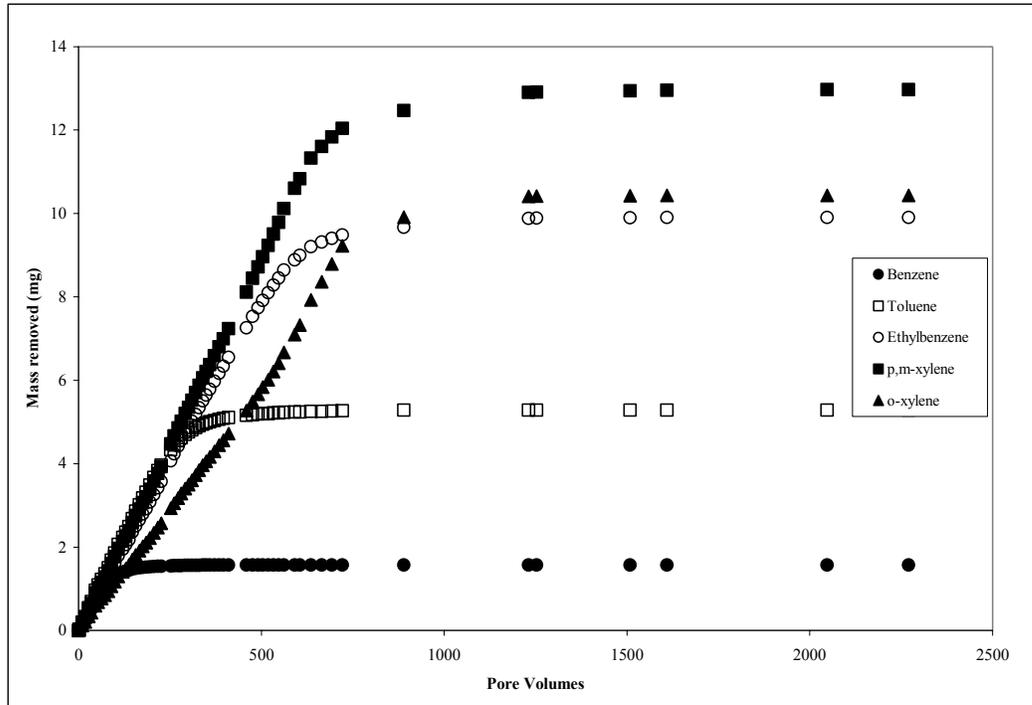


Figure 5.25 BTEX Mass Removed from SMZ in the Lab Column by Air-Sparging.

BTEX breakthrough in the regenerated column is shown in Figure 5.26. The estimated mass of BTEX sorbed to the SMZ and estimated K_d values are shown in Table 5.37. The breakthroughs of benzene and toluene for the regenerated SMZ are similar to their breakthroughs with virgin SMZ. Figure 5.27 shows a comparison of benzene breakthrough in the two columns. The breakthrough curves for ethylbenzene and the xylenes seem to plateau at a relative concentration of 0.8. We hypothesize the low plateau concentrations to be a result of enhanced cosorption effects in the regenerated columns. Others have noted that an increase of bound organic carbon due to BTEX sorption will enhance partitioning of additional BTEX (Jaynes and Vance, 1996; Sharmasardar et al., 2000). These effects would be more significant in the regenerated column since there is a higher hydrocarbon content on the SMZ, as not all of the BTEX mass was removed during air-sparging. These effects are most pronounced on the compounds with highest K_{ow} and lowest S_w . Because the relative concentrations indicate that equilibrium between the SMZ and these compounds was not reached, K_d values were not calculated for ethylbenzene and xylenes in the regenerated column.

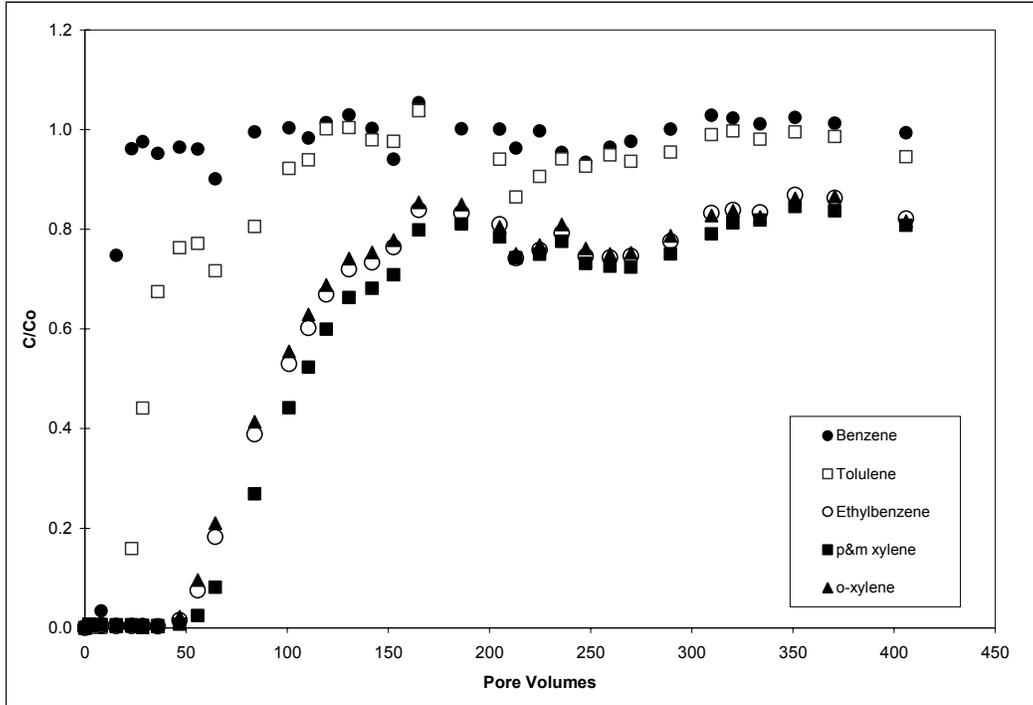


Figure 5.26 BTEX Breakthrough in the Lab Column with Regenerated SMZ

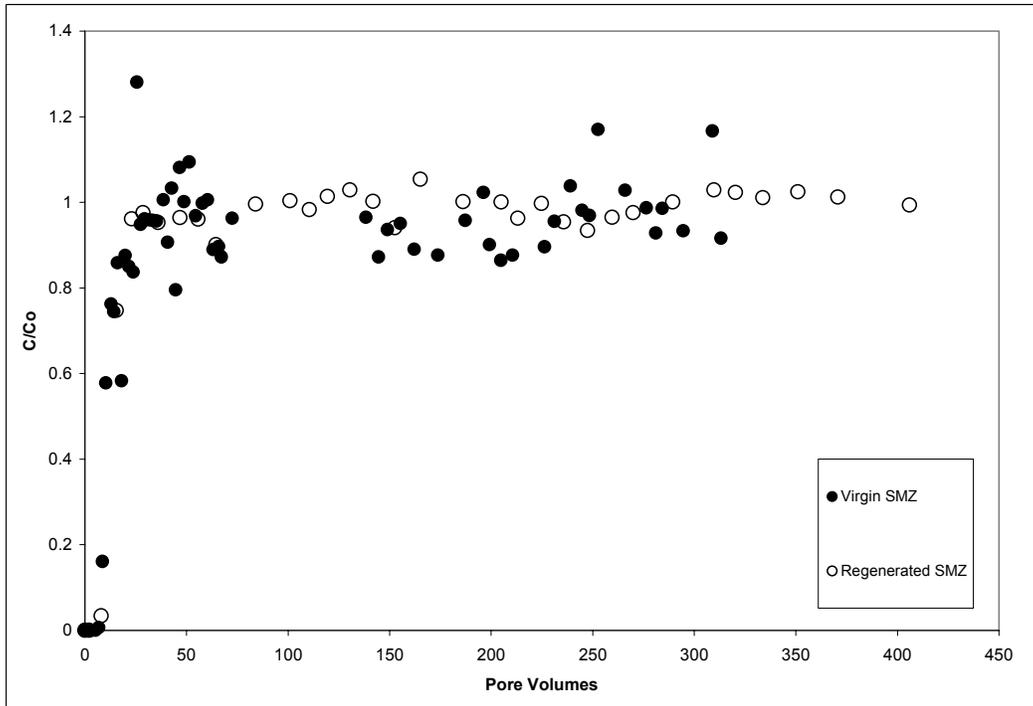


Figure 5.27 Comparison of Benzene Breakthrough in Lab Column for Virgin and Regenerated SMZ

Table 5.37 Amount of BTEX Sorbed in Laboratory Columns and Comparison of K_d Values

	Mass sorbed to virgin SMZ (mg)	Virgin SMZ K_d (L/kg)	Mass sorbed to regen. SMZ (mg)	Regen. SMZ K_d (L/kg)	Batch K_d (L/kg)
Benzene	1.9	7.8	1.8	8.2	9.9
Toluene	4.4	23	4.2	23.0	27
Ethylbenzene	15.5	85	12.6	--	69
p&m-xylene	15.1	90	12.8	--	75
o-xylene	16.1	85	12.8	--	66

5.4 Field Experiments

The BTEX concentrations in the produced water used in the field testing varied over time. Table 5.38 shows the average and range of values of the BTEX component concentrations throughout the duration of the test of the field-scale columns. The breakthrough of BTEX in the virgin 14-inch field system is shown in Figure 5.28. The effluent concentrations of all compounds remained below the influent concentrations for the duration of the test. Little ethylbenzene or xylene had appeared in the effluent after 80 pore volumes. Benzene and toluene concentrations in the effluent appeared to plateau at relative concentrations of 0.8 and 0.6, respectively. A possible reason for the failure of benzene and toluene to reach saturation may be the cosorption described above. The dissolved organic carbon of this produced water was 470 mg/L, of which only 110 mg/L was BTEX, thus providing additional hydrocarbons that were not present in the laboratory experiments. These additional, primarily higher molecular weight hydrocarbons may have added to the cosorption effects. Laboratory batch tests comparing BTEX sorption to SMZ in both pure and produced waters showed similar results. The K_d values were higher in produced water, which contained higher dissolved organic carbon.

Table 5.38 Average and range of BTEX component concentrations in WY Produced Water

	Average concentration in WY Produced water (mg/L)	Range of concentration (mg/L)
Benzene	25.1	18.9-36.4
Toluene	40.7	31.0-61.3
Ethylbenzene	4.7	1.8-19.9
p&m-xylene	30.6	8.8-78.9
o-xylene	9.5	3.7-40.8

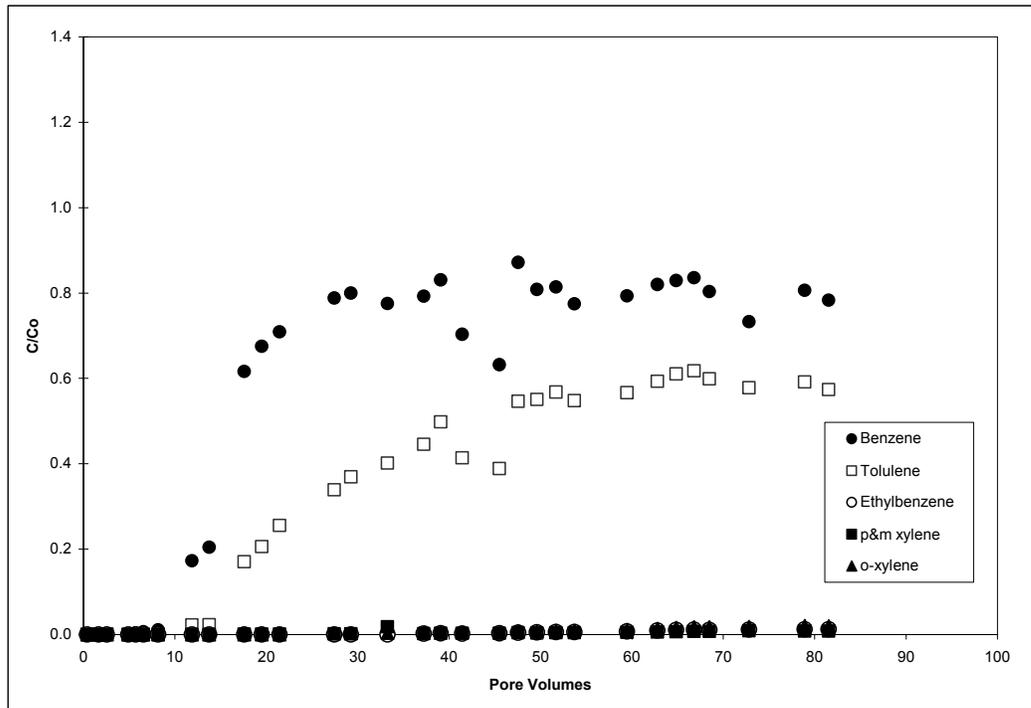


Figure 5.28 BTEX Breakthrough in the 14-inch Field Column with Virgin SMZ

Figure 5.29 shows a comparison of benzene sorption between the lab trial and 14-inch column field trial, both with virgin SMZ. Benzene breakthrough is later in the field column and does not reach the influent value. The results of the 12-inch column with virgin SMZ are similar. Figure 5.30 shows a comparison of toluene sorption between the lab trial and 12-inch field column with virgin SMZ.

Regeneration of the 14-inch column showed results similar to regeneration of the lab column, as shown in Figure 5.31. Benzene was the first to be removed, and was the only compound that fully stripped from the column. As mentioned above, air-sparging of the field column was terminated sooner than desired due to equipment failure.

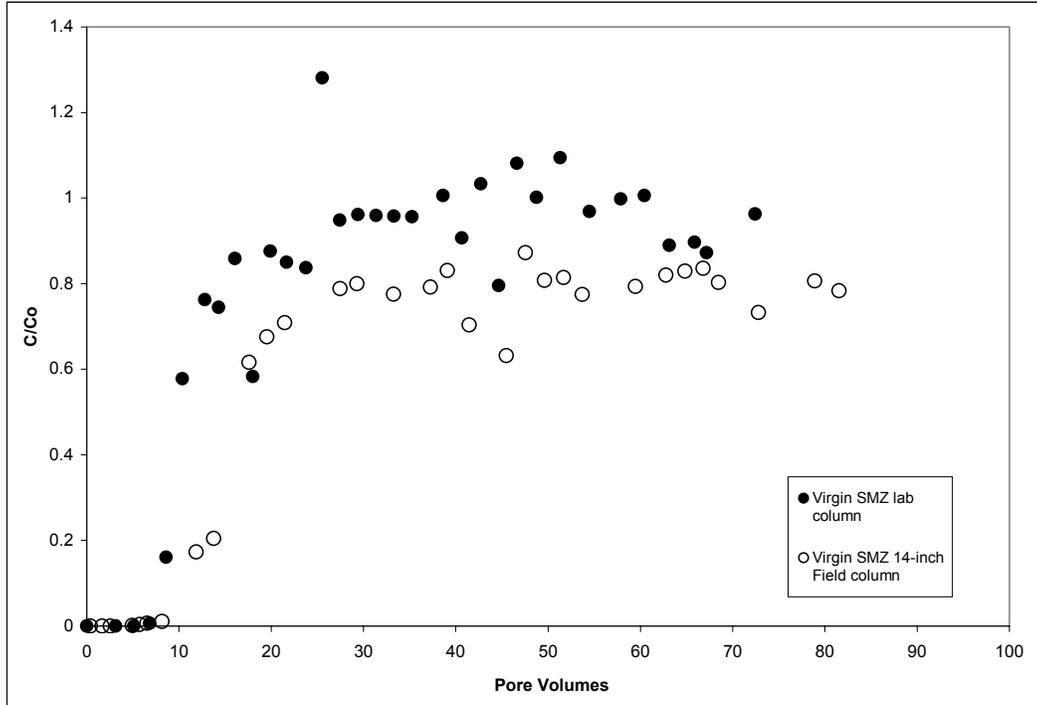


Figure 5.29 Comparison of Benzene Breakthrough in Lab Column with Virgin SMZ and 14-inch Field Column with Virgin SMZ.

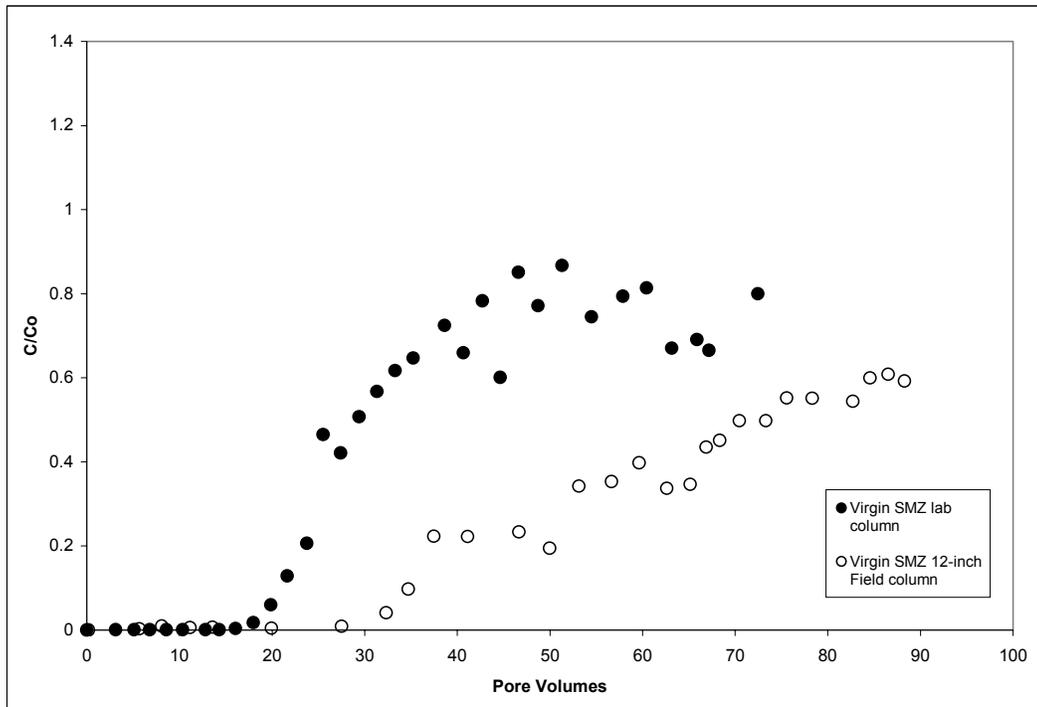


Figure 5.30 Comparison of Toluene Breakthrough in Lab Column with Virgin SMZ and 12-inch Field Column with Virgin SMZ

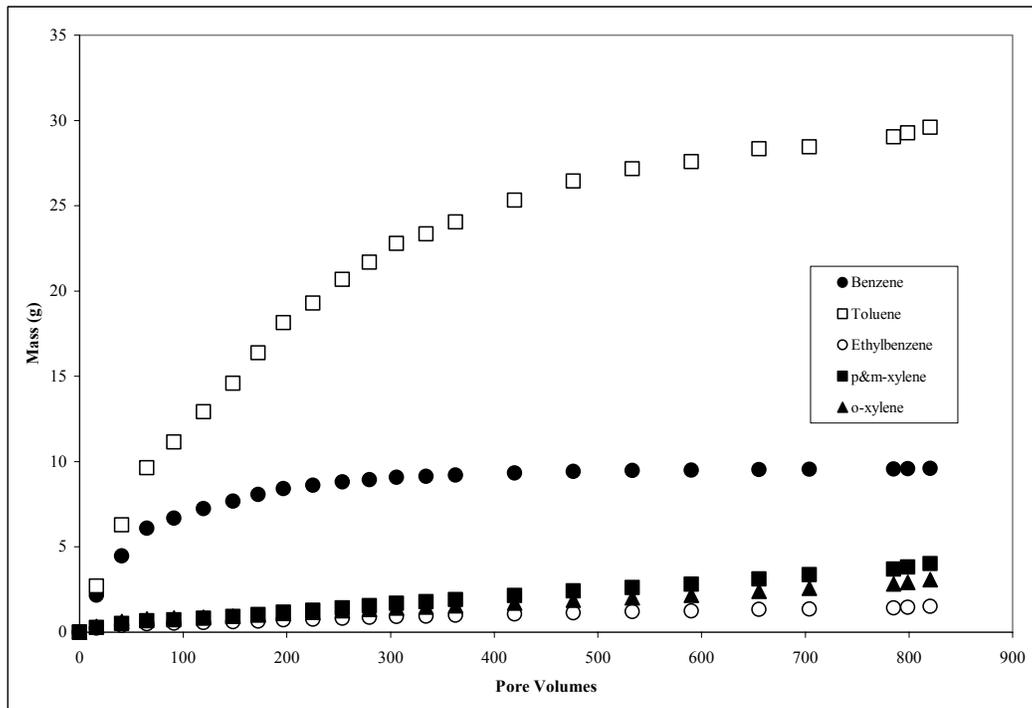


Figure 5.31 BTEX Mass Removed from SMZ in 14-inch Field Column by Air-sparging.

Figure 5.32 shows the breakthrough of BTEX in the regenerated 14-inch column. The relative concentrations of all of the compounds except for benzene are above background (and higher for ethylbenzene and the xylenes than during any stage of the initial sorption experiment). We believe the high initial concentrations were due to the incomplete regeneration of the SMZ. During regeneration, air was pushed into the column in the same flow direction as water. Therefore, the influent end of the column was regenerated first and the BTEX was pushed toward the effluent end of the column. The compounds with higher K_{ow} are less readily air sparged from the SMZ and were not completely removed from the column when regeneration terminated, but instead concentrated near the effluent end. Thus, when produced water was again flushed through the column, these higher concentrations eluted. If flow was reversed during regeneration, residual BTEX would be concentrated towards the influent end of the column and less readily eluted during the next saturation step.

Except for the high initial concentrations, the regenerated SMZ was even more effective than the virgin SMZ at BTEX removal. A comparison of toluene removal from the virgin and regenerated 14-inch column trials is shown in Figure 5.33. As was noted in the lab columns, the regenerated column removes higher amounts of BTEX from the water than the original column.

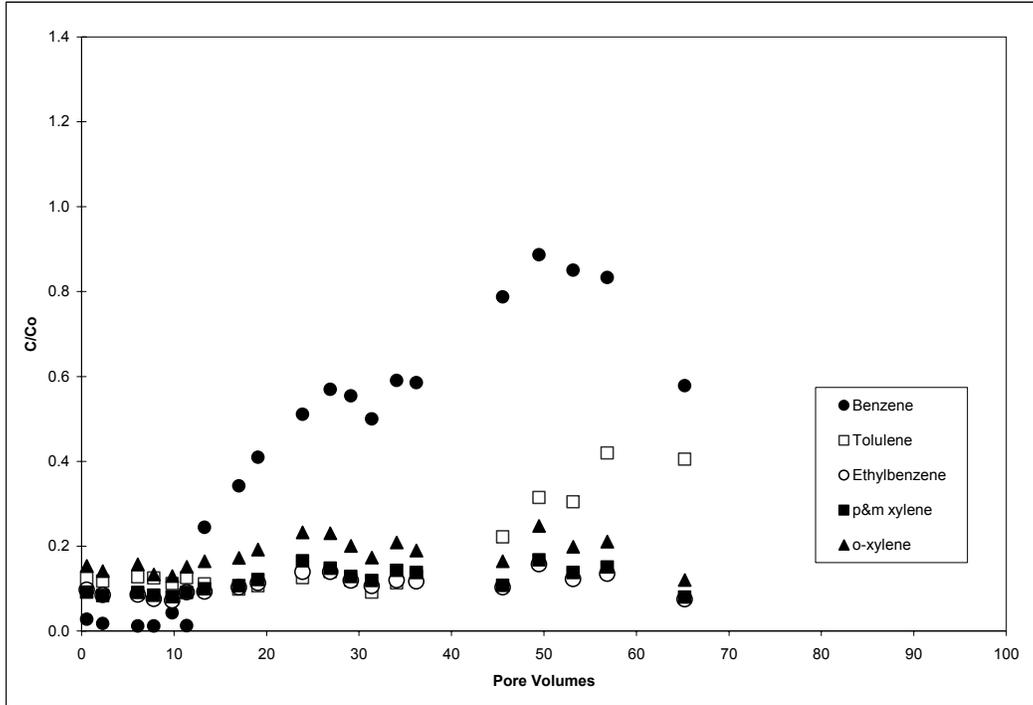


Figure 5.32 BTEX Breakthrough in 14-inch Field Column with Regenerated SMZ

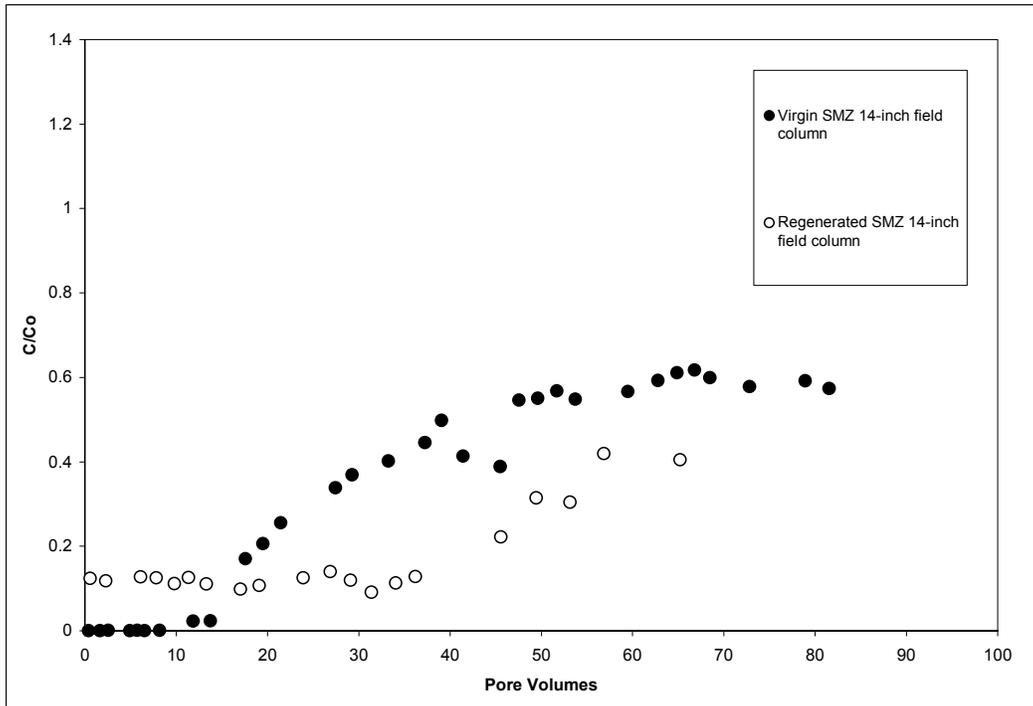


Figure 5.33 Comparison of Toluene Breakthrough in 14-inch Field Column with Virgin SMZ and 14-inch Field Column with Regenerated SMZ

5.5 Cost Analyses

The original pilot scale system used for the Wyoming tests considered two columns: one 14" diameter and 48" in height, and one 12" diameter and 44" in height. These columns were run with average flow rates of 25 and 19 gph respectively as described above. According to the U.S. Department of Energy, as of 1996 the state of Wyoming discharges approximately 121,300 bbl per day of produced water amongst 586 permits (Doyle and Brown, 1997). According to the American Petroleum Institute, the average offshore oil platform produces between 2,500 and 5,000 barrels of produced water per day (API, 1995). Thus, an industrial scale treatment system would need to be able to handle an average flow rate of 362 gph onshore and between 4375 and 8750 gph for offshore use. These flow values are summarized in Table 5.39.

Table 5.39 Industrial Produced Water Discharge Flow Rates

Flowrate, Q	Onshore	Offshore	
		Low	High
bbls/d	207	2500	5000
gph	362	4375	8750
lph	1371	16559	33119

The field test prototypes had an average hydraulic loading rate in the columns of approximately 0.5 gpm/ft². It was found from this work that this hydraulic loading rate provided good flow, and gave an average of almost 100 percent benzene removal after 6 hours. As such, the industrial columns were designed to operate at a similar hydraulic loading rate in order to provide a reasonable time before regeneration would be required. For the purposes of this project, the columns were designed to be regenerated at the point of near 100 percent benzene removal. Since benzene broke through much sooner than the other components of BTEX, their removal rate was near 100 percent as well. For the prototype SMZ system, the columns were obtained from a local Culligan distributor in Austin, TX. The columns were originally designed for ion exchange systems and were used by substituting the ion exchange resin for SMZ. Culligan produces the same type of columns for industrial scale use, and the recommended size available for the flow rates presented in Table 5.39 would be columns 36" in diameter and 72" in height (personal communication).

The prototype test showed that an air flow rate of 3 – 3.5 scfm provided by an air compressor was sufficient to regenerate the columns over a time period of 10 hours. For the larger, industrial scale system, an air compressor would need to provide approximately 25-30 scfm in order to provide the same air-flow rate through the column. In order to meet these requirements, a 7.5 horsepower rotary screw compressor is recommended, and can be purchased from various vendors, including Kaeser Compressors, Inc (personal communication).

Finally, the industrial scale SMZ system would require columns in series so that produced water could be treated continuously while the one set of columns is being regenerated. Thus, the system on which the cost analysis was based consisted of three 36" diameter by 72" height columns in series, with each set of columns being run for 6-8 hours followed by a 12 hour regeneration by air sparging with an air compressor.

5.5.1 Cost Analysis for Industrial Scale SMZ System

Based on an example onshore produced water treatment facility with flow rates given in Table 5.39, a series of 3 columns could be used to treat water continuously. This example industrial treatment system would therefore consist of 3 columns filled with SMZ and one industrial size air compressor for regeneration. As one column reached the benzene breakthrough point at 6 - 8 hours, it could be switched off and regenerated for 12 hours while the other columns continue to treat the influent flow. Thus, this system would allow continuous treatment.

In order for the SMZ filtration system to work effectively, pretreatment of the produced water is necessary. In particular, the use of an oil/water separation process is necessary to avoid fouling the SMZ. Due to the need for pretreatment and the large flow rates of produced water associated with offshore oil platforms, the SMZ system is most likely not a viable treatment option for offshore applications. Therefore, the preliminary design presented here is recommended for onshore use.

The initial capital costs for the SMZ system comprise the bulk of the costs. The costs of the columns are approximately \$4500 per column including fittings and filters (Culligan International Company). Furthermore, the initial cost of the air compressors required to regenerate the columns is \$5000 per air compressor (Kaeser Compressors, Inc.). Amortized over ten years at an interest rate of 5 percent, the yearly capital expenditures for a three-column system would be approximately \$2400. This figure includes the capital costs of the columns and air compressor for regeneration, but does not include treatment costs.

Power and energy costs associated with the SMZ system would be potentially very low. Head loss through the columns was calculated to be approximately 6 feet H₂O, so no pumping would be required if the influent of the system was connected to the bottom of a separation tank as it was in the pilot test. Moreover, the cost of running the air compressors to regenerate the columns was also low, at approximately \$10 per day. The capital costs and operating costs are summarized in Table 5.40.

Table 5.40 Capital and Operating Costs of Industrial SMZ Column

Component	Cost
Adsorption column	\$4500
SMZ fill	\$500
Air Compressor	\$5000
Daily Power Use	\$10 / day

The total treatment costs of such a system would depend on the frequency that the SMZ is replaced or re-flushed with surfactant. Each column would contain approximately 1100 kg of SMZ at a cost of \$460 per metric ton, resulting in a total material cost of about \$500 per column. Table 5.41 summarizes the cost of an industrial-

scale SMZ system based on different replacement intervals of the SMZ fill. The replacement intervals are based on 350 operating days per year. It is likely these costs would be lower if the SMZ were renewed by pumping surfactant through the columns rather than merely replacing the bulk of the zeolite.

Table 5.41 Total Cost of Industrial SMZ System

Replacement Interval	Capitol Costs	Treatment Costs / 1000 gal
1 month	\$18,500	\$5.80
3 months	\$18,500	\$1.96
6 months	\$18,500	\$0.98
1 year	\$18,500	\$0.49

When compared to other existing treatment technologies, the cost of the SMZ system is very competitive. In 1995, the American Petroleum Institute organized a workshop to analyze technologies for treating produced water toxicity (API, 1995). Table 5.42 provides a brief summary of the treatment technologies discussed, including the estimated costs associated with each. Of the technologies presented, the use of SMZ has the potential of being one of the most cost effective treatment options available. Furthermore, the SMZ system is relatively compact, does not require the storage of potentially hazardous chemicals, and could be readily adapted to an automated system. When compared with the most common offshore treatment method, reinjection, the use of SMZ would be substantially cheaper. Finally, the cost analysis performed here is based on removing all BTEX compounds to nearly undetectable levels, the total cost of such a system could be potentially much lower if it were used to treat to “acceptable” levels in order to meet any state of federal guidelines.

Table 5.42 Summary of Treatment Costs of Other Technologies (API, 1995)

Technology	Comments	Treatment Costs
Membrane Filtration	Likely to require pretreatment	\$1.90-2.38 / 1000 gal
Carbon Adsorption	Requires deoiling pretreatment of water to avoid fouling media, costs w/ pretreatment estimated by PWMOM	\$1.19-8.33 / 1000 gal
Chemical Oxidation	Cost estimated for Hydrogen Peroxide system at 50 ppm dosage rate, ozone would be double this cost	\$0.20-0.40 / 1000 gal
Air Stripping	Off gas treatment required	\$0.03-0.05 plus \$0.50-1.00 / 1000 gal
UV Oxidation	Designed to treat 10,000 barrels per day at 350 days per year	\$350,000-\$600,000 capital costs plus \$0.60 / 1000 gal
Reinjection	Most common treatment for offshore use, cost estimated by the API SWIM model	\$3.00-5.00 with up to over \$72 per 1000 gal in some cases

6. Conclusions

6.1 Batch Equilibrium Studies

6.1.1 Batch Equilibrium Sorption Studies Conducted in Ultrapure Water

Single-solute and multi-solute sorption tests showed that the partitioning of BTEX compounds remained linear through concentrations ranging over five orders of magnitude. As proven through hypothesis testing, the distribution coefficients for benzene and toluene were not significantly changed by the addition of the remaining BTEX compounds. Distribution coefficients for ethylbenzene and the xylenes were substantially greater than those for benzene and toluene which is typical for sorption of hydrophobic compounds onto organic carbon surfaces. Due to their lower aqueous solubilities, the driving force for partitioning of ethylbenzene and the xylenes out of the aqueous phase was greater. As a result, ethylbenzene and the xylenes will be removed to a higher extent than the remaining BTEX compounds in SMZ adsorption systems. Because benzene demonstrated the least affinity for SMZ and effluent criteria for benzene are generally more stringent, this compound was used as the target compound for design of the SMZ treatment system.

The distribution coefficients for benzene and toluene were underestimated by typical published correlations relating organic carbon normalized partition coefficients to either aqueous solubility or octanol water partition coefficients. These published correlations were developed for soils that contain organic matter which acts as an adsorbent for non-polar organic compounds. The failure of the correlations to validate results from sorption onto SMZ signifies the chemical and physical differences between soil organic matter and SMZ. Hence, correlations specific to SMZ were developed with the data generated during this project. These correlations are:

$$\log K_d = 0.84 \log K_{ow} - 0.81 \quad R^2 = 0.9987 \quad (6.1)$$

$$\log K_d = -0.75 \log S - 0.26 \quad R^2 = 0.9868 \quad (6.2)$$

where K_d is expressed in L/kg SMZ, K_{ow} in L octanol/L water, and S in mol/L.

6.1.2 Batch Equilibrium Sorption Studies Conducted in Saline Solutions

The sorption isotherms for every BTEX compound in the saline solutions continued to show strong linearity as demonstrated by high correlation coefficients for isotherms on SMZ and by the y-intercepts that were not statistically different from zero. Hypothesis testing showed that all of the BTEX compounds demonstrated increased affinity for SMZ when the salt concentration in solution was increased to 100,000 ppm. Thus, the presence of high levels of salts did enhance linear partitioning of the BTEX compounds.

However, results comparing isotherms generated in ultrapure water and those generated in a 30,000 ppm saline solution were mixed. Statistical differences between the two isotherms were found for benzene and toluene, but the isotherms for the

ethylbenzene and the xylenes were determined to be statistically equivalent. Hence, a baseline salt concentration may be required to yield a significant increase in sorption of BTEX compounds.

Attempts to predict distribution coefficients with the Setchenow equation and regressions developed both through this research and by Schwarzenbach, *et al.* (1993) were unsuccessful. As a result, empirical regression equations were developed based on observed distribution coefficient values and corresponding salt concentrations. These regressions fit the collected data well, as demonstrated by correlation coefficient values. Hence, these regressions can be used to provide estimates of the salt concentration required for BTEX effluent standards to be met. The general regression is:

$$\log K_{d,salt,observed} = a[salt]_M + b \quad (6.3)$$

The specific parameters, a and b , for each BTEX compound are included in Table 6.1.

Table 6.1 Calculated Values for a and b

Compound	a (M^{-1})	b
Benzene	0.118	0.948
Toluene	0.135	1.39
Ethylbenzene	0.155	1.79
m- & p-Xylenes	0.159	1.83
o-Xylene	0.154	1.78

6.1.3 Batch Equilibrium Sorption Studies Conducted in Produced Water

The methods used for sorption studies in produced water were similar to those used in the studies conducted in ultrapure water and saline solutions. However, small differences in these methods were present because of the unique nature of produced water. These differences could have affected the accuracy of the results for the batch studies. Nevertheless, the sorption isotherms for all of the compounds remained linear throughout at least two orders of magnitude.

Comparison of BTEX sorption in produced water and ultrapure water suggested that BTEX compounds had a higher affinity for SMZ in produced water than ultrapure water. In all cases, the distribution coefficients increased in the produced water background. However, hypothesis testing indicated that the differences in distribution coefficients were only significant for benzene and m and p-xylene.

6.1.4 Studies of Temperature Effects on Batch Equilibrium Sorption

The distribution coefficients for BTEX compounds sorbed onto SMZ increased with increasing temperature. This means that for BTEX compounds temperature does have to be considered when designing field scale systems. Van't Hoff plots of $\ln K_d$ vs. $1/T$ were used to estimate enthalpy values for the same mesh size material considered. The process

proved to be endothermic and consistent with a partitioning mechanism for sorption. Greater sorption capacity of SMZ for BTEX compounds can be achieved by increasing temperature. This finding is of particular interest because produced water temperatures can be extremely high for some off-shore operations.

6.2 Laboratory Scale Column Studies and Field Studies

6.2.1 Column Studies with Ultrapure Water, Saline Water, and Produced Water

A summary of the distribution coefficients for BTEX sorption to SMZ obtained from column studies in ultrapure water, saline water and produced water are shown in Table 6.2.

Table 6.2 K_d Values from Ultrapure, Saline, and Produced Water Column Studies

Compounds	K_d from Ultrapure Water (L/Kg)	K_d from Produced Water (L/Kg)	K_d from Saline Water (L/Kg) ^a
Benzene	5.7	8.2	8.7
Toluene	16.1	23.1	26.4
Ethylbenzene	40.9	68.3	84.9
m- & p- Xylene	46.5	72.9	96.4
o-Xylene	38.2	58.2	78.2

^aSalt concentration was 100,000 ppm

Note: SMZ mesh size was 80x100 in all laboratory column experiments.

Comparison of the K_d values obtained from the ultrapure batch isotherms and the ultrapure column breakthrough curve showed good agreement between the two experimental methods. In addition, breakthrough curves derived from the breakthrough data using CTXFIT2 matched the experimental data reasonably well for both the produced water and saline water backgrounds. These results suggest that the local equilibrium assumption provided a reasonable fit to the data for the conditions tested.

As shown in Table 6.2, the K_d values for the tests conducted in different background waters increased from ultrapure water to produced water to water containing 100,000 ppm TDS. While the increase in sorption capacity for the saline water can be attributed to a salting out effect, this phenomenon can not explain the increase in BTEX sorption for produced water since the TDS concentration in the produced water was relatively low.

The column studies laid the foundation for the design of pilot-scale column design based on benzene sorption capacities and assumed local equilibrium kinetics. Benzene was selected for the design basis because it is the weakest sorbing BTEX species and typically has the most stringent regulatory limits.

6.2.1 Regeneration Studies with Ultrapure Water

Regeneration was successfully achieved using an air stripping approach. Upon completion of the adsorption phase of a laboratory column experiment, regeneration successfully removed both the benzene and toluene. Indeed, the compounds with the

lowest K_{ow} were the most readily removed. While air sparging was effective in stripping all of the benzene and toluene from the column, not all of the ethylbenzene and the xylenes were removed under the conditions employed.

The breakthrough profiles of benzene and toluene for the regenerated SMZ were similar to their breakthroughs with virgin SMZ; however, the breakthrough curves for ethylbenzene and the xylenes plateaued at $C/Co = 0.8$. Others have noted that an increase of bound organic carbon due to BTEX sorption will enhance partitioning of additional BTEX (Jaynes and Vance, 1996; Sharmasardar et al., 2000). These effects would be more significant in the regenerated column since there is a higher hydrocarbon content on the SMZ, as not all of the BTEX mass was removed during air-sparging. These effects are most pronounced on the compounds with highest K_{ow} and lowest S_w .

6.2.3 Summary of Field Test

The field test conducted at the BC Technologies site in Wamsutter, WY successfully verified the laboratory findings. The SMZ treatment system removed BTEX using virgin SMZ and regenerated SMZ. Benzene breakthrough in the field column occurred after a greater number of pore volumes than observed in the laboratory columns, suggesting that the background produced water increased the sorption capacity of the SMZ for benzene.

Regeneration of a 14-inch column showed results similar to regeneration of the lab column. Benzene was the first compound to be removed from the spent SMZ, and was the only compound that fully stripped from the column. Air sparging of the field column was terminated sooner than desired due to equipment failure; therefore, the more hydrophobic BTEX compounds were not completely stripped from the column.

Comparison of breakthrough profiles from the regenerated SMZ to the virgin SMZ suggested that the regenerated SMZ had a greater capacity for benzene. This result was consistent with a cosorption effect observed for the more hydrophobic compounds in the laboratory columns.

6.3 Cost Analysis

When compared to other existing treatment technologies, the cost of the SMZ system is very competitive. In comparison to other technologies including carbon adsorption, membrane filtration and oxidation, the use of SMZ has the potential to be one of the most cost effective treatment options available. Furthermore, the SMZ system is relatively compact, does not require the storage of potentially hazardous chemicals, and could be readily adapted to an automated system.

The analysis also demonstrated that the cost of the system would depend on the need for off-gas treatment and the replacement interval for the SMZ.

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Appendices

Appendix A: Input and Output Files in Column Studies

Appendix A-1: Input Files for Predicting BTEX Breakthrough Curves in the Column Study Conducted with ultrapure Water

The distribution coefficients K_d and retardation factors R applied in the CXTFIT direct problem are:

Compounds	K_d (L/Kg)	Retardation Factor (R)
Benzene	5.7	11.9
Toluene	16.1	15.6
Ethylbenzene	40.9	38.4
m,p-Xylene	46.5	43
o-Xylene	38.2	37.9

Benzene breakthrough curve prediction.

```

*** BLOCK A: MODEL DESCRIPTION*****
BENZENE BREAKTHROUGH CURVE PREDICTION (Kd=5.7L/KG)
(DIMENSIONAL V D L T; CM MIN G)
INVERSE MODE NREDU
  0   1   1
MODC   ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK C: TRANSPORT PARAMETERS*****
  V   D   R   Mu
  84  210 11.9 0.0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB   =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0  100.0
* BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL ***
MODP
  0
*** BLOCK H: POSITION AND TIME FOR DIRECT PROBLEM *****
  NZ   DZ   ZI   NT   DT   TI   MPRINT
  1    0.0  25   100  1    0    1

```

Toluene breakthrough curve prediction.

```

*** BLOCK A: MODEL DESCRIPTION*****
TOLUENE BREAKTHROUGH CURVE PREDICTION (Kd=15.6L/KG)
(DIMENSIONAL V D L T; CM MIN G)
INVERSE MODE NREDU
  0   1   1
MODC   ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK C: TRANSPORT PARAMETERS*****
  V   D   R   Mu
  84  210 32  0.0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE ***
MODB   =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0  100.0
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK H: POSITION AND TIME FOR DIRECT PROBLEM*****
  NZ   DZ   ZI   NT   DT   TI   MPRINT
  1    0.0  25   100  1    0    1

```

Ethylbenzene breakthrough curve prediction.

```

*** BLOCK A: MODEL DESCRIPTION*****
ETHYLBENZENE BREAKTHROUGH CURVE PREDICTION (Kd=38.4L/KG)
(DIMENSIONAL V D L T; CM MIN G)
INVERSE  MODE  NREDU
  0        1      1
MODC     ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK C: TRANSPORT PARAMETERS*****
  V    D    R    Mu
  84   210  74.1  0.0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB      =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0   100.0
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL ***
MODP
  0
*** BLOCK H: POSITION AND TIME FOR DIRECT PROBLEM*****
  NZ    DZ    ZI    NT    DT    TI    MPRINT
  1     0.0  25    100   1     0     1

```

M-P-xylene breakthrough curve prediction

```

*** BLOCK A: MODEL DESCRIPTION*****
M,P-XYLENE BREAKTHROUGH CURVE PREDICTION (Kd=43 L/KG)
(DIMENSIONAL V D L T; CM MIN G)
INVERSE  MODE  NREDU
  0        1      1
MODC     ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK C: TRANSPORT PARAMETERS*****
  V    D    R    Mu
  84   210  82.9  0.0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB      =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0   100.0
***BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL ***
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL ***
MODP
  0
*** BLOCK H: POSITION AND TIME FOR DIRECT PROBLEM*****
  NZ    DZ    ZI    NT    DT    TI    MPRINT
  1     0.0  25    100   1     0     1

```

O-xylene breakthrough curve prediction

```

*** BLOCK A: MODEL DESCRIPTION*****
O-XYLENE BREAKTHROUGH CURVE PREDICTION (Kd=37.9 L/KG)
(DIMENSIONAL V D L T; CM MIN G)
INVERSE  MODE  NREDU
  0    1    1
MODC    ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK C: TRANSPORT PARAMETERS*****
  V    D    R    Mu
  84  210  73.2  0.0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB          =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0  100.0
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK H: POSITION AND TIME FOR DIRECT PROBLEM *****
  NZ    DZ    ZI    NT    DT    TI    MPRINT
  1    0.0  25    100    1    0    1

```

□

Appendix A-2: Output files of BTEX Breakthrough Curve in Column Study in ultrapure Water

Benzene breakthrough curve prediction

```

*****
*
* CXTFIT VERSION 2.0 (1/2/95) *
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* DIRECT PROBLRM *
* *
* Benzene Breakthrough curve prediction (Kd=5.7L/Kg) *
* (dimensional V D L T; cm min g) *
* *
* DATA INPUT FILE: ben-di.in *
* *
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE
V.....  .8400E+02
D.....  .2100E+03
R.....  .1190E+02
mu.....  .0000E+00

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 100.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM
    
```

\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 95.4587	
\$TIME	C
.0000	.00000E+00
1.0000	.20134E-02
2.0000	.13313E+00
3.0000	.43445E+00
4.0000	.68934E+00
5.0000	.84312E+00
6.0000	.92405E+00
7.0000	.96403E+00
8.0000	.98316E+00
9.0000	.99216E+00
10.0000	.99636E+00
11.0000	.99831E+00
12.0000	.99922E+00
13.0000	.99964E+00
14.0000	.99983E+00
15.0000	.99992E+00
16.0000	.99996E+00
17.0000	.99998E+00
18.0000	.99999E+00
19.0000	.10000E+01
20.0000	.10000E+01
21.0000	.10000E+01
22.0000	.10000E+01
23.0000	.10000E+01
24.0000	.10000E+01
25.0000	.10000E+01
26.0000	.10000E+01
27.0000	.10000E+01
28.0000	.10000E+01
29.0000	.10000E+01
30.0000	.10000E+01
31.0000	.10000E+01
32.0000	.10000E+01
33.0000	.10000E+01
34.0000	.10000E+01
35.0000	.10000E+01
36.0000	.10000E+01
37.0000	.10000E+01
38.0000	.10000E+01
39.0000	.10000E+01
40.0000	.10000E+01
41.0000	.10000E+01
42.0000	.10000E+01
43.0000	.10000E+01
44.0000	.10000E+01
45.0000	.10000E+01
46.0000	.10000E+01
47.0000	.10000E+01
48.0000	.10000E+01
49.0000	.10000E+01
\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 95.4587	
\$TIME	C
50.0000	.10000E+01
51.0000	.10000E+01
52.0000	.10000E+01
53.0000	.10000E+01

54.0000	.10000E+01
55.0000	.10000E+01
56.0000	.10000E+01
57.0000	.10000E+01
58.0000	.10000E+01
59.0000	.10000E+01
60.0000	.10000E+01
61.0000	.10000E+01
62.0000	.10000E+01
63.0000	.10000E+01
64.0000	.10000E+01
65.0000	.10000E+01
66.0000	.10000E+01
67.0000	.10000E+01
68.0000	.10000E+01
69.0000	.10000E+01
70.0000	.10000E+01
71.0000	.10000E+01
72.0000	.10000E+01
73.0000	.10000E+01
74.0000	.10000E+01
75.0000	.10000E+01
76.0000	.10000E+01
77.0000	.10000E+01
78.0000	.10000E+01
79.0000	.10000E+01
80.0000	.10000E+01
81.0000	.10000E+01
82.0000	.10000E+01
83.0000	.10000E+01
84.0000	.10000E+01
85.0000	.10000E+01
86.0000	.10000E+01
87.0000	.10000E+01
88.0000	.10000E+01
89.0000	.10000E+01
90.0000	.10000E+01
91.0000	.10000E+01
92.0000	.10000E+01
93.0000	.10000E+01
94.0000	.10000E+01
95.0000	.10000E+01
96.0000	.10000E+01
97.0000	.10000E+01
98.0000	.10000E+01
99.0000	.10000E+01

Toluene breakthrough curve prediction.

```
*****
*
* CXTFIT VERSION 2.0 (1/2/95)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* DIRECT PROBLRM
*
* Toluene Breakthrough curve prediction (Kd=15.6L/Kg)
* (dimensional V D L T; cm min g)
*
* DATA INPUT FILE: ben-di.in
*
*****
```

Model Description

```
=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE
V.....  .8400E+02
D.....  .2100E+03
R.....  .3200E+02
mu.....  .0000E+00

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 100.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM
```

\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 89.4762	
\$ TIME	C
.0000	.0000E+00
1.0000	.59684E-09
2.0000	.96960E-04
3.0000	.49526E-02
4.0000	.33269E-01
5.0000	.99128E-01
6.0000	.19697E+00
7.0000	.31117E+00
8.0000	.42689E+00
9.0000	.53424E+00
10.0000	.62820E+00
11.0000	.70724E+00
12.0000	.77187E+00
13.0000	.82368E+00
14.0000	.86457E+00
15.0000	.89649E+00
16.0000	.92119E+00
17.0000	.94018E+00
18.0000	.95470E+00
19.0000	.96577E+00
20.0000	.97416E+00
21.0000	.98053E+00
22.0000	.98534E+00
23.0000	.98896E+00
24.0000	.99170E+00
25.0000	.99376E+00
26.0000	.99531E+00
27.0000	.99648E+00
28.0000	.99735E+00
29.0000	.99801E+00
30.0000	.99851E+00
31.0000	.99888E+00
32.0000	.99916E+00
33.0000	.99937E+00
34.0000	.99952E+00
35.0000	.99964E+00
36.0000	.99973E+00
37.0000	.99980E+00
38.0000	.99985E+00
39.0000	.99989E+00
40.0000	.99991E+00
41.0000	.99994E+00
42.0000	.99995E+00
43.0000	.99996E+00
44.0000	.99997E+00
45.0000	.99998E+00
46.0000	.99998E+00
47.0000	.99999E+00
48.0000	.99999E+00
49.0000	.99999E+00
50.0000	.99999E+00
\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 89.4762	
\$ TIME	C
51.0000	.10000E+01
52.0000	.10000E+01
53.0000	.10000E+01
54.0000	.10000E+01
55.0000	.10000E+01

56.0000	.10000E+01
57.0000	.10000E+01
58.0000	.10000E+01
59.0000	.10000E+01
60.0000	.10000E+01
61.0000	.10000E+01
62.0000	.10000E+01
63.0000	.10000E+01
64.0000	.10000E+01
65.0000	.10000E+01
66.0000	.10000E+01
67.0000	.10000E+01
68.0000	.10000E+01
69.0000	.10000E+01
70.0000	.10000E+01
71.0000	.10000E+01
72.0000	.10000E+01
73.0000	.10000E+01
74.0000	.10000E+01
75.0000	.10000E+01
76.0000	.10000E+01
77.0000	.10000E+01
78.0000	.10000E+01
79.0000	.10000E+01
80.0000	.10000E+01
81.0000	.10000E+01
82.0000	.10000E+01
83.0000	.10000E+01
84.0000	.10000E+01
85.0000	.10000E+01
86.0000	.10000E+01
87.0000	.10000E+01
88.0000	.10000E+01
89.0000	.10000E+01
90.0000	.10000E+01
91.0000	.10000E+01
92.0000	.10000E+01
93.0000	.10000E+01
94.0000	.10000E+01
95.0000	.10000E+01
96.0000	.10000E+01
97.0000	.10000E+01
98.0000	.10000E+01
99.0000	.10000E+01

Ethylbenzene breakthrough curve prediction.

```

*****
*
* CXTFIT VERSION 2.0 (1/2/95) *
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* DIRECT PROBLRM *
* *
* Ethylbenzene Breakthrough curve prediction (Kd=40.9L/kg) *
* (dimensional V D L T; cm min g) *
* *
* DATA INPUT FILE: ben-di.in *
* *
*****

```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE
V.....  .8400E+02
D.....  .2100E+03
R.....  .7960E+02
mu.....  .0000E+00

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 100.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

```

\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 75.3103	
\$TIME	C
.0000	.00000E+00
1.0000	.18465E-24
2.0000	.17003E-11
3.0000	.36284E-07
4.0000	.52620E-05
5.0000	.10291E-03
6.0000	.73650E-03
7.0000	.29641E-02
8.0000	.83189E-02
9.0000	.18354E-01
10.0000	.34211E-01
11.0000	.56413E-01
12.0000	.84858E-01
13.0000	.11895E+00
14.0000	.15778E+00
15.0000	.20026E+00
16.0000	.24528E+00
17.0000	.29178E+00
18.0000	.33882E+00
19.0000	.38559E+00
20.0000	.43142E+00
21.0000	.47579E+00
22.0000	.51832E+00
23.0000	.55872E+00
24.0000	.59683E+00
25.0000	.63253E+00
26.0000	.66580E+00
27.0000	.69664E+00
28.0000	.72512E+00
29.0000	.75132E+00
30.0000	.77534E+00
31.0000	.79730E+00
32.0000	.81733E+00
33.0000	.83555E+00
34.0000	.85209E+00
35.0000	.86709E+00
36.0000	.88065E+00
37.0000	.89291E+00
38.0000	.90397E+00
39.0000	.91394E+00
40.0000	.92291E+00
41.0000	.93098E+00
42.0000	.93824E+00
43.0000	.94475E+00
44.0000	.95059E+00
45.0000	.95583E+00
46.0000	.96053E+00
47.0000	.96474E+00
48.0000	.96850E+00
49.0000	.97187E+00
50.0000	.97489E+00
\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 75.3103	
\$TIME	C
51.0000	.97758E+00
52.0000	.97999E+00
53.0000	.98215E+00
54.0000	.98407E+00
55.0000	.98579E+00

56.0000	.98732E+00
57.0000	.98869E+00
58.0000	.98992E+00
59.0000	.99101E+00
60.0000	.99198E+00
61.0000	.99285E+00
62.0000	.99362E+00
63.0000	.99432E+00
64.0000	.99493E+00
65.0000	.99548E+00
66.0000	.99597E+00
67.0000	.99641E+00
68.0000	.99680E+00
69.0000	.99715E+00
70.0000	.99746E+00
71.0000	.99773E+00
72.0000	.99798E+00
73.0000	.99820E+00
74.0000	.99839E+00
75.0000	.99857E+00
76.0000	.99872E+00
77.0000	.99886E+00
78.0000	.99899E+00
79.0000	.99910E+00
80.0000	.99919E+00
81.0000	.99928E+00
82.0000	.99936E+00
83.0000	.99943E+00
84.0000	.99949E+00
85.0000	.99955E+00
86.0000	.99960E+00
87.0000	.99964E+00
88.0000	.99968E+00
89.0000	.99971E+00
90.0000	.99974E+00
91.0000	.99977E+00
92.0000	.99980E+00
93.0000	.99982E+00
94.0000	.99984E+00
95.0000	.99986E+00
96.0000	.99987E+00
97.0000	.99989E+00
98.0000	.99990E+00
99.0000	.99991E+00

M-P-xylene breakthrough curve prediction

```

*****
*
* CXTFIT VERSION 2.0 (1/2/95) *
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* DIRECT PROBLRM *
* *
* m,p-Xylene Breakthrough curve prediction (Kd=46.5L/Kg) *
* (dimensional V D L T; cm min g) *
* *
* DATA INPUT FILE: ben-di.in *
* *
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE
V.....  .8400E+02
D.....  .2100E+03
R.....  .9040E+02
mu.....  .0000E+00

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 100.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM
    
```

\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 72.0987	
\$TIME	C
.0000	.00000E+00
1.0000	.56832E-28
2.0000	.29450E-13
3.0000	.24269E-08
4.0000	.69530E-06
5.0000	.20543E-04
6.0000	.19413E-03
7.0000	.95516E-03
8.0000	.31228E-02
9.0000	.77711E-02
10.0000	.15971E-01
11.0000	.28557E-01
12.0000	.46000E-01
13.0000	.68379E-01
14.0000	.95439E-01
15.0000	.12667E+00
16.0000	.16141E+00
17.0000	.19890E+00
18.0000	.23839E+00
19.0000	.27914E+00
20.0000	.32050E+00
21.0000	.36187E+00
22.0000	.40276E+00
23.0000	.44276E+00
24.0000	.48155E+00
25.0000	.51887E+00
26.0000	.55454E+00
27.0000	.58844E+00
28.0000	.62048E+00
29.0000	.65064E+00
30.0000	.67892E+00
31.0000	.70533E+00
32.0000	.72992E+00
33.0000	.75276E+00
34.0000	.77392E+00
35.0000	.79347E+00
36.0000	.81150E+00
37.0000	.82810E+00
38.0000	.84336E+00
39.0000	.85737E+00
40.0000	.87021E+00
41.0000	.88196E+00
42.0000	.89270E+00
43.0000	.90252E+00
44.0000	.91148E+00
45.0000	.91965E+00
46.0000	.92709E+00
47.0000	.93387E+00
48.0000	.94003E+00
49.0000	.94564E+00
50.0000	.95074E+00
\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 72.0987	
\$TIME	C
51.0000	.95537E+00
52.0000	.95957E+00
53.0000	.96339E+00
54.0000	.96685E+00
55.0000	.96999E+00

56.0000	.97284E+00
57.0000	.97542E+00
58.0000	.97776E+00
59.0000	.97988E+00
60.0000	.98180E+00
61.0000	.98354E+00
62.0000	.98511E+00
63.0000	.98654E+00
64.0000	.98783E+00
65.0000	.98899E+00
66.0000	.99005E+00
67.0000	.99100E+00
68.0000	.99187E+00
69.0000	.99265E+00
70.0000	.99335E+00
71.0000	.99399E+00
72.0000	.99457E+00
73.0000	.99509E+00
74.0000	.99556E+00
75.0000	.99599E+00
76.0000	.99638E+00
77.0000	.99672E+00
78.0000	.99704E+00
79.0000	.99732E+00
80.0000	.99758E+00
81.0000	.99781E+00
82.0000	.99803E+00
83.0000	.99822E+00
84.0000	.99839E+00
85.0000	.99854E+00
86.0000	.99868E+00
87.0000	.99881E+00
88.0000	.99892E+00
89.0000	.99903E+00
90.0000	.99912E+00
91.0000	.99921E+00
92.0000	.99928E+00
93.0000	.99935E+00
94.0000	.99941E+00
95.0000	.99947E+00
96.0000	.99952E+00
97.0000	.99957E+00
98.0000	.99961E+00
99.0000	.99965E+00

O-xylene breakthrough curve prediction

```
*****
*   CXTFIT VERSION 2.0 (1/2/95)   *
*   ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
*   DIRECT PROBLRM               *
*   *                             *
*   o-Xylene Breakthrough curve prediction (Kd=38.2 L/Kg) *
*   (dimensional V D L T; cm min g) *
*   *                             *
*   DATA INPUT FILE: ben-di.in  *
*   *                             *
*****
```

Model Description

```
=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE
V.....  .8400E+02
D.....  .2100E+03
R.....  .7450E+02
mu.....  .0000E+00

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 100.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM
```

\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 76.8277	
\$ TIME	C
.0000	.00000E+00
1.0000	.84227E-23
2.0000	.11549E-10
3.0000	.13007E-06
4.0000	.13663E-04
5.0000	.21971E-03
6.0000	.13778E-02
7.0000	.50390E-02
8.0000	.13148E-01
9.0000	.27387E-01
10.0000	.48719E-01
11.0000	.77277E-01
12.0000	.11249E+00
13.0000	.15331E+00
14.0000	.19843E+00
15.0000	.24651E+00
16.0000	.29626E+00
17.0000	.34652E+00
18.0000	.39633E+00
19.0000	.44493E+00
20.0000	.49172E+00
21.0000	.53627E+00
22.0000	.57830E+00
23.0000	.61764E+00
24.0000	.65420E+00
25.0000	.68799E+00
26.0000	.71905E+00
27.0000	.74749E+00
28.0000	.77342E+00
29.0000	.79699E+00
30.0000	.81835E+00
31.0000	.83766E+00
32.0000	.85507E+00
33.0000	.87073E+00
34.0000	.88481E+00
35.0000	.89743E+00
36.0000	.90873E+00
37.0000	.91884E+00
38.0000	.92787E+00
39.0000	.93593E+00
40.0000	.94311E+00
41.0000	.94951E+00
42.0000	.95521E+00
43.0000	.96028E+00
44.0000	.96478E+00
45.0000	.96879E+00
46.0000	.97234E+00
47.0000	.97550E+00
48.0000	.97830E+00
49.0000	.98078E+00
50.0000	.98299E+00
\$ Z= 25.0000 (FLUX CONC. VS. TIME)	
\$ Sum(C*dT)= 76.8277	
\$ TIME	C
51.0000	.98494E+00
52.0000	.98667E+00
53.0000	.98820E+00
54.0000	.98956E+00
55.0000	.99076E+00

56.0000	.99183E+00
57.0000	.99277E+00
58.0000	.99360E+00
59.0000	.99434E+00
60.0000	.99499E+00
61.0000	.99557E+00
62.0000	.99608E+00
63.0000	.99654E+00
64.0000	.99694E+00
65.0000	.99729E+00
66.0000	.99760E+00
67.0000	.99788E+00
68.0000	.99813E+00
69.0000	.99834E+00
70.0000	.99853E+00
71.0000	.99870E+00
72.0000	.99885E+00
73.0000	.99899E+00
74.0000	.99910E+00
75.0000	.99921E+00
76.0000	.99930E+00
77.0000	.99938E+00
78.0000	.99945E+00
79.0000	.99951E+00
80.0000	.99957E+00
81.0000	.99962E+00
82.0000	.99966E+00
83.0000	.99970E+00
84.0000	.99974E+00
85.0000	.99977E+00
86.0000	.99979E+00
87.0000	.99982E+00
88.0000	.99984E+00
89.0000	.99986E+00
90.0000	.99987E+00
91.0000	.99989E+00
92.0000	.99990E+00
93.0000	.99991E+00
94.0000	.99992E+00
95.0000	.99993E+00
96.0000	.99994E+00
97.0000	.99995E+00
98.0000	.99995E+00
99.0000	.99996E+00

Appendix A-3: Input Files for Predicting BTEX Sorption Distribution Coefficients in
Column Study with Saline Water

Benzene sorption coefficient Kd in 100,000 PPM salt water evaluation

```

*** BLOCK A: MODEL DESCRIPTION*****
Conc. vs. time at 25 cm (dimensional V D L T; cm min g)
INVERSE  MODE   NREDU
  1      1      1
MODC     ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK B: INVERSE PROBLEM*****
MIT      ILMT  MASS
  30     0     0
*** BLOCK C: TRANSPORT PARAMETERS*****
V        D      R      Mu
  84     210    1.0    0.0
  0      0      1      0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB     =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0    55
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK G: DATA FOR INVERSE PROBLEM*****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
  1
  25.0
TIME     CONC   (Give "0 0 0" after last data set.)
.0000    0.0000
1.0000    0.0008
4.0000     0.4565
8.0000    0.9340
12.0000   0.9747
16.0000   0.9931
20.0000   1.0104
24.0000   1.0041
28.0000   0.9747
32.0000   0.9612
36.0000   0.9840
40.0000   1.0228
44.0000   1.0061
48.0000   0.9614
52.0000   0.9836
56.0000   1.0181
  0      0

```

Toluene sorption coefficient Kd in 100,000 PPM salt water evaluation

```

*** BLOCK A: MODEL DESCRIPTION*****
Toluene sorption coefficient Kd in 100,000 PPM salt water evaluation
Conc. vs. time at 25 cm (dimensional V D L T; cm min g)
INVERSE  MODE  NREDU
  1      1      1
MODC     ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK B: INVERSE PROBLEM*****
MIT      ILMT  MASS
30      0      0
*** BLOCK C: TRANSPORT PARAMETERS*****
  V      D      R      Mu
  84     210    1.0    0.0
  0      0      1      0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB     =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0    55
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK G: DATA FOR INVERSE PROBLEM*****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
  1
  25.0
  TIME   CONC   (Give "0 0 0" after last data set.)
  0      0
  1      0.0007
  4      0.012
  8      0.2176
  12     0.5737
  16     0.7011
  20     0.8144
  24     0.8492
  28     0.8644
  32     0.9053
  36     0.9505
  40     0.9414
  44     0.9252
  48     0.9152
  52     0.9430
  55     0.9846
  0      0

```

Ethylbenzene sorption coefficient Kd in 100,000 PPM salt water evaluation

```

*** BLOCK A: MODEL DESCRIPTION*****
Ethylbenzene sorption coefficient Kd in 100,000 PPM salt water evaluation
Conc. vs. time at 25 cm (dimensional V D L T; cm min g)
INVERSE  MODE  NREDU
  1    1    1
MODC  ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK B: INVERSE PROBLEM*****
MIT  ILMT  MASS
30   0    0
*** BLOCK C: TRANSPORT PARAMETERS*****
  V    D    R    Mu
  84   210  1.0  0.0
  0    0    1    0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB      =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0   55
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK G: DATA FOR INVERSE PROBLEM*****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
  1
  25.0
TIME  CONC  (Give "0 0 0" after last data set.)
  0      0
  1      0
  4      0
  8      0.0009
  12     0.0186
  16     0.0649
  20     0.1374
  24     0.2213
  28     0.3025
  32     0.3842
  36     0.4887
  40     0.5315
  44     0.5755
  48     0.6055
  52     0.6625
  55     0.7220
  0      0

```

m,p-Xylene sorption coefficient Kd in 100,000 PPM salt water evaluation

```

*** BLOCK A: MODEL DESCRIPTION*****
m,p-Xylene sorption coefficient Kd in 100,000 PPM salt water evaluation
Conc. vs. time at 25 cm (dimensional V D L T; cm min g)
INVERSE  MODE  NREDU
  1    1    1
MODC    ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK B: INVERSE PROBLEM*****
MIT  ILMT  MASS
30   0    0
*** BLOCK C: TRANSPORT PARAMETERS*****
  V    D    R    Mu
84   210  1.0  0.0
  0    0    1    0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB      =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
1.0   55
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK G: DATA FOR INVERSE PROBLEM*****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
  1
25.0
TIME  CONC  (Give "0 0 0" after last data set.)
  0    0
  1    0
  4    0
  8    0
 12   0.0089
 16   0.0358
 20   0.0847
 24   0.1492
 28   0.2181
 32   0.2908
 36   0.3898
 40   0.4364
 44   0.4876
 48   0.5241
 52   0.5848
 55   0.6457
  0    0

```

o-Xylene sorption coefficient Kd in 100,000 PPM salt water evaluation

```

*** BLOCK A: MODEL DESCRIPTION*****
o-Xylene sorption coefficient Kd in 100,000 PPM salt water evaluation
Conc. vs. time at 25 cm (dimensional V D L T; cm min g)
INVERSE  MODE  NREDU
  1      1      1
MODC     ZL(BLANK IF MODE=NREDU=1)
  1
*** BLOCK B: INVERSE PROBLEM*****
MIT      ILMT  MASS
30      0      0
*** BLOCK C: TRANSPORT PARAMETERS*****
  V      D      R      Mu
  84     210    1.0    0.0
  0      0      1      0
*** BLOCK D: BVP; MODB=0 ZERO; =1 Dirac ; =2 STEP; =3 A PULSE***
MODB     =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0    55
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK G: DATA FOR INVERSE PROBLEM*****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
  1
  25.0
  TIME   CONC   (Give "0 0 0" after last data set.)
  0      0
  1      0
  4      0
  8      0.0016
  12     0.0269
  16     0.0854
  20     0.1715
  24     0.2657
  28     0.3531
  32     0.4403
  36     0.5494
  40     0.5909
  44     0.6339
  48     0.6630
  52     0.7209
  55     0.7819
  0      0

```

Appendix A-4: Output files for Predicting BTEX Sorption Distribution Coefficients in Column Study with Saline Water.

Predicting benzene sorption coefficient K_d in 100,000 PPM salt water

```

*****
*   CXTFIT VERSION 2.0 (1/2/95)           *
*   ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE   *
*   NON-LINEAR LEAST-SQUARES ANALYSIS           *
*                                           *
*   Predicting benzene sorption coefficient  $K_d$  in 100,000 PPM salt water *
*   Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
*                                           *
*   DATA INPUT FILE: sat7-3a.in           *
*                                           *
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02   N
D.....  .2100E+03   N
R.....  .1000E+01   Y
mu.....  .0000E+00   N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. =  1.0000 & DURATION =  55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS =  30

ITER  SSQ      R....
0     .2337E+01 .100E+01
1     .2126E+01 .633E+02
2     .2556E+00 .262E+02
3     .5611E-02 .156E+02
    
```

4 .5570E-02 .155E+02
 5 .5570E-02 .155E+02

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .99697862
 (COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

NAME	VALUE	95% CONFIDENCE LIMITS		
		S.E.COEFF.	LOWER	UPPER
R....	.1549E+02	.1927E-01	.1545E+02	.1553E+02

-----ORDERED BY COMPUTER INPUT-----

\$	NO	DISTANCE	CONCENTRATION		RESI-	DUAL
			TIME	OBS		
1	25.0000	.0000	.0000	.0000	.0000	
2	25.0000	1.0000	.0008	.0001	.0007	
3	25.0000	4.0000	.4565	.4562	.0003	
4	25.0000	8.0000	.9340	.9318	.0022	
5	25.0000	12.0000	.9747	.9934	-.0187	
6	25.0000	16.0000	.9931	.9994	-.0063	
7	25.0000	20.0000	1.0104	.9999	.0105	
8	25.0000	24.0000	1.0041	1.0000	.0041	
9	25.0000	28.0000	.9747	1.0000	-.0253	
10	25.0000	32.0000	.9612	1.0000	-.0388	
11	25.0000	36.0000	.9840	1.0000	-.0160	
12	25.0000	40.0000	1.0228	1.0000	.0228	
13	25.0000	44.0000	1.0061	1.0000	.0061	
14	25.0000	48.0000	.9614	1.0000	-.0386	
15	25.0000	52.0000	.9836	1.0000	-.0164	
16	25.0000	56.0000	1.0181	.9999	.0182	

Predicting toluene K_d in 100,000 PPM saline water

```

* CXTFIT VERSION 2.0 (1/2/95) *
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS *
* Predicting toluene  $K_d$  in 100,000 PPM saline water *
* Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
* * DATA INPUT FILE: sat7-3a.in
*
*
*
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02   N
D.....  .2100E+03   N
R.....  .1000E+01   Y
mu.....  .0000E+00   N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS = 30

ITER  SSQ    R...
0 .2963E+01 .100E+01
1 .2504E+01 .124E+03
2 .2632E+00 .620E+02
3 .7319E-01 .483E+02
4 .6391E-01 .455E+02
5 .6349E-01 .450E+02
6 .6347E-01 .449E+02
7 .6346E-01 .449E+02
8 .6346E-01 .449E+02

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .97035822
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
=====
    
```

		95% CONFIDENCE LIMITS				
NAME	VALUE	S.E.COEFF.	LOWER	UPPER		
R....	.4485E+02	.6505E-01	.4471E+02	.4499E+02		
-----ORDERED BY COMPUTER INPUT-----						
		CONCENTRATION	RESI-			
\$	NO	DISTANCE	TIME	OBS	FITTED	DUAL
	1	25.0000	.0000	.0000	.0000	.0000
	2	25.0000	1.0000	.0007	.0000	.0007
	3	25.0000	4.0000	.0120	.0033	.0087
	4	25.0000	8.0000	.2176	.1659	.0517
	5	25.0000	12.0000	.5737	.4886	.0851
	6	25.0000	16.0000	.7011	.7358	-.0347
	7	25.0000	20.0000	.8144	.8740	-.0596
	8	25.0000	24.0000	.8492	.9422	-.0930
	9	25.0000	28.0000	.8644	.9740	-.1096
	10	25.0000	32.0000	.9053	.9884	-.0831
	11	25.0000	36.0000	.9505	.9949	-.0444
	12	25.0000	40.0000	.9414	.9977	-.0563
	13	25.0000	44.0000	.9252	.9990	-.0738
	14	25.0000	48.0000	.9152	.9996	-.0844
	15	25.0000	52.0000	.9430	.9998	-.0568
	16	25.0000	55.0000	.9846	.9999	-.0153
\$						

Predicting ethylbenzene K_d in 100,000ppm salt water

```

* CXTFIT VERSION 2.0 (1/2/95) *
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS *
* Predicting ethylbenzene  $K_d$  in 100,000ppm salt water *
* Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
* DATA INPUT FILE: sat7-3a.in *
*
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02    N
D.....  .2100E+03    N
R.....  .1000E+01    Y
mu.....  .0000E+00    N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS = 30

ITER  SSQ    R....
0     .8058E+01 .100E+01
1     .1370E+00 .125E+03
2     .5120E-01 .139E+03
3     .4879E-01 .142E+03
4     .4877E-01 .143E+03
5     .4877E-01 .143E+03

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .95571232
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
=====
                                     95% CONFIDENCE LIMITS
NAME      VALUE    S.E.COEFF.    LOWER    UPPER
R....     .1426E+03  .5702E-01    .1425E+03  .1427E+03
    
```

-----ORDERED BY COMPUTER INPUT-----

\$	NO	DISTANCE	CONCENTRATION		RESI-	DUAL
			TIME	OBS	FITTED	
	1	25.0000	.0000	.0000	.0000	.0000
	2	25.0000	1.0000	.0000	.0000	.0000
	3	25.0000	4.0000	.0000	.0000	.0000
	4	25.0000	8.0000	.0009	.0000	.0009
	5	25.0000	12.0000	.0186	.0020	.0166
	6	25.0000	16.0000	.0649	.0175	.0474
	7	25.0000	20.0000	.1374	.0607	.0767
	8	25.0000	24.0000	.2213	.1338	.0875
	9	25.0000	28.0000	.3025	.2284	.0741
	10	25.0000	32.0000	.3842	.3323	.0519
	11	25.0000	36.0000	.4887	.4357	.0530
	12	25.0000	40.0000	.5315	.5318	-.0003
	13	25.0000	44.0000	.5755	.6171	-.0416
	14	25.0000	48.0000	.6055	.6904	-.0849
	15	25.0000	52.0000	.6625	.7520	-.0895
	16	25.0000	55.0000	.7220	.7909	-.0689

\$

Predicting m,p-xylene K_d in 100,000 PPM saline water

```

*****
*
*   CXTFIT VERSION 2.0 (1/2/95)
*   ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
*   NON-LINEAR LEAST-SQUARES ANALYSIS
*
*   Predicting m,p-xylene  $K_d$  in 100,000 PPM saline water
*   Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
*
*   DATA INPUT FILE: sat7-3a.in
*
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02   N
D.....  .2100E+03   N
R.....  .1000E+01   Y
mu.....  .0000E+00   N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS = 30

ITER  SSQ    R...
0   .9063E+01 .100E+01
1   .3628E+00 .125E+03
2   .4419E-01 .153E+03
3   .3234E-01 .160E+03
4   .3221E-01 .161E+03
5   .3221E-01 .161E+03

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .96199420
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
=====
    
```

		95% CONFIDENCE LIMITS				
NAME	VALUE	S.E.COEFF.	LOWER	UPPER		
R....	.1611E+03	.4634E-01	.1610E+03	.1612E+03		
-----ORDERED BY COMPUTER INPUT-----						
		CONCENTRATION	RESI-			
\$	NO	DISTANCE	TIME	OBS	FITTED	DUAL
	1	25.0000	.0000	.0000	.0000	
	2	25.0000	1.0000	.0000	.0000	
	3	25.0000	4.0000	.0000	.0000	
	4	25.0000	8.0000	.0000	.0000	
	5	25.0000	12.0000	.0089	.0007	.0082
	6	25.0000	16.0000	.0358	.0076	.0282
	7	25.0000	20.0000	.0847	.0320	.0527
	8	25.0000	24.0000	.1492	.0804	.0688
	9	25.0000	28.0000	.2181	.1510	.0671
	10	25.0000	32.0000	.2908	.2366	.0542
	11	25.0000	36.0000	.3898	.3287	.0611
	12	25.0000	40.0000	.4364	.4206	.0158
	13	25.0000	44.0000	.4876	.5074	-.0198
	14	25.0000	48.0000	.5241	.5862	-.0621
	15	25.0000	52.0000	.5848	.6558	-.0710
	16	25.0000	55.0000	.6457	.7017	-.0560
\$						

o-Xylene sorption coefficient Kd in 100,000 PPM salt water

```

*
* CXTFIT VERSION 2.0 (1/2/95)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS
*
* o-Xylene sorption coefficient Kd in 100,000 PPM salt water e
* Conc. vs. time at 25 cm (dimentional V D L T; cm min g) *
*
* DATA INPUT FILE: sat7-3a.in
*
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02   N
D.....  .2100E+03   N
R.....  .1000E+01   Y
mu..... .0000E+00   N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS = 30

ITER  SSQ    R...
0    .7479E+01 .100E+01
1    .5991E-01 .125E+03
2    .4712E-01 .130E+03
3    .4689E-01 .131E+03
4    .4689E-01 .131E+03

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .96406136
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
=====

NAME      VALUE      95% CONFIDENCE LIMITS
          S.E.COEFF.  LOWER      UPPER
    
```

R....	.1313E+03	.5591E-01	.1311E+03	.1314E+03			
-----ORDERED BY COMPUTER INPUT-----							
		CONCENTRATION	RESI-				
\$	NO	DISTANCE	TIME	OBS	FITTED	DUAL	
	1	25.0000	.0000	.0000	.0000	.0000	
	2	25.0000	1.0000	.0000	.0000	.0000	
	3	25.0000	4.0000	.0000	.0000	.0000	
	4	25.0000	8.0000	.0016	.0001	.0015	
	5	25.0000	12.0000	.0269	.0041	.0228	
	6	25.0000	16.0000	.0854	.0288	.0566	
	7	25.0000	20.0000	.1715	.0889	.0826	
	8	25.0000	24.0000	.2657	.1809	.0848	
	9	25.0000	28.0000	.3531	.2908	.0623	
	10	25.0000	32.0000	.4403	.4043	.0360	
	11	25.0000	36.0000	.5494	.5113	.0381	
	12	25.0000	40.0000	.5909	.6062	-.0153	
	13	25.0000	44.0000	.6339	.6871	-.0532	
	14	25.0000	48.0000	.6630	.7540	-.0910	
	15	25.0000	52.0000	.7209	.8082	-.0873	
	16	25.0000	55.0000	.7819	.8416	-.0597	

Appendix A-5: Output files for Predicting BTEX Sorption Distribution Coefficients in Column Study with Produced Water.

Benzene sorption coefficient Kd in produced water

```

*****
*
* CXTFIT VERSION 2.0 (1/2/95)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS
*
* Benzene sorption coefficient Kd in produced water
* Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
*
* DATA INPUT FILE: pw-CSL.in
*
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02   N
D.....  .2100E+03   N
R.....  .1000E+01   Y
mu.....  .0000E+00   N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. =  1.0000 & DURATION =  55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS =  30

ITER  SSQ    R...
0    .1872E+01 .100E+01
1    .3848E+00 .319E+02
2    .4842E-01 .207E+02
3    .3604E-01 .188E+02
4    .3566E-01 .185E+02
5    .3565E-01 .185E+02
    
```

6 .3565E-01 .185E+02

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .98406392
 (COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

95% CONFIDENCE LIMITS
 NAME VALUE S.E.COEFF. LOWER UPPER
 R.... .1846E+02 .4720E-01 .1836E+02 .1856E+02

-----ORDERED BY COMPUTER INPUT-----

		CONCENTRATION		RESI-		
\$	NO	DISTANCE	TIME	OBS	FITTED	DUAL
	1	25.0000	.0000	.0000	.0000	
	2	25.0000	1.0000	.0000	.0000	
	3	25.0000	3.0000	.1520	.1165	.0355
	4	25.0000	6.0000	.6892	.6615	.0277
	5	25.0000	9.0000	.8494	.9120	-.0626
	6	25.0000	12.0000	.8738	.9794	-.1056
	7	25.0000	15.0000	.9190	.9953	-.0763
	8	25.0000	18.0000	1.0058	.9989	.0069
	9	25.0000	21.0000	.9863	.9998	-.0135
	10	25.0000	24.0000	.9983	.9999	-.0016
	11	25.0000	27.0000	1.0347	1.0000	.0347
	12	25.0000	30.0000	1.0113	1.0000	.0113
	13	25.0000	33.0000	1.0171	1.0000	.0171
	14	25.0000	36.0000	1.0543	1.0000	.0543
	15	25.0000	39.0000	1.0766	1.0000	.0766
	16	25.0000	42.0000	1.0453	1.0000	.0453
	17	25.0000	45.0000	.9972	1.0000	-.0028

\$

Toluene sorption coefficient Kd in produced water

```

*
* CXTFIT VERSION 2.0 (1/2/95) *
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS *
* *
* Toluene sorption coefficient Kd in produced water *
* Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
* *
* DATA INPUT FILE: pw-CSL.in *
* *
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02    N
D.....  .2100E+03    N
R.....  .1000E+01    Y
mu.....  .0000E+00    N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. =  1.0000 & DURATION =  55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS =  30

ITER  SSQ    R...
0   .4116E+01 .100E+01
1   .3126E+01 .125E+03
2   .2293E-01 .506E+02
3   .2274E-01 .503E+02
4   .2273E-01 .502E+02
5   .2273E-01 .502E+02

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .99091125
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
    
```

```

=====
          95% CONFIDENCE LIMITS
NAME      VALUE      S.E.COEFF.  LOWER      UPPER
R....    .5021E+02   .3769E-01  .5013E+02  .5029E+02

-----ORDERED BY COMPUTER INPUT-----
          CONCENTRATION  RESI-
$ NO  DISTANCE  TIME  OBS  FITTED  DUAL
1  25.0000   .0000 .0000 .0000 .0000
2  25.0000   1.0000 .0002 .0000 .0002
3  25.0000   3.0000 .0012 .0001 .0011
4  25.0000   6.0000 .0680 .0257 .0423
5  25.0000   9.0000 .2447 .1688 .0759
6  25.0000  12.0000 .4059 .3866 .0193
7  25.0000  15.0000 .5736 .5886 -.0150
8  25.0000  18.0000 .7421 .7394 .0027
9  25.0000  21.0000 .7915 .8405 -.0490
10 25.0000  24.0000 .8865 .9044 -.0179
11 25.0000  27.0000 .9381 .9435 -.0054
12 25.0000  30.0000 .9083 .9669 -.0586
13 25.0000  33.0000 .9470 .9807 -.0337
14 25.0000  36.0000 .9695 .9888 -.0193
15 25.0000  39.0000 .9511 .9935 -.0424
16 25.0000  42.0000 .9723 .9962 -.0239
17 25.0000  45.0000 .9306 .9978 -.0672
$
    
```

Ethylbenzene sorption coefficient Kd in produced water

```

*****
*
* CXTFIT VERSION 2.0 (1/2/95)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS
*
* Ethylbenzene sorption coefficient Kd in produced water
* Conc. vs. time at 25 cm (dimentional V D L T; cm min g) *
*
* DATA INPUT FILE: pw-CSL.in
*
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02   N
D.....  .2100E+03   N
R.....  .1000E+01   Y
mu.....  .0000E+00   N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS = 30

ITER  SSQ   R...
0  .1073E+02 .100E+01
1  .1769E+00 .125E+03
2  .4429E-01 .143E+03
3  .4039E-01 .146E+03
4  .4035E-01 .147E+03
5  .4035E-01 .147E+03

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .93377468
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
=====
    
```

95% CONFIDENCE LIMITS				
NAME	VALUE	S.E.COEFF.	LOWER	UPPER
R....	.1467E+03	.5022E-01	.1466E+03	.1468E+03

-----ORDERED BY COMPUTER INPUT-----

\$	NO	CONCENTRATION		RESI-	DUAL	
		DISTANCE	TIME	OBS		FITTED
	1	25.0000	.0000	.0000	.0000	.0000
	2	25.0000	1.0000	.0000	.0000	.0000
	3	25.0000	3.0000	.0000	.0000	.0000
	4	25.0000	6.0000	.0000	.0000	.0000
	5	25.0000	9.0000	.0000	.0001	-.0001
	6	25.0000	12.0000	.0097	.0016	.0081
	7	25.0000	15.0000	.0374	.0094	.0280
	8	25.0000	18.0000	.0853	.0300	.0553
	9	25.0000	21.0000	.1318	.0670	.0648
	10	25.0000	24.0000	.1784	.1199	.0585
	11	25.0000	27.0000	.2794	.1852	.0942
	12	25.0000	30.0000	.3132	.2583	.0549
	13	25.0000	33.0000	.3459	.3346	.0113
	14	25.0000	36.0000	.4275	.4104	.0171
	15	25.0000	39.0000	.4342	.4830	-.0488
	16	25.0000	42.0000	.4999	.5506	-.0507
	17	25.0000	45.0000	.5047	.6122	-.1075

\$

m,p-Xylene sorption coefficient Kd in produced water

```

*****
*
* CXTFIT VERSION 2.0 (1/2/95)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS
*
* m,p-Xylene sorption coefficient Kd in produced water
* Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
*
* DATA INPUT FILE: pw-CSL.in
*
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02   N
D.....  .2100E+03   N
R.....  .1000E+01   Y
mu.....  .0000E+00   N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS = 30

ITER  SSQ    R...
0    .9498E+01 .100E+01
1    .2538E-01 .125E+03
2    .2528E-01 .125E+03
3    .2528E-01 .125E+03

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .97553946
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
=====

NAME      VALUE      95% CONFIDENCE LIMITS
          S.E.COEFF.  LOWER      UPPER
    
```

R.... .1251E+03 .3975E-01 .1250E+03 .1252E+03

-----ORDERED BY COMPUTER INPUT-----

		CONCENTRATION	RESI-			
\$	NO	DISTANCE	TIME	OBS	FITTED	DUAL
	1	25.0000	.0000	.0000	.0000	.0000
	2	25.0000	1.0000	.0000	.0000	.0000
	3	25.0000	3.0000	.0000	.0000	.0000
	4	25.0000	6.0000	.0000	.0000	.0000
	5	25.0000	9.0000	.0000	.0005	-.0005
	6	25.0000	12.0000	.0204	.0059	.0145
	7	25.0000	15.0000	.0571	.0262	.0309
	8	25.0000	18.0000	.1230	.0686	.0544
	9	25.0000	21.0000	.1852	.1325	.0527
	10	25.0000	24.0000	.2441	.2123	.0318
	11	25.0000	27.0000	.3695	.3003	.0692
	12	25.0000	30.0000	.4156	.3897	.0259
	13	25.0000	33.0000	.4568	.4757	-.0189
	14	25.0000	36.0000	.5573	.5551	.0022
	15	25.0000	39.0000	.5873	.6262	-.0389
	16	25.0000	42.0000	.6470	.6884	-.0414
	17	25.0000	45.0000	.6508	.7420	-.0912

\$

o-Xylene sorption coefficient Kd in produced water

```

*****
*
* CXTFIT VERSION 2.0 (1/2/95)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS
*
* o-Xylene sorption coefficient Kd in produced water
* Conc. vs. time at 25 cm (dimensional V D L T; cm min g) *
*
* DATA INPUT FILE: pw-CSL.in
*
*****
    
```

Model Description

```

=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REAL TIME (t), POSITION(x)
(D,V,mu, AND gamma ARE ALSO DIMENSIONAL)

INITIAL VALUES OF COEFFICIENTS
=====
NAME      INITIAL VALUE  FITTING
V.....  .8400E+02    N
D.....  .2100E+03    N
R.....  .1000E+01    Y
mu.....  .0000E+00    N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 55.0000
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE
=====
MAXIMUM NUMBER OF ITERATIONS = 30

ITER  SSQ    R....
0    .9498E+01 .100E+01
1    .2538E-01 .125E+03
2    .2528E-01 .125E+03
3    .2528E-01 .125E+03

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .97553946
(COEFFICIENT OF DETERMINATION)

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS
=====
    
```

95% CONFIDENCE LIMITS						
NAME	VALUE	S.E.COEFF.	LOWER	UPPER		
R....	.1251E+03	.3975E-01	.1250E+03	.1252E+03		
-----ORDERED BY COMPUTER INPUT-----						
		CONCENTRATION	RESI-			
\$	NO	DISTANCE	TIME	OBS	FITTED	DUAL
	1	25.0000	.0000	.0000	.0000	.0000
	2	25.0000	1.0000	.0000	.0000	.0000
	3	25.0000	3.0000	.0000	.0000	.0000
	4	25.0000	6.0000	.0000	.0000	.0000
	5	25.0000	9.0000	.0000	.0005	-.0005
	6	25.0000	12.0000	.0204	.0059	.0145
	7	25.0000	15.0000	.0571	.0262	.0309
	8	25.0000	18.0000	.1230	.0686	.0544
	9	25.0000	21.0000	.1852	.1325	.0527
	10	25.0000	24.0000	.2441	.2123	.0318
	11	25.0000	27.0000	.3695	.3003	.0692
	12	25.0000	30.0000	.4156	.3897	.0259
	13	25.0000	33.0000	.4568	.4757	-.0189
	14	25.0000	36.0000	.5573	.5551	.0022
	15	25.0000	39.0000	.5873	.6262	-.0389
	16	25.0000	42.0000	.6470	.6884	-.0414
	17	25.0000	45.0000	.6508	.7420	-.0912

Appendix B: Batch Studies**Appendix B-1: Isotherm Data and Percent Differences for Single-Solute Test****Table B.1 Isotherm Data for Benzene in Saline Solutions**

Millipore Water		30,000 ppm		231,000 ppm	
C _e μg/L	q _e μg/g	C _e μg/L	q _e μg/g	C _e μg/L	q _e μg/g
4.5	0.05	0	0	0	0
45	0.44	0	0	0	0
4642	44.07	2.5	0.02	0.86	0.03
32130	337.64	2.6	0.02	0.86	0.03
		4.5	0.05	1.8	0.07
		4.7	0.04	1.7	0.07
		47	0.43	18	0.66
		47	0.42	17	0.65
		480	4.28	187	6.65
		474	4.19	182	6.74
		4716	43.20	1844	67.91
		4690	43.78	1761	67.75
		18783	173.23	6915	259.45
		19692	167.76	7118	271.73
		35148	316.29	12203	497.97
		broken	broken	11661	500.07

Table B.2 Percent Differences Between Duplicates

C _o μg/L	30,000 ppm		231,000 ppm	
	C _e μg/L	q _e μg/g	C _e μg/L	q _e μg/g
5	1.8	4.5	0.2	1.9
10	5.1	5.7	5.4	2.0
100	1.3	2.1	3.0	0.5
1000	1.2	2.3	2.6	1.2
10000	0.5	1.3	4.5	0.2
40000	4.8	3.2	2.9	4.7
75000	broken	broken	4.4	0.4

Appendix B-2: Isotherm Data and Percent Differences for Multi-Solute Test**Table B.3 - Isotherm Data for Multi-Solutes in Saline Solutions**

Compound	Millipore Water		30,000 ppm		100,000 ppm		200,000 ppm	
	C _e μg/L	q _e μg/g						
Benzene	7	0.06	0	0	0	0	0	0
	453	4.34	0	0	0	0	0	0
	4597	44.58	7	0.06	6	0.07	3	0.10
			7	0.06	6	0.07	3	0.10
			470	4.20	369	5.22	200	6.51
			477	4.34	377	5.09		
		4644	43.94	3590	53.27			
		4720	43.57	3628	52.46			
Toluene	4	0.09	0	0	0	0	0	0
	237	6.07	0	0	0	0	0	0
	2351	62.72	5	0.08	3	0.10	2	0.11
			5	0.08	3	0.10	2	0.10
			247	5.98	167	6.87	71	7.54
			249	6.19	171	6.74		
		2392	62.25	1569	69.65			
		2388	62.42	1561	69.32			
Ethylbenzene	1	0.11	0	0	0	0	0	0
	113	7.08	0	0	0	0	0	0
	1106	72.94	1.0	0.11	0	0.12	0	0.12
			1.0	0.11	0	0.12	0	0.12
			115.9	7.03	68	7.70	24	7.93
			116.8	7.28	69	7.57		
		1071.5	73.16	620	77.51			
		1088.0	73.08	626	77.10			
m- and p-Xylenes	2	0.11	0	0	0	0	0	0
	102	7.15	0	0	0	0	0	0
	1001	73.61	2	0.11	0.55	0.11	0	0.12
			2	0.11	0.64	0.11	0	0.12
			104	7.11	59	7.75	21	7.94
			105	7.36	60	7.62		
		962	73.87	542	77.96			
		975	73.82	546	77.58			
o-Xylene	0	0.12	0	0	0	0	0	0
	115	7.06	0	0	0	0	0	0
	1132	72.66	0	0.12	0	0.12	0	0.12
			0	0.12	0	0.12	0	0.12
			117	7.02	70	7.68	25	7.92
			119	7.25	71	7.55		
		1094	72.90	647	77.22			
		1117	72.77	652	76.81			

Table B.4 - Percent Differences Between Replicates in Multi-Solute Salinity Studies

Compound	C _o μg/L	30,000 ppm		100,000 ppm		200,000 ppm	
		C _e μg/L	q _e μg/g	C _e μg/L	q _e μg/g	C _e μg/L	q _e μg/g
Benzene	15	4	4	0	2	10	2
Toluene	15	1	1	0	1	16	2
Ethylbenzene	15	3	1	-	1	-	0
m- & p-Xylenes	15	1	1	18	1	-	0
o-Xylene	15	-	1	-	1	-	0
Benzene	1000	2	3	2	3	-	-
Toluene	1000	1	4	2	2	-	-
Ethylbenzene	1000	1	3	2	2	-	-
m- & p-Xylenes	1000	1	3	1	2	-	-
o-Xylene	1000	1	3	1	2	-	-
Benzene	10000	2	1	1	2	-	-
Toluene	10000	0	0	1	0	-	-
Ethylbenzene	10000	2	0	1	1	-	-
m- & p-Xylenes	10000	1	0	1	0	-	-
o-Xylene	10000	2	0	1	1	-	-

Appendix B-3: Multi-Solute Isotherms for Ethylbenzene, m- & p-Xylenes, and o-Xylene

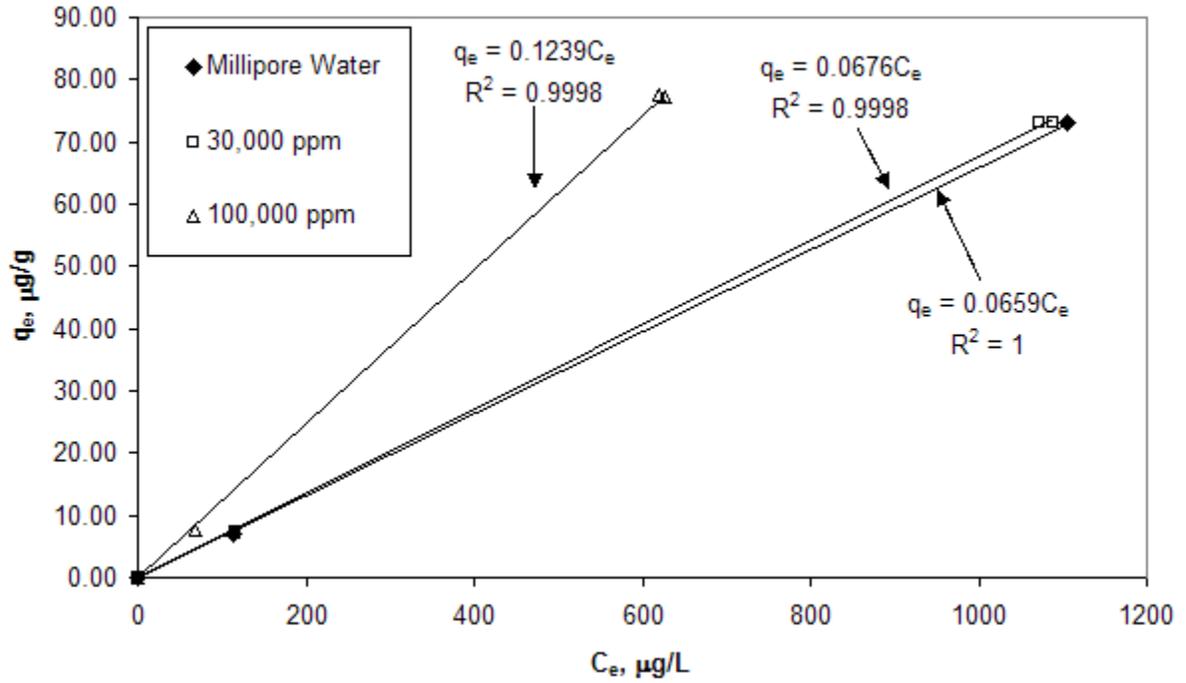


Figure B.1 - Ethylbenzene Sorption Isotherms in Aqueous Solutions of Varying Salinities

Appendix B-4: Isotherm Data for Benzene, Toluene, Ethylbenzene, m- & p-Xylene, and o-Xylene at Different Temperature in ultrapure Water

Table B.5 – Isotherm Data at 4°C

Benzene		Toluene		Ethylbenzene		m- & p-Xylene		o-Xylene	
C _e μg/L	q _e μg/g								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44.57	0.44	27.36	0.58	12.95	0.70	12.40	0.70	13.17	0.69
52.53	0.37	32.47	0.54	16.23	0.67	15.16	0.68	16.15	0.67
52.14	0.38	32.22	0.54	15.88	0.67	14.99	0.68	15.70	0.67
570.80	3.66	351.73	5.49	189.65	6.80	169.91	6.96	184.98	6.84
581.61	3.59	358.89	5.44	193.78	6.77	173.57	6.93	188.42	6.81
552.22	3.47	339.05	5.24	182.60	6.50	163.30	6.66	177.68	6.54
5564.44	33.92	3374.67	52.09	1791.94	64.90	1598.58	66.48	1731.49	65.40
5570.72	34.32	3350.22	52.69	1783.01	65.33	1594.93	66.87	1731.81	65.75
5569.82	33.99	3327.55	52.55	1742.98	65.34	1553.34	66.88	1686.55	65.80
18907.82	165.66	10447.82	234.79	5053.02	277.63	4574.03	281.47	5000.21	278.06
18920.37	165.77	10409.61	235.79	5006.01	279.00	4526.59	282.87	4863.60	280.16
19499.09	168.66	10753.41	240.79	5134.34	285.85	4617.98	290.02	4988.30	287.04

Table B.6 – Isotherm Data at 10°C

Benzene		Toluene		Ethylbenzene		m- & p-Xylene		o-Xylene	
C _e	q _e								
μg/L	μg/g								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53.41	0.36	32.62	0.53	15.59	0.67	14.79	0.68	15.52	0.67
52.13	0.38	31.65	0.54	15.11	0.68	14.38	0.68	15.18	0.68
52.42	0.37	32.03	0.54	15.77	0.67	14.54	0.68	15.34	0.67
538.44	3.95	319.61	5.78	166.06	7.02	148.97	7.16	163.11	7.05
519.70	3.79	306.23	5.54	157.42	6.72	141.79	6.85	156.01	6.73
515.51	3.82	300.08	5.57	153.17	6.73	137.99	6.85	152.11	6.74
5399.90	35.34	3092.21	54.73	1560.12	67.28	1401.06	68.59	1539.72	67.45
5320.82	35.77	3042.70	54.73	1526.58	67.04	1368.57	68.33	1505.86	67.21
5220.52	37.18	2950.51	55.82	1479.66	67.59	1326.47	68.83	1457.07	67.77
18431.70	176.66	9733.65	248.11	4536.74	289.56	4139.82	292.75	4517.20	289.72
18035.25	180.02	9536.54	250.41	4409.31	291.62	4018.48	294.78	4357.75	292.04
18522.08	174.47	9762.21	247.74	4473.17	290.72	4065.93	294.05	4439.25	291.00

Table B.7 – Isotherm Data at 15°C

Benzene		Toluene		Ethylbenzene		m- & p-Xylene		o-Xylene	
C _e	q _e								
μg/L	μg/g								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53.06	0.37	30.92	0.55	14.67	0.68	13.79	0.69	14.53	0.68
50.28	0.39	29.73	0.56	14.00	0.68	13.16	0.69	13.72	0.68
53.34	0.36	30.99	0.55	14.39	0.68	13.60	0.69	14.37	0.68
538.51	3.60	305.50	5.53	152.48	6.77	137.45	6.90	152.58	6.77
514.96	3.82	290.39	5.67	145.31	6.84	130.74	6.96	145.17	6.84
514.66	4.15	283.92	6.07	138.90	7.25	124.99	7.36	139.76	7.24
972.29	0.00	2842.82	56.90	1400.75	68.33	1260.28	69.45	1397.72	68.35
5142.23	38.17	2840.63	57.04	1397.22	68.58	1256.32	69.72	1390.96	68.63
5125.41	38.28	2899.00	56.36	1385.59	68.41	1246.00	69.53	1393.30	68.35
17645.44	182.46	9246.04	252.39	4322.47	292.14	3892.13	295.65	4290.83	292.41
18339.69	177.41	9199.87	253.10	4135.56	293.83	3707.57	297.30	4144.14	293.76
19079.52	164.46	9347.59	243.77	4140.13	285.04	3726.43	288.35	4272.61	283.98

Table B.8 – Isotherm Data at 20°C

Benzene		Toluene		Ethylbenzene		m- & p-Xylene		o-Xylene	
C _e	q _e								
μg/L	μg/g								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47.31	0.42	26.39	0.59	11.94	0.70	11.35	0.71	11.82	0.70
47.95	0.41	26.89	0.58	11.83	0.70	11.25	0.71	12.08	0.70
49.29	0.40	27.23	0.58	11.93	0.70	11.59	0.70	12.12	0.70
498.60	4.27	270.37	6.18	130.86	7.31	118.37	7.41	132.34	7.30
489.38	4.04	265.38	5.87	129.06	6.95	116.78	7.05	129.98	6.94
489.80	4.06	264.61	5.87	128.20	6.94	115.94	7.04	129.40	6.93
4831.43	41.30	2576.33	59.52	1242.19	70.00	1126.91	70.91	1248.09	69.95
5035.76	38.44	2653.75	58.11	1257.20	69.34	1136.67	70.31	1282.77	69.13
4811.27	40.32	2574.80	58.93	1236.38	69.76	1116.25	70.74	1240.30	69.72
17242.80	179.60	8628.19	249.74	3930.08	286.81	3564.84	289.72	3994.33	286.30
16779.73	191.11	8419.83	259.96	3838.81	296.47	3461.86	299.51	3843.40	296.44
16465.36	194.00	8271.47	261.33	3787.00	296.97	3417.44	299.94	3797.36	296.89

Table B.9 – Isotherm Data at 25°C

Benzene		Toluene		Ethylbenzene		m- & p-Xylene		o-Xylene	
C _e	q _e								
μg/L	μg/g								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44.74	0.43	24.00	0.61	11.13	0.71	10.79	0.71	11.71	0.70
45.15	0.43	24.43	0.60	10.62	0.71	10.52	0.71	11.09	0.71
43.95	0.44	23.53	0.61	10.41	0.71	9.96	0.72	10.46	0.71
451.11	4.31	233.68	6.11	110.29	7.09	99.78	7.18	111.93	7.08
473.08	4.47	245.03	6.37	115.62	7.41	104.54	7.50	117.31	7.40
456.49	4.26	235.79	6.07	111.11	7.06	100.66	7.14	112.94	7.04
4662.81	42.11	2398.05	60.83	1136.53	70.96	1026.92	71.85	1148.97	70.86
4673.76	41.37	2397.56	60.34	1122.49	70.67	1015.61	71.54	1137.22	70.55
4608.59	41.94	2383.32	60.63	1128.77	70.87	1019.67	71.77	1144.47	70.74
16115.36	197.06	7960.02	263.97	3585.86	298.65	3240.74	301.42	3633.61	298.27
16492.91	192.35	8254.15	260.75	3770.85	296.77	3414.57	299.66	3798.83	296.55
16184.42	194.81	8006.08	261.44	3643.86	295.79	3298.46	298.53	3665.18	295.62

Table B.10 – Isotherm Data at 36°C

Benzene		Toluene		Ethylbenzene		m- & p-Xylene		o-Xylene	
C _e	q _e								
μg/L	μg/g								
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42.83	0.45	22.13	0.62	9.30	0.72	9.00	0.72	9.44	0.72
42.57	0.46	22.31	0.62	9.22	0.73	9.01	0.73	9.41	0.73
41.98	0.45	21.62	0.62	9.03	0.73	8.83	0.73	9.18	0.72
438.80	4.44	222.99	6.21	103.18	7.16	93.95	7.23	106.33	7.13
449.43	4.70	227.94	6.56	105.68	7.55	96.16	7.63	108.51	7.53
464.90	4.56	237.18	6.46	110.45	7.48	100.23	7.57	113.36	7.46
4454.32	43.44	2261.84	61.43	1056.61	71.03	958.77	71.82	1080.07	70.84
4590.72	42.83	2316.18	61.40	1067.14	71.31	968.33	72.10	1088.83	71.13
4504.73	43.22	2267.86	61.64	1047.58	71.40	949.55	72.19	1064.77	71.26
16010.21	194.44	7887.01	262.18	3492.10	297.63	3267.91	299.45	3652.93	296.31
16081.88	195.27	7908.41	262.71	3479.38	298.05	3232.51	300.03	3578.93	297.24
15930.95	197.78	7836.73	263.92	3450.54	298.56	3181.58	300.70	3546.81	297.78

Appendix B-5: Isotherms for Benzene, Toluene, Ethylbenzene, m- & p-Xylene and o-Xylene in Produced Water

Benzene		Toluene		Ethylbenzene		m- & p- Xylene		o-Xylene	
C _e μg/L	q _e μg/g								
5442	79.73	6324	168.83	116	9.83	906	64.61	410	20.29
4793	84.74	5171	177.68	86	10.05	517	67.57	215	21.80
5341	81.79	5977	174.25	81	10.26	776	66.66	334	21.22
5459	81.71	6007	174.98	138	10.61	673	68.36	296	22.35
5538	80.32	5947	173.84	131	10.58	604	68.28	293	22.17
5285	83.37	6067	175.00	89	11.04	777	67.71	324	22.19
5668	86.08	5861	180.88	195	17.21	755	73.93	376	28.60
5602	87.75	6034	181.97	184	17.43	851	74.10	435	28.41
5797	84.79	5824	180.57	167	17.40	648	74.55	369	28.58
				1196	81.16	1363	141.79	1270	93.56
9382	129.01	7562	241.68	998	82.77	1596	140.00	1303	93.32
10000	123.90	7532	241.53	1196	81.16	1572	140.05	1420	92.33
21973	242.80	12383	441.97	3576	301.79	3881	360.91	3895	312.15
22438	272.80	12416	450.37	3848	307.48	4026	367.94	4086	318.55
19611	292.15			4003	306.36	3955	368.28	4112	318.40

Appendix C: Column StudiesAppendix C-1: Breakthrough Data in Column Study Conducted with ultrapure Water

T	C/C0				
min	Benzene	Toluene	Ethylbenzene	m-&p-Xylene	o-Xylene
0	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.0122	0.0000	0.0000	0.0000	0.0000
4	0.6104	0.0210	0.0000	0.0000	0.0000
6	0.8388	0.1312	0.0000	0.0000	0.0000
8	0.9369	0.3756	0.0045	0.0024	0.0066
10	0.9471	0.5645	0.0234	0.0119	0.0313
12	0.9517	0.7116	0.0705	0.0401	0.0881
14	0.9671	0.7813	0.1379	0.0868	0.1633
16	0.9796	0.8779	0.2284	0.1544	0.2598
18	1.0005	0.9328	0.3431	0.2510	0.3779
20	0.9782	0.9461	0.3733	0.2823	0.4009
22	0.9634	0.9226	0.5131	0.4169	0.5415
24	0.9749	0.9281	0.5777	0.4870	0.6086
26	0.9558	0.9253	0.6330	0.5455	0.6513
28	0.9835	0.9672	0.7182	0.6365	0.7427
30	0.9763	0.9543	0.7454	0.6715	0.7616
32	0.9819	0.9373	0.7665	0.7041	0.7835
34	0.9913	0.9588	0.8188	0.8067	0.8279
36	1.0239	1.0098	0.8788	0.8232	0.8816
38	1.0186	1.0118	0.9021	0.8546	0.9085
40	0.9904	0.9233	0.9009	0.8587	0.9076
42	0.9845	0.9724	0.9004	0.8650	0.9042
44	1.0087	1.0018	0.9392	0.9069	0.9360
46	1.0041	1.0210	0.9621	0.8851	0.9991
48	0.9935	1.0511	8.4168	0.9345	0.9956
50	1.0012	0.9902	0.9476	0.9251	0.9447
52	0.9970	0.9592	0.9229	0.8949	0.9730
54	0.9951	0.9784	0.9498	0.9318	0.9416
56	1.0114	0.9997	0.9753	0.9598	0.9670
58	1.0437	1.0383	1.0134	0.9996	1.0081
60	1.0002	0.9862	0.9658	0.9517	0.9568

Appendix C-2: Breakthrough Data in Column Study Conducted with Saline Water

T (min)	Benzene	Toluene	Ethylbenzene	m-&p-Xylene	o-Xylene
0	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.0008	0.0007	0.0000	0.0000	0.0000
4	0.4565	0.0120	0.0000	0.0000	0.0000
8	0.9340	0.2176	0.0009	0.0000	0.0016
12	0.9747	0.5737	0.0186	0.0089	0.0269
16	0.9931	0.7011	0.0649	0.0358	0.0854
20	1.0041	0.8144	0.1374	0.0847	0.1715
24	1.0104	0.8492	0.2213	0.1492	0.2657
28	0.9612	0.8644	0.3025	0.2181	0.3531
32	0.9840	0.9053	0.3842	0.2908	0.4403
36	1.0228	0.9509	0.4887	0.3898	0.5494
40	1.0041	0.9414	0.5315	0.4364	0.5909
44	1.0061	0.9252	0.5755	0.4876	0.6339
48	0.9614	0.9152	0.6055	0.5241	0.6630
52	0.9836	0.9430	0.6625	0.5848	0.7209
55	1.0181	0.9846	0.7220	0.6457	0.7819

Note: the concentration is fractional.

Appendix C-3: Breakthrough Data in Column Study Conducted with Produced Water

T	C/C0				
Min	Benzene	Toluene	Ethylbenzene	m-&p-Xylene	o-Xylene
0	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.0000	0.0002	0.0000	0.0000	0.0000
3	0.1520	0.0012	0.0000	0.0000	0.0000
6	0.6892	0.0680	0.0000	0.0000	0.0000
9	0.8494	0.2447	0.0000	0.0023	0.0000
12	0.8738	0.4059	0.0097	0.0102	0.0204
15	0.9190	0.5736	0.0374	0.0277	0.0571
18	1.0058	0.7421	0.0853	0.0624	0.1230
21	0.9863	0.7915	0.1318	0.0991	0.1852
24	0.9983	0.8865	0.1784	0.1378	0.2441
27	1.0347	0.9381	0.2749	0.2185	0.3695
30	1.0113	0.9083	0.3132	0.2553	0.4156
33	1.0171	0.9470	0.3459	0.2883	0.4568
36	1.0543	0.9695	0.4275	0.3624	0.5573
39	1.0766	0.9511	0.4342	0.4238	0.5873
42	1.0453	0.9723	0.4999	0.4415	0.6470
45	0.9972	0.9306	0.5047	0.4509	0.6508

Note: the concentration is fractional.

**Appendix D Averages and Standard Deviations for BTEX Sorption Study in
ultrapure Water at 20°C**

Compounds	Initial Concentration ($\mu\text{g/L}$)	Final Concentration ($\mu\text{g/L}$)	Sorption Density ($\mu\text{g/g}$)
		Average \pm Std. Dev.	Average \pm Std. Dev.
Benzene	0	0 \pm 0	0 \pm 0
	100	48.2 \pm 1.01	0.406 \pm 0.01
	1000	492.6 \pm 5.21	4.12 \pm 0.129
	10000	4892.8 \pm 124.2	40.0 \pm 1.45
	40000	16829.3 \pm 391.1	188.2 \pm 7.62
Toluene	0	0 \pm 0	0 \pm 0
	100	26.8 \pm 0.42	0.58 \pm 0.0047
	1000	266.8 \pm 3.13	5.97 \pm 0.18
	10000	2601.6 \pm 45.15	58.85 \pm 0.71
	40000	8439.8 \pm 179.2	257.0 \pm 6.33
Ethylbenzene	0	0 \pm 0	0 \pm 0
	100	11.9 \pm 0.06	0.70 \pm 0.0011
	1000	129.4 \pm 1.40	7.07 \pm 0.21
	10000	1245.3 \pm 10.7	69.7 \pm 0.34
	40000	3852.0 \pm 72.4	293.4 \pm 5.70
m,p-Xylene	0	0 \pm 0	0 \pm 0
	100	11.4 \pm 0.17	0.71 \pm 0.0015
	1000	117.0 \pm 1.24	7.17 \pm 0.21
	10000	1126.6 \pm 10.2	70.6 \pm 0.31
	40000	3481.4 \pm 75.6	296.4 \pm 5.8
O-Xylene	0	0 \pm 0	0 \pm 0
	100	12 \pm 0.17	0.7 \pm 0.0026
	1000	130.6 \pm 1.56	7.06 \pm 0.21
	10000	1257 \pm 22.6	69.6 \pm 0.43
	40000	3878 \pm 103	293.2 \pm 6.0

NOTE: SMZ'S MESH SIZE IS 14x40.