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VAPOUR PHASE INVESTIGATION OF THE IMPACT OF SOIL ORGANIC MATTER ON THE SORPTION AND PHASE DISTRIBUTION OF 20% ETHANOL-BLENDED GASOLINE IN THE VADOSE ZONE

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ABSTRACT
Laboratory batch microcosm experiments were conducted to quantify the impact of soil organic matter (SOM) on the sorption and phase distribution of 20% ethanol-blended gasoline (E20) in the vadose zone. SOM was found to increase the sorption of all E20 gasoline compounds, thereby altering their mass distribution between the vadose zone phases. This impact, quantified by the sorption coefficient (K_d) of E20 gasoline compounds, increased with decreasing hydrophobicity, hence affected the aromatics to a greater extent of 7 times than the cycloalkanes (4 times) and the alkanes (2 times). However, when compared with unblended gasoline, the ethanol in E20 generally reduced the sorptive capability of SOM for gasoline compounds by a maximum of 76% for the cycloalkanes, 73% for the aromatics and 60% for the alkanes.Therefore, the full sorptive capability of SOM for gasoline compounds is unlikely to be realized for E20 gasoline compounds.

KEYWORDS: Soil organic matter; Ethanol-blended gasoline; Sorption; Phase distribution; Vadose zone

INTRODUCTION
Ethanol is largely used in the transport sector as a fuel oxygenate, and its usage is likely to increase as new legislations requiring more biofuels come into effect (Powers et al., 2001). Ethanol is been used as a fuel oxygenate because it addresses air quality objectives without seriously deteriorating groundwater quality compared to methyl tertiary butyl ether (Beller et al., 2001; Dakhel et al., 2003). Studies on the impact of ethanol on gasoline compounds, especially with 10 and 20% ethanol blends, have shown that ethanol affects the infiltration, distribution, sorption and biodegradation of gasoline compounds (Powers and McDowell, 2001; Adam et al., 2002; McDowell and Powers, 2003; Mackay et al., 2006; Österreicher-Cunha et al., 2007; Lawrence et al., 2009; Österreicher-Cunha et al., 2009). As a hydrophilic compound, ethanol partitions almost instantly and totally into the aqueous phase, thereby increasing the solubility of gasoline in water, as well as reducing surface and interfacial tensions. Consequently, these processes alter the overall interactions between gasoline, soil water and soil particles. Although mounting evidence have shown that hydrophobic organic compounds, like gasoline compounds, have high octanol-water partition coefficient and will tend to be retained by soil organic matter (SOM) (Marchetti et al., 1999; Weber et al., 2001; Chiou, 2002; Celis et al., 2006; Chen et al., 2007; Joo et al., 2008; Liu et al., 2008; Wang et al., 2008a; Guo et al., 2010), it is still unclear how SOM will impact the sorption and phase distribution of a complex mixture like 20% ethanol-blended gasoline in the vadose zone.

Sorption by soils is a fundamental process controlling the fate of less polar and non-polar organic contaminants in the subsurface environment (Huang et al., 2003). Soils in the natural environment consist of an inorganic component (soil minerals) and an organic component (SOM). These components affect the sorption of organic contaminants differently (Joo et al., 2008; Liu et al., 2008). Generally, the sorption of non-polar organic contaminants by natural soil often correlates well with the content of SOM (Huang and Weber, 1997; Chiou, 2002; Celis et al., 2006; Liu et al., 2008; Li et al., 2009; Shi et al., 2010). According to Shi et al. (2010), the removal of SOM from a soil decreased sorption by approximately 86% for non-polar 1,3,5-trichlorobenzene (TCB), but only by 34-54% for highly polar 1,3,5-trinitrobenzene (TNB). Viewed from the physiology of SOM, it is rational to believe that the alkyl chains and aromatic rings contained in the SOM may invoke various degree of sorption on different organic contaminants.

Although the reviewed sorption studies may have shed light on the contribution of SOM to the overall sorption of hydrophobic organic compounds (HOCs) by soils, the findings may not be applicable to gasoline and gasoline blends due to the single HOC generally used in those studies. Such single HOC lacks the intermolecular interactions that exists amongst gasoline compounds (Lawrence et al., 2009), and has been found to result in different shapes of concentration profile and overestimation of vapour concentration (Karapanagioti et al., 2004). Gasoline is a complex mixture of volatile and semi-volatile hydrocarbons, predominantly composed of paraffins, olefins, naphthenes and aromatics (Speight, 2002). Thus, for a reasonable conclusion to be made about the behaviour of gasoline, it must be composed of the different hydrocarbon types (Speight, 2002). More so, the addition of oxygenate such as ethanol, which is completely miscible in water, to gasoline will further impact the characteristics of the gasoline as well as the intermolecular interactions amongst the gasoline compounds.

A good understanding of the phase distribution of ethanol-blended gasoline released into the vadose zone would provide a significant insight on groundwater contamination potential and in determining which tools are viable options regarding site characterization and remediation. Once introduced into the vadose zone, ethanol-blended gasoline is expected to gradually partition into the soil solids, soil water, soil air and nonaqueous phase liquid. Such distribution between phases will depend on the physicochemical properties of the ethanol-blended gasoline and the characteristics of the geologic media (Yu, 1995), and can be represented by empirical relationships referred to as partition coefficients (Huling and Weaver, 1991). One of the characteristics of the geologic media that could affect phase distribution is SOM. To the best of our knowledge, no work has addressed the impact of SOM on the phase distribution of either single or mixed gasoline compounds in the vadose zone.

In this study, a number of laboratory batch experiments were performed to investigate the impact of SOM on the sorption and phase distribution of E20 gasoline compounds in the vadose zone. The porous media used consisted of uncontaminated sand mixed with 0 - 5% SOM. Contamination involved a vapour phase injection of synthetic gasoline blended with 0 and 20% ethanol, referred to as E0 and E20 respectively, into the headspace of microcosms and allowing sorption to and phase distribution within the porous media. The data obtained indicated that the ethanol in E20 generally reduced the sorption capability of SOM for E20 gasoline compounds.

Experimental
Fuel composition
The fuel used in this study was a synthetic gasoline blended with 20% ethanol, referred to as E20. The synthetic gasoline, referred to as E0, was prepared from six typical fuel compounds (Table 1). The six fuel compounds were all of high purity (>99.5%) and were purchased from Sigma-Aldrich chemical company, UK. These fuel compounds are typical constituents of petroleum fuel (Pasteris et al., 2002; Speight, 2002; Dakhel et al., 2003; Höhener et al., 2003; Christophersen et al., 2005) and represent the three major hydrocarbon groups in gasoline, namely alkanes or paraffins, cycloalkanes or naphthenes and aromatics. The ethanol (>99.5%) was purchased from Sigma-Aldrich chemical company, UK.

Table 1 Ethanol-blended gasoline composition

Gasoline compounds	Formula	Weight in mixture, %	Volume, ml	Vapour pressure at 20°C, Pa[a]	Density at 25°C, g/ml[a]	Henry's law constant, -[c]
Pentane	C_5H_{12}	9.6	15.3	57900	0.626	51.4
Octane	C_8H_{18}	25.8	36.7	1470	0.703	211
MCP	C_6H_{12}	19.5	26.0	17732[b]	0.75	14.7
MCH	C_7H_{14}	32.3	41.9	4930	0.77	17.5
Benzene	C_6H_6	3.2	3.7	9950	0.874	2.26E-01
Toluene	C_7H_8	3.2	11.1	2910	0.865	2.65E-01
Gasoline oxygenate						
Ethanol	C_2H_5OH	-	0 - 20%	5950	0.789	2.94E-04

MCP – Methylcyclopentane; MCH – Methylcyclohexane; [a] values obtained from Sigma Aldrich Material Safety Data Sheet; [b] value obtained from Pasteris et al. (2002) Supporting Information; [c] obtained from Yaws (2008)

Description of the porous media
A mixture of sand and peat the source of SOM was used as the porous media. The sand was obtained from Nottingham (UK) and contained approximately 0% SOM. The sand has a particle size distribution of coarse (20%), medium (53%), and fine (27%). According to the BS 1377-1 (1990) soil classification, the sand could be

classified as a fine-grained sandy soil. The Peat was also obtained from Nottingham (UK) and contained approximately 96% SOM in its dry state as determined by the "Loss on Ignition" (LOI) method (Sutherland, 1998). The peat has a particle size distribution of 2 - 0.71 mm (26%) and <0.71 mm (74%). The sand and the peat were mixed to obtain porous media consisting of 0, 1, 3 and 5% SOM fraction by weight, referred to as 0%f_{om}, 1%f_{om}, 3%f_{om} and 5%f_{om}, respectively. The SOM percentages were chosen because they are within the reported range of SOM fraction for typical soils (Sparks, 2003). Table 2 shows the changing properties of the porous media with changing SOM fraction.

Table 2 Properties of porous media

Porous media	Porous media properties					
	Porosity, -	Surface area, m^2/g	Particle density, g/ml	Dry bulk density, g/ml	Total pore volume, cm^3/g	Volumetric water content at field capacity, %
5%f_{om}	0.54	1.91	2.1	0.97	6.20E-3	16
3%f_{om}	0.53	1.47	2.3	1.07	5.33E-3	14
1%f_{om}	0.52	1.04	2.4	1.17	4.47E-3	12
0%f_{om}	0.51	0.82	2.5	1.22	4.04E-3	11

Batch microcosm experiments
The batch microcosm experiments were performed with 60 ml glass vials (H*Ø = 140*27.5 mm) capped with 24 mm screw caps with 3.2 mm seal. The porous media used were sterilised by heating in an oven set at 160°C for approximately 16 h and then wetted with hot water of approximately 50°C to a volumetric water content of 11%. The wetted porous media (65 g) were packed into the glass vials and compacted alike by tapping vials on the worktable until stable heights were obtained. Heights in vials were 80 mm for 0%f_{om}, 84 mm for 1%f_{om}, 92 mm for 3%f_{om} and 100 mm for 5%f_{om}, leaving headspaces of 60, 56, 48, and 40 mm, respectively, for vapour phase sampling. The porosities of the porous media were 0.45, 0.46, 0.48 and 0.48 for 0%f_{om}, 1%f_{om}, 3%f_{om} and 5%f_{om}, respectively. The 0%f_{om} experiment was the control experiment. All experiments were performed in triplicates. Before contamination with either E0 or E20 vapours, the microcosms were stored in a Thermostatic bath/circulator (L*W*H = 52*32*21.5 cm) set at 25°C for 24 h. Then 10 ml of air were extracted from the microcosms and 10 ml headspace of a glass vial containing E0 or E20 at 25°C were injected using a stainless steel hypodermic needle (L*Ø = 50*0.63 mm) fitted to a 10 ml gas-tight syringe. The decrease in concentrations of the gasoline compounds in the microcosm headspaces were monitored for 15 days. The microcosms were maintained at 25°C in the Thermostatic bath/circulator throughout the experimental period. The changes in sorption and phase distribution of E20 gasoline compounds due to SOM was obtained by comparing data from the SOM-containing porous media (1%f_{om}, 3%f_{om} and 5%f_{om}) with the SOM-free porous medium (0%f_{om}). The impact of ethanol on the sorption capability of SOM was obtained by comparing the increase in sorption between 0%f_{om} and 5%f_{om} porous media for E0 and E20 gasoline compounds.

Vapour phase analysis
The concentrations of gasoline compounds in the headspace of the microcosms were analysed by injecting 40µl of vapour samples into a HR-5300 mega series Gas Chromatography (Carlo Erba, UK) equipped with a ChrompackPoraploto column (27.5m * 0.32mm * 10µm) and Flame Ionization Detector (FID). The injector was heated to 200°C, and the column temperature held at 200°C for 16 min. The carrier gas was helium at a flow rate of 4 ml/min.

Estimation of mass of gasoline compounds in soil air, water and solid
The mass of gasoline compounds in the soil air (M_a), water (M_w) and solids (M_s) were estimated from the total mass of gasoline compound injected into the microcosm (M_t), mass of gasoline compound lost via sampling (M_L), concentration of gasoline compound measured at the headspace of microcosm (C_a), volumes of air (V_a) and water (V_w) in the microcosm and dimensionless Henry's law constant (H) as follows:

$$M_a = C_a * V_a \qquad\qquad\qquad (1)$$

$$M_w = \frac{C_a}{H} * V_w \qquad\qquad\qquad (2)$$

$$M_s = M_t - M_a - M_w - M_L \qquad (3)$$

Estimation of sorption coefficient and retardation factor of gasoline compounds
The sorption coefficient (K_d) was estimated as the ratio of the concentration of gasoline compound in the soil solids (C_s) to the concentration in the soil water (C_w):

$$K_d = \frac{C_s}{C_w} \qquad (4)$$

The retardation factor (R) or the degree of retardation of the migration of gasoline compounds as a result of sorption was estimated from (K_d) and the bulk density (ρ_b) and porosity (n) of the vadose zone as (Site, 2001):

$$R = 1 + \left(\frac{\rho_b}{n}\right) K_d \qquad (5)$$

RESULTS AND DISCUSSION
Impact of SOM on the sorption and phase distribution of E20 gasoline compounds
E20 gasoline compounds sorption by porous media
The headspace concentrations of E20 gasoline compounds in microcosms with time as a function of SOM fraction of porous media is presented in Figure 1. Octane was not included in Figure 1 due to poor detection by the GC-FID used for the headspace vapour sample analysis. All E20 gasoline compounds persisted at detectable concentrations at the headspace throughout the 15 days duration of the experiment except for ethanol that decreased continuously with time and completely disappeared from the headspace on Day 13. The decrease in the headspace concentration of all E20 gasoline compounds followed the first order rate law and indicates sorption to the porous media since biodegradation is not expected to occur due to the cautious sterilization of the porous media. Generally, two phases of sorption were observed. A rapid sorption during the first three days after contamination followed by a slower sorption from Day 6 to Day 13 for the alcohol, to Day 15 for the alkane and to when equilibrium were reached for the cycloalkanes and aromatics. The two phases of sorption observed in the present study is a common observation in sorption studies (Allen-King et al., 1994; Gaston and Locke, 1995; Höhener et al., 2003). The slower sorption has been interpreted as intraparticle diffusion-limited approach of equilibrium between soil phases (Site, 2001; Höhener et al., 2003).

The increase in the SOM fraction of porous media resulted in rapid and greater sorption of all E20 gasoline compounds except for ethanol that had similar sorption for all SOM fractions. Ethanol has low octanol-water partition coefficient (K_{ow}) of 0.5 compared to the gasoline compounds that have K_{ow} ranging from 134.9 to 7585.8 (Yaws, 2008), hence partitioned readily to soil water and was not affected by SOM. Since SOM has high specific surface area and porosity that can promote sorption (Allen-King et al., 2002), the increasing sorption of all gasoline compounds by porous media with increasing SOM fraction could be due to the increase in the surface area and porosity of the porous media as listed in Table 2. Although the impact of SOM on the sorption of gasoline compounds varied with time and compounds, it was generally more on Day 1 and affected the aromatics to a greater extent (76 – 89%) than the cycloalkanes (46 – 59%) and the alkane (29%). However, from Day 1 to Day 15, a huge reduction in SOM impact was observed for the aromatics (10 – 19%) whereas negligible reductions were observed for the cycloalkanes (0 – 2%) and the alkane (≈0%). This implies that bonding forces between the aromatics and the SOM are weaker than those between either the cycloalkanes or alkanes and the SOM. Thus, any aromatics retained by SOM are more likely to undergo faster leaching with time than would any cycloalkanes or alkanes. Overall, the data indicate that SOM promoted the sorption of all gasoline compounds but had no significant impact on the sorption of ethanol. Among the gasoline compounds, the cycloalkanes and the alkanes are more likely to be tightly retained by SOM than would the aromatics by SOM.
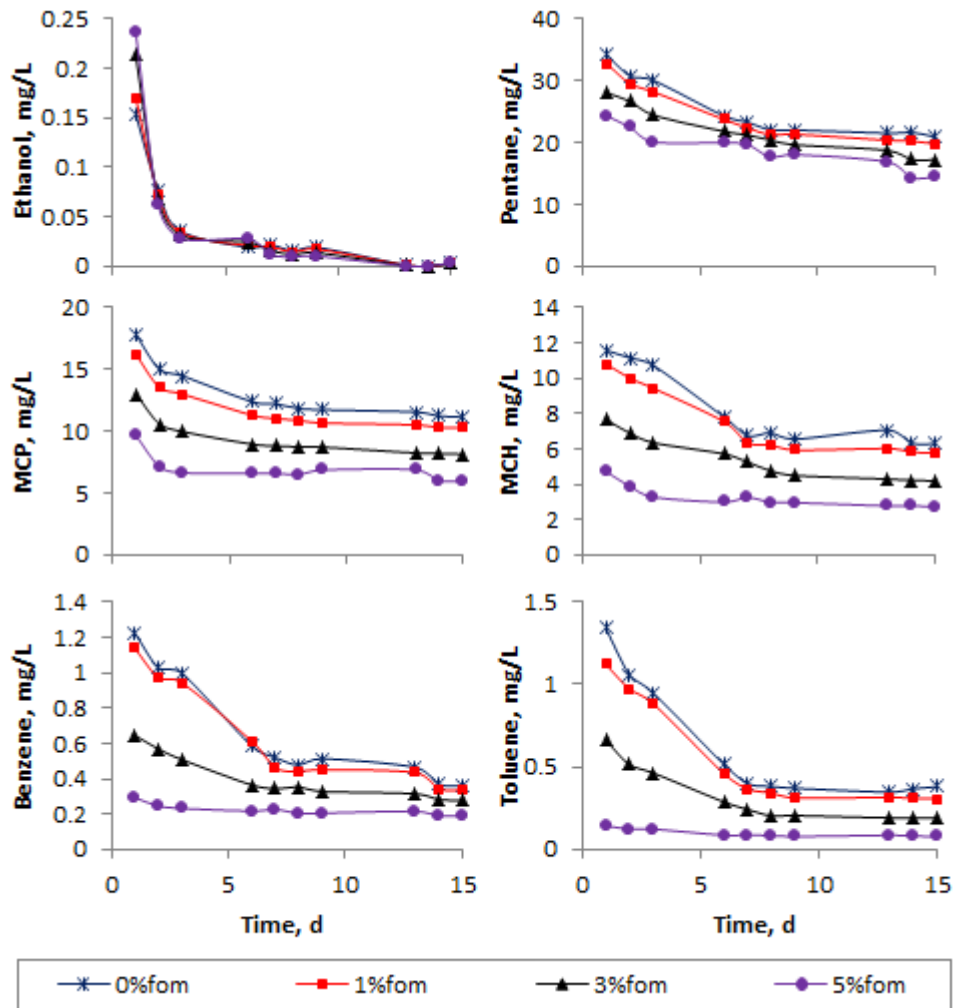
Figure 1 Headspace concentrations of E20 gasoline compounds with time as a function of SOM fraction of porous media

E20 gasoline compounds soil-water interaction in the vadose zone

The distribution of a contaminant between the soil solids and water, commonly referred to as sorption, results from its relative affinity for each phase or its sorption coefficient (K_d) (Weber et al., 1991). The K_d of each gasoline compound was calculated on a daily basis using Equation [4] and the average K_d used as the representative K_d. The changes in the average K_d values for all gasoline compounds with changing SOM fraction (f_{om}) of porous media are shown in Figure 2. The K_d of all E20 gasoline compounds increased with increasing f_{om}, suggesting an increase in the adsorption of gasoline compounds to the soil solids or a reduction in the concentrations of gasoline compounds in the soil water. This impact was greatest for the aromatics, with K_d increased by a maximum of 7 times, compared with the cycloalkanes (4 times) and the alkanes (2 times), for 0 to 5% increase in f_{om}. As reported by Site (2001), the K_d values for benzene, toluene and xylenes were increased with increasing surface area (SA) of adsorbents. The K_d value of pyrene was also found to increase with increasing SA of adsorbents (Wang et al., 2008b). Therefore, one explanation for the observed increase in K_d with increasing f_{om} of porous media could be due to the increase in the surface area of the porous media (see Table 2). Another explanation could be due to the reduction in available soil water in the porous media with increasing f_{om}. Since the porous media were wetted to the same volumetric water content, and SOM has a high water absorption capacity (Page, 1982), it is likely that lesser water were available for the gasoline compounds to dissolve in with increasing f_{om} of porous media. Shoemaker et al. (1990) have reported that sorption under dry or low moisture conditions would be substantially greater than sorption under saturated conditions. As listed in Table 2, the volumetric water contents of the porous media at field capacity were 11% and 16% for 0%f_{om} and 5%f_{om}, respectively. Since the porous media were wetted to a volumetric water content of 11%, it therefore implies that the 0%f_{om} was at saturated condition hence the lower K_d obtained from it as compared to those from

5

5% f_{om}. Despite the difference in contaminant mixtures, the K_d values obtained for 0% f_{om} in the present study, 0.4 l/kg for benzene and 0.5 l/kg for toluene, were qualitatively and quantitatively comparable to those reported for sand in the literature. For example Joo et al. (2008) reported K_d values of 0.2 l/kg for benzene and 0.3 l/kg for toluene, and Christophersen et al. (2005) reported K_d values of 0.02 – 0.3 l/kg for benzene and 0.04 – 0.5 l/kg for toluene. Similar observations on the direct relationship between K_d and SOM have been reported for a wide range of organic contaminants and sorbents (Celis et al., 2006; Chen et al., 2007; Shi et al., 2010). Therefore, the data suggest that SOM increased the adsorption of gasoline compounds to the soil solids but reduced their dissolution in the soil water. This impact increased with decreasing hydrophobicity of gasoline compounds.
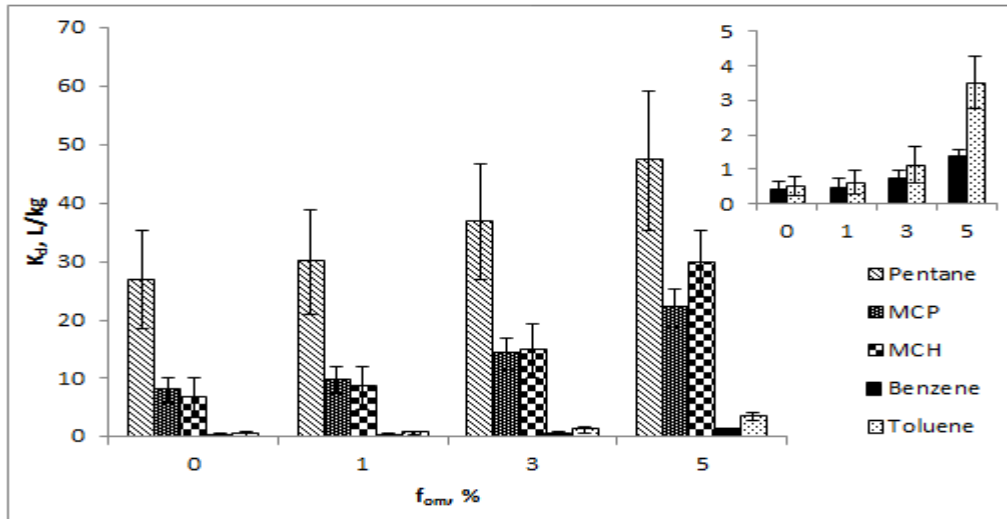

Figure 2 Sorption coefficient (K_d) of E20 gasoline compounds as a function of SOM fraction (f_{om}) of porous media

Retardation of the migration of E20 gasoline compounds in the vadose zone

Figure 3 shows the changes in the retardation factor (R) values for E20 gasoline compounds with varying SOM fraction (f_{om}) of porous media. R was estimated from Equation [5] and represents the degree of retardation of the migration of the gasoline compounds due to sorption on soil solids. The figure shows that SOM promoted the R of all E20 gasoline compounds, implying a reduction in the migration of E20 gasoline compounds in the vadose zone. This effect increased with decreasing solubility of gasoline compounds hence was in the order: cycloalkanes (0 – 46.8)>alkane (0 – 25.7)>aromatics (0 – 6.5). The R of gasoline compounds with similar solubility, such as pentane and MCP (0.04 g/l) (Yaws, 2008), were similarly impacted. Generally, SOM promoted the R of E20 gasoline compounds in a similar way as it promoted their K_d values, probably due to the dependence of R on K_d as can be seen in Equation [5]. By substituting Joo et al. (2008) K_d values of 0.2 l/kg for benzene and 0.3 l/kg for toluene into Equation [5] for 0% f_{om} porous medium which is similar in SOM fraction to the aquifer sand used by the researchers, R values of 1.61 for benzene and 1.91 for toluene were obtained. These values, though obtained from a contaminant mixture comprising only aromatics, were found qualitatively and quantitatively similar to the R values of 2.29 for benzene and 2.53 for toluene obtained in the present study which used a contaminant mixture consisting of alkanes, cycloalkanes, aromatics and alcohol. Also, our benzene and toluene R values in 0% f_{om} were in good agreement with the R values of 1.24 for benzene and 1.93 for toluene in sand reported by Höhener et al. (2006). However, our R values were found to be only qualitatively similar to those reported by Myrand et al. (1992), 117.2 for benzene and 734 for toluene, which used clay as the porous medium. The vast difference between the R values from different soils, as compared to the R values from different contaminant mixture, suggest that R of gasoline compounds could be highly site specific and that the types and properties of soils are likely to have a greater influence on the R of gasoline compounds than the composition of contaminants.
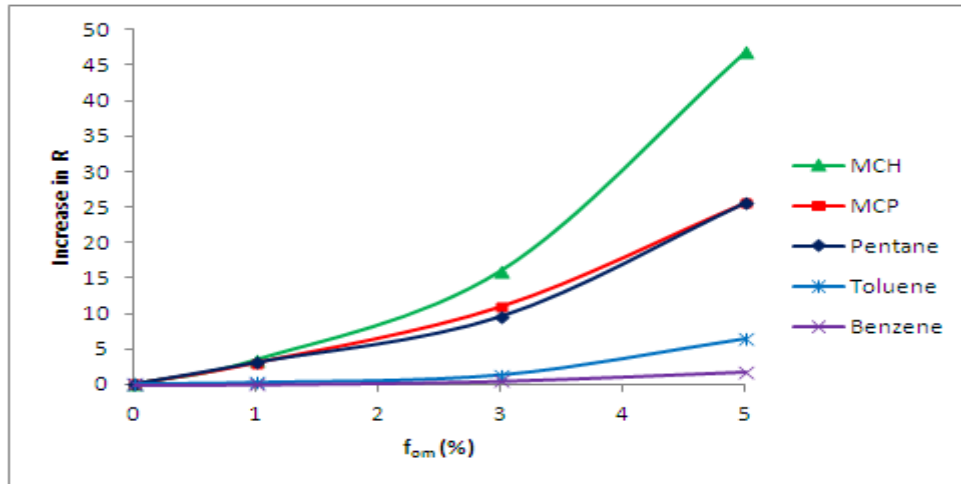
Figure 3 Retardation factors (R) of E20 gasoline compounds as a function of SOM fraction of porous media

Distribution of E20 gasoline compounds amongst vadose zone phases

The mass distribution of E20 representative gasoline compounds to the soil air, solids and water as a function of SOM fraction (f_{om}) of porous media is presented in Table 3. The masses were estimated by fitting measured data into Equations [1] to [3]. The mass distribution of gasoline compounds to the vadose zone phases changed with time. While the mass of gasoline compounds on the soil solids increased with time, the mass in the soil air and water decreased with time, for all porous media tested. The increase in f_{om} of porous media increased mass distribution to the soil solids and caused a rapid uptake of all gasoline compounds 4 h after contamination on Day 1. This effect was greater on the aromatics representative (with increase in adsorption to soil solids ranging from 6 to 55% for 1 to 5% increase in f_{om} of porous media) than on the cycloalkanes representative (8 to 35%) and alkanes representative (5 to 26%). Water solubility seemed to be an important property determining the impact of SOM on the adsorption of gasoline compounds to the soil solids. The mass distribution in 0%f_{om} porous medium on Day 1 shows that the aromatics had higher mass in the soil water compared to the cycloalkanes and the alkanes. It is then likely that the addition of SOM to porous media affected the available water in the experimental system more than it affected the available air due to the high water absorption capability of SOM (Page, 1982). Consequently, most of the dissolved masses were adsorbed to the soil solids. The adsorption of some of the masses in the soil air may have been prompted by the increase in the surface area of porous media with increasing f_{om} as shown in Table 2 (Site, 2001; Wang et al., 2008b). In contrast to impact on Day 1, SOM impacted a general lower mass distribution to the soil solids for all gasoline compounds on Day 15, suggesting that the sorption influence of SOM is likely to be predominant on Day 1 of spills. More so, the mass distribution to the soil solids of the cycloalkanes was impacted to a greater extent (4 – 23%) than those of the alkanes (3 – 17%) and aromatics (2 – 11%), suggesting that the degree of impact of SOM on the mass distribution of gasoline compounds could vary with time. Therefore, the data show that SOM could enhance the mass distribution of E20 gasoline compounds to the soil solids in the vadose zone. The degree of the impact is likely to vary with time among the gasoline compounds. The less hydrophobic compounds such as the aromatics are more likely to be impacted to a greater extent before equilibrium, while the more hydrophobic compounds such as the cycloalkanes could be impacted to a larger extent at equilibrium. Hence, this result offers an understanding into the mass distribution of E20 gasoline compounds to the vadose zone phases following a spill on soils with varying SOM contents.

Table 3 Mass distribution of E20 representative gasoline compounds in the vadose zone as a function of SOM fraction of porous media

Day	Pentane			MCP			Benzene		
	Air	Solid	Water	Air	Solid	Water	Air	Solid	Water
	%	%	%	%	%	%	%	%	%
$0\%f_{om}$									
1	66.2	33.6	0.3	64.6	34.5	0.8	38.0	29.8	32.2
8	42.8	56.7	0.2	43.0	56.0	0.6	14.9	72.4	12.6
15	40.6	58.6	0.2	40.5	58.3	0.5	11.2	79.1	9.5
$1\%f_{om}$									
1	61.5	38.3	0.2	56.9	42.3	0.8	34.2	35.9	29.9
8	39.9	59.5	0.2	38.3	60.8	0.5	13.3	74.8	11.7
15	37.2	62.0	0.1	36.2	62.7	0.5	10.1	80.8	8.8
$3\%f_{om}$									
1	50.4	49.4	0.2	43.8	55.6	0.6	18.6	64.5	17.0
8	36.7	62.8	0.2	29.5	69.8	0.4	10.2	80.4	9.3
15	31.0	68.3	0.1	27.5	71.8	0.4	8.0	84.4	7.3
$5\%f_{om}$									
1	40.4	59.5	0.2	30.0	69.6	0.5	7.8	84.5	7.7
8	29.3	70.3	0.1	20.3	79.2	0.3	5.4	89.1	5.4
15	24.0	75.4	0.1	18.6	80.8	0.3	5.1	89.8	5.1

Impact of ethanol on SOM sorptive capability for gasoline compounds

Figure 4 shows the impact of ethanol on the SOM-induced increase in K_d of gasoline compounds. The SOM-induced increase in K_d was obtained by comparing the K_d of gasoline compounds in $0\%f_{om}$ and $5\%f_{om}$ porous media for unblended gasoline (E0) and E20. The presence of ethanol reduced the SOM-induced increase in K_d of E20 gasoline compounds, implying a reduction in the SOM sorptive capability for gasoline compounds. This impact of ethanol on the sorptive capability of SOM could be due to changes in conformation of the SOM matrix induced by changes in gasoline polarity resulting from the presence of ethanol (Brusseau et al., 1991; Ju and Young, 2005). Previous studies have shown that low polarity of SOM could lead to high sorption of contaminant and vice versa (Chefetz et al., 2000; Guo et al., 2010). Therefore, it is likely that the presence of ethanol increased the polarity of the SOM which resulted in the reduction of K_d. The change in gasoline polarity with 20% ethanol addition was expected since ethanol effect on gasoline has been reported to be significant for concentrations higher than 10% (Corseuil et al., 2004). Among the gasoline compounds, the cycloalkanes were impacted to a greater extent, with a maximum decrease in the SOM-induced increase in K_d of 46 and 76%, than the aromatics of 43 and 73% and the alkanes of 36 and 60%. This reduction in the SOM sorptive capability signifies reduction in the amount of gasoline compounds retained by the soil solids in the vadose zone. It also denotes increase in the amount of gasoline compounds in the mobile phases (water and air) which in turn represents increase in groundwater contamination potential (Yu, 1995).
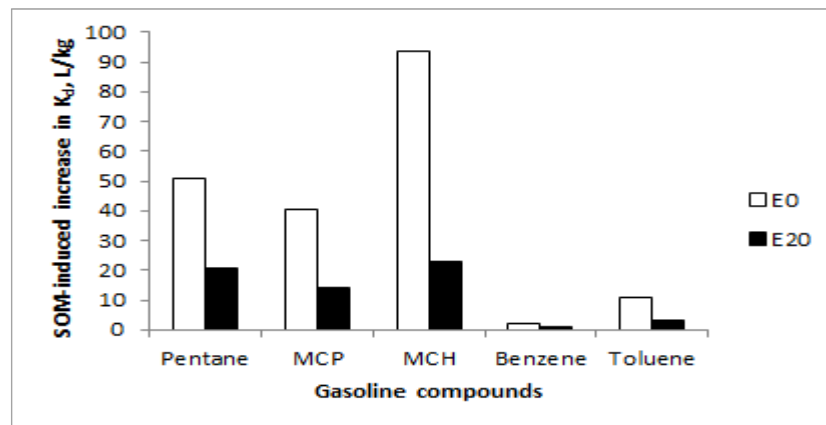

Figure 4 Impact of ethanol on the SOM sorptive capability for gasoline compounds

CONCLUSIONS

The results of this study indicate that the addition of SOM to sand changed the conformation of the sand to higher porosity and greater surface area porous medium, hence increased the sorption of all E20 gasoline compounds and altered their mass distribution between the vadose zone phases. This impact, quantified by the sorption coefficient (K_d) of E20 gasoline compounds, increased with decreasing hydrophobicity, hence affected the aromatics to a greater extent than the cycloalkanes and the alkanes. By increasing the SOM fraction of sand from 0 to 5%, the K_d of E20 gasoline compounds increased by about 7 times for the aromatics, 4 times for cycloalkanes and 2 times for the alkanes. However, when compared with unblended gasoline, the ethanol in E20 generally reduced the sorptive capability of SOM for gasoline compounds by a maximum of 76% for the cycloalkanes, 73% for the aromatics and 60% for the alkanes. Therefore, the full sorptive capability of SOM for gasoline compounds is unlikely to be realized for E20 gasoline compounds. This would mean greater groundwater contamination with E20 gasoline compounds than with E0 gasoline compounds even in soils with high SOM content. This behaviour of E20 is of great significance in determining its fate in soils with varying SOM fractions.

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