

## Sorption of benzene, toluene, ethylbenzene and xylenes to various media

Richard G. Zytner

*School of Engineering, University of Guelph, Guelph, Ontario, N1G 2W1 Canada*

Received 25 October 1993; accepted in revised form 10 February 1994

---

### Abstract

The sorption and desorption characteristics of the major components of gasoline were determined for five media; sandy loam soil, organic top soil, clay soil, peat moss and granular activated carbon (GAC). Emphasis was placed on the sorption of benzene, toluene, ethylbenzene and xylenes (BTEX), the aromatic hydrocarbons contained in gasoline. The results showed that the Freundlich isotherm satisfactorily described the sorption and desorption of dissolved BTEX on the media tested. The organic carbon content of the media was an important factor in both sorption and desorption, with the order of sorption preference being GAC, peat moss, organic top soil, clay soil and sandy loam soil. The soil–water partition coefficient ( $K_{oc}$ ) for the BTEX compounds and Total BTEX suggests that the BTEX compounds will migrate quickly through soil, with benzene being the fastest followed by toluene, *m*-, *p*- and *o*-xylenes and ethylbenzene.

---

### 1. Introduction

The United States Environmental Protection Agency (US EPA) has stated that approximately 25% of all underground storage tanks (USTs) are leaking [1]. Once released, the gasoline contaminates the soil, volatilizes into the atmosphere and has the potential to migrate through the soil and contaminate the groundwater. Because gasoline is a mixture of many volatile and semi-volatile hydrocarbons, including benzene, toluene, ethylbenzene *m*-, *p*- and *o*-xylene (BTEX), spills pose health risks to the public. The greatest health risks occur at sites where residents rely on groundwater for their drinking water supply [2].

At the time of release, the immiscible gasoline disperses into the unsaturated soil pores as it migrates towards the groundwater. The dispersed gasoline, referred to as residual saturation, can be a long-term contamination source as it remains stationary until it volatilizes into the atmosphere or is transported to the groundwater by infiltrating water [3]. This transport of gasoline is a complex process as it is a function

of the different soil properties and the four different phases of gasoline: aqueous, vapour, sorbed and immiscible. Consequently there exist a large number of possible reactions in the subsurface [4, 5]. However, limited information exists to describe the migration of gasoline through unsaturated soil [2, 4, 6]. Therefore, an experimental program was developed to gather information on how gasoline behaves in the soil environment, specifically the sorption and desorption characteristics of BTEX.

The sorption/desorption experiments are required as each soil sorbs and retains different amounts of the major components of dissolved gasoline under varying environmental conditions [7]. To evaluate the sorption and desorption characteristics, batch sorption experiments were conducted with sandy loam soil, organic top soil, clay soil, peat moss and granular activated carbon (GAC). These media were mixed with an aqueous BTEX solution derived from commercially available unleaded gasoline, to determine the mass of BTEX sorbed and subsequently desorbed. The use of the BTEX solution (a multi-solute solution) differs from existing studies where single-solute systems are traditionally used. The multi-component solution was used, as it is important to understand how the soluble BTEX compounds behave in the presence of the other dissolved gasoline compounds.

## 2. Theory

Sorption is the process through which the majority of spilled chemicals are removed from the soil environment [8]. This sorption is a combination of adsorption and absorption. Adsorption is defined as the condensation of gases on the free surfaces of the soils or the fixation of solutes from a solution onto the surface of a solid [9], while absorption is the uptake of solute by the solid. Sorption can be positive or negative. Positive sorption occurs when there is an attraction between the sorbate and the sorbent, resulting in a higher concentration of sorbate at the surface-liquid interface than in the bulk solution. Negative sorption, commonly referred to as desorption, is the opposite situation with the repelling of the sorbate.

To explain the sorption process and permit comparisons between different chemicals and media, equilibrium equations or isotherms have been developed. These equations relate the mass of solute sorbed per unit of sorbent to the equilibrium concentration in the liquid phase. An isotherm successfully used to express the sorption of organic chemicals onto soil particles is the Freundlich isotherm [10–12]. The Freundlich isotherm is used as it describes the multi-layer sorption occurring on the soil surface. According to the Freundlich isotherm, sorption at equilibrium is expressed by:

$$\frac{X_a}{m} = K_f C_e^{1/n_f} \quad (1)$$

where  $X_a$  = mass of sorbate sorbed (mg);  $m$  = mass of sorbent (kg);  $K_f$  = sorption equilibrium constant  $(\text{mg kg}^{-1})(\text{mg l}^{-1})^{-1/n_f}$ ;  $C_e$  = solution concentration at equilibrium after sorption  $(\text{mg l}^{-1})$ ;  $n_f$  = constant indicative of sorption intensity.

The constants defined in Eq. (1) are determined by regressing the log of mass of sorbate sorbed on the sorbent ( $X_a/m$ ) and the log of the equilibrium concentration ( $C_e$ ). The intercept is  $K_f$  which gives an indication of sorptive capacity, while  $1/n_f$ , the slope, indicates sorption intensity. The higher the values for  $K_f$  and  $n_f$ , the greater the sorption capacity for the medium [13]. Theoretically, Eq. (1) predicts that the sorption is indefinite. Therefore, it should not be extrapolated past the solute concentration for which it was developed.

Similarly, Eq. (1) can be modified to express the mass of chemical desorbed (released) from the medium back into solution. This isotherm, referred to as the desorption isotherm, is expressed by:

$$\frac{X_{des}}{m} = K_{fd} C_e^{1/n_{fd}} \quad (2)$$

where  $X_{des}$  = mass of sorbate desorbed (released) mg;  $K_{fd}$  = desorption equilibrium constant ( $\text{mg kg}^{-1})(\text{mg l}^{-1})^{-1/n_{fd}}$ ;  $C_{ed}$  = solution concentration at equilibrium after desorption  $\text{mg l}^{-1}$ ;  $n_{fd}$  = constant indicative of desorption intensity.

Additional details on the interaction of synthetic organic chemicals with different soils has been described in detail elsewhere [10–12, 14].

### 3. Materials and methods

The procedures used to determine the sorption characteristics are similar to those described in Zytner [15] with some modifications. The following sections outline the important differences.

#### 3.1. Media tested

Three different types of soils were selected for this study; sandy loam soil, organic top soil and clay soil. The sandy loam soil and clay soil are typical soils present in Essex County, Province of Ontario. The organic top soil was purchased from an Essex County nursery selling organic enriched top soil. In addition to the three soils, two other media were selected to ensure that the media selected exhibited a wide variety of physical and chemical properties. One was commercial peat moss, which was purchased from an Essex County nursery, while the other, granular activated carbon (GAC, Nuclear 4 × 10 mesh), was purchased from Westvaco.

Prior to using, the soils and peat moss were air dried and sieved to pass a 2.00 mm sieve. The GAC was used as purchased. All five media were analyzed for their important physical and chemical properties according to the *Methods of Soil Analysis* [16]. The results are summarized in Table 1.

#### 3.2. BTEX stock solution

The BTEX stock solution was prepared by mixing 2 l of de-ionized water with 100 ml of commercially available unleaded gasoline in a closed 2 l separatory funnel.

Table 1  
Properties of media used for sorption/desorption studies

Medium	Organic C (%)	CEC (meq/100 g)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
Clay soil	0.25	30.1	91
Sandy loam soil	1.0	14.2	22
Organic top soil	11.7	23.3	N.A.
Peat moss	49.4	Approx. 150	0.4 [11]
GAC	74.1	N.A. <sup>a</sup>	1300 [28]

<sup>a</sup> N.A. Not available.

These volumes ensured that the de-ionized water would become saturated with gasoline at room temperature. This mixture was then vigorously shaken three times a day over a five day period. After five days, the gasoline saturated de-ionized water was drained from the bottom of the funnel and transferred into appropriate containers. These containers were stored at 4°C to minimize volatilization losses. The average concentration of the dissolved BTEX in the stock solution was measured as follows: benzene, 55 mg/l, toluene, 425 mg/l, ethylbenzene, 17 mg/l, *m*- and *p*-xylene, 85 mg/l and *o*-xylene, 75 mg/l. To ensure a sufficient and consistent supply of stock solution for the duration of the experiments, 4 l of solution was prepared prior to starting the experiments.

### 3.3. Sorption

The sorption experiments were conducted at room temperature by taking the air dried media, weighing out an appropriate amount and placing it in glass containers with Teflon liners in the caps. The containers used were 14 ml culture tubes for the sandy loam soil, organic top soil, clay soil and peat moss, and 45 ml square bottles for the GAC. The quantity of sandy loam soil, organic top soil, clay and peat moss placed in the containers was 5, 4, 4 and 0.3 g, respectively. Only 30 mg of GAC was used, as it was expected to have a high sorption capacity for dissolved BTEX.

Various concentrations of aqueous solutions were added to the medium. These concentrations were obtained by diluting the gasoline stock solution. The dilution percentages were as follows: Conc 1, 0%, Conc 2, 20%, Conc 3, 40%, Conc 4, 60% and Conc 5, 80%.

The volume of aqueous solution added to each medium was 11.5, 11, 12, 13 and 34 ml, respectively, for sandy loam soil, organic top soil, clay soil, peat moss and GAC. The volumes varied with each medium to maintain a minimum headspace. The headspace was important as it not only affected the degree of mixing during shaking, but also controlled the mass of gasoline lost through volatilization. Shaking of aqueous blanks, gasoline solutions with no medium, allowed the measurement of volatilization losses. The concentrations selected for the volatilization blanks were identical to those used in the sorption study. One blank was prepared for every concentration.

To ensure that the solution and medium attained equilibrium, the containers were placed in a tumbler. The mixing times, estimated through preliminary experiments, were 165, 84, 240, 92 and 185 h, respectively, for sandy loam soil, organic top soil, clay soil, peat moss and GAC. After mixing, the sealed containers were centrifuged in a refrigerated centrifuge to separate the fluid and suspended soil particles. Even though sandy loam soil, organic top soil and clay were the only media requiring separation, the GAC and peat moss samples and blanks were also centrifuged to maintain procedural similarities. The collected supernatant was analyzed for the corresponding BTEX concentrations.

The concentration of BTEX in the solution after equilibrium is reached, is referred to as the equilibrium concentration ( $C_e$ ), and is used to calculate the mass of BTEX sorbed by the different media. The mass of BTEX sorbed is the difference between the initial aqueous concentration and final equilibrium concentration (corrected for volatilization losses), times the volume of solution added to each medium.

### 3.4. Desorption

In evaluating the desorption isotherms, each medium was first subjected to sorption as indicated in Section 3.3. After the sorption samples were centrifuged, equilibrium was attained, all the free supernatant was removed and replaced with clean de-ionized water. The sorption procedure was then repeated with minor changes; the mixing times to reach equilibrium were longer and the mass of chemical desorbed from the soil was determined. The desorption equilibrium times used, based on preliminary experiments, were 212, 108, 260, 138 and 168 h, respectively, for sandy loam soil, organic top soil, clay soil and peat moss and GAC. The mass of BTEX desorbed was calculated by multiplying the equilibrium concentration after desorption ( $C_{ed}$ ) with the volume of de-ionized water added to each medium. A volatilization correction was also made.

### 3.5. Analysis

The method used to analyze the aqueous BTEX concentrations was a liquid extraction procedure using carbon disulphide ( $CS_2$ ). Eleven ml of sample were extracted with 2 ml of  $CS_2$ . Standards were extracted using a similar procedure. The gas chromatograph (GC) used for extract analysis was a HP-5890A, equipped with a Flame Ionization Detector (FID), a SPB-1 capillary column (60 m  $\times$  0.32  $\times$  1.0 mm) and an HP 3393A integrator. The following GC conditions were used throughout the study: initial column temperature: 50 °C for 7.0 min; final temperature: 120 °C for 2.0 min; detector temperature: 200 °C; detector gas (H): 30 ml min<sup>-1</sup>; temperature rate: 5 °C min<sup>-1</sup>; injector temperature: 150 °C; carrier gas (N): 30 ml min<sup>-1</sup>; detector gas (Air): 200 ml min<sup>-1</sup>.

Using the HP-5890A with the above conditions, the BTEX retention times were as follows: benzene, 7.3 min, toluene, 12.1 min, ethylbenzene, 16.6 min, *m*- and *p*-xylene, 17.0 min, and *o*-xylene, 17.9 min.

#### 4. Results and discussion

The data collected from the sorption and desorption experiments were correlated using the Freundlich isotherm outlined in Section 2. Typical sorption and desorption isotherms are shown in Figs. 1-5. The symbols are the actual data points, with the solid lines representing the least squares fit. Tables 2 and 3 contain the respective Freundlich coefficients based on the least squares fit. For Total BTEX, all the individual compound masses were summed together. These results will be discussed in the subsequent sections in the following order, sorption, desorption, soil-water partition coefficient and application of results.

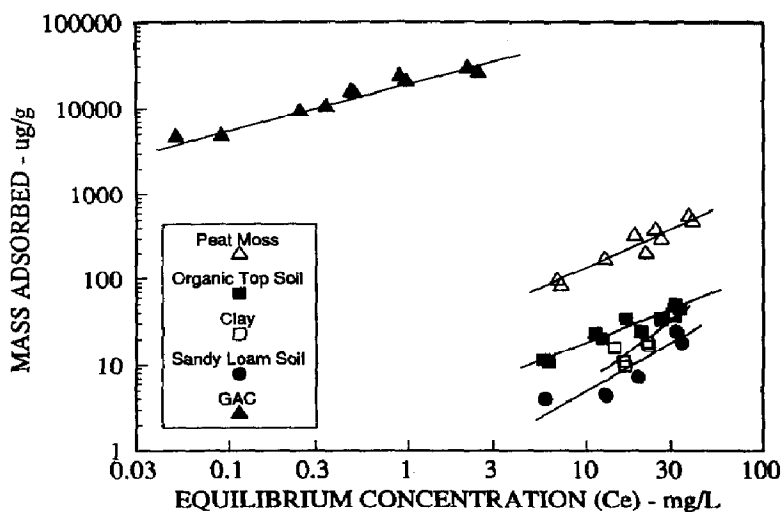


Fig. 1. Sorption of benzene on different media.

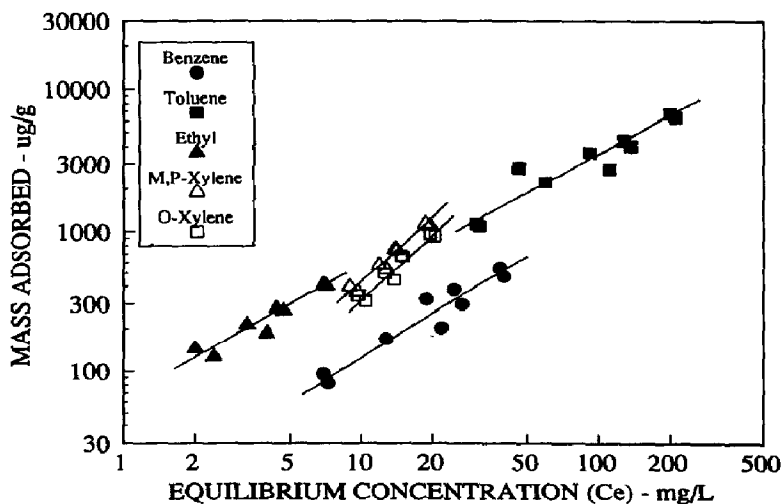


Fig. 2. Sorption of BTEX compounds onto peat moss.

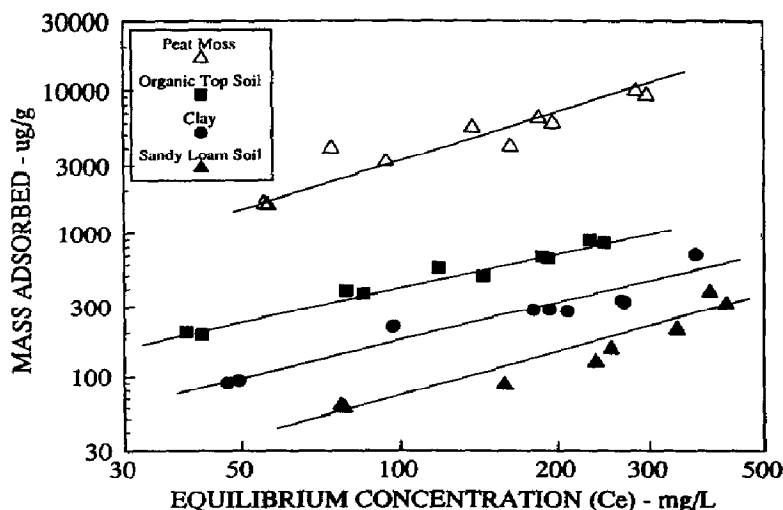


Fig. 3. Sorption of Total BTEX on different media.

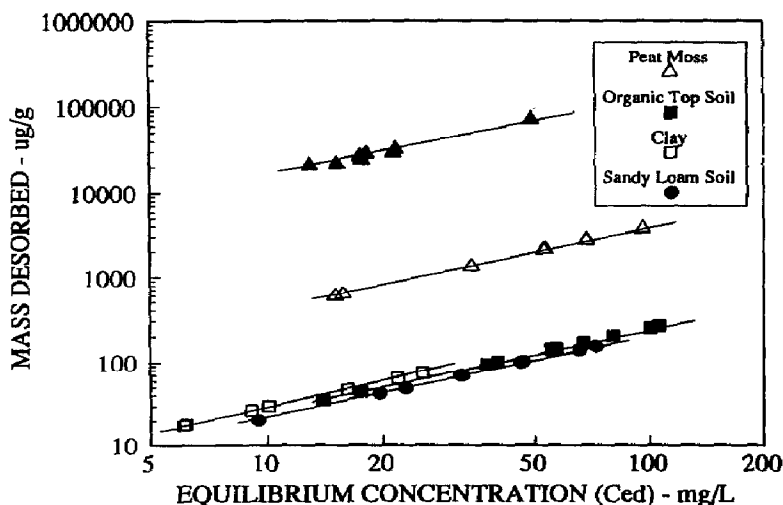


Fig. 4. Desorption of toluene from different media.

#### 4.1. Sorption

The results given in Table 2 show that the sorption of the BTEX compounds from aqueous solutions by clay soil, sandy loam soil, organic top soil, peat moss and GAC are well represented by the Freundlich isotherm. This is shown by the correlation coefficient values ( $r$ ) being in excess of 0.87. Sorption coefficients were not obtained for ethylbenzene, *m*-, *p*- and *o*-xylene on GAC as the GAC was very effective in sorbing all the compounds that were in solution, i.e., the equilibrium concentrations were measured as less than detection. It should be noted that the experiments with GAC were repeated three times, with each successive attempt having a larger sorption volume

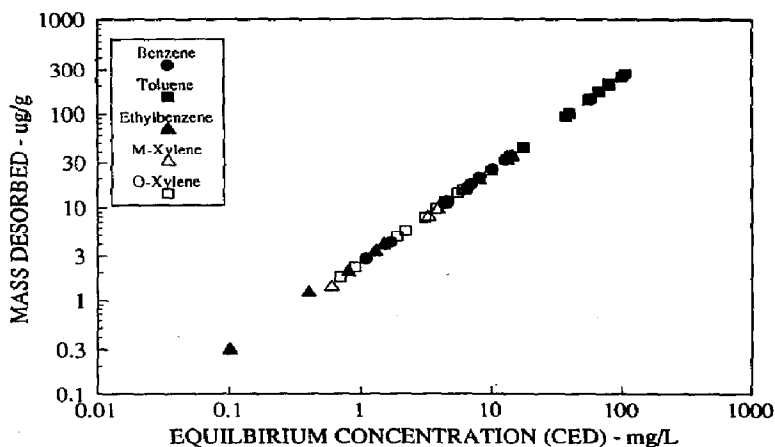


Fig. 5. Desorption of BTEX compounds from organic top soil.

Table 2  
Freundlich sorption coefficients

Media	Coef.	Benzene	Toluene	Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene	Total <sup>a</sup> BTEX
Clay	$1/n_f$	1.55	0.66	1.01	1.22	1.22	0.87
	$K_f$	0.17	8.47	1.64	0.80	0.81	3.08
	$r$	0.89	0.94	0.89	0.95	0.87	0.96
GAC	$1/n_f$	0.51	1.03	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
	$K_f$	19649	115974	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
	$r$	0.98	0.91	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
Organic top soil	$1/n_f$	0.78	0.83	0.34	0.60	0.79	0.81
	$K_f$	2.97	7.58	18.74	30.82	11.49	10.36
	$r$	0.96	0.98	0.89	0.99	0.99	0.99
Peat moss	$1/n_f$	1.0	0.83	0.93	1.49	1.56	0.97
	$K_f$	13.0	74.06	63.99	13.89	9.25	39.44
	$r$	0.96	0.95	0.96	0.98	0.97	0.94
Sandy loam soil	$1/n_f$	0.95	0.94	1.20	1.24	1.17	1.00
	$K_f$	0.58	0.82	0.45	0.44	0.38	0.66
	$r$	0.89	0.91	0.93	0.97	0.93	0.95

<sup>a</sup> Total BTEX; sum of all compounds.

<sup>b</sup> Value not determined.

and a smaller mass of GAC. However, after the third attempt, the  $C_e$  values for ethylbenzene and the xylenes were still less than detection. Since it was not possible to use a larger container for a larger sorption volume, or use a smaller mass of GAC, no further attempts were made.

The Freundlich sorption coefficients,  $K_f$  and  $1/n_f$  given in Table 2 for the various media suggest that the order of sorption preference is GAC, peat moss, organic top



Table 3  
Freundlich desorption coefficients

Media	Coef.	Benzene	Toluene	Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene
Clay	$1/n_{fd}$	1.07	1.01	— <sup>a</sup>	1.01	1.00
	$K_{fd}$	2.53	2.88	— <sup>a</sup>	2.82	2.81
	$r$	0.98	1.00	— <sup>a</sup>	0.99	1.0
GAC	$1/n_{fd}$	0.96	0.97	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
	$K_{fd}$	1981.0	1596.0	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
	$r$	0.91	0.99	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
Organic top soil	$1/n_{fd}$	1.0	1.0	1.0	1.0	1.0
	$K_{fd}$	2.48	2.54	2.6	2.42	2.54
	$r$	1.0	1.0	1.0	1.0	1.0
Peat moss	$1/n_{fd}$	1.0	1.0	1.01	1.0	0.99
	$K_{fd}$	38.74	39.33	40.76	37.80	40.13
	$r$	1.0	1.0	1.0	0.99	1.00
Sandy loam soil	$1/n_{fd}$	1.0	1.0	1.0	1.0	1.0
	$K_{fd}$	2.12	2.18	2.30	2.07	2.18
	$r$	1.0	1.0	0.98	1.0	1.0

<sup>a</sup> Value not determined.

soil, clay soil and sandy loam soil. This ranking is based on the earlier findings of Reynolds [13], where larger the  $K_f$  value and smaller the  $1/n_f$  value, the more effective the medium is in sorption. A clearer representation of sorption affinity for each BTEX compound was obtained by plotting on one graph the sorption isotherms obtained for a particular compound on a specific media. Plots similar to Fig. 1 were obtained, which confirmed the sorption preference suggested by the isotherm data in Table 2.

Comparison of the sorption ranking to the media characteristics listed in Table 1 suggests that sorption is related to the physical/chemical properties of the media. As the sorption affinity increased there was a corresponding increase in organic C content, cation exchange capacity (CEC) and surface area. Of the three soil properties, previous research has shown that sorption of organic chemicals is strongly influenced by the organic C content of the medium [12, 14, 17].

Karichoff et al. [18] showed that hydrophobic chemicals are readily adsorbed by organic C. Literature shows the log octanol–water partition coefficient ( $\log(K_{ow})$ ) for the BTEX compounds to be as follows: benzene, 2.13, toluene, 2.69, ethylbenzene, 3.15, *o*-xylene, 3.15; *m*-xylene, 3.20 [19] and *p*-xylene, 3.10 [20]. These values indicate that the BTEX compounds are moderately hydrophobic, and can be used to explain the sorption difference exhibited by the different compounds as seen in Fig. 2. Fig. 2 is a typical plot of the sorption isotherms for all BTEX compounds on a particular medium, and suggests that the sorption affinity of each compound is ranked as follows: toluene, *m*- and *p*-xylene, *o*-xylene, ethylbenzene and benzene.

The differences in sorption affinity are minor between toluene, *m*-, *p*- and *o*-xylene and ethylbenzene. This is consistent with the similar  $\log K_{ow}$  values (2.69–3.2) for the

group. However, comparison of sorption affinity for this group to benzene shows a difference (see Fig. 2). This sorption difference may be attributed to  $\log(K_{ow})$ , where benzene, having the lowest sorption affinity also has the lowest  $\log K_{ow}$  value (2.13) (i.e., the least hydrophobic).

Of the remaining two sorption factors, CEC and surface area, it is believed that CEC may have the greatest impact on sorption. CEC is a measure of the readily exchangeable cations neutralizing the negative charges in the soil and is usually given in terms of milliequivalents (meq) per 100 g of soil. CEC in arable soils varies from 0.5 to 50 meq/100 g, with the highest values present in organic and clay soils [21]. Felsot and Dahm [22] observed that the higher the CEC value, the greater the amount of sorption. However, studies have shown that all soil properties are interrelated, making it difficult to separate their influences [14]. The sorption affinities exhibited by BTEX in this study are consistent with these findings.

Comparison of the data in Table 2 to existing data is difficult due to the limited information in the literature. Most previous studies evaluated one or more of the BTEX compounds as individual compounds and not as a BTEX solution derived from commercial gasoline [7, 23, 24]. However, the sorption trends of the single solute studies generally agree with the sorption ranking in this study.

The American Petroleum Institute (API) [25] reported that sorption increases with an increase in molecular weight of the chemical and organic matter content of the soil. The API study also reported that the clay soil had a higher sorption tendency than sandy loam soil as the clay soil had a higher organic C content. Stuart et al. [23] studied competitive benzene, toluene and xylene sorption on sandy loam soil. Their sorption results showed the same sorption magnitude as the values listed in Table 2, except for benzene and toluene. The difference for toluene between both studies was two orders of magnitude, with this study having a higher sorption capacity. This difference can be attributed to the lower organic C content in the sandy loam soil used by Stuart et al. [23]. Stuart's soil had an organic C content of 0.62% while the sandy loam soil in this study had an organic C of 1.0%.

Fig. 3 shows the isotherms of Total BTEX on the media tested. Consistent with the individual compounds, the ranking is peat moss, organic top soil, clay soil and sandy loam soil. This order of affinity is consistent with the increase in organic carbon content, except for clay soil and sandy loam soil. One possibility for the switch is the higher CEC and surface area present in the clay soil as compared to the sandy loam soil. Another possibility is the work of Stuart et al. [23], who showed that competitive sorption can have an impact on the BTEX behaviour in soil and that single component sorption data are not useful as a predictive tool. This confirms the findings of Bouchard et al. [7], who showed that each soil behaves differently and that the sorption coefficients should be determined for each soil and chemical compound.

#### 4.2. Desorption

Fig. 4 shows typical desorption isotherms obtained for the mass of toluene desorbed (released) from the media tested. Review of the desorption isotherm coefficients in Table 3 and the soil properties in Table 1 suggest that the mass of BTEX desorbed is

related to the medium's organic carbon content, CEC and surface area. The ability to retain an organic chemical is based on the strength of bond developed between the sorbent and sorbate [26]. To understand or gain a feel for the retention capacity of BTEX by the media tested, the ratio of  $K_f$  to  $K_{fd}$  can be used [12]. The higher the ratio, the greater the retention of the chemical by the medium. However, when this ratio approaches unity or less, the medium has no retention capabilities. In other words, the medium exhibits reversible sorption.

Table 4 contains the  $K_f$  to  $K_{fd}$  ratios for this study. As expected, GAC has the highest  $K_f/K_{fd}$  value because of the high organic C content and large surface area. After GAC it was expected that peat moss would have the next highest retention ratio as has been found for PCE [12] and TCE [15]. However, in this study it was seen that organic top soil typically had the second greatest ratio. Without further investigation, possible reasons for the change are unknown except for experimental error in determining the sorption/desorption isotherms for peat moss or the work of Anderson et al. [24], who showed that the individual BTEX compounds exhibit nonreversible sorption.

An additional desorption figure is given in Fig. 5, where the desorption isotherm for each BTEX compound is plotted for one medium. Interestingly it shows that the mass released can be described by one desorption isotherm. The other four media exhibited similar behaviour as shown by the desorption coefficients ( $K_{fd}$ ) listed in Table 3. It should also be noted that the equilibrium concentrations are related to the sorption coefficient  $K_f$ . That is, higher the initial  $K_f$  value, larger the mass of chemical desorbed.

#### 4.3. Soil–water partition coefficient

The soil–water partition coefficient,  $K_{oc}$ , is useful in determining the mobility of organic chemicals in soil.  $K_{oc}$  is determined by normalizing the linear partition coefficient,  $K_p$ , with the organic C content of the soil [27]. The linear partition coefficient is equal to the Freundlich sorption coefficient,  $K_f$ , when  $1/n_f$  approaches 1.0. For comparison purposes the  $K_{oc}$  values were calculated for those compounds

Table 4  
 $K_f/K_{fd}$  values for media studied

Media	Benzene	Toluene	Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene
Clay	0.1	3.0	— <sup>a</sup>	0.3	0.3
GAC	9.9	72.0	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
Organic top soil	1.2	3.0	7.2	11.9	4.8
Peat moss	0.3	1.9	1.6	0.4	0.2
Sandy loam soil	0.3	7.1	0.3	0.2	0.2

<sup>a</sup> Values not determined.

Table 5  
 $K_{oc}$  values ( $l\text{ kg}^{-1}$ ) for the different compounds

Medium	$K_{oc}^a$	Lit. $K_{oc}$ [29]
Benzene	26–59	12–340
Toluene	65–151	13–710
Ethylbenzene	45–656	95–1095
<i>m,p</i> -Xylene	44–320	110–1200
<i>o</i> -Xylene	38–324	48–540
Total BTEX	66–1232	Unavailable

having  $1/n_f$  values between 0.75 and 1.25. Table 5 contains the calculated  $K_{oc}$  values. Comparison of the calculated values with those reported in the literature (Table 5), show that they were similar. Variation did exist, but this was expected because each soil consists of a complex matrix, i.e., organic C content, surface area, CEC, etc.

Kenaga [27] suggested that the soil–water partition coefficient is a useful indicator for mobility: a  $K_{oc}$  of  $100\text{ l kg}^{-1}$  indicates high chemical mobility in soil, while a  $K_{oc}$  in excess of  $1000\text{ l kg}^{-1}$  indicates chemical immobility in soil. Comparison of the  $K_{oc}$  values determined in this study to Kenaga's limits, suggest that the BTEX compounds have high to moderate mobility in soil and can quickly migrate into the groundwater. Accordingly, the mobility can be ranked from highest to lowest as follows: benzene, *m*-, *p*- and *o*-xylene, ethylbenzene and toluene.

#### 4.4. Application of isotherm data

The sorption and desorption isotherm coefficients evaluated in this study, indicate that materials high in organic C content are effective in adsorbing and retaining dissolved BTEX. This was shown by the GAC, as it had a significantly higher  $K_f/K_{fd}$  value when compared to the other media tested. This information is useful when a gasoline spill occurs and it dissolves in the water present. A material high in organic C content like GAC or peat moss can be applied to the aqueous solution, to sorb and retain the gasoline, especially BTEX.

The sorption and desorption characteristics can also be used to estimate the effectiveness of soil washing as a remediation tool. When contaminated soil is excavated and the free product removed, calculations can be made on how many wash cycles are required to desorb the remaining gasoline fractions [30].

The soil–water partition coefficient values show that once the BTEX compounds go into solution, especially benzene and toluene, they have the potential to quickly migrate into the groundwater following a spill. Thus, quick response is required after a spill to remove the free product, to minimize the mass of gasoline that will dissolve into the water present. If not, a constant source of gasoline would be present, which would continually dissolve into infiltrating water and migrate into the groundwater [3]. The mobility results also suggest that when investigating the extent of subsurface contamination through groundwater sampling, it is important to analyze for the BTEX compounds. It is insufficient to test just for total petroleum hydrocarbons.

## 5. Conclusions

- (1) The sorption/desorption processes of BTEX in different media were well represented by the Freundlich isotherm, for the range of aqueous concentrations studied.
- (2) The soil–water partition coefficient,  $K_{oc}$ , for all the BTEX compounds ranged between 26 and  $656 \text{ l kg}^{-1}$ , indicating that the BTEX compounds have high to moderate mobility in soil. According to the  $K_{oc}$  values measured, benzene has the greatest migration potential, followed by toluene, *m*-, *p*- and *o*-xylene and ethylbenzene.
- (3) The organic C content of the medium appears to be the most significant controlling factor in sorption and desorption. Both the sorption and retention potentials of BTEX increased with an increase in organic carbon content. The order of sorption preference was GAC, peat moss, organic top soil, clay soil and sandy loam soil.
- (4) The order of preferential sorption on component basis when comparing  $K_f$  values for different media is toluene, *m*-, *p*- and *o*-xylene, ethylbenzene and benzene. This trend follows the  $\log K_{ow}$  predications.

## Acknowledgements

This research was made possible through an Industrial Research Fellowship (IRF) funded by the Natural Sciences and Engineering Research Council of Canada and by the equipment and support provided by Clayton Environmental Consultants, Ltd. of Windsor, Ont., where the IRF was completed. Special thanks go to Mrs. Balbir of Clayton Environmental Consultants, Ltd., for assistance in sample preparation and analysis.

## References

- [1] USEPA, Rules and Regulations on Underground Storage Tanks, December 1988.
- [2] M.Y. Corapcioglu and A.L. Baehr, A compositional multiphase model for groundwater contamination by petroleum products 1. Theoretical considerations, *Water Res. Resources*, 23 (1987) 191–200.
- [3] R.G. Zytner, N. Biswas and J.K. Bewtra, Retention capacity of dry soils for NAPLs, *Environ. Technol.* 14 (1993) 1073–1080.
- [4] D. Mackay, in: E.J. Calabrese and P.T. Kosteci, (Eds) *Soils Contaminated by Petroleum: Environmental and Public Health Effects*, 1988, 458 p.
- [5] R.E. Hinchee and H.J. Reisinger, A practical application of multiphase transport theory to groundwater contamination problems, *Ground Water Monitoring Rev.*, 84 (1987) 84–92.
- [6] D.Y. Lee and A.C. Chang, Evaluating transport of organic chemicals in soil, In: 46th Annual Purdue Waste Conference, 1991.
- [7] D.C. Bouchard, S.C. Mravik and G.B. Smith, Benzene and naphthalene solution on soil contaminated with high molecular weight residual hydrocarbons from unleaded gasoline, *Chemosphere*, 21 (1990) 975–989.
- [8] O.C. Braids, In: *Subsurface Seminar on the Fundamentals of Groundwater Quality Protection*, Geraghty and Miller Inc. and Am. Ecology Services Inc., Oct. 5–6, 1981.

- [9] L.G. Morrill, B.C. Mahlum and S.H. Mohiuddin, *Organic Compounds in Soils: Sorption, Degradation and Persistence*, Ann Arbor Science, Ann Arbor, MI, 1982, 326 p.
- [10] R.G. La Poe, *Sorption and Desorption of Volatile Chlorinated Aliphatic Compounds by Soils and Soil Components*, Ph.D. Dissertation, Cornell University, 1985, 306 p.
- [11] D.A. Dzombak and R.G. Luthy, Estimating adsorption of polycyclic aromatic hydrocarbons on soils, *Soil Sci.*, 137 (1984) 292–308.
- [12] R.G. Zytner, N. Biswas and J.K. Bewtra, Adsorption and desorption of perchloroethylene in soils, peat moss and granular activated carbon, *Can. J. Civil Eng.*, 16 (1989) 798–806.
- [13] T.D. Reynolds, *Unit Operations and Processes in Environmental Engineering*, Brooks/Cole Eng. Div., 1982, 576 p.
- [14] T.J. Walker, *Fate and Disposition of Trichloroethylene in Surface Soils*, Ph.D. Dissertation, Purdue University, 1984, 350 p.
- [15] R.G. Zytner, Adsorption–desorption of trichloroethylene in granular media, *Water, Air and Soil Pollut.*, 65 (1992) 245–255.
- [16] C.A. Black, *Methods of Soil Analysis: Part I*, Am. Society of Agronomy, 1965, 770 p.
- [17] W.A. Jury, W.F. Spencer and W.J. Farmer, Behaviour assessment model for trace organics in soil: IV review of experimental evidence, *JEQ*, 13 (1984) 580–586.
- [18] S. Karichoff, D.S. Brown and T.A. Scott, Sorption of hydrophobic pollutants on natural sediments, *Water Res.*, 13 (1979) 241–248.
- [19] C. Hansch, J.E. Quinlan and G.L. Lawrence, The linear free-energy relationship between partition coefficients and the aqueous solubility of organic liquids, *J. Am. Chem. Soc.*, 4 (1968) 345–350.
- [20] S. Banerjee and P.H. Howard, Improved estimation of solubility and partitioning through correction of UNIFAC-derived activity coefficients, *E.S. and T.*, 22 (1988) 839–841.
- [21] P.V. Roberts, M. Reinhard and A.J. Valocchi, Movement of organic contaminants in groundwater: Implications for water supply, *J. AWWA*, 74 (1982) 408–413.
- [22] A. Felsot and P.A. Dahm, Sorption of organophosphorous and sarbmate insecticides by soil, *J. Agric. Food Chem.*, 27 (1979) 394.
- [23] B.J. Stuart, G.F. Bowlen and D.S. Kosson, Competitive sorption of benzene, toluene, and xylenes onto soil, *Environ. Prog.*, 10 (1991) 104–109.
- [24] T.A. Anderson, J.J. Beauchamp and B.J. Walton, Organic chemicals on the environment, *JEQ*, 20 (1991) 420–424.
- [25] American Petroleum Institute, *Literature Survey, Hydrocarbon Solubilities and Attenuation Mechanisms*, API Publication No. 4414, 1985.
- [26] W.R. Roy and R.A. Griffin, Mobility of organic solvents in water saturated soil materials, *Environ. Geol. Water Sci.*, 7 (1985) 241–247.
- [27] E.E. Kenaga, Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals, *Ecotoxicol. Environ. Saf.*, 4 (1980) 26–38.
- [28] C.C. Broughton, Principles of liquid-phase adsorption, in: W.W. Eckenfelder, Jr. (Ed.), *Application of Adsorption to Wastewater Treatment*, Enviro Press Inc., Nashville (1981) 29–66.
- [29] D. Mackay, W.Y. Shiu and K.C. Mai, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*, Lewis, 1992, 697 p.
- [30] N. Biswas, R.G. Zytner and J.K. Bewtra, Model for predicting PCE desorption from contaminated soils, *Water Environ. Res.*, 64 (1992) 170–178.