QUANTIFICATION
OF BTX SORPTION TO
SURFACE-ALTERED ZEOLITES

By

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Dedication

This report, representing a great deal
of effort, time, and sometimes heartache,
is dedicated to

Patrick Drew McCarter

in the hope that the fruits of this labor
will someday make up for all that I've missed
in the beginning.

Acknowledgements

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1. INTRODUCTION

INTRODUCTION

Zeolite Formation and Characteristics

Natural zeolites have emerged in the past thirty years as an easily accessible and relatively inexpensve natural resource. They are used successfully in many applications as cation-exchangers, adsorbents, molecular sieves and dessicants. The use of zeolites is particularly important where large quantities of material are required (Kallo and Sherry, 1988).

By 1984, some 40-50 naturally-occurring zeolites having 25 different structures were identified. Chemically, zeolites are alkali and alkaline earth hydro-aluminosilicates. They occur as crystals in volcanic rocks and sedimentary formations (Tsitsishvili, 1985). In terms of volume and frequency of occurrence, laumonite, heulandite-clinoptilolite, and analcime are the most common (Boles, 1985). The species and amount of zeolite vary primarily as a function of texture and composition of the host rock, composition of interstitial water, age, and temperature (Hay, 1976).

Zeolites are crystalline materials composed of tetrahedral structures that combine to form open frameworks. Because of these voids and channels that penetrate the whole crystal, zeolites are microporous bodies that maintain regular structures. The voids and channels contain cations that counterbalance the negative charge of the framework, caused by isomorphic substitution of aluminum into the tetrahedral unit (Tsitsishvili, 1985). These cations are available for exchange. The microporous structure yields materials with high cation exchange capacities (CEC's), which has generated an intense interest in the scientific, industrial and agricultural communities for the possible use of zeolites in the remediation or contamination field.

Openings in the channels of the zeolite structure allow for molecular sieving. The openings are on the order of nanometers and are fixed in size. In order for a molecule to penetrate the zeolitic voids, it must be smaller than these openings; otherwise, it will be excluded from the primary porosity of the zeolite. This molecular sieving effect is characteristic of all zeolites (Tsitsishvili, 1985).

Large molecules, such as certain quaternary amines, are excluded from the interior zeolitic chambers because of their size. Hence, only the external surface is available to these molecules for sorption and exchange. Adsorption of these large molecules significantly alters the surface of the mineral from hydrophillic to hydrophobic. Through synthetic alteration of mineral surfaces with quaternary amines, both Mortland et al. (1986) and Boyd et al. (1988) have shown that the more hydrophobic the mineral surface the greater sorption of organic chemicals.

Clinoptilolite, used in the experiments described in this paper, is one of the most common natural zeolites. Average opening size is approximately 0.20 nm^2 (Ming and Mumpton, 1989).

It occurs as an alteration product of volcanic ash in saline alkaline lakes, as an authigenic silicate in marine deposits, and as a product of hydrothermal alteration of vitric tuffs in geothermal areas (Hawkins, 1976).

In general, previous research on zeolites was focused primarily on industrial and agricultural applications. However, in light of the growing concern over environmental pollutants and their effect on the earth's ecosystem, zeolite research has been expanded to include environmental applications. The high CEC's, low expense, and relative availablity of these materials make the use of zeolites for environmental applications an attractive alternative to more conventional - and perhaps more expensive - treatments. Although few practical applications are available as yet, the heightened awareness of the versatility and effectiveness of zeolites has sparked much research in the academic community.

Although natural zeolites have been used with great success for some time in the sorption of heavy metals (Semmens & Seyfarth, 1976), they do not share the same propensity for organic compounds. Boyd et al. (1989) and Lee et al. (1989) have shown that a marked increase in the sorption of non-ionic organic compounds from solution can be achieved by surface-alteration of clays and soils by quaternary amines. Additionally, a recent study by Huddleston (1990) also demonstrated the effectiveness of a surface-altered zeolite in the sorption of halogenated hydrocarbons.

The ability of surface-modified (or tailored) zeolites to sorb halogenated hydrocarbons from aqueous solutions led the writer to expand this application to other common groundwater contaminants, namely, benzene, toluene and p-xylene (BTX).

The objectives of this study were several:

1) To quantify the amount of sorption of BTX compounds to zeolites using quaternary amines as the tailoring (or surface-altering) agents;
2) To determine the mechanism of sorption of these compounds to the zeolites, i.e., partitioning or adsorption;
3) To compare and contrast the experimental distribution coefficients with those obtained from the literature; and,
4) To establish a correlation between the distribution coefficient, soil organic carbon content and tailoring agent for future prediction of these parameters for any given zeolite, solute and tailoring agent.

2. PARTITIONING THEORY

PARTITIONING THEORY

The degree of sorption of nonionic organic compounds to a soil surface in aqueous solution has been shown by many (Chiou, 1979; Karickhoff, 1981; Chiou et al., 1983; Rutherford et al., 1992) to be controlled by the organic matter content. Lee et al. (1989), Boyd et al. (1988), and Huddleston (1990) have determined that the uptake of nonionic organic compounds can be greatly enhanced by exchanging organic cations onto the soil surface. The mechanism by which nonionic organic compound sorption occurs is thought by Chiou (1989) and others (Rutherford et al., 1992; Lee et al., 1989) to be a partitioning process, not an adsorption process. Lee et al. (1989) suggest that this is a process of solubilization of these chemicals into the synthetic organic phase formed by the conglomeration of the alkyl tails of the exchanged quaternary amines, i.e., partitioning. In order to clarify any misconceptions about the mechanisms associated with organic chemical partitioning, some definitions are presented below (Chiou, 1989):

1) *sorption* - a general term used to designate the uptake of a solute by soil without regard to the mechanism.

2) *adsorption* - refers to the condensation of vapors or solutes on surfaces or interior pores of a solid by physical or chemical bonding forces.

3) *partitioning* - designates an uptake in which the sorbed organic compound permeates into the organic medium by forces common to solution, such as Van der Waals forces.

Several points are used to distinguish partitioning from adsorption (Chiou, 1989): (i) the high linearity of the sorption isotherm; (ii) the inverse relationship between the sorption (or partition) coefficient (K_d) and the aqueous solubility of the solute (S_w); (iii) the low exothermic heat exhibited during sorption of solutes in solvent-water and soil-water equilibria; and (iv) the absence of sorption competition among solutes. In addition to the above characteristics, the apparent solubility of the solutes into the soil organic matter also provides evidence of partitioning (Chiou, 1989). The demonstrated presence of low exothermic heats seen during sorption of nonionic organic compounds was not evaluated in the experiments for this paper, therefore, evidence of this effect will not be presented. Discussions on the other applicable characteristics of partitioning are presented below.

Isotherm Shape

A number of studies have shown that the equilibrium isotherms for the sorption of nonionic organic compounds to soils are virtually linear (Chiou, et al., 1979, 1983; Mingelgrin & Gerstl, 1983; Huddleston, 1990; Rutherford, et al., 1992). For water-soluble nonionic organics and pesticides, this linearity holds true even when concentration levels are relatively high. Coupled with the recognized role of sorption dependence on soil organic matter (Bonazountas, 1990), the mechanism by which sorption occurs it is thought by many (Chiou, 1989; Lee et al., 1989) to be a partitioning process and not adsorption. Although linearity of the sorption isotherm is a good indicator of partitioning, caution is advised to the reader when using this characteristic as a tool for evaluating sorption isotherms since *adsorption* isotherms at low concentrations (sometimes referred to as the Henry's-law region) can also yield a linear plot (Chiou, 1989).

Sorption Coefficient and Water Solubility

Chiou (1989) showed that a relationship existed between the organic matter partitioning coefficient (K_{om}) and the aqueous solubility (S_w) of an organic compound for any given soil. The plot of log K_{om} versus the log (S_wV), where V is the molar volume of solute (L/mol), was linear. Since the variation of V is small for most organics, then a linear relationship should also exist between log K_{om} and log S_w for any particular soil (Chiou, et al., 1979, 1983; Briggs, 1981). One should remember, however, that the slope of the equation is dependent on the organic matter composition; therefore, the relationship of these parameters is unique for each soil (Briggs, 1981).

Given that a linear relationship existed between K_{om} and S_w, Chiou (1989) surmised that a relationship between K_{om} and the octanol-water partition coefficient (K_{ow}) also existed. Partitioning into soil organic matter is analogous to the partitioning of a chemical into an organic solvent such as octanol. However, the soil organic matter is not as suitable a partitioning medium as octanol, therefore, K_{om} values are expected to be significantly lower than the corresponding K_{ow}

values. In fact, Chiou (1989) found that for compounds with log K_{om} = 2-5, the corresponding log K_{ow} values are approximately one order of magnitude higher than the log K_{om} values.

Chiou (1989) determined that the primary factor affecting sorption of slightly water-soluble nonionic organic compounds into organic soil matter is the aqueous solubility of the compound. The dominance of this factor was illustrated by the fact that solutes with lower aqueous solubilities showed higher equilibrium sorption coefficients.

Competitive Effects

Adsorption (by definition) is a process whereby the solute is bonded to the surface by physical or chemical processes. In adsorption processes, i.e., Langmuir (Veith et al., 1977) or Freundlich type sorption, specific sites are available for adsorption. It follows from this logic that in an adsorption process, multiple solutes in solution would compete for sorption sites. Therefore, the amount of sorption of any one solute is directly related to the concentrations and number of constituents available in solution for competition.

Conversely, the partitioning process is envisioned to be similar to a diffusion process whereby the organic solute distributes itself throughout the organic medium (soil organic matter). This type of process is not site-dependent, therefore, the amount of sorption of any one solute is completely independent of the other constituents in solution, as suggested by Chiou, et al. (1983) and Boyd, et al. (1989).

Solubility of Organic Compounds in Soil Organic Matter

The final characteristic that indicates partitioning is the estimated magnitude of the solute solubility in the soil organic matter (Chiou, 1989). The solubility of the solute is defined by the following equation:

$$S_{om} - K_{om}S_w \tag{2-1}$$

where S_{om} is the solubility of the solute in the organic matter. Following partitioning theory, one expects organic compounds with higher aqueous solubilities to give lower K_{om} values but higher S_{om} values, because these compounds are more compatible with organic solvents. However, the S_{om} values in organic soil mediums should be lower than those in organic solvents, since the solvents are better partitioning mediums than organic soil matter. In fact, Chiou (1989) declared that if one finds S_{om} values to be greater than or about equal to the solute solubility in an organic phase (such as octanol), then the validity of the assumed partitioning process should be seriously examined.

3. MATERIALS AND METHODS

Materials

Sorbent Selection

The zeolite used for these experiments was clinoptilolite. The typical unit cell formula is shown below:

$$Na_6[Al_6Si_{30}O_{72}]\ 24H_2O$$

Although other exchangeable cations can exist in this structure, sodium is the most common (Gottardi, 1976).

The Tilden zeolite was supplied by Zeotech Minerals of Albuquerque, New Mexico, from their mine in Tilden, Texas. Table 3-1 shows the characteristics of the Tilden zeolite as provided in Huddleston (1990). The material used was not pure zeolite but contained a high percentage of clay (montmorillonite), also known to exhibit high sorption and exchange capacities. The combination of these minerals yielded a mineral surface that had a high CEC, which provided an ideal surface for sorption of quaternary amines. This same zeolite was used in previous studies performed by Huddleston (1990).

The St. Cloud zeolite was supplied by the St. Cloud Mining Company (Truth of Consequences, New Mexico), from their mine near Winston, New Mexico. This zeolite was chosen for its marked differences from the Tilden zeolite; the zeolite purity was much higher, with little or no clay content (Table 3-2). It was thought that this material could serve to confirm the role of the clay versus zeolitic material in the sorption process. The external CEC of the St. Cloud zeolite was slightly less than that of the Tilden zeolite, which was expected to play a role in the possible correlation between external CEC, tailoring agent, and solutes used for any given experiment.

Table 3-1. Characteristics of the Tilden, Texas zeolite[a].

60 % Clinoptilolite
20 % Montmorillonite
16 % Amorphous
4 % Carbonates
Total CEC: ~ 60 me/100 g [b]
External CEC: ~ 30 me/100 g [b]
Grain Size: 0.2 - 2.0 mm

[a] Composition determined by X-ray Diffraction (XRD) by the New Mexico Bureau of Mines, Socorro, New Mexico.

[b] Determined by Huddleston (1990) using the Ming and Dixon procedure (1987).

Table 3-2. Characteristics of the St. Cloud zeolite[a].

84 % Clinoptilolite
12 % Volcanic Glass
3 % Feldspar
1 % Hematite
Total CEC: ~ 65-75 me/100 g [b]
External CEC: ~ 23-25 me/100 g [b]
Grain Size: 0.2 - 2.0 mm

[a] Composition furnished by St. Cloud Mining Company.

[b] Determined by Flynn (personal communication, 1992) using the Ming and Dixon procedure (1987).

Surface-Modifying Agents

Figure 1-1 shows the molecular structure of the two quaternary amines chosen as the surface-modifying agents for use

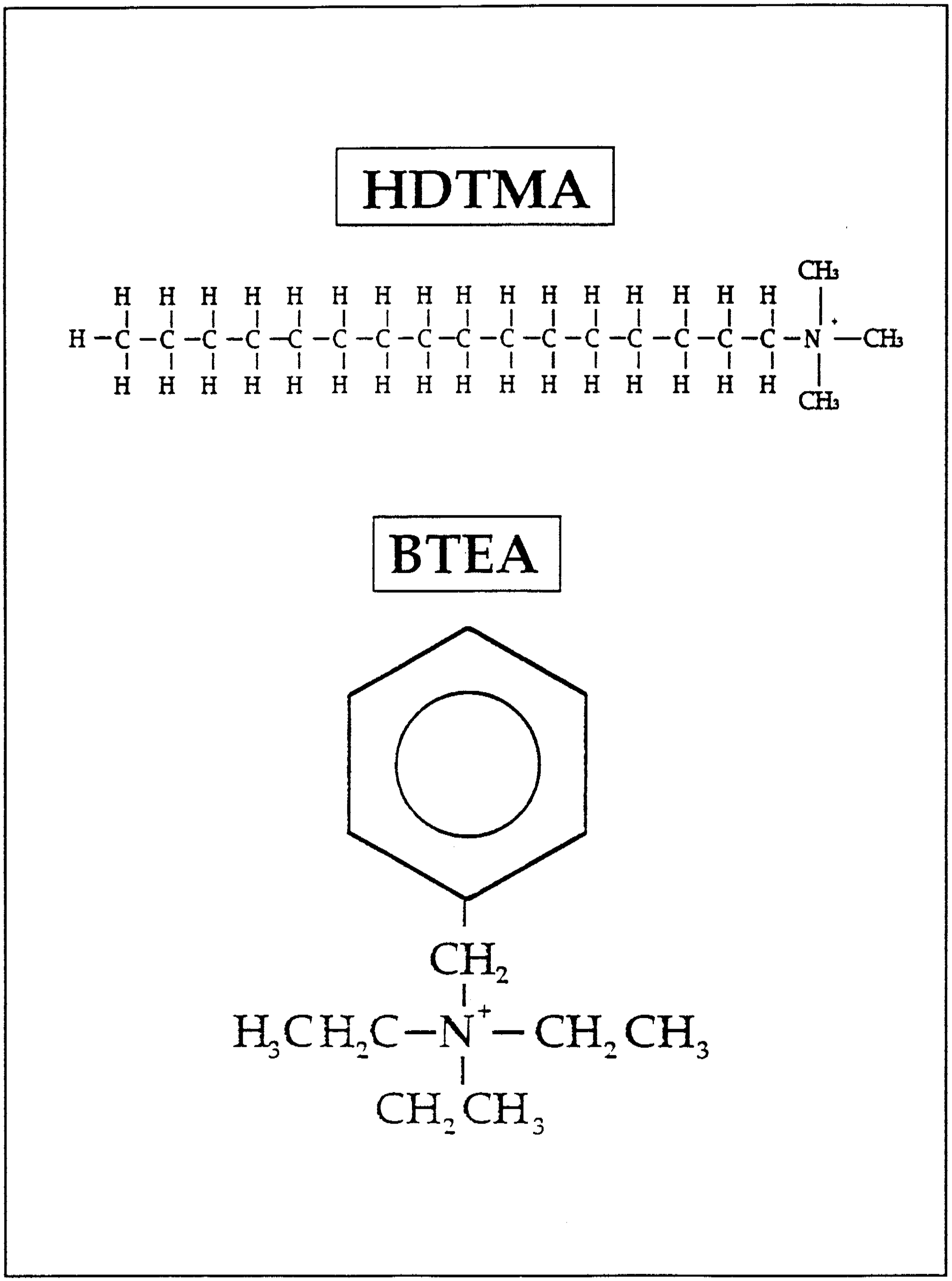

Figure 1-1. Molecular Structure of Surface-Modifying Quaternary Amines.

with the Tilden zeolite: Hexadecyltrimethylammonium (HDTMA) and Benzyltriethylammonium (BTEA). HDTMA was chosen to represent a long chain, aliphatic organic because of its wide availability, relatively low cost, and its demonstrated effectiveness as a surface-modifying agent (Huddleston, 1990; Boyd, et al., 1989). An aromatic tailoring agent, BTEA, was chosen to compare and contrast with the efficiency of the aliphatic surface-altering agent, HDTMA. The selection of BTEA was more difficult since aromatic quaternary amines are more scarce and, unquestionably, more expensive. Fortunately, an adequate supply of both HDTMA and BTEA in the form of chloride salts was located from Aldrich Chemical Company in Milwaukee, Wisconsin. The use of HDTMA (with 19 carbons) and BTEA (with 13 carbons) allowed the organic carbon content of the altered zeolite to be significantly increased. This increase has a direct effect on the partitioning of organic sorbates (Chiou, 1989).

Organic Carbon Content

By performing equilibrium isotherm experiments with ^{14}C-labelled HDTMA, Huddleston (1990) found the organic carbon content (OCC) of the Tilden zeolite modified with HDTMA to be approximately 6.33 % by weight. This number agrees well with the calculated value of 6.31 %, based on a CEC of 30 me/100 grams of HDTMA-modified Tilden zeolite. The OCC of the BTEA-modified Tilden zeolite was calculated to be 5.46 % by weight.

The OCC of St. Cloud zeolite modified with HDTMA was calculated to be 5.00 % by weight, based on a CEC of 23 me/100 g of zeolite. To date, no experimental evidence has been generated in support of this calculation, although Huddleston's (1990) conclusions of irreversible exchange of HDTMA to the zeolite surface indicates that this estimate is reasonable.

Organic Solute and Solvent Selection

Three organic solutes were chosen for the sorption experiments: benzene, toluene, and para-xylene. Table 3-3 shows the characteristics of these chemicals, referred to in this paper as BTX compounds. These chemicals were chosen because they are major constituents of gasoline, which has become of increasing environmental interest due to the large number of leaking underground storage tanks. These chemicals, since commonly found together in groundwater, also provided an opportunity to examine the sorption effects of multiple solutes in solution.

The solvent chosen for the experiments was 0.005 M $CaCl_2$ solution. This solvent was chosen because it is similar in composition to many groundwaters.

Table 3-3. Properties of BTX Compounds at 25° C.

Name	Chemical Formula	Mol. Weight, (g)	log K_{ow}[a]	Aqueous Solubility S_w, (mg/L)	Henry's Law Const., K_H[a]
Benzene	C_6H_6	78.11	2.13	1791[a]	0.222
Toluene	C_7H_8	92.13	2.73	535[a]	0.243
p-Xylene	C_8H_{10}	106.17	3.15	200[b]	0.314

[a] Howard, 1990.
[b] Dean, 1985.

Methods

Surface Modification of the Zeolites

The surfaces of both the Tilden and St. Cloud zeolites were modified by the procedure described in Huddleston (1990). This method entails the exchange of large organic molecules (i.e., HDTMA and BTEA) onto the surface of the zeolite. The exchange appears to be irreversible (Huddleston, 1990), with the permanently bonded cation further enhancing the sorption of other organic molecules by the partitioning process previously described in Chapter 2. The surface modification is briefly described below. See Huddleston (1990) for a detailed description of the method.

1. Carbonates were removed from the zeolites by the use of a pH 5 buffered solution of 1.0 M sodium acetate-acetic acid. The zeolite/buffered solution mixture was allowed to

effervesce for 24 hours, with occassional stirring. This process was repeated for another 24 hours, after which the zeolite was rinsed several times with distilled water, vacuum filtered and air-dried in a Buchner funnel.

2. 6.66 g of the air-dried Tilden zeolite or 8.70 g of the St. Cloud zeolite was measured into 50 mL teflon centrifuge tubes. Different weights of the zeolites were used so that an equal amount (20mL) of organic cation solution (0.1 M concentration) could be added to each tube to satisfy the external CEC. After adding the solution, each tube was put on a mechanical shaker for at least 24 hours, a period previously shown to be sufficient to attain equilibrium.

3. The tubes were centrifuged for approximately 15 minutes at 7294 g's (Ohanian, 1985) to yield a clear supernatant solution, after which the supernatant was decanted and discarded. For the St. Cloud zeolite, three additional rinses of the zeolite with subsequent centrifuging was performed to ensure that no excess organic cations were available to interfere with the sorption results. The Tilden zeolite was rinsed once with distilled water and centrifuged.

4. The zeolite was then filtered and air-dried in a Buchner funnel, with several rinsings (at least three) with distilled water. After complete air drying, the modified zeolite was ready to use.

The above process was used for both HDTMA and BTEA alteration of Tilden and St. Cloud zeolites.

Quantification of Organic Solute Sorption to Modified Zeolites

Quantification of organic solute sorption to modified zeolites was accomplished through the use of batch isotherm studies. Isotherms using the untreated (or natural) zeolite were performed concurrently to illustrate the overall effectiveness of the altered zeolites for the sorption of organic solutes. Except in the case of p-xylene, each isotherm consisted of five nominal initial concentrations in aqueous solution: 10 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 250 mg/L. Concentrations of the p-xylene experiments were as follows: 10 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L, since the maximum attainable concentration of the p-xylene solution (due to the aqueous solubility) was approximately 200 mg/L (Table 3-3). The procedure used for the batch isotherm studies was developed by Huddleston (1990). Slight modifications of the procedure were necessary for the BTX compounds, due to their relatively low aqueous solubilities and their tendency to volatilize (see Table 3-3). The method used for the batch isotherms is outlined below:

1. Saturated solutions of each compound were prepared in 1.0 L amber glass bottles. Each bottle was filled approximately three-fourths full of distilled water; a head of at least one half-inch of each chemical was poured into the bottles. The head of free organic liquid ensured a saturated aqueous solution available for preparing the five experimental concentrations.

2. Prior to preparing the experimental solutions, the free organic liquid and distilled water mixtures were stirred overnight in the amber bottles using a stir bar and magnetic stirrer.

3. Individual concentrations of BTX compounds in aqueous solution were prepared by dilution of the saturated solutions with 0.005 M $CaCl_2$. Since the saturated solutions were prepared in distilled water, this resulted in different concentrations of $CaCl_2$ solution being used for each solution concentration. The $CaCl_2$ concentrations used are listed below. For each chemical, the solution concentration is followed by the $CaCl_2$ concentration. For example, the terminology 10/ 0.005 M refers to a solution concentration of 10 mg/L containing a $CaCl_2$ solution of 0.005 M. BTX solutions were obtained as follows - benzene: 10-150/ 0.005 M $CaCl_2$ solution, and 250/ 0.004 M; toluene: 10-50/ 0.005M, 100-150/ 0.004 M, and 250/ 0.003 M; xylene: 10/ 0.005 M, 50/ 0.004 M, 100/ 0.003 M, 150/ 0.001 M; the final concentration of xylene (200 mg/L) contained no $CaCl_2$ solution since this concentration was equivalent to the aqueous solubility. The saturated solution was injected by means of a Brinkmann dispenser (VWR Scientific, Philadelphia, Pennsylvania) into 160-mL Wheaton (Millville, New Jersey) crimp top bottles containing the appropriate volume of $CaCl_2$ solution and a magnetic stir bar. Each bottle was then capped with a

teflon-coated butyl rubber septum provided by Supelco, Inc. (Bellafonte, Pennsylvania). Each bottle was stirred for a minimum of 24 hours using a magnetic stirrer to allow the solution to reach equilibrium.

4. The equilibrated organic chemical solution was extracted from the 160-mL bottles using a 100 mL Hamilton gas tight syringe (Fisher Scientific, Pittsburgh, Pennsylvania). From the syringe, solution was added to 15-mL Wheaton crimp-top vials containing 2.50 g of zeolite. Each bottle was weighed before and after filling to determine the volume of solution present, for sorption calculations. The vials were capped (prior to filling) with teflon-coated silicone septa, also provided by Supelco. The solution was injected through the silicone cap while an additional needle provided the vent for exiting air. Although some air remained in the samples after filling (estimated to be < 0.5 mL), this process minimized the amount of air remaining in the vials and, therefore, the amount of volatilization of the chemicals. Two samples prepared at each concentration without zeolite by the same method served as blanks. Two 2-mL gas chromatography (GC) crimp-top vials were also filled with the equilibrated solution to serve as standards. These samples were not vented and therefore, were not subject to volatization losses that were experienced in subsequent steps of the method. These samples also served as a check on the concentration accuracy of the prepared solutions. After filling the samples and blanks with a given concentration solution, the gas-tight syringe was rinsed twice with methanol and dried to minimize cross contamination of the solutions. All samples and blanks were prepared in duplicate.

5. The zeolite samples and blanks were then placed on a mechanical shaker for 24 hours to allow them to come to equilibrium at room temperature. Huddleston (1990) determined that this was sufficient time for other nonpolar organics to reach equilibrium.

6. After equilibration, the zeolite samples were centrifuged at 7294 g's for approximately 15 minutes. Approximately 2.3-mL of solution was withdrawn from each bottle and placed in pre-capped GC crimp-top vials for analysis using a 5-mL Hamilton gas tight syringe and vent. The syringe was rinsed twice with methanol and once with the succeeding sample after each bottle to minimize cross contamination.

7. The samples were analyzed with a 0.53-mm I.D. 10-m HP-5 capillary column using a 5890A GC with a flame ionization detector (FID) and a 3396A integrator, all from Hewlett Packard, Palo Alto, California. A HP 7376A autosampler injector was used for all experiments since manual injection

could not provide adequate reproducibility. The settings for the instrument and the integrator are shown in Table 3-4.

8. Data was analyzed as peak areas and compared to standards of 200 mg/L purchased from Supelco.

9. Multiple-solute solutions were also prepared with Brinkmann dispensers in the same manner as outlined above with each saturated solution being added separately to the $CaCl_2$ solution. The most volatile solution was added last to minimize volatilization losses.

Table 3-4. Operating Conditions for Gas Chromatography Equipment for Analysis of BTX in Aqueous Solution.

Carrier Gas:	Helium: 5.56 - 5.88 mL/min
Make-up Gas:	Nitrogen: 33 mL/min
Hydrogen:	59.32 - 60.34 mL/min
Air:	390 - 400 mL/min
Septum Purge:	1.21 mL/min
Split Vent:	33.5 - 35.3 mL/min
Threshold:	0
Attenuation:	2
Zero:	0
Peak Width:	0.04
Area Rej.	0
Chart Speed:	1.0
Inital Oven Temperature:	50° C
Injector Temperature:	200° C
Detector Temperature:	250° C
Split Ratio:	7:1
Purge A:	On
Purge B:	On

Temperature Program: Initial temperature 50° C, ramped 10° C/minute from 0-4 minutes, then 20° C/minute from 4-6 minutes to a maximum oven temp. of 125° C. Total run time for each sample was approximately 10 minutes (including the time required for the oven temperature to be reset to the intial temperature).

4. RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Quantification of Organic Solute Sorption to Modified Zeolites

Sorption isotherms were prepared for each chemical in aqueous solution, as well as for pairs of chemicals to determine the effect of multiple solutes in solution.

The sorption isotherms generated from experiments with the surface-modifying agent HDTMA were linear for both zeolites, as will be seen in the following sections. However, the isotherms produced from data involving the BTEA-modified Tilden zeolite were more typical of Freundlich-type sorption. Therefore, the BTEA sorption of BTX compounds, along with possible explanations for the deviation from the anticipated results, will be discussed independently of the other sorption experiments.

BTX Sorption to BTEA-treated Tilden Zeolite

BTEA was chosen to represent an aromatic surface-modifying agent to compare with the alkyl chain agent, HDTMA. Figure 4-1 shows the non-linearity of the sorption data of BTX compounds to the BTEA-modified surface. The actual sorption data is presented in Appendix A, Tables A.1-A.9. The data for this graph was a result of sorption experiments for individual chemicals in aqueous solutions. A logrithmic line was best-fit to the given data. Although the toluene data does not exhibit the same well-evidenced non-linear behavior of the benzene and xylene data, neither does it exhibit true linearity either. It is the error caused by manual GC injection of these samples during a time when the autosampler was under repair. Therefore, the focus of the discussion will be on the benzene and xylene data.

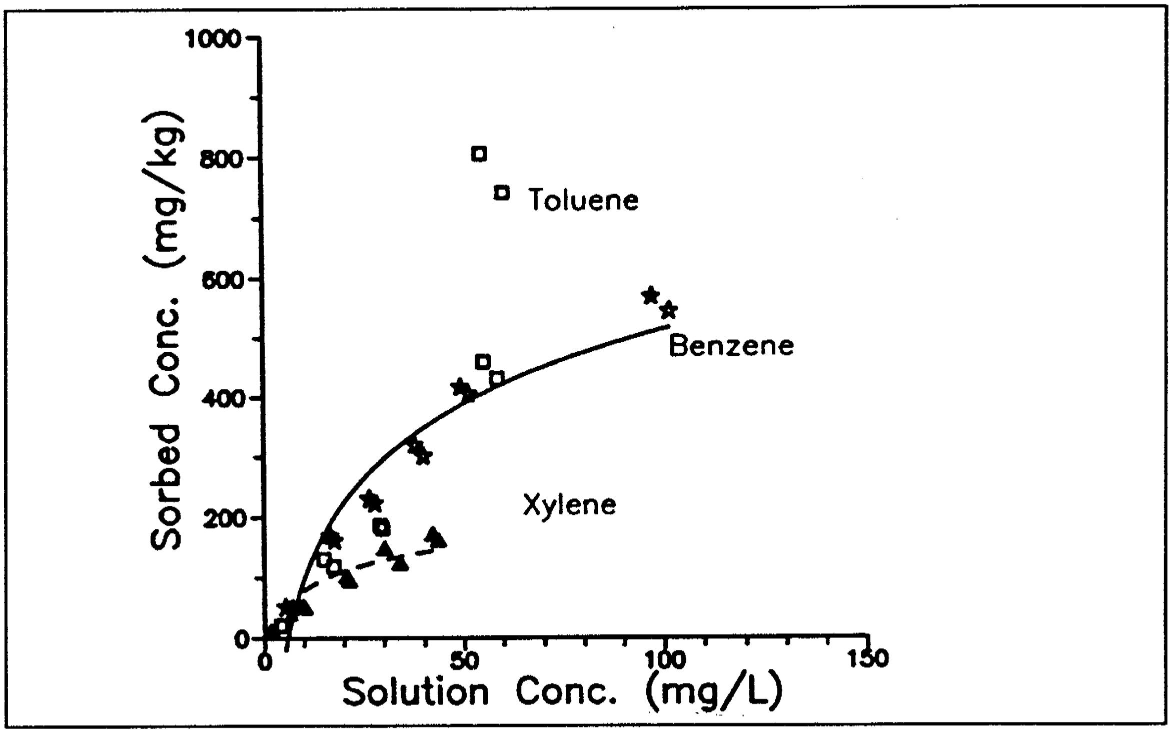

Figure 4-1. BTX Sorption to BTEA-modified Tilden Zeolite.

Sorption isotherm experiments with multiple solutes were performed to determine if competition existed. One experiment was performed by holding benzene constant at approximately 100 ppm, while varying the concentration of toluene. All other competitive experiments were performed by varying the concentration of both compounds in solution at the same level. Results for benzene sorption are shown in Figure 4-2, toluene in Figure 4-3, and xylene in Figure 4-4. As seen in these figures, the data also exhibit Freundlich-type sorption. The sorption of benzene in the presence of both toluene and xylene appears to be

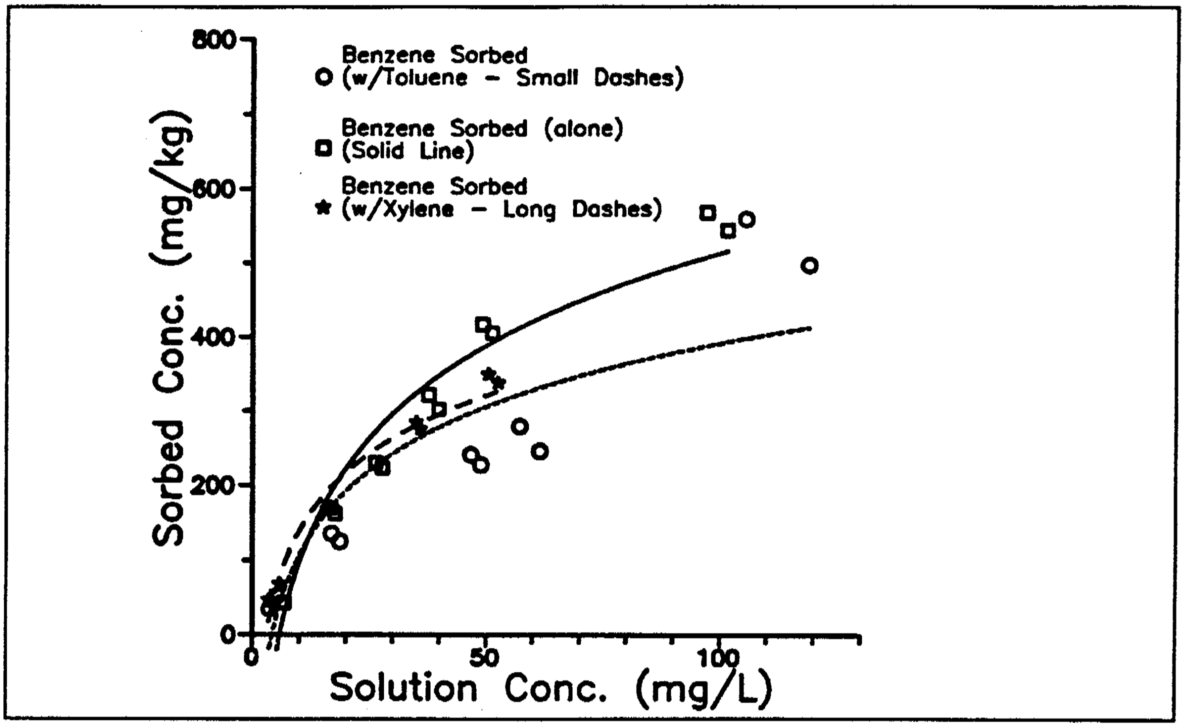

Figure 4-2. Benzene Sorption to BTEA-modified Tilden zeolite.

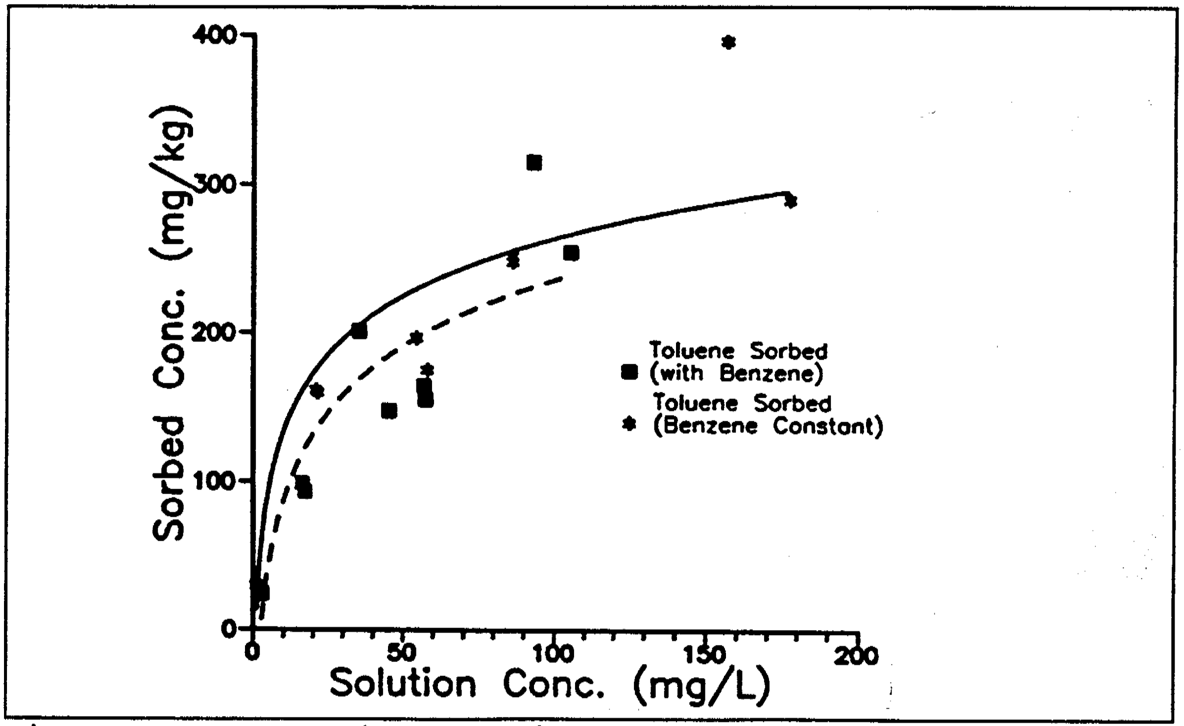

Figure 4-3. Competitve Studies of Toluene using BTEA-modified Tilden zeolite.

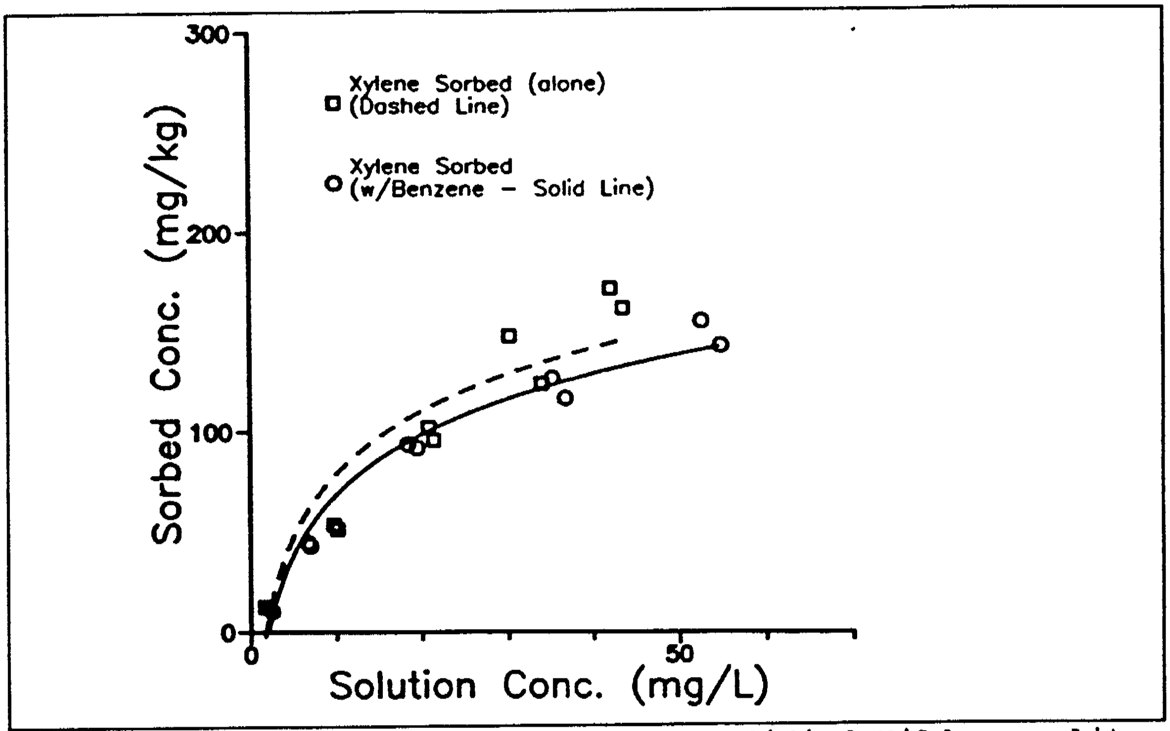

Figure 4-4. Xylene Sorption to BTEA-modified Tilden zeolite.

benzene in the presence of both toluene and xylene appears to be slightly affected by these chemicals. The sorption of toluene and xylene appears to be less affected by the presence of benzene, and all the isotherms for each chemical are consistent with one another. Since it was not the goal of this study to determine K_F parameters for BTX compounds, they are not presented here.

It is unclear what may have caused the Freundlich-type sorption behavior experienced by BTX sorption to BTEA-altered zeolite. However, this type of sorption behavior is frequently encountered in adsorption experiments, where the molecules have to compete for sorption sites. It is possible that the BTEA caused adsorption of the BTX molecules to occur instead of partitioning.

Clearly, this theory is speculative, however, a surface stability experiment as performed for the HDTMA-modified surface by Huddleston (1990) would aid in determining if the BTEA sorption is permanent. Exchange of BTEA off the surface would indicate instability of the organic surface required for partitioning, but could provide more insight into the mechanism for the apparent irreversibility of the HDTMA exchange (or other large cations).

Since such unusual results were obtained for the BTEA-modified Tilden zeolite experiments, the remainder of the research was focused on the HDTMA-modified Tilden and St. Cloud zeolites.

BTX Sorption to HDTMA-treated Tilden and St. Cloud Zeolites

Tilden Assessment

In contrast to the BTEA-zeolite experiments, the sorption isotherms produced from HDTMA-modified surfaces were quite linear. The sorption of benzene, toluene, and p-xylene to both HDTMA-treated and untreated Tilden zeolite are shown in Figures 4-5, 4-6, and 4-7, respectively. For the sake of comparison, Figure 4-8 shows the isotherms for all three compounds, without their corresponding untreated zeolite isotherms. In all cases, the untreated zeolite showed much lower sorption of the BTX

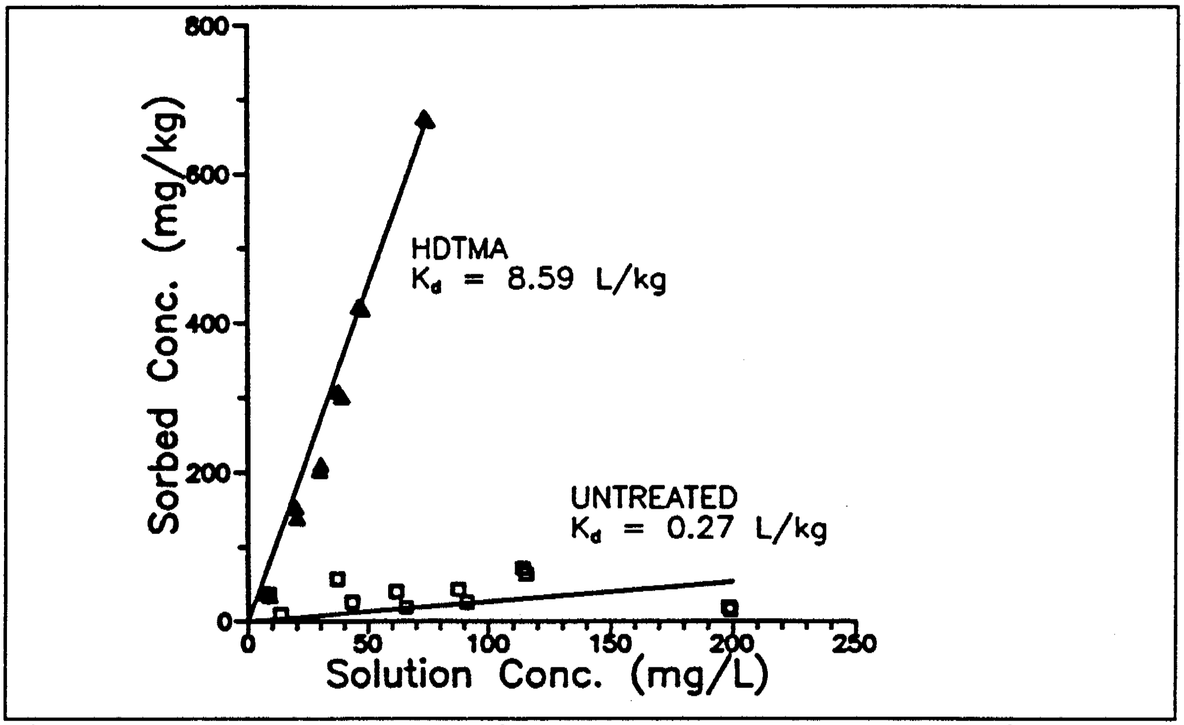

Figure 4-5. Benzene Sorption to HDTMA & Untreated Tilden Zeolite.

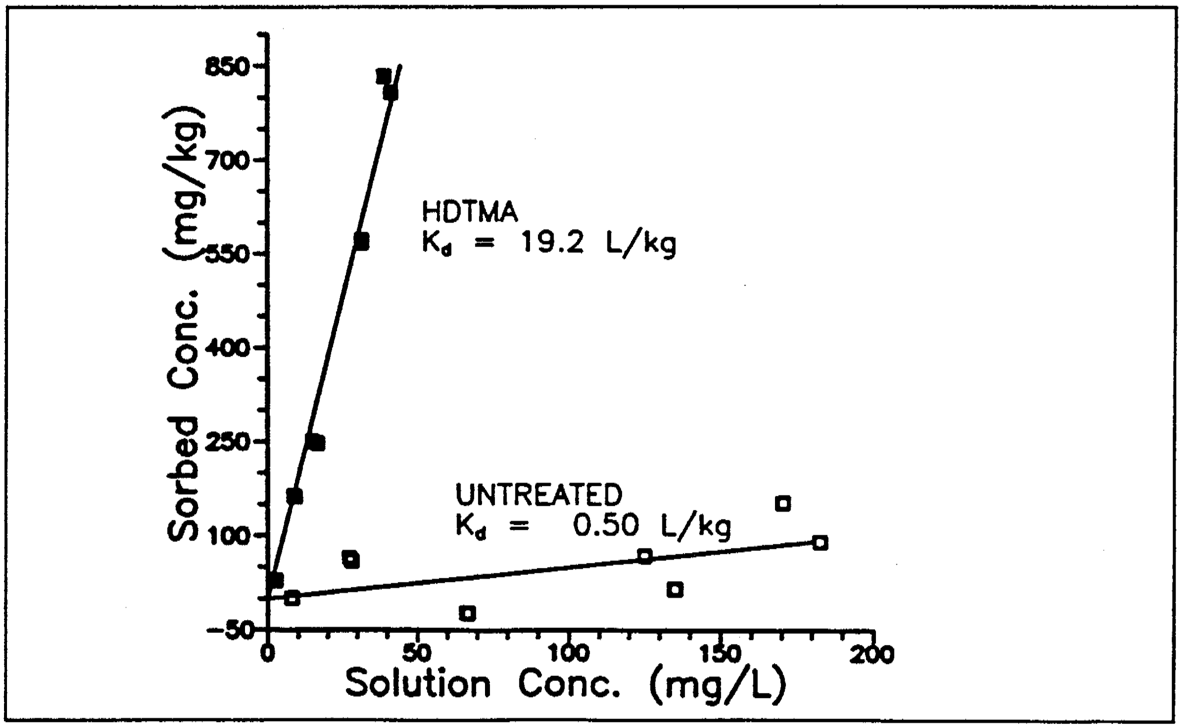

Figure 4-6. Toluene Sorption to HDTMA-treated Tilden Zeolite.

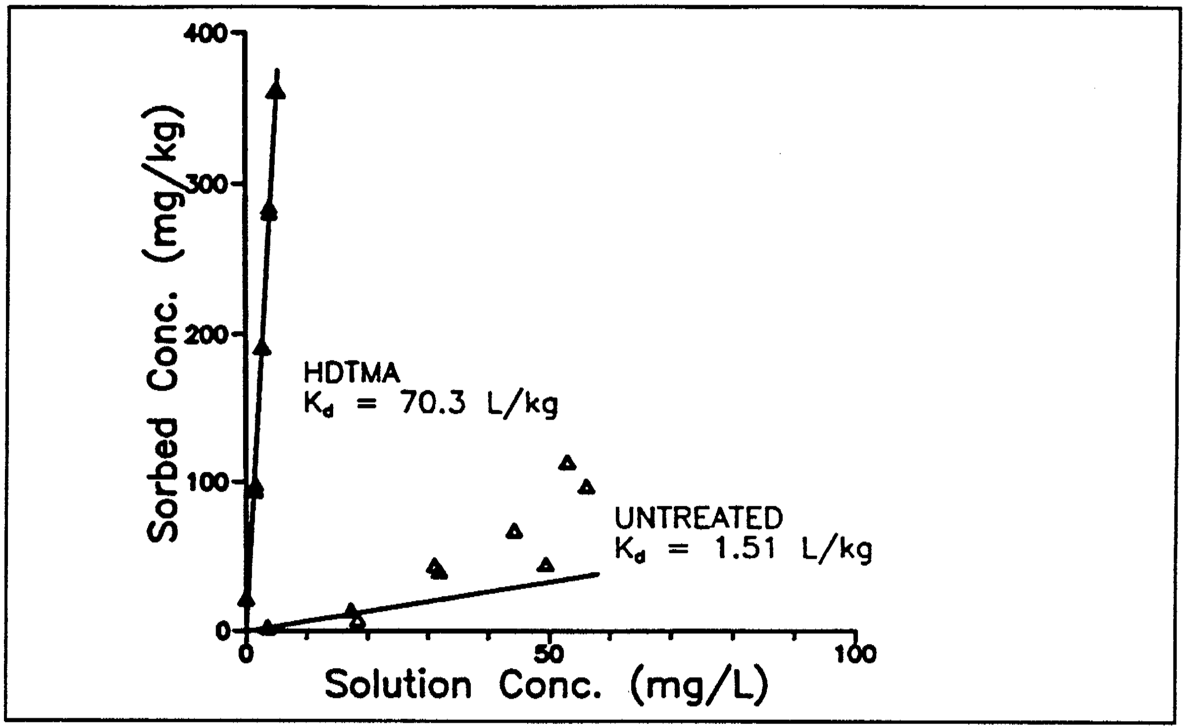

Figure 4-7. p-Xylene Sorption to HDTMA-treated Tilden Zeolite.

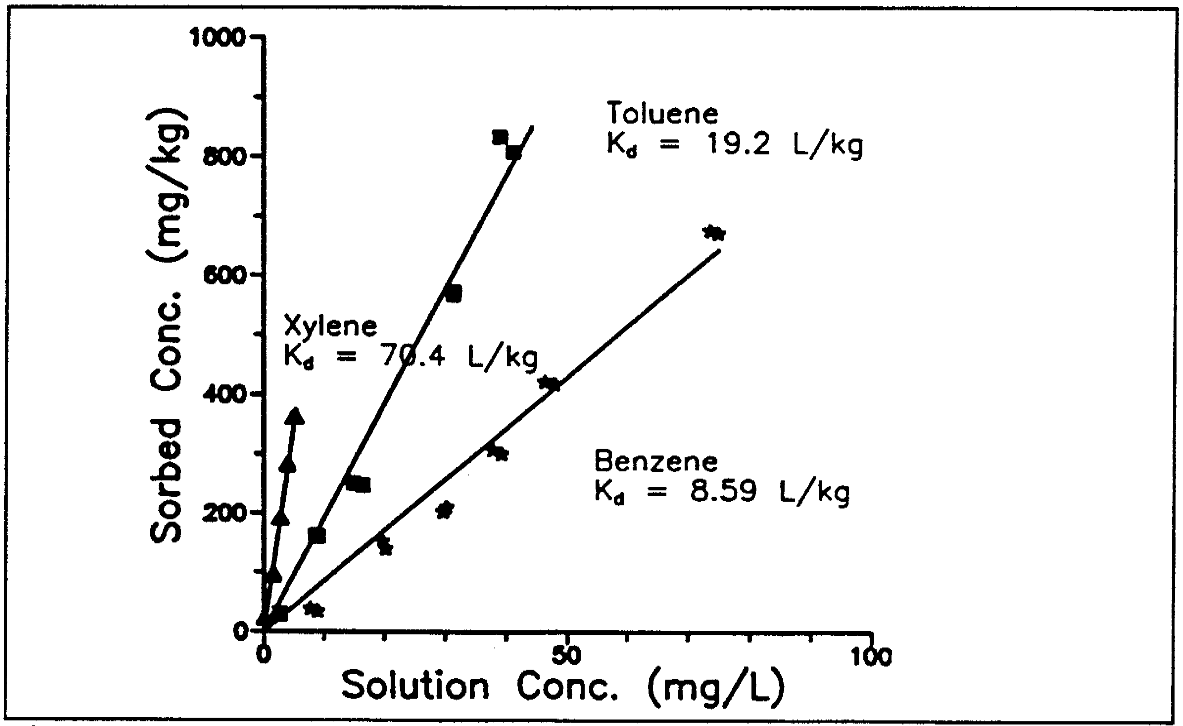

Figure 4-8. BTX Sorption to HDTMA-treated Tilden Zeolite.

chemicals than did the modified zeolite. This phenomenon is an expected result of the partitioning theory, since the natural zeolite has such a low OCC (0.16%), as determined by Huddleston (1990). Sorption data for generating these graphs is presented in Appendix B, Tables B.1-B.6.

Examination of the distribution coefficients (K_d) for each chemical and the overall amount of sorption also indicates that partitioning is the dominant mechanism present (see Figure 4-8). The degree (or quantification) of sorption is represented by the distribution coefficient; K_d is the slope of the line formed by plotting the concentration of chemical remaining in solution at equilibrium versus the amount of chemical sorbed at equilibrium. Chiou (1989) proposed that the amount of partitioning of a non-ionic compound is inversely related to the aqueous solubility of that chemical. In other words, the chemical with the lowest solubility should exhibit the greatest partitioning (K_d), and vice versa. The aqueous solubilities of BTX compounds are in descending order (see Table 3-3), i.e., benzene is more soluble than toluene, and both are more soluble than p-xylene. As seen in Figure 4-8, the K_d for toluene is over two times greater than that of benzene; likewise, the K_d of p-xylene is more than eight times greater than benzene and over twice that of toluene.

Competitive Results (Pairs of Solutes in Solution)

A lack of competition between solutes is evidence of the partitioning process (Chiou, 1989). Therefore, experiments were performed using the Tilden HDTMA-modified zeolite and pairs of solutes in order to examine this phenomenon. Figure 4-9 illustrates the sorption of toluene in the presence of benzene. These chemicals were together in solution at equal increasing initial concentrations. As shown by this figure, the sorption of toluene was unaffected by the presence of benzene, illustrated by comparing the K_d's for toluene: for toluene alone in solution, the K_d = 19.2 L/kg, while in solution with equal concentrations of benzene, the K_d = 19.1 L/kg. The distribution coefficient from the combined data was determined to be 19.2 L/kg.

The sorption of xylene in the presence of benzene is illustrated in Figure 4-10. A slight difference in the sorption coefficients obtained from xylene alone and xylene with benzene was seen. The K_d for p-xylene in solution with benzene was 56.6 L/kg, while the K_d of p-xylene alone was 70.4 L/kg. Based on a t-test using a 95 % confidence interval, (Loftus and Loftus, 1982) the K_d values for xylene were not found to be statistically different. The writer believes that the slight discrepancy in the data is due to the low aqueous solubility of p-xylene and the difficulty found during experimentation with this chemical due to its tendency to volatilize during the experimental process. As such, the writer believes that the incongruity in the xylene data is not a deviation of the partitioning theory, but a reflection of the imperfections of performing sorption isotherms without the benefit of a totally closed system.

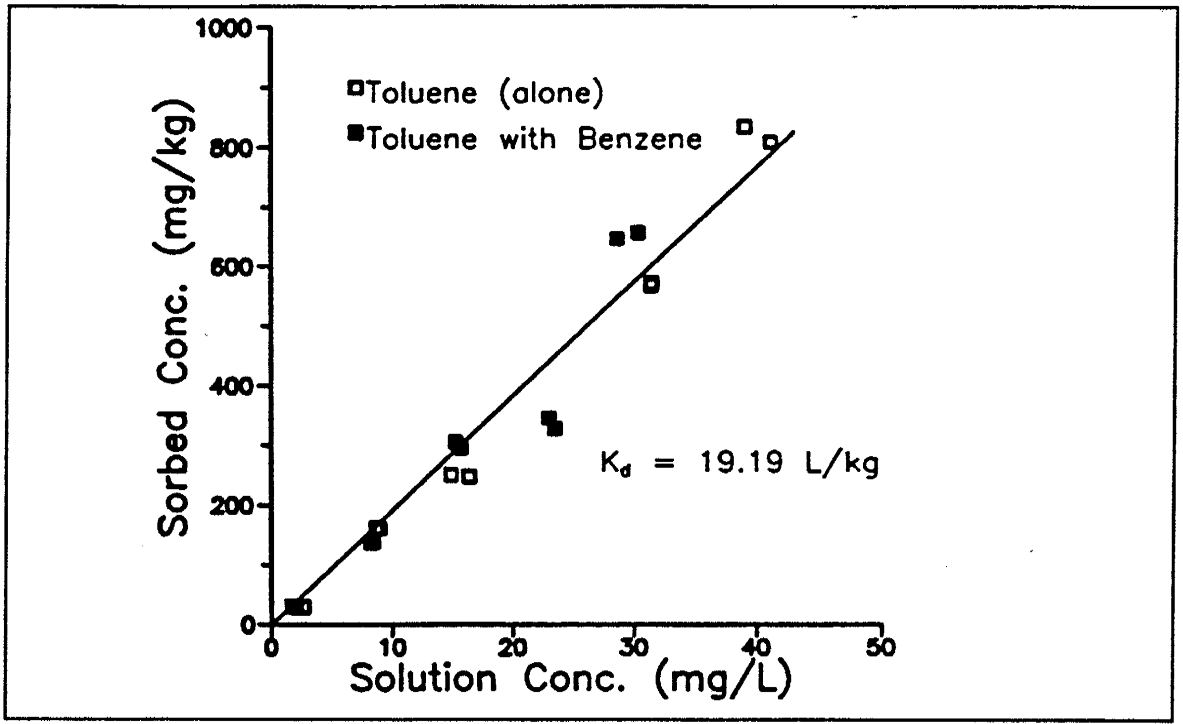

Figure 4-9. Competitive Effects on Toluene Sorption.

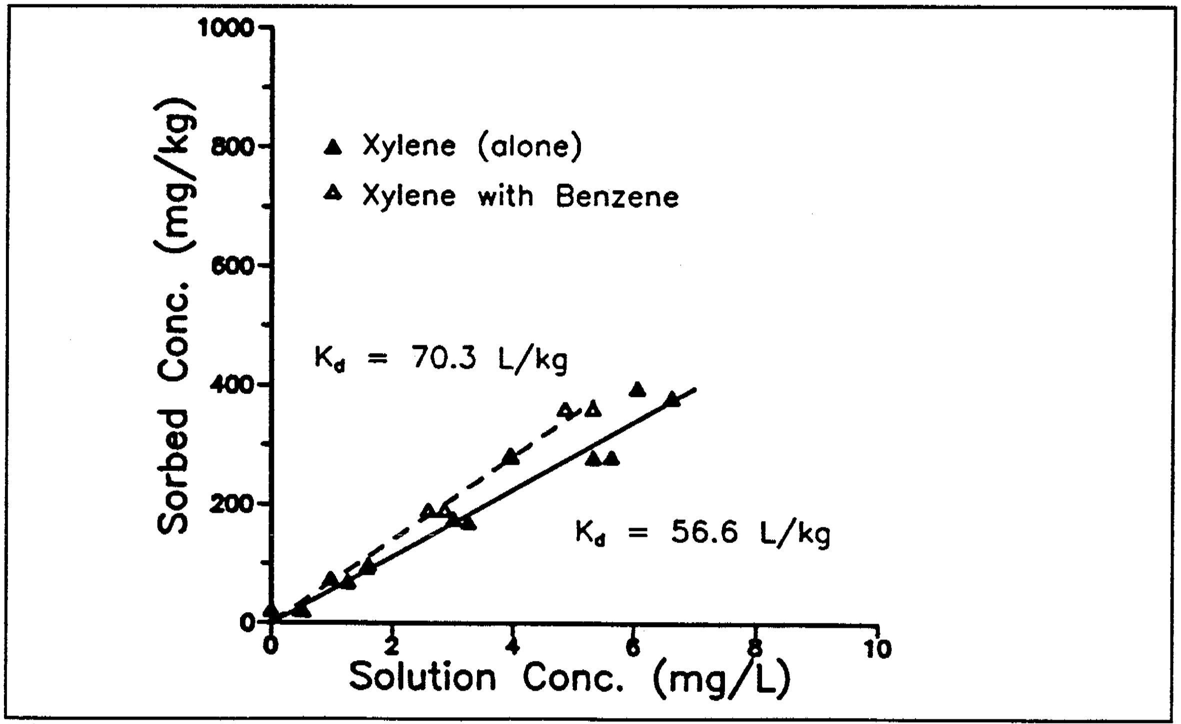

Figure 4-10. Competitive Effects on p-Xylene Sorption.

Another consequence of volatilatization is a higher apparent sorption coefficient for the untreated zeolite. The K_d for untreated zeolite for xylene alone was determined to be 1.51 L/kg. While this value is significantly less than that of the modified zeolite, it still indicates that meaningful sorption is occurring. Although some sorption is expected from the untreated material, the K_d values are usually less than one (see Table 4-1), due to the low OCC for the natural zeolite. Volatilization would result in a smaller amount of xylene present in the equilibrated solution, which directly affects the amount of sorption calculated for the zeolite, i.e., a loss of chemical due to volatilization will result in a higher apparent K_d for that chemical. As such, the writer believes the higher than expected K_d for xylene alone is due to volatilization of the chemical. The reader will note from Table 4-1 that the high K_d for untreated material corresponds to the highest K_d for HDTMA-treated zeolite, where the influence of volatilization was previously discussed.

Figure 4-11 shows the sorption results for benzene alone in solution, benzene in solution with toluene, and benzene in solution with p-xylene. By plotting the combined sorption data, an overall K_d value of 9.13 L/kg was obtained. This value corresponds reasonably well to the values obtained for benzene with xylene (9.40 L/kg), benzene with toluene (8.44 L/kg), and benzene alone in solution (8.59 L/kg). A t-test performed on

Table 4-1. Partitioning Coefficients for the Sorption of BTX Compounds to Surface-Altered Tilden Zeolite.

Chemical	K_d (L/kg) for HDTMA-altered Zeolite	K_d (L/kg) for Untreated Zeolite
Benzene[a]	8.59	0.27
Benzene[t]	8.44	0.39
Benzene[x]	9.40	-0.22
Toluene[a]	19.2	0.50
Toluene[b]	19.1	0.70
p-Xylene[a]	70.4	1.51
p-Xylene[b]	56.6	0.42

[a] K_d determined while the chemical was in solution alone.

[b] K_d determined while the chemical was in solution with initial concentrations equal to that of benzene.

[t] K_d determined while the chemical was in solution with initial concentrations equal to that of toluene.

[x] K_d determined while the chemical was in solution with initial concentrations equal to that of p-xylene.

all three sets of data using a 95 % confidence interval determined that these results are not statistically different from one another.

As previously mentioned in Chapter 2, a finite amount of sites available for sorption (as in the adsorption process) would cause the chemicals to compete for the same sites. This would result in lowering the overall sorption (and the K_d) for each chemical. Clearly, this is not the case for these compounds and

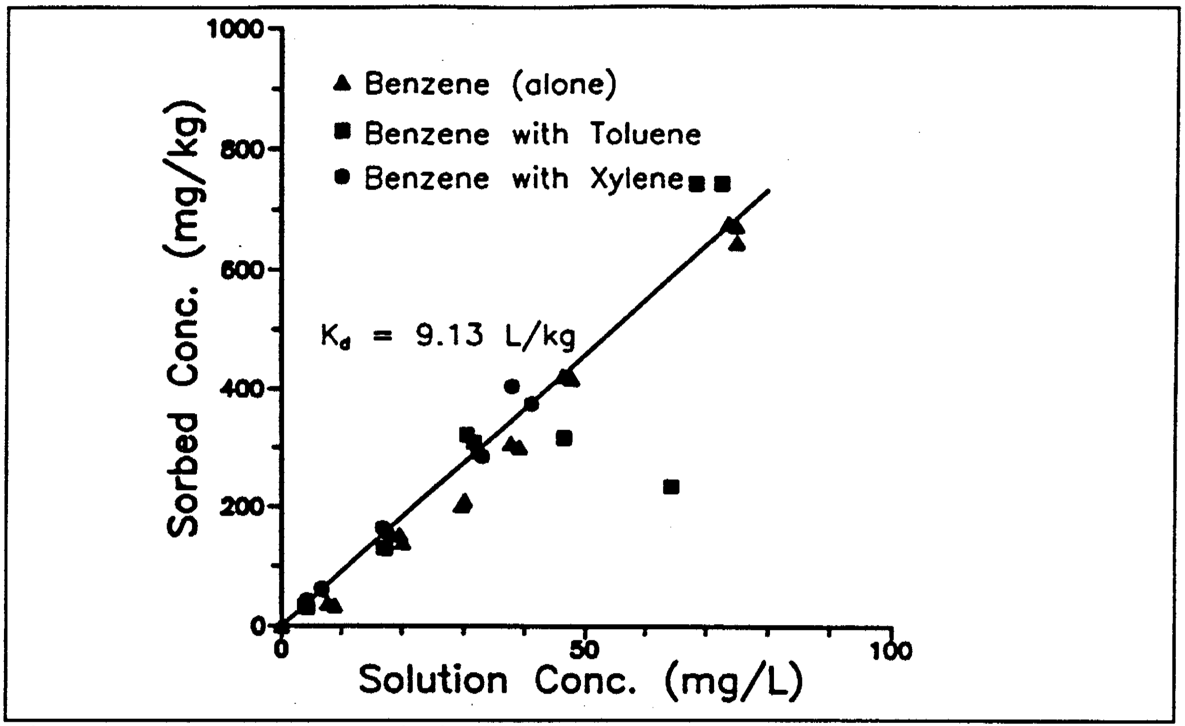

Figure 4-11. Competitive Effects on Benzene Sorption.

the modified zeolite chosen. The above data are strong evidence that a partitioning process is the dominant mechanism for these sorption experiments. K_d values for both treated and untreated Tilden zeolite are presented in Table 4-1. Raw data for these isotherms are shown in Appendix C, Tables C.1-C.12.

Comparison to Literature K_d Values

In order to confirm the experimental results of this paper, a comparison of experimental to literature partition coefficents was essential. Unfortunately, K_d's were scarce in the literature; frequently used for comparison is the organic carbon distribution coefficient (K_{oc}), which is a normalized parameter based on the organic carbon content of the soil. As such, values obtained for a specific chemical are relatively constant and reasonably independent of the soil or sediment used. The K_{oc}s are calculated values; the relationship between the two parameters is given below (Lyman, et al., 1982) in Equation 4-1:

$$K_{oc} = \frac{K_d}{\%O.C.} \ x \ 100 \qquad (4\text{-}1)$$

where % O.C. is the percent organic carbon (by weight) in the soil.

Literature values of K_{oc} also tend to be sparse, therefore, a method of reasonable estimation of this parameter was needed. The sorption of non-ionic compounds onto soil particle surfaces is well-correlated with two measurements of organic chemical hydrophobicity: the aqueous solubility of the chemical S_w, and the octanol-water partition coefficient, K_{ow} (Dragun, 1988). Dragun (1988) provided numerous methods for the calculation of log K_{oc} from these parameters, however, care must be taken when choosing an estimation equation since the equations can not be universally applied to all organic chemicals in all soil systems. Therefore, the estimation equation must not be used without knowing its limitations. The chemical structures of the compounds and the OCC used to develop the equation are important factors to consider when choosing an estimation equation (Dragun, 1988). With these limitations in mind, the writer chose Eqn.

6-20 of Dragun (1988), which most closely matched the experimental conditions used here. This equation, presented as Equation 4-2, was tested over a wide variety of OCC's (<0.01 - 33.0 %); the chemicals used for testing the equation were halogenated hydrocarbons and toluene, which are similar in chemical structure to BTX (or the same, in the case of toluene). The estimation equation as given by Dragun (1988) is listed as follows:

$$\log K_{oc} = 0.72 \log K_{ow} + 0.49 \qquad (4\text{-}2)$$

A comparison of literature to experimental K_{oc} values can be seen by examination of Tables 4-2 and 4-3. These tables show that the experimental results are consistent with those obtained from the literature. Because of the difficulties encountered in the experimental method due to volatilization, one would expect the percent difference to increase with increasing K_H values (see Table 3-3 for values). Volatilization would lead to higher apparent K_d's, which in turn would lead to higher apparent K_{oc} values. This phenomenon is evident with the xylene data, which exhibits the highest K_H of the three chemicals used. As such, K_{oc} values for both xylene experiments were calculated to compare to literature values. Both experimental log K_{oc} values for xylene were higher than the corresponding literature value, however, the small deviation from the literature results (approximately 10% or less) obtained with the experimental data indicates that the results are still reliable and should not be discounted.

Table 4-2. Literature values of K_{oc} for BTX Compounds.

Chemical	Literature log K_{ow} [a]	Literature log K_{oc}
Benzene	2.13	1.56 - 2.25[b]
Toluene	2.73	2.46[c]
p-Xylene	3.15	2.76[c]

[a] See Table 3-3 for reference.
[b] Howard, 1990.
[c] Calculated from Equation 4-2.

Table 4-3. Experimental values of K_{oc} for BTX Compounds.

Chemical	Experimental K_d value	Exp. K_{oc} [a]	Exp. log K_{oc}	% Difference[c]
Benzene	8.59	136.35	2.13	4.9[b]
Toluene	19.2	304.76	2.48	0.8
p-Xylene	70.4	1117.46	3.05	10.5
p-Xylene	56.6	898.4	2.95	6.9

[a] Calculated from Equation 4-1 using a value of 6.3% OCC for HDTMA-Tilden modified zeolite.
[b] Based on comparison to an average literature log K_{oc} value of 2.03
[c] % Difference calculated as $\frac{\text{Exp. Values - Lit. Values}}{\text{Lit. Values}}$ x 100

According to Chiou (1989), another indicator of partitioning is the comparison of log K_{om} values to log K_{ow} values. If true partitioning is the mechanism of sorption, then the log K_{ow} values should be approximately one order of magnitude higher than log K_{om} values, since the octanol is a preferred partitioning medium over the organic matter. In order to investigate this aspect of partitioning, K_{om} values were calculated from previously calculated K_{oc} values. The relationship between these parameters is assumed to be constant as stated by Dragun (1988) and as illustrated below in Equation 4-3:

$$K_{om} = \frac{K_{oc}}{1.724} \tag{4-3}$$

Table 4-4 shows the values obtained for log K_{om} and log K_{ow}. The log K_{om} values obtained experimentally vary from 0.2-0.5 orders of magnitude lower than their corresponding log K_{ow} values. Since K_{om} values were lower than their corresponding K_{ow} values, the solubility of BTX compounds into the organic matter (S_{om}) would also be lower than their solubility into octanol, as predicted by partitioning theory. This information suggests partitioning as the dominant mechanism for the sorption of these chemicals into the surface-altered medium.

Table 4-4. Comparison of experimental log K_{om} values and literature log K_{ow} values for BTX Compounds.

Chemical	Exp. K_{oc}	Exp. K_{om}[a]	Exp. log K_{om}	Lit. log K_{ow}[b]
Benzene	136.35	79.09	1.90	2.13
Toluene	304.76	176.77	2.25	2.73
p-Xylene	898.4	521.1	2.72	3.15

[a] Calculated from Equation 4-3.
[b] See Table 3-3 for reference.

St. Cloud Assessment

The St. Cloud zeolite was used to determine if a possible correlation between zeolite CEC, the solute used and the surface-modifying agent could be found to allow prediction of the sorption for variations of CEC's using BTX compounds. The correlation would enable one to estimate (roughly) the amount of sorption expected without the time and expense of experimental procedures. As the goal of these experiments was different from the Tilden zeolite experiments, the only surface-modifying agent used was HDTMA. Initially, one experiment was performed using treated and untreated St. Cloud zeolite with benzene as the solute. In this experiment, the untreated material showed the same trends as the Tilden experiments, i.e., (no discernable sorption of benzene was obtained). As such, further experiments with untreated St. Cloud zeolite were deemed unnecessary. Data from the initial experiment is not presented in this paper because it was later discovered that the tailoring agent HDTMA was present in excess of the CEC, (and not simply equal to the CEC). Subsequent experiments were performed with HDTMA-modified St. Cloud zeolite where the amount of tailoring agent added was equivalent to the CEC.

Figure 4-12 illustrates the sorption results of BTX to HDTMA-modified St. Cloud zeolite. The same overall trends observed with the Tilden zeolite were seen with the purer St. Cloud zeolite, although the magnitude of the K_d values was lessened somewhat due to the lower external CEC of the St. Cloud material. The K_d values followed the expected increase as the aqueous solubility of the compounds decreased. Raw data for the generation of these isotherms is available in Appendix D, Tables D.1-D.3.

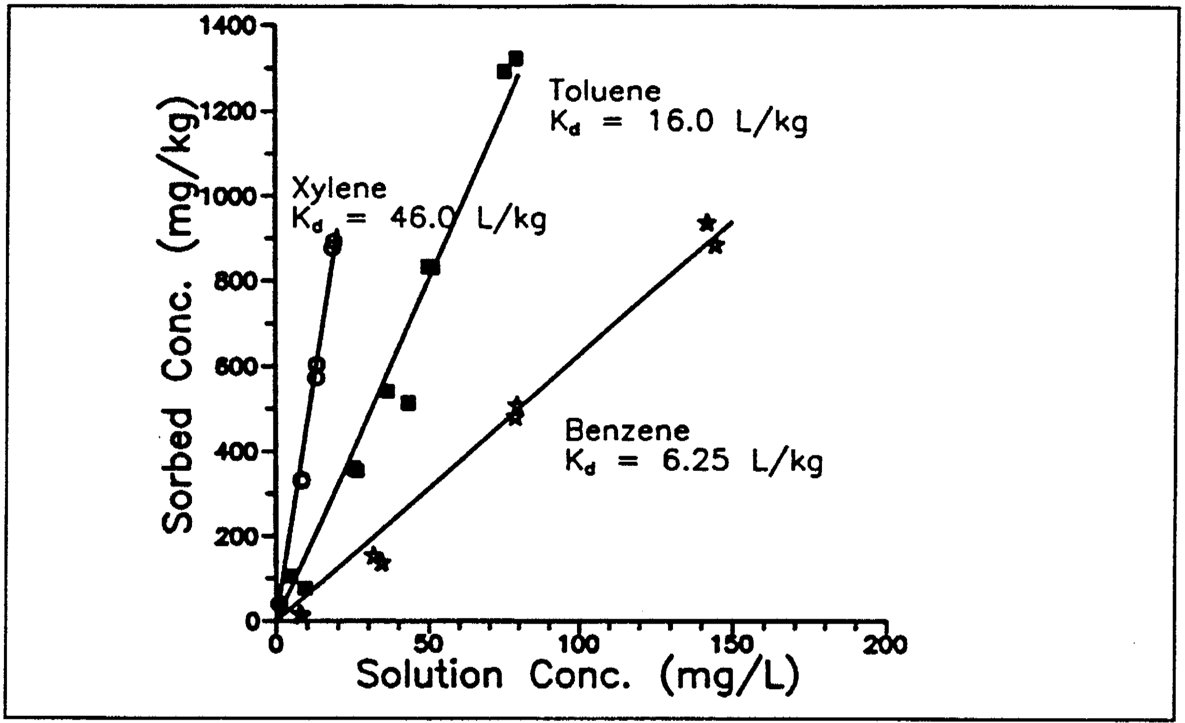

Figure 4-12. BTX Sorption to HDTMA-treated St. Cloud Zeolite.

Correlation

The reader will recall from Tables 3-1 and 3-2 that the external CEC of St. Cloud is approximately 17-23% lower than that of the Tilden zeolite. As such, the OCC was reduced from 6.3% for the HDTMA-Tilden zeolite to 5.0-5.3% for the HDTMA-St. Cloud zeolite. Since partitioning is a linear process, one would expect to be able to directly predict (within reason) the amount of sorption of the St. Cloud zeolite from the Tilden results, based on the difference in the external CEC between the two materials. Figure 4-13 compares the predicted sorption of St. Cloud based on an external CEC of 23 me/100 g to the actual sorption results obtained experimentally. This correlation can be seen more clearly by comparing the predicted K_d's to the actual K_d's obtained experimentally (Table 4-5). As expected, the estimated sorption results correspond well to the experimental results obtained for the St. Cloud zeolite, as shown in Table 4-5 below. In fact, estimation of K_d values for the St. Cloud zeolite based on the CEC could have been predicted to within 10 % of the actual sorption results obtained experimentally.

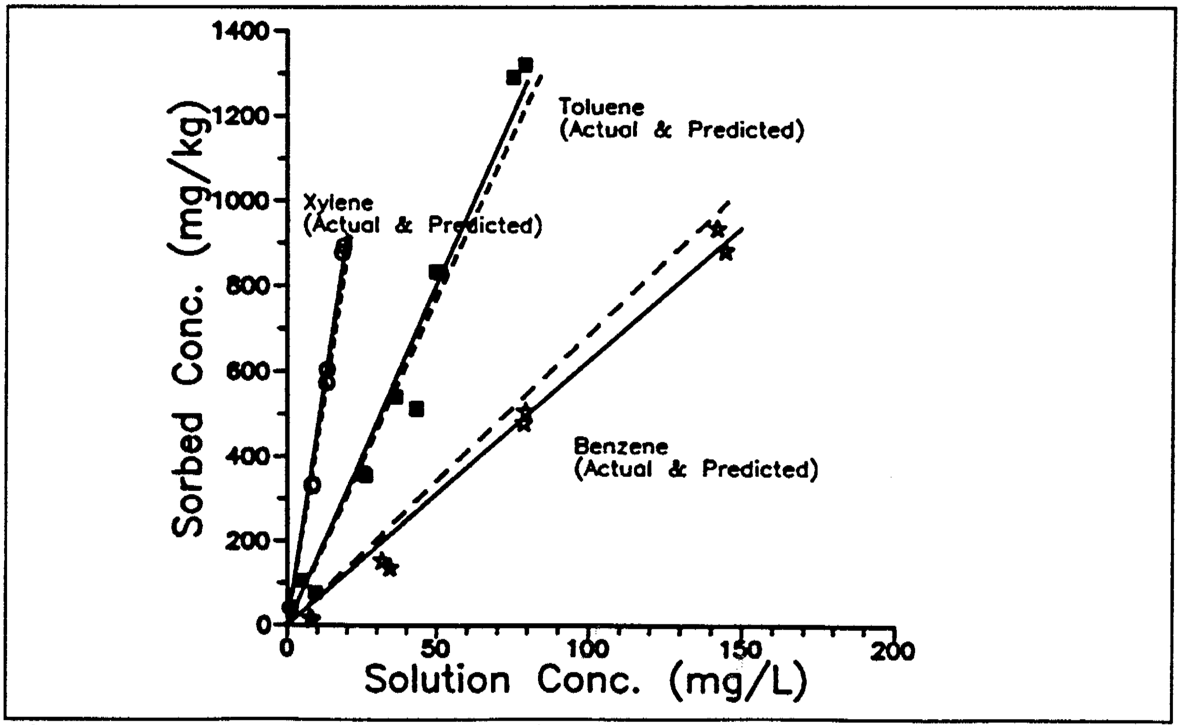

Figure 4-13. Actual & Predicted (dashed lines) Sorption of BTX Compounds to HDTMA-treated St. Cloud Zeolite.

Table 4-5. Predicted and experimental K_d's for the St. Cloud-HDTMA modified zeolite.

Chemical	Predicted K_d based on CEC	Experimental K_d	% Difference
Benzene	6.59	6.25	5.4
Toluene	14.7	16.0	8.1
p-Xylene	43.4	46.0	5.7

Examination of both Figure 4-13 and Table 4-5 illustrates that the amount of sorption of BTX compounds can be reasonably predicted without an exhaustive investigation, provided the same tailoring agent is used. A t-test performed for each chemical using a 99 % confidence interval determined that the predicted K_d values for St. Cloud-treated material are not statistically different from the experimental results obtained for this zeolite. From a practical standpoint, the amount of sorption to be expected from a particular zeolite modified with HDTMA could be used as a first cut analysis in a treatment or remediation process. If the estimated sorption indicated that the contaminants could be effectively removed by the altered zeolite, then experiments could be performed to accurately determine the partition coefficients and the overall amount of sorption to be expected for each contaminant, or group of contaminants. This ability to predict the sorption could save remediation investigators much time and money during the feasibility studies of contaminated site investigations.

5. SUMMARY AND CONSLUSIONS

Summary

Evidence presented in this paper shows that a marked increase in the removal of non-ionic organic compounds from aqueous solution can be achieved through the use of surface-altered zeolites. Thus far, Huddleston's study (1990) and experiments performed in this paper indicate that the long chain alkyl quaternary amine HDTMA allows the greatest amount of chemicals to be sorbed. In particular, some smaller quaternary amines (such as BTEA) may not be irreversibly exchanged onto the zeolite surface.

Clearly, experimental evidence demonstrates that multiple solutes can be sorbed without interference from each other. The amount of sorption experienced is directly proportional to the CEC and thus, the OCC of the zeolite. As such, a correlation can be made from experimental evidence obtained from one altered zeolite to another zeolite, provided the same tailoring agent is used for both. This correlation allows one to accurately predict the results anticipated for the second zeolite, without performing the time consuming experimental procedures.

Impurities in the material, such as clay, appear to have little or no effect on the partitioning of BTX compounds, which increases the potential use of different zeolite materials for practical applications. Possible practical applications include packed columns for the removal of contaminants from wastewater effluents or waste streams and for pump and treat systems at remediation sites. In the future, it is feasible to imagine surface-altered zeolites as part of the clean-up solution for some of today's complicated contamination sites since they are capable of sorbing organics and many heavy metals as well (Flynn, 1992, personal communication).

Conclusions

From the evidence presented herein, it is possible to derive the following conclusions:

- Altered zeolites, and in particular, HDTMA-modified zeolites, show significantly enhanced sorption of nonionic organic chemicals from aqueous solution compared to natural zeolites;
- Partitioning is the likely dominant mechanism for the sorption of BTX compounds from aqueous solution on HDTMA-modified zeolites;
- The tailoring agent chosen for modifying the zeolites is important since it affects the altered OCC of the zeolite used and the stability (irreversibility) of the partitioning medium;
- Multiple solutes in solution can be sorbed without interference from each other, i.e., sorption is not site dependent;
- Experimental K_{oc}'s correspond well to those obtained from the literature;
- Experimental results for the HDTMA-modified St. Cloud material can be predicted from the HDTMA-Tilden results using the difference in the external CEC of the materials.

Suggestions for Future Work

Based on the findings of this work, the following are recommended for future studies:

- Studies involving small columns using BTX compounds and various HDTMA-treated zeolites should be performed first to determine the feasibility of treated zeolites in this manner;
- Column studies should be continuous to provide information on continuous exposure to contaminated waters, instead of batch studies as analyzed in this paper - this should also provide information on the saturation points of the treated zeolite;
- Treatment of the saturated zeolites should be performed (i.e., high temperatures to volatilize contaminants), to determine the feasibility of reusing the HDTMA-treated zeolites;
- Based on results of these experiments, if possible a field site contaminated with gasoline should be obtained to examine the idea of *in situ* treatment of contaminated groundwater with treated zeolites - this may be somewhat impractical depending on the size of the contaminated plume, however, the writer believes that this type of information would be invaluable to the future of new contaminant technology;
- Additional batch studies should be useful to study the mechanisms associated with surface-modification of zeolite surfaces, i.e., aliphatic versus aromatic quaternary amines;
- In the future, if more volatile compounds than BTX organics are planned for investigation, development of a new methodology employing the use of a closed system may be in order to minimize the possible error associated with volatilization.

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APPENDICES

Introduction/Definitions for Appendices

The amount of soil added to each bottle for the generation of sorption isotherms was 2.5 g.

Where possible, the experimental data were calibrated by comparison to a known standard of 200 mg/L. When the known standard was unavailable, the data were calibrated by preparation of laboratory standards by the dissolution of the chemicals in methanol. A linearly regressed line through this data defined the calibration curve (equation).

The postscript "D" signifies the duplicate sample.

"Actual Conc." defines the initial concentration of the chemical in aqueous solution.

The date on the spreadsheet refers to the date the experiment was performed, not the date of analysis.

Appendix A

Table A.1. Isotherm Data for Benzene in Water (alone)

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g) - 2.5
Calibration Equation: y= 1.4769 + 1.1275e-3x
DATE: 7/18/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbed, S mg/kg
43	13572	15.105636	3322	5.222455	9.883181	13.31	52.6180556
43D	13572	15.105636	4693	6.7682575	8.3373785	13.1	43.6878633
44	43156	48.032628	13452	16.64403	31.388598	13.51	169.623984
44D	43156	48.032628	14401	17.7140275	30.3186005	13.39	162.386424
45	62054	69.066102	22142	26.442005	42.624097	13.51	230.34062
45D	62054	69.066102	23358	27.813045	41.253057	13.54	223.426557
46	85984	95.700192	34106	39.931415	55.768777	13.54	302.043696
46D	85984	95.700192	32165	37.7429375	57.9572545	13.85	321.08319
47	114066	126.955458	42400	49.2829	77.672558	13.43	417.256982
47D	114066	126.955458	44216	51.33044	75.625018	13.41	405.652597
48	181432	201.933816	88797	101.595518	100.338299	13.58	545.037637
48D	181432	201.933816	84896	97.19714	104.736676	13.59	569.348571

Table A.2. Isotherm Data for Toluene in Water (alone)

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g) - 2.5
Calibration Equation: y= 1.4227 + 4.3041e-4 x
Date: 7/31/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbed, S mg/kg
21	15457	8.07554737	7015	4.44202615	3.63352122	13.71	19.9262304
21D	15457	8.07554737	6236	4.10673676	3.96881061	13.6	21.5903297
22	88216	39.39174856	31539	14.997401	24.3943476	13.39	130.656126
22D	88216	39.39174856	37328	17.4890445	21.9027041	13.56	118.800267
23	142206	62.62958446	64432	29.1548771	33.4747073	13.86	185.583777
23D	142206	62.62958446	65839	29.760464	32.8691205	13.72	180.385733
24	318533	138.5224885	124691	55.0909533	83.4315352	13.73	458.205991
24D	318533	138.5224885	132803	58.5824392	79.9400493	13.45	430.077465
25	460400	199.583464	123650	54.6428965	144.940568	13.89	805.289793
25D	460400	199.583464	136764	60.2872932	139.296171	13.3	741.055628

Table A.3. Isotherm Data for p-Xylene in Water (alone)

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g) - 2.5
Calibration Equation: y= x*(200/181160)
DATE: 8/22/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbed, S mg/kg
21	3598	3.972179289	1518	1.67586664	2.29631265	13.47	12.3725326
21D	3598	3.972179289	1547	1.70788253	2.26429675	13.72	12.4264606
22	17881	19.74056083	8812	9.72841687	10.012144	13.34	53.4248002
22D	17881	19.74056083	9204	10.1611835	9.57937735	13.38	51.2688276
23	35554	39.2514904	19349	21.3612276	17.8902628	13.39	95.8202473
23D	35554	39.2514904	18858	20.8191654	18.432325	13.88	102.336268
24	52095	57.51269596	27373	30.2196953	27.2930007	13.56	148.037236
24D	52095	57.51269596	30779	33.9799073	23.5327887	13.17	123.970731
25	67030	74.0008832	38158	42.1262972	31.874586	13.48	171.867768
25D	67030	74.0008832	39444	43.5460367	30.4548465	13.28	161.776145

Table A.4. Isotherm Data for Benzene (100 ppm) & Toluene in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g)- 2.5
Calibration Equation: N/A - Benzene Constant
Date:8/23/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, mL	Amt. Sorbed, S mg/kg
36	75591	81	23803	25.5084982	55.4915018	13.9	308.53275
36D	75591	81	26965	28.8970572	52.1029428	13.49	281.147479
37	75591	81	28268	30.2934179	50.7065821	13.64	276.655112
37D	75591	81	27138	29.0824528	51.9175472	13.74	285.338839
38	75591	81	34049	36.4886298	44.5113702	13.36	237.868762
38D	75591	81	34480	36.9505112	44.0494888	13.54	238.572031
39	75591	81	33154	35.5295025	45.4704975	13.48	245.176922
39D	75591	81	33575	35.9806674	45.0193326	13.65	245.805556
40	75591	81	38054	40.7805903	40.2194097	13.54	217.828323
40D	75591	81	43628	46.7539705	34.2460295	13.83	189.449035

Table A.5. Isotherm Data for Benzene (100 ppm) & Toluene in Water: Toluene Data

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = -3.5368 + 1.1312e-3 x
Date: 8/23/91

Vial #	Avg. Area of Blanks Toluene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
36	9011	6.6564432	4178	1.1893536	5.4670896	13.9	30.3970182
36D	9011	6.6564432	4176	1.1870912	5.469352	13.49	29.5126234
37	47752	50.4802624	21603	20.9005136	29.5797488	13.64	161.387109
37D	47752	50.4802624	22047	21.4027664	29.077496	13.74	159.809918
38	83414	90.8211168	54456	58.0638272	32.7572896	13.36	175.054956
38D	83414	90.8211168	51313	54.5084656	36.3126512	13.54	196.669319
39	120142	132.3678304	79445	86.331384	46.0364464	13.48	248.228519
39D	120142	132.3678304	79278	86.1424736	46.2253568	13.65	252.390448
40	206616	230.1872192	141802	156.869622	73.3175968	13.54	397.088104
40D	206616	230.1872192	160109	177.578501	52.6087184	13.83	291.03143

Table A.6. Isotherm Data for Benzene & Toluene (both varying) in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/117163)
DATE:8/9/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
36	5928	10.11923559	2127	3.63083909	6.48839651	13.35	34.6480373
36D	5928	10.11923559	2169	3.70253408	6.41670152	13.72	35.2148579
37	24572	41.94498263	9909	16.9148963	25.0300863	13.58	135.963429
37D	24572	41.94498263	10950	18.6919079	23.2530748	13.49	125.473591
38	53170	90.76244207	27404	46.7792733	43.9831687	13.72	241.37963
38D	53170	90.76244207	28654	48.9130528	41.8493893	13.63	228.162871
39	63169	107.8309705	33572	57.3081946	50.522776	13.85	279.896179
39D	63169	107.8309705	36076	61.5825815	46.248389	13.32	246.411417
40	122747	209.5320195	69789	119.131466	90.4005531	13.79	498.649451
40D	122747	209.5320195	61851	105.581113	103.950906	13.48	560.503285

Table A.7. Isotherm Data for Benzene & Toluene (both varying) in Water:Toluene Data

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/162466)
DATE:8/9/91 Date: 8/9/91

Vial #	Avg. Area of Blanks Toluene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
36	6022	7.413243386	2336	2.8756786	4.53756478	13.35	24.2305959
36D	6022	7.413243386	2331	2.86952347	4.54371992	13.72	24.9359349
37	28042	34.52045351	13259	16.3221843	18.1982692	13.58	98.8529982
37D	28042	34.52045351	13977	17.2060616	17.3143919	13.49	93.4284589
38	58630	72.17510125	36769	45.2636244	26.9114769	13.72	147.690185
38D	58630	72.17510125	28654	35.2738419	36.9012593	13.63	201.185666
39	70394	86.65690052	46244	56.9276033	29.7292972	13.85	164.700307
39D	70394	86.65690052	46690	57.4766413	29.1802593	13.32	155.472421
40	123158	151.6107986	85599	105.374663	46.2361356	13.79	255.038524
40D	123158	151.6107986	75611	93.0791673	58.5316312	13.48	315.602556

Table A.8. Isotherm Data for Benzene & p-Xylene (both varying) in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/117163)
DATE:8/13/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
6	7088	12.09938291	2355	4.02004046	8.07934245	13.84	44.7272398
6D	7088	12.09938291	2004	3.42087519	8.67850772	13.59	47.176368
7	10682	18.23442554	3421	5.83972756	12.394698	13.87	68.7657844
7D	10682	18.23442554	3390	5.78680983	12.4476157	13.82	68.8104197
8	27918	47.65668342	10029	17.1197392	30.5369443	13.9	169.78541
8D	27918	47.65668342	9425	16.0886969	31.5679865	13.34	168.446776
9	51292	87.55665184	20542	35.0656777	52.4909741	13.54	284.291116
9D	51292	87.55665184	21056	35.9430878	51.613564	13.35	275.616432
10	67214	114.7358808	29639	50.594471	64.1414098	13.63	349.698966
10D	67214	114.7358808	30832	52.63095	62.1049307	13.61	338.099243

Table A.9. Isotherm Data for Benzene & p-Xylene (both varying) in Water: Xylene Data

Soil Type - Tilden

Tailoring Agent - BTEA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/181160)
DATE:8/13/91

Vial #	Avg. Area of Blanks Xylene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
6	3926	4.33429013	2242	2.47516008	1.85913005	13.84	10.292144
6D	3926	4.33429013	1952	2.1550011	2.17928903	13.59	11.8466151
7	13347	14.73504085	6062	6.69242658	8.04261426	13.87	44.6204239
7D	13347	14.73504085	6302	6.95738574	7.77765511	13.82	42.9948775
8	32600	35.99028483	17616	19.4480018	16.5422831	13.9	91.9750938
8D	32600	35.99028483	16677	18.4113491	17.5789357	13.34	93.8012011
9	53091	58.61227644	31878	35.1931994	23.4190771	13.54	126.837721
9D	53091	58.61227644	33286	36.7476264	21.86465	13.35	116.757231
10	73568	81.2188121	47737	52.7014794	28.5173327	13.63	155.476498
10D	73568	81.2188121	49733	54.9050563	26.3137558	13.61	143.252087

Appendix B

Table B.1. Isotherm Data for Benzene in Water

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = 1.4769 + 1.1275e-3x
Date: 7/18/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
37	13572	15.105636	6567	8.8811925	6.2244435	13.56	33.7613815
37D	13572	15.105636	5478	7.653345	7.452291	12.72	37.9172566
38	43156	48.032628	16566	20.155065	27.877563	12.51	139.499325
38D	43156	48.032628	16136	19.67024	28.362388	13.47	152.816547
39	62054	69.066102	25076	29.75009	39.316012	12.89	202.713358
39D	62054	69.066102	25503	30.2315325	38.8345695	13.53	210.17269
40	85984	95.700192	33475	39.2199625	56.4802295	13.32	300.926663
40D	85984	95.700192	32197	37.7790175	57.9211745	13.27	307.445594
41	114066	126.955458	39784	46.33336	80.622098	13.07	421.492328
41D	114066	126.955458	41114	47.832935	79.122523	13.19	417.450431
42	181432	201.933816	64014	73.652685	128.281131	13.18	676.298123
42D	181432	201.933816	65123	74.9030825	127.030734	13.22	671.738519

Table B.2. Isotherm Data for Benzene in Water

Soil Type - Tilden

Tailoring Agent: None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = 1.4769 = 1.1275e-3x
Date: 7/18/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbed, S mg/kg
43	13572	15.105636	7499	8.47387	6.631766	13.9	36.872619
43D	13572	15.105636	11795	13.32835	1.777286	13.59	9.6613267
44	43156	48.032628	32931	37.21203	10.820598	13.17	57.0029103
44D	43156	48.032628	38381	43.37053	4.662098	13.62	25.3991099
45	62054	69.066102	58202	65.76826	3.297842	13.82	18.2304706
45D	62054	69.066102	54669	61.77597	7.290132	13.84	40.3581708
46	85984	95.700192	77628	87.71964	7.980552	13.5	43.0949808
46D	85984	95.700192	80581	91.05653	4.643662	13.87	25.7630368
47	114066	126.955458	100964	114.08932	12.866138	13.87	71.3813336
47D	114066	126.955458	102140	115.4182	11.537258	13.8	63.6856642
48	181432	201.933816	175616	198.44608	3.487736	13.6	18.9732838
48D	181432	201.933816	176244	199.15572	2.778096	13.47	14.9683812

Table B.3. Isotherm Data for Toluene in Water

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: $y = 1.4227 + 4.3041e-4\ x$
Date: 7/31/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbed, S mg/kg
16	15457	8.07554737	2760	2.6106316	5.46491577	13.56	29.6417031
16D	15457	8.07554737	2796	2.62612636	5.44942101	13.09	28.5331684
17	88216	39.39174856	16830	8.6665003	30.7252483	13.25	162.843816
17D	88216	39.39174856	17489	8.95014049	30.4416081	13.26	161.462289
18	142206	62.62958446	34829	16.4134499	46.2161346	13.38	247.348752
18D	142206	62.62958446	31256	14.875595	47.7539895	13.11	250.421921
19	318533	138.5224885	69566	31.3646021	107.157886	13.26	568.36543
19D	318533	138.5224885	69647	31.3994653	107.123023	13.36	572.465436
20	460400	199.583464	87302	38.9983538	160.58511	12.98	833.757892
20D	460400	199.583464	92234	41.1211359	158.462328	12.75	808.157873

Table B.4. Isotherm Data for Toluene in Water

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y= 1.4227 + 4.3041e-4 x
Date: 7/31/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbed, S mg/kg
26	15457	8.07554737	15386	8.04498826	0.03055911	13.82	0.16893076
26D	15457	8.07554737	15054	7.90209214	0.17345523	13.48	0.9352706
27	88216	39.39174856	59973	27.2356789	12.1560696	13.42	65.2537818
27D	88216	39.39174856	61786	28.0160123	11.3757363	13.35	60.7464318
28	142206	62.62958446	151580	66.6642478	-4.0346633	13.89	-22.41659
28D	142206	62.62958446	152276	66.9638132	-4.3342287	13.22	-22.919401
29	316927	137.8312501	287360	125.105318	12.7259325	13.45	68.4655167
29D	316927	137.8312501	310258	134.960846	2.87040429	13.66	15.683889
30	460400	199.583464	392684	170.43782	29.1456436	13.14	153.189503
30D	460400	199.583464	421194	182.70881	16.8746545	13.5	91.1231341

Table B.5. Isotherm Data for p-Xylene in Water

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y= X*(200/181160)
Date: 8/22/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbed, S mg/kg
16	3598	3.972179289	0	0	3.97217929	13.29	21.1161051
16D	3598	3.972179289	0	0	3.97217929	13.54	21.513323
17	17881	19.74056083	1449	1.59969088	18.1408699	13.5	97.9606977
17D	17881	19.74056083	1431	1.57981894	18.1607419	12.95	94.072643
18	35554	39.2514904	2587	2.85603886	36.3954515	13.1	190.712166
18D	35554	39.2514904	2348	2.59218371	36.6593067	13.01	190.775032
19	52095	57.51269596	3580	3.95230735	53.5603886	13.28	284.512784
19D	52095	57.51269596	3600	3.97438728	53.5383087	13.11	280.754891
20	67030	74.0008832	4819	5.32015898	68.6807242	13.15	361.260609
20D	67030	74.0008832	4405	4.86310444	69.1377788	13.07	361.452307

Table B.6. Isotherm Data for p-Xylene in Water

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y= X*(200/181160)
DATE:8/22/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/L	Volume of Sample, ml	Amt. Sorbe mg/kg
26	3598	3.972179289	3219	3.55376463	0.41841466	13.54	2.2661338
26D	3598	3.972179289	3172	3.50187679	0.4703025	13.62	2.56220799
27	17881	19.74056083	16636	18.3660852	1.3744756	13.61	7.48264518
27D	17881	19.74056083	15612	17.2355928	2.50496798	13.61	13.6370457
28	35554	39.2514904	28951	31.9618017	7.28968867	13.72	40.0058114
28D	35554	39.2514904	28247	31.1845882	8.06690219	13.57	43.7871451
29	52095	57.51269596	44795	49.4535217	8.05917421	13.86	44.6800618
29D	52095	57.51269596	40157	44.3331861	13.1795098	12.83	67.6372444
30	67030	74.0008832	50941	56.238684	17.7621992	13.7	97.3368514
30D	67030	74.0008832	48072	53.0713182	20.929565	13.59	113.773115

Appendix C

Table C.1. Isotherm Data for Benzene (100 ppm) & Toluene in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: N/A - Benzene Constant
Date: 8/23/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
31	75591	81	23524	25.2095077	55.7904923	13.34	297.698067
31D	75591	81	22047	23.6266798	57.3733202	13.18	302.472144
32	75591	81	22222	23.8142187	57.1857813	13.12	300.11098
32D	75591	81	24066	25.7903423	55.2096577	13.49	297.911313
33	75591	81	24331	26.0743297	54.9256703	13.27	291.545458
33D	75591	81	23362	25.0359003	55.9640997	13.13	293.923452
34	75591	81	21664	23.2162376	57.7837624	12.89	297.933079
34D	75591	81	22870	24.5086482	56.4913518	13.27	299.856095
35	75591	81	27810	29.802602	51.197398	13.52	276.875529
35D	75591	81	21979	23.5538076	57.4461924	13.01	298.949985

Table C.2. Isotherm Data for Benzene (100 ppm) & Toluene in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: N/A - Benzene Constant
Date: 8/23/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
41	75591	81	63036	67.5525645	13.4474355	13.2	71.0024597
41D	75591	81	65108	69.7730244	11.2269756	13.18	59.1886153
42	75591	81	71398	76.5137064	4.48629359	13.93	24.9976279
42D	75591	81	73430	78.6913003	2.30869966	13.7	12.6516741
43	75591	81	63548	68.1012495	12.8987505	13.88	71.6138625
43D	75591	81	82360	88.2611398	-7.2611398	13.93	-40.459071
44	75591	81	72579	77.7793257	3.22067428	13.6	17.5204681
44D	75591	81	78492	84.1159955	-3.1159955	13.75	-17.137975
45	75591	81	69466	74.4432775	6.55672246	13.6	35.6685702
45D	75591	81	65608	70.3088497	10.6911503	13.87	59.3145019

Table C.3. Isotherm Data for Benzene (100 ppm) & Toluene in Water: Toluene Data

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: $y = -3.5368 + 1.1312e\text{-}3\, x$
Date: 8/23/91

Vial #	Avg. Area of Blanks Toluene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
31	9011	6.6564432	1602	-1.7246176	8.3810608	13.34	44.7213404
31D	9011	6.6564432	1363	-1.9949744	8.6514176	13.18	45.6102736
32	47752	50.4802624	6884	4.2503808	46.2298816	13.12	242.614419
32D	47752	50.4802624	7153	4.5546736	45.9255888	13.49	247.814477
33	83414	90.8211168	14308	12.6484096	78.1727072	13.27	414.94073
33D	83414	90.8211168	14089	12.4006768	78.42044	13.13	411.864151
34	120142	132.3678304	20181	19.2919472	113.075883	12.89	583.019254
34D	120142	132.3678304	21106	20.3383072	112.029523	13.27	594.652709
35	206616	230.1872192	38625	40.1558	190.031419	13.52	1027.68992
35D	206616	230.1872192	30995	31.524744	198.662475	13.01	1033.83952

Table C.4. Isotherm Data for Benzene (100 ppm) & Toluene in Water: Toluene Data

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = -3.5368 + 1.1312e-3 x
Date: 8/23/91

Vial #	Avg. Area of Blanks Toluene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
41	9011	6.6564432	6971	4.3487952	2.307648	13.2	12.1843814
41D	9011	6.6564432	7105	4.500376	2.1560672	13.18	11.3667863
42	47752	50.4802624	39456	41.0958272	9.3844352	13.93	52.2900729
42D	47752	50.4802624	40761	42.5720432	7.9082192	13.7	43.3370412
43	83414	90.8211168	69647	75.2478864	15.5732304	13.88	86.4625752
43D	83414	90.8211168	89682	97.9114784	-7.0903616	13.93	-39.507495
44	120142	132.3678304	116543	128.296642	4.0711888	13.6	22.1472671
44D	120142	132.3678304	121917	134.37571	-2.00788	13.75	-11.04334
45	206616	230.1872192	176835	196.498952	33.6882672	13.6	183.264174
45D	206616	230.1872192	189207	210.494158	19.6930608	13.87	109.257101

Table C.5. Isotherm Data for Benzene & Toluene (both varying) in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y=x(200/117163)
DATE:8/9/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
31	5928	10.1192356	2521	4.30340637	5.81582923	13.25	30.823895
31D	5928	10.1192356	2265	3.86640834	6.25282726	13.4	33.515154
32	24572	41.9449826	9985	17.0446301	24.9003525	13.14	130.87625
32D	24572	41.9449826	10160	17.3433593	24.6016234	13.25	130.3886
33	53170	90.7624421	17940	30.6240025	60.1384396	13.4	322.34204
33D	53170	90.7624421	18588	31.7301537	59.0322884	13.13	310.03758
34	63169	107.830971	27308	46.6153991	61.2155715	12.96	317.34152
34D	63169	107.830971	37754	64.446967	43.3840035	13.57	235.48837
35	122747	209.532019	40079	68.4157968	141.116223	13.15	742.27133
35D	122747	209.532019	42514	72.5723991	136.95962	13.55	742.32114

Table C.6. Isotherm Data for Benzene & Toluene (both varying) in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/117163)
DATE:8/9/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
41	5928	10.11923559	5294	9.03698267	1.08225293	13.8	5.97403617
41D	5928	10.11923559	4565	7.7925625	2.3266731	13.39	12.4616611
42	24572	41.94498263	22350	38.1519763	3.79300632	13.68	20.7553306
42D	24572	41.94498263	20623	35.2039466	6.74103599	13.79	37.1835545
43	53170	90.76244207	43383	74.0558026	16.7066395	13.67	91.3519046
43D	53170	90.76244207	41519	70.8739107	19.8885314	13.4	106.602528
44	63169	107.8309705	63792	108.894446	-1.0634757	13.89	-5.9086708
44D	63169	107.8309705	64204	109.59774	-1.7667694	13.4	-9.4698838
45	122747	209.5320195	114946	196.215529	13.3164907	13.9	74.0396883
45D	122747	209.5320195	114546	195.532719	13.9993001	13.93	78.0041003

Table C.7. Isotherm Data for Benzene & Toluene (both varying) in Water: Toluene Data

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/162466)
DATE:8/1/91

Vial #	Avg. Area of Blanks Toluene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
31	6022	7.413243386	1650	2.03119422	5.38204917	13.25	28.5248606
31D	6022	7.413243386	1372	1.68896877	5.72427462	13.4	30.6821119
32	28042	34.52045351	6684	8.22818313	26.2922704	13.14	138.192173
32D	28042	34.52045351	6831	8.40914407	26.1113094	13.25	138.38994
33	58630	72.17510125	12377	15.2364187	56.9386826	13.4	305.191338
33D	58630	72.17510125	12762	15.710364	56.4647372	13.13	296.5528
34	70394	86.65690052	19061	23.4646018	63.1922987	12.96	327.588876
34D	70394	86.65690052	18667	22.9795773	63.6773233	13.57	345.640511
35	123158	151.6107986	23240	28.6090628	123.001736	13.15	646.98913
35D	123158	151.6107986	24621	30.3091108	121.301688	13.55	657.455148

Table C.8. Isotherm Data for Benzene & Toluene (both varying) in Water: Toluene Data

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/162466)
DATE:8/1/91

Vial #	Avg. Area of Blanks Toluene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
41	6022	7.413243386	4995	6.14897886	1.26426452	13.8	6.97874017
41D	6022	7.413243386	3908	4.81085273	2.60239065	13.39	13.9384043
42	28042	34.52045351	22898	28.1880517	6.33240186	13.68	34.650903
42D	28042	34.52045351	19346	23.8154445	10.705009	13.79	59.0488299
43	58630	72.17510125	43957	54.112245	18.0628562	13.67	98.7676979
43D	58630	72.17510125	40252	49.5512907	22.6238105	13.4	121.263624
44	70394	86.65690052	66555	81.9309886	4.72591188	13.89	26.2571664
44D	70394	86.65690052	67000	82.4787956	4.17810496	13.4	22.3946426
45	123158	151.6107986	110339	135.830266	15.7805325	13.9	87.7397609
45D	123158	151.6107986	111506	137.266874	14.3439243	13.93	79.924346

Table C.9. Isotherm Data for Benzene & Xylene (both varying) in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/117163)
DATE:8/12/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
1	7088	12.09938	2432	4.1514813	7.9479016	13.18	41.90134
1D	7088	12.09938	2425	4.1395321	7.9598508	13.56	43.17423
2	10682	18.23443	3914	6.6812902	11.553135	12.92	59.7066
2D	10682	18.23443	3887	6.6352005	11.599225	13.5	62.63582
3	27918	47.65668	9878	16.861979	30.794705	13.34	164.3205
3D	27918	47.65668	10293	17.570393	30.08629	13.01	156.5691
4	51292	87.55665	19369	33.063339	54.493313	13.12	285.9809
4D	51292	87.55665	19034	32.491486	55.065166	13.23	291.4049
5	67214	114.7359	24132	41.193892	73.541989	12.74	374.77
5D	67214	114.7359	22242	37.967618	76.768263	13.18	404.7223

Table C.10. Isotherm Data for Benzene & p-Xylene (both varying) in Water: Benzene Data

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/117163)
DATE: 8/13/91

Vial #	Avg. Area of Blanks Benzene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
11	7088	12.09938291	6970	11.8979541	0.20142878	13.69	1.10302399
11D	7088	12.09938291	6918	11.8091889	0.290194	13.05	1.5148127
12	10682	18.23442554	10327	17.6284322	0.60599336	13.7	3.32084361
12D	10682	18.23442554	10105	17.249473	0.98495259	13.66	5.38178094
13	27918	47.65668342	27046	46.1681589	1.48852453	13.58	8.08566527
13D	27918	47.65668342	27608	47.1275061	0.5291773	13.85	2.93164224
14	51292	87.55665184	55080	94.022857	-6.4662052	13.58	-35.124427
14D	51292	87.55665184	54100	92.349974	-4.7933221	13.65	-26.171539
15	67214	114.7358808	69617	118.837858	-4.1019776	13.9	-22.806995
15D	67214	114.7358808	70080	119.62821	-4.8923295	13.26	-25.948916

Table C.11. Isotherm Data for Benzene & Xylene (both varying) in Water: Xylene Data

Soil Type - Tilden

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/181160)
DATE:8/13/91

Vial #	Avg. Area of Blanks Xylene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
1	3926	4.3342901	476	0.52550232	3.808787812	13.18	20.0799293
1D	3926	4.3342901	432	0.47692647	3.857363656	13.56	20.9223405
2	13347	14.735041	1137	1.25524398	13.47979686	12.92	69.6635902
2D	13347	14.735041	887	0.97924487	13.75579598	13.5	74.2812983
3	32600	35.990285	2723	3.00618238	32.98410245	13.34	176.003171
3D	32600	35.990285	2949	3.25568558	32.73459925	13.01	170.350854
4	53091	58.612276	4825	5.32678295	53.28549349	13.12	279.64227
4D	53091	58.612276	5103	5.63369397	52.97858247	13.23	280.362658
5	73568	81.218812	6008	6.63281078	74.58600132	12.74	380.090263
5D	73568	81.218812	5489	6.05983661	75.15897549	13.18	396.238119

Table C.12. Isotherm Data for Benzene & Xylene (both varying) in Water: Xylene Data

Soil Type - Tilden

Tailoring Agent - None

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/181160)
DATE:8/13/91

Vial #	Avg. Area of Blanks Xylene	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
11	3926	4.33429013	4178	4.61249724	-0.2782071	13.69	-1.5234621
11D	3926	4.33429013	4132	4.5617134	-0.2274233	13.05	-1.1871495
12	13347	14.73504085	11552	12.7533672	1.98167366	13.7	10.8595716
12D	13347	14.73504085	11414	12.6010157	2.13402517	13.66	11.6603135
13	32600	35.99028483	28123	31.0476926	4.94259218	13.58	26.8481607
13D	32600	35.99028483	28750	31.7398984	4.2503864	13.85	23.5471406
14	53091	58.61227644	53251	58.7889159	-0.1766394	13.58	-0.9595054
14D	53091	58.61227644	50903	56.1967322	2.41554427	13.65	13.1888717
15	73568	81.2188121	65128	71.9010819	9.31773018	13.9	51.8065798
15D	73568	81.2188121	69150	76.3413557	4.87745639	13.26	25.8700287

Appendix D

Table D.1. Isotherm Data for Benzene in Water

Soil Type - St. Cloud

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: $y = X(200/102093)$
DATE: 11/16/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
6	5460	10.69613	4199	8.22583331	2.47029669	13.15	12.9937606
6D	5460	10.69613	3906	7.65184685	3.04428315	13.31	16.2077635
7	30660	60.062884	16171	31.6789594	28.3839245	13.61	154.522085
7D	30660	60.062884	17550	34.3804179	25.682466	13.44	138.068937
8	88928	174.20979	40567	79.4706787	94.7391104	13.42	508.559545
8D	88928	174.20979	40257	78.8633893	95.3463999	12.63	481.690012
9	164068	321.40891	72497	142.02149	179.387421	13.08	938.554988
9D	164068	321.40891	73861	144.693564	176.715348	12.53	885.697323

Table D.2. Isotherm Data for Toluene in Water

Soil Type - St. Cloud

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/127685)
DATE:11/22/91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
11	15592	24.422602	2927	4.58472021	19.8378823	13.3	105.537534
11D	15592	24.422602	5931	9.29004973	15.1325528	12.72	76.9944285
12	60220	94.32588	16041	25.1258958	69.1999843	13.02	360.393518
12D	60220	94.32588	16648	26.0766731	68.249207	13.02	355.44187
13	89162	139.65932	23256	36.4271449	103.232173	13.1	540.936586
13D	89162	139.65932	27664	43.3316364	96.3276814	13.31	512.848576
14	134753	211.071	31876	49.9291224	161.141873	12.93	833.425765
14D	134753	211.071	32717	51.2464268	159.824568	13	831.087755
15	210470	329.67067	50525	79.1400713	250.530603	13.19	1321.79946
15D	210470	329.67067	48064	75.2852723	254.385402	12.7	1292.27784

Table D.3. Isotherm Data for p-Xylene in Water

Soil Type - St. Cloud

Tailoring Agent - HDTMA

Amt. of Soil Added (g)- 2.5
Calibration Equation: y = X*(200/124673)
DATE: 11\24\91

Vial #	Avg. Area of Blanks	Actual Conc., Ci mg/l	Area of Samples	Equil. Conc., Co mg/l	Conc. Sorbed, A mg/l	Volume of Sample, ml	Amt. Sorbed, S mg/kg
21	5516	8.8487483	657	1.05395715	7.79479117	13.02	40.5952724
21D	5516	8.8487483	607	0.97374732	7.875001	12.64	39.8160051
22	45890	73.616581	5145	8.2535914	65.3629896	12.79	334.397055
22D	45890	73.616581	5134	8.23594523	65.3806357	12.63	330.302972
23	79422	127.4085	8128	13.0389098	114.369591	12.52	572.762911
23D	79422	127.4085	8240	13.2185798	114.189921	13.22	603.836301
24	118586	190.23526	11718	18.7979755	171.43728	13.03	893.531103
24D	118586	190.23526	11397	18.2830284	171.952227	12.76	877.644167