Full Length Research Paper

Impact of soil organic matter on the sorption and phase distribution of 20% butanol-blended gasoline in the vadose zone

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Batch microcosm experiments were conducted to examine the impact of soil organic matter (SOM) on the sorption and phase distribution of 20% butanol-blended gasoline (B20) compounds in the vadose zone. SOM was found to promote the sorption of B20 gasoline compounds in the vadose zone. It also affected the phase distribution of B20 gasoline compounds in the vadose zone by increasing adsorption on the soil solid and reducing concentrations in the soil air and soil water. These impacts increased with decreasing hydrophobicity of gasoline compounds. However, when compared with unblended gasoline, the SOM-induced increase in sorption coefficient for B20 gasoline compounds was reduced by a maximum of 66% for the cycloalkanes, 60% for the aromatics and 37% for the alkanes, implying a general reduction in the sorptive capability of SOM. Therefore, the use of high butanol volume such as 20% in gasoline to combat climate change is likely to reduce the retentive capability of SOM in the vadose zone and thus may increase groundwater contamination with gasoline compounds.

Key words: Butanol-blended gasoline, sorption, phase distribution, vadose zone, soil organic matter.

INTRODUCTION

Biobutanol is now gaining increasing interest as a gasoline oxygenate following butanol production from renewable and cost-effective cellulosic materials (Kumar and Gayen, 2011). Companies such as BP, Cobalt Biofuels, DuPont, Gevo, Green Biologics, METabolic Explorer and Tetravitae Bioscience plan to produce biobutanol on industrial scale to be used as a new gasoline extender (EBTP, 2009) where the first commercial-scale biobutanol facility are expected to be operational by 2013. With this near future commercialization of butanol-blended gasoline, potential large spills will be likely. Therefore, knowing the sorption and phase distribution of butanol-blended gasoline in the vadose zone will be useful both in making informed decision on its use and in assessing risks from spills.

As a fuel alcohol, butanol has several advantages over ethanol. These advantages include higher energy content,

higher miscibility with gasoline, lower vapour pressure, lower water absorption and higher compatibility with existing gasoline pipelines (EBTP, 2009; USEPA, 2005). In a direct comparison of 20% blends in gasoline, Mariano et al. (2009) found that butanol may enhance the biodegradation of gasoline compounds in soil more than ethanol. As ethanol has been in the fuel market for decades, several studies on its impact on gasoline compounds transport in the vadose zone have been conducted (Adam et al., 2002; Chen et al., 2008; Corseuil et al., 2004; Dakhel et al., 2003; Lahvis, 2003; McDowell and Powers, 2003; Powers et al., 2001; Yu et al., 2009). These studies, especially with 10 and 20% ethanol blends, have shown that ethanol can reduce the interfacial and surface tensions of gasoline with respect to water, thereby increasing the rate of gasoline transport from the vadose zone to the saturated zone (McDowell

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and Powers, 2003; Yu et al., 2009). Also, ethanol enhances the mobility of dissolved gasoline compounds by exerting a cosolvent effect that decreases retention in the vadose zone (Alvarez et al., 2001; Powers et al., 2001; Yu et al., 2009). This leads to reduced retention capability of the soil (Adam et al., 2002). However, since butanol is still new in the fuel market, little is known about its potential impact on the transport of gasoline in the vadose zone. More so, to the best of our knowledge, the extent that soil organic matter (SOM) will impact the sorption and phase distribution of gasoline compounds in the vadose zone has not been addressed in the literature. Recent studies on butanol and butanol-blended gasoline have focused on the biodegradation of butanol and the effect of butanol on the biodegradation of gasoline compounds. These studies have revealed that butanol is readily biodegraded (Fairbanks et al., 1985; Mariano et al., 2009) and can affect the biodegradation of gasoline compounds in soil (Gomez and Alvarez, 2010; Mariano et al., 2009).

The SOM content of soils is the component that primarily regulates the sorption of organic contaminants by soils (Bohn et al., 2001; Celis et al., 2006; Chen et al., 2007; Li et al., 2009; Liu et al., 2008; Shi et al., 2010; Sparks, 1989). Consequently, the total removal of SOM from natural soils has been found to decrease sorption substantially (Shi et al., 2010). Besides the SOM content of soils, contaminant hydrophobicity is another important factor that can influence the sorption of contaminants in the vadose zone (Chen et al., 2007; Liu et al., 2008). Since butanol is a hydrophilic compound, its addition to gasoline could reduce the hydrophobicity of gasoline, thereby affecting the sorption of gasoline compounds by soils. Such impact could also alter the overall interactions between gasoline, soil water and soil particles.

Considering the near use of butanol-blended gasoline and the poor knowledge associated with its sorption by soil and phase distribution in the vadose zone, this study aimed to evaluate the impact of SOM on the sorption and phase distribution of butanol-blended gasoline in the vadose zone. The study also examined the effect of butanol on the SOM sorption potency. To achieve these aims, a number of laboratory batch microcosm experiments were performed. The soils used consisted of uncontaminated sand mixed with 0 to 5% SOM. Contamination involved a vapour phase injection of 20% butanol-blended gasoline as well as unblended gasoline into the headspace of microcosms, and allowing sorption to and distribution among the phases in the soils. The data obtained indicated that the addition of 20% butanol in gasoline could reduce the sorptive capability of SOM thereby increasing the risk of groundwater contamination with gasoline compounds.

MATERIALS AND METHODS

Butanol-gasoline blend composition

The butanol-blended gasoline used in this study was a synthetic gasoline blended with 20% butanol, referred to as B20. The butanol (99.8%) was purchased from Sigma-Aldrich chemical company, UK.The synthetic gasoline (referred to as B0) 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. The selected fuel compounds are typical constituents of petroleum fuel (Christophersen et al., 2005; Dakhel et al., 2003; Höhener et al., 2003; Pasteris et al., 2002; Speight, 2002) and represent the three major hydrocarbon groups in gasoline, namely alkanes, cycloalkanes (or naphthenes) and aromatics. The weight percentages of the fuel compounds have been chosen according to the typical fuel composition noted by Pasteris et al. (2002) and Höhener et al. (2003). The high blending of 20% butanol by volume was motivated by the consistent increase in the utilization of ethanol as gasoline oxygenate since the phase out of methyl tertiary butyl ether (MTBE) as gasoline oxygenate in the early 2000s.

Description of the soils

The soils used in this study comprised a mixture of SOM-free sand and peat as the source of SOM. The sand was oven dried and sieved through a 2 mm sieve to obtain uniform sand with a particle size distribution of coarse (20%), medium (53%) and fine (27%). The Peat was obtained from Westland Horticulture, UK and contained ≈96% SOM in its dry state, as determined by the "Loss on Ignition" (LOI) method (Sutherland, 1998). The peat was sieved through a 2 mm sieve to obtain particles generally regarded as SOM (Page, 1982). The sand and the peat were mixed on a dry basis to obtain soils consisting of 0 to 5% SOM fraction by weight (Table 2). These percentages of SOM were chosen because they are within the reported range of SOM fraction for typical soils (Bohn et al., 2001; Sparks, 2003).

Batch microcosm experiments

All microcosm experiments were performed with glass vials of 60 mL (H*Ø = 140*27.5 mm) sealed with a polytetrafluoroethylene screw cap for injection and extraction without leaks. The soils ($1\%f_{om}$, $3\%f_{om}$ and $5\%f_{om}$) were autoclaved by heating in an oven set at 160°C for 16 h and thereafter wetted with hot water (50°C) to a volumetric water content of 11%, similar to the water content used by Höhener et al. (2006). A 65 g mass of the wetted soils were packed into the glass vials and compacted alike by tapping vials on the worktable until stable heights were obtained. Heights in vials were 84 mm for $1\%f_{om}$, 92 mm for $3\%f_{om}$ and 100 mm for $5\%f_{om}$, leaving headspaces of 56, 48, and 40 mm, respectively, in the glass vials for vapour phase sampling. The porosities of the soils are 0.46, 0.48 and 0.48 for $1\%f_{om}$, $3\%f_{om}$ and $5\%f_{om}$, respectively. The control experiments were prepared with $0\%f_{om}$, similarly treated and packed. Height in vial was 80 mm leaving a headspace of 60 mm. The porosity of the $0\%f_{om}$ was 0.45. All experiments were performed in triplicates. Before adding the B20 vapours, the vials 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 the B20 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 decreases of the gasoline compounds in the headspace of the microcosms were measured for up to 15 days as described in "Vapour phase analysis by gas chromatography" part of this work. The microcosms were maintained at 25°C in the Thermostatic bath/circulator throughout the duration of the experiment to enhance the unbiased extraction of both the highly and less volatile gasoline compounds. The increase in sorption resulting from SOM was obtained by comparing the average sorption in SOM-

Table 1. Synthetic gasoline composition.

Gasoline compound	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 additive						
Butanol	C_4H_9OH	-	0 &20%	500	0.81	4.99E-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).

Table 2. Soil composition and characterisation.

Soils	Description	Properties					
		pH -	ρ_s g/mL	ρ_b g/mL	n -	SA m^2/g	TPV cm^3/g
$0\%f_{om}$	Sand + 0% SOM	9.10	2.5	1.22	0.51	0.82	4.04E-3
$1\%f_{om}$	Sand + 1% SOM	8.51	2.4	1.17	0.52	1.04	4.47E-3
$3\%f_{om}$	Sand + 3% SOM	7.34	2.3	1.07	0.53	1.47	5.33E-3
$5\%f_{om}$	Sand + 5% SOM	6.17	2.1	0.97	0.54	1.91	6.20E-3

ρ_s = Particle density; ρ_b = Dry bulk density; n = Porosity; SA = Surface area; TPV = Total pore volume.

containing porous media with that in $0\%f_{om}$. The impact of butanol on the sorptive capability of SOM for gasoline compound was obtained by establishing a baseline from experiments using unblended gasoline (B0).

Vapour phase analysis by gas chromatography

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

Estimation of mass distribution of gasoline compounds amongst phases

The mass of gasoline compounds that partitioned to the air and water phases of the vadose zone were estimated using Equations (1) and (2) (Kerfoot, 1991).

$$M_a = C_a * V_a \tag{1}$$

$$M_w = \frac{C_a}{H} * V_w \tag{2}$$

where M_a, and M_w are the masses of gasoline compound in the air

and water phase, respectively, C_a is the concentration of gasoline compound measured at the headspace of microcosm, V_a and V_w are the volumes of air and water in the microcosm, respectively, and H is the dimensionless Henry's law constant.

By applying mass balance in a closed system, the mass adsorbed on the soil solids (M_s) was estimated using Equation (3).

$$M_s = M_t - M_a - M_w - M_L \tag{3}$$

where M_t is the total mass of gasoline compound injected into the microcosm and M_L is the mass of gasoline compound lost via sampling.

Estimation of sorption coefficient of gasoline compounds

Sorption coefficient (K_d), also called the soil-water distribution coefficient, was estimated as the ratio of the concentration of gasoline compound in the soil solid (C_s) to the concentration in the soil water (C_w) (Kerfoot, 1991):

$$K_d = \frac{C_s}{C_w} \tag{4}$$

Estimation of retardation factor of gasoline compounds

The degree of retardation, called retardation factor (R), of the migration of gasoline compounds in the vadose zone as a result of sorption on soil solid was estimated using Equation (5) (Site, 2001).
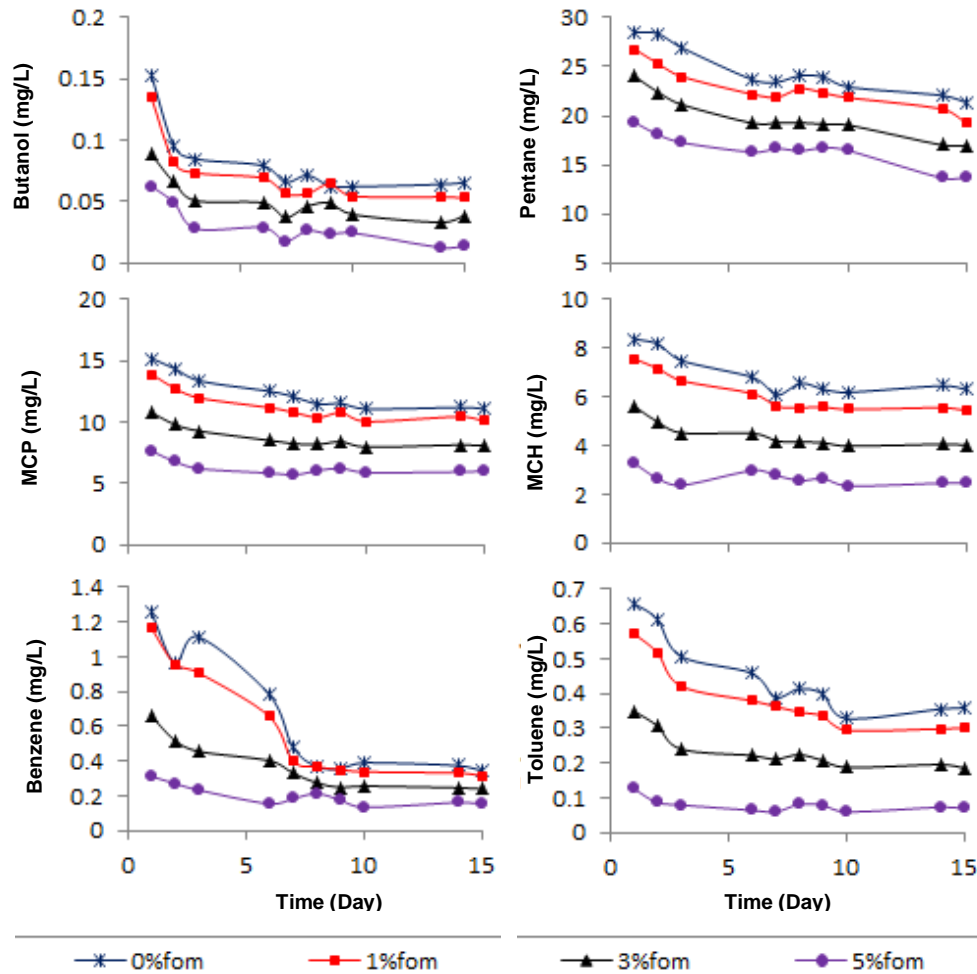
Figure 1. Headspace concentrations of B20 gasoline compounds with time as a function of SOM fraction of soils.

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

where ρ_b and n are the bulk density and porosity of the vadose zone, respectively.

RESULTS AND DISCUSSION

Impact of SOM on the sorption and phase distribution of B20 gasoline compounds

Sorption of B20 gasoline compounds

Figure 1 presents the concentrations of B20 gasoline compounds in the headspace of microcosms as a function of time and SOM fraction of soils. Octane, the second alkane in the gasoline mixture, was poorly detected by the GC-FID used for analysis hence was not

included in Figure 1. The headspace concentration of the different gasoline compounds decreased with specific trend. All gasoline compounds attained equilibrium within the 15 days duration of the experiment, except for pentane that still maintained an approximate linear concentration decrease with time. The decrease in the headspace concentration of gasoline compounds observed indicated increase in sorption to the soils.

The increase in the SOM fraction of soils resulted in greater sorption of all compounds. This enhanced sorption of compounds by SOM could be due to the increased porosity, surface area, and total pore volume of soils with increasing SOM fraction as listed in Table 2. Our ethanol-blended gasoline study indicated that SOM had no significant impact on the sorption of ethanol. Therefore, the impact of SOM on the sorption of butanol confirmed that butanol has lower water absorption than ethanol, as published by the United States Environmental protection Agency (USEPA, 2005), and higher octanol-water partition coefficient (K_{ow}) as reported by Yaws (2008). Therefore, butanol is likely to have less adverse

effect, compared with ethanol, on the sorption of gasoline compounds by SOM. Among the gasoline compounds, SOM impacted the sorption of the aromatics to a greater extent (75 to 81%) than the cycloalkanes (50 to 61%) and the alkanes (32%). This impact was relatively consistent throughout the duration of the experiment except for benzene that dwindled from 75% 4 h after contamination to 55% on Day 15, suggesting that the sorption of benzene by SOM was via physisorption. Since physisorption involves relatively weak bonding forces between dipole moments of contaminant and soil molecules (Bhandari et al., 2007; Weber et al., 1991), it therefore implies that benzene retained by SOM in the vadose zone after a spill of B20 is likely to leach out with time.

Overall, this result indicates that SOM promoted the sorption of all B20 gasoline compounds. This effect was more on the aromatics than on the cycloalkanes and alkanes. Also, it indicates that SOM-compound bonding forces would be stronger for the more hydrophobic gasoline compounds than for the less hydrophobic gasoline compounds. Hence, less hydrophobic gasoline compounds retained by SOM are more likely to undergo leaching with time.

Soil-water interaction of B20 gasoline compounds in the vadose zone

The impact of SOM on the soil-water interaction of B20 gasoline compounds was examined by comparing the sorption coefficient (K_d) values estimated from 0, 1, 3 and 5%f_{om} soils as shown in Figure 2. K_d was estimated for each sampling day and the average K_d was used as the representative K_d. The standard deviation of all the K_d was calculated and used as the error bar. The K_d values obtained are comparable to those reported in the literature. For example, Joo et al (2008) reported K_d values of 0.2 and 0.3 L/kg for benzene and toluene, respectively, with aquifer sand of negligible SOM fraction. In contrast, we have K_d values of 0.6 and 0.7 L/kg for benzene and toluene, respectively, with 0%f_{om} soil which is comparable to aquifer sand in terms of SOM content. The slight difference in the K_d values can be attributed to the difference in the soil and contaminant mixture used (Allen-King et al., 2002). Joo et al. (2008) mixture consisted of only aromatics, while our mixture consisted of aromatics, cycloalkanes, alkanes and alcohol.

The K_d values for all gasoline compounds increased with increasing SOM fraction (f_{om}) of soils, suggesting increase in adsorption on soil solid and decrease in dissolution into the soil water. The increased surface area (SA) of the soils associated with increasing f_{om} could be the possible reason for the observed increase in K_d. As reported by Site (2001), the K_d values for benzene, toluene and xylenes were lower in kaolinite ($SA = 3*10^4$ m^2kg^{-1}) than in illite ($SA = 10^5$ m^2kg^{-1}) and montmorillonite

($SA = 8*10^6$ m^2kg^{-1}), indicating that increase in SA of soils could result in increase in K_d of gasoline compounds. The impact of SOM was greatest for the aromatics where the K_d increased 7 times, compared with the 4 times for the cycloalkanes and 2 times for the alkanes, as the f_{om} increased from 0 to 5%. This direct relationship between K_d and SOM have also been reported for a wide range of single organic contaminants and adsorbents, but it is to the authors knowledge shown for the first time for butanol-blended gasoline. Thus, the data indicate that SOM increased the adsorption of B20 gasoline compounds on the soil solid, but reduced their dissolution into the soil water. This effect is likely to be greatest for the aromatics compared with the alkanes and cycloalkanes.

Retardation of the migration of B20 gasoline compounds in the vadose zone

The degree of retardation of the migration of gasoline compounds in the vadose zone by SOM was investigated by observing the variations in the retardation factor (R) of gasoline compounds in 0, 1, 3 and 5%f_{om} soils. Figure 3 shows the variations in R with increasing SOM fraction (f_{om}) of soils for the B20 gasoline compounds. Generally, the R values for all gasoline compounds increased with increasing f_{om}, suggesting that partitioning into SOM is a major process causing retardation. This effect increased with increasing hydrophobicity, hence was greatest for the cycloalkanes (0 to 64) and least for the aromatics (0 to 9.4). The difference in the R values for gasoline compounds would result in different distributions for the gasoline compounds in soils (Johnson and Perrott, 1991).

A comparison of our R values for benzene and toluene in 0%f_{om} with those reported by Höhener et al. (2006) in sand shows a good agreement despite the slight difference in contaminant mixture. We obtained R values of 2.29 for benzene and 2.53 for toluene while Höhener and co-workers reported R values of 1.24 for benzene and 1.93 for toluene. Also, the R values of 1.61 for benzene and 1.91 for toluene obtained from Joo et al. (2008) K_d values of 0.2 L/kg for benzene and 0.3 L/kg for toluene were in good agreement with our R values. However, our R values were found to differ greatly with those reported for clay, 117.2 for benzene and 734 for toluene (Myrand et al., 1992), and for fine silty loam, 193.0 for benzene and 218.0 for toluene (Johnson and Perrott, 1991). 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 properties of soils is likely to have a greater influence on the R of gasoline compounds than the composition of contaminants. Overall, our data indicate that SOM reduced the migration of B20 gasoline compounds in the vadose zone. This effect increased with increasing
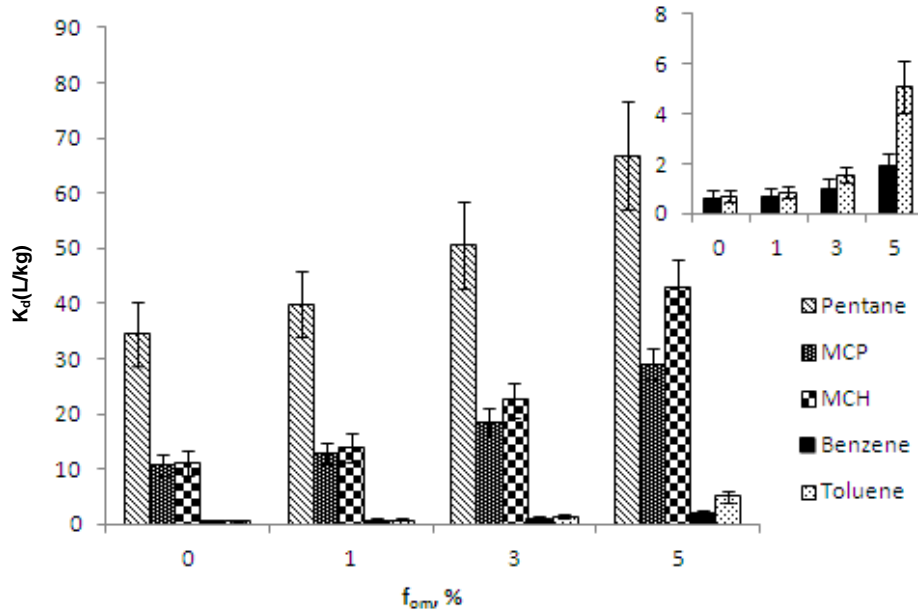
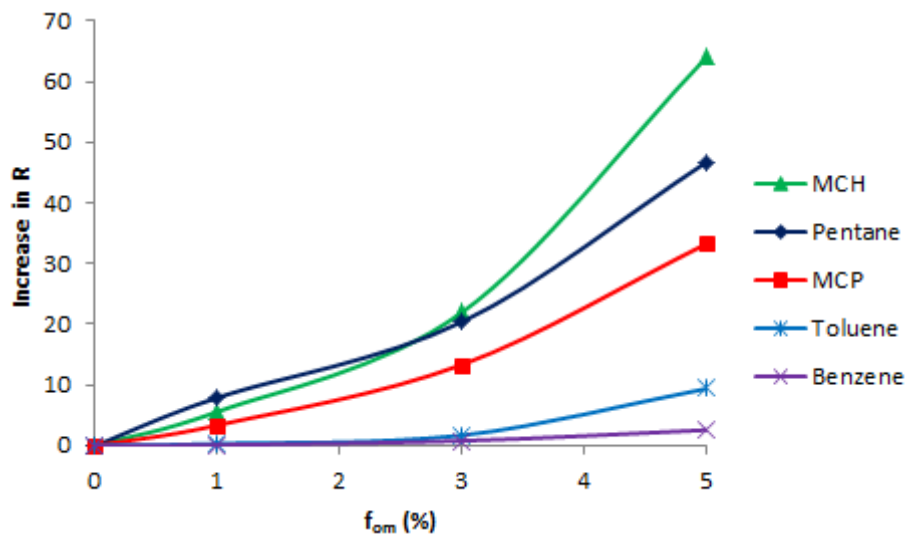**Figure 2.** Sorption coefficient (K_d) of B20 gasoline compounds as a function of SOM fraction of soils.

Figure 3. Impact of SOM on the retardation factor (R) of B20 gasoline compounds.

hydrophobicity of gasoline compounds.

Mass distribution of B20 gasoline compounds amongst the vadose zone phases

Table 3 lists the changing masses of B20 gasoline compounds in the soil air, soil solid and soil water with changing SOM fraction of soils. The increase in the SOM fraction of soils resulted in an increased mass distribution of gasoline compounds from the soil air to the soil solid,

and in a reduced mass distribution to the soil water. Although this effect was observed throughout the duration of the experiment, it was generally greatest on Day 1 and affected the aromatics (29 to 49%) more than the cycloalkanes (28 to 35%) and the alkanes (20%). The reduction in the amount of available soil water in the microcosm with increasing SOM fraction of the soils could be the possible reason for the greater impact of SOM on the adsorption of the less hydrophobic gasoline compounds such as the aromatics. However, on Day 15, when equilibrium is assumed to have been reached, SOM

Table 3. Mass distribution of B20 gasoline compounds in the vadose zone as a function of SOM fraction of soils.

Day	Pentane			MCP			MCH			Benzene			Toluene		
	Air	Solid	Water	Air	Solid	Water	Air	Solid	Water	Air	Solid	Water	Air	Solid	Water
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
							$0\%f_{om}$								
1	48.3	51.6	0.2	48.2	51.1	0.6	52.1	47.3	0.8	34.1	37.0	28.9	20.7	64.4	14.9
8	40.8	58.7	0.2	36.5	62.8	0.5	40.8	58.4	0.5	10.0	81.3	8.5	13.0	77.6	9.4
15	32.8	60.6	0.1	35.3	63.7	0.5	39.3	59.7	0.4	9.4	82.5	7.9	11.3	80.4	8.1
							$1\%f_{om}$								
1	43.9	56.0	0.2	42.7	56.8	0.6	45.5	54.0	0.5	30.7	42.5	26.8	17.4	69.6	13.0
8	37.3	62.2	0.1	31.9	67.3	0.4	33.5	65.8	0.4	9.7	81.6	8.5	10.5	81.5	7.9
15	31.5	67.9	0.1	31.1	68.0	0.4	32.8	66.4	0.4	8.3	84.2	7.3	9.2	83.8	6.8
							$3\%f_{om}$								
1	37.6	62.2	0.2	31.6	67.9	0.4	32.3	67.3	0.4	16.6	68.2	15.2	10.2	81.9	7.9
8	30.3	69.3	0.1	24.2	75.3	0.3	24.0	75.5	0.3	7.0	86.6	6.4	6.5	88.3	5.1
15	26.6	72.9	0.1	23.8	75.4	0.3	23.2	75.1	0.3	6.1	88.3	5.6	5.4	90.3	4.2
							$5\%f_{om}$								
1	28.0	71.9	0.1	20.7	79.0	0.3	17.4	82.4	0.2	7.3	85.5	7.2	3.4	93.7	2.9
8	23.8	75.9	0.1	16.5	83.0	0.3	13.7	86.0	0.2	5.0	90.0	4.9	2.2	95.9	1.9
15	19.9	79.6	0.1	16.4	83.1	0.3	13.2	86.5	0.2	3.6	92.7	3.6	1.9	96.4	1.6

promoted the adsorption of gasoline compounds based on hydrophobicity, with the cycloalkanes promoted to greater extent (19 to 26%) than the alkanes (19%) and the aromatics (10 to 16%). This implies that the bonding forces between the dipole moments of the SOM and the aromatics are weaker than those of the cycloalkanes and the alkanes. Hence, any aromatics retained by SOM in the vadose zone after a spill of B20 are more likely to leach out with time faster than would any cycloalkanes or alkanes. Overall, the data indicate that SOM could impact the phase distribution of B20 gasoline compounds in the vadose zone. Among the gasoline compounds, the impact is likely to vary with time. While the less hydrophobic gasoline compounds may be impacted to a greater extent few hours after spills, the more hydrophobic gasoline compounds are likely to be impacted to a greater extent afterwards.

Impact of butanol on SOM sorptive capability

The impact of butanol on SOM sorptive capability for gasoline compounds was investigated by comparing the K_d of B0 and B20 gasoline compounds in $0\%f_{om}$ and $5\%f_{om}$ soils. The difference in K_d increase with increasing SOM for B0 and B20 gasoline compounds is presented in Figure 4. The presence of butanol caused a substantial reduction in the K_d of all gasoline compounds in both 0 and $5\%f_{om}$, signifying reduction in the amount of

gasoline compounds adsorbed on the soil solid. The presence of butanol also caused a significant reduction in the SOM-induced increase in K_d for all B20 gasoline compounds, implying reduction in the SOM sorptive capability for gasoline compounds. This effect increased with increasing molecular weight and thus was greatest for the cycloalkanes compared with the aromatics and alkanes. The SOM-induced increase in K_d for B20 gasoline compounds decreased by 55 to 66% for the cycloalkanes, 43 to 60% for the aromatics and 37% for the alkanes. Generally, the reduction in the K_d and in the SOM-induced increase in K_d of gasoline compounds would mean decrease in the amount of gasoline compounds retained in the vadose zone. Therefore, the data indicate that the full sorptive capability of SOM for gasoline compounds is unlikely to be realised for B20 gasoline compounds.

Conclusions

Soil organic matter (SOM) showed a great impact on the sorption and phase distribution of B20 gasoline compounds in the vadose zone. This impact increased with decreasing hydrophobicity of gasoline compounds. By increasing the SOM fraction of sand from 0 to 5%, the sorption coefficient (K_d) of B20 gasoline compounds increased 7 times for the aromatics, 4 times for the cycloalkanes and 2 times for the alkanes. However, when
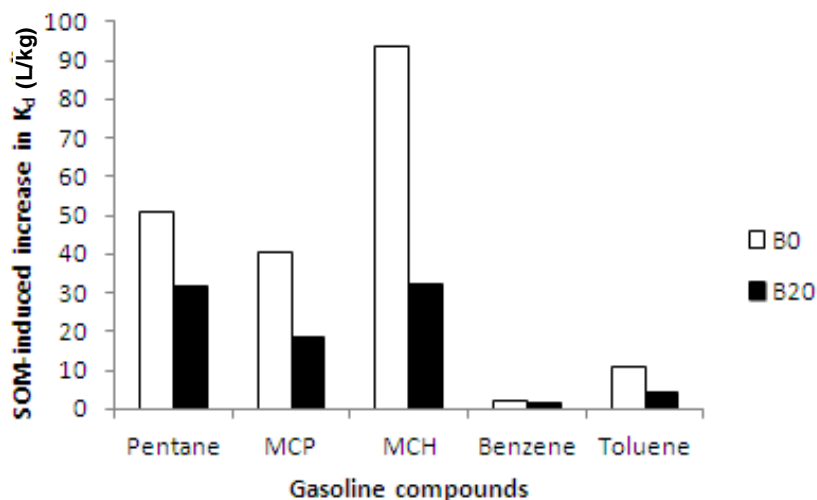
Figure 4. Impact of butanol on SOM capability to increase the K_d of gasoline compounds.

compared with B0 gasoline compounds, the SOM-induced increase in K_d for B20 gasoline compounds decreased by 55 to 66% for the cycloalkanes, 43 to 60% for the aromatics and 37% for the alkanes, implying a general reduction in the sorptive capability of SOM. Therefore, the use of high butanol volume such as 20% in gasoline to combat climate change is likely to reduce the retentive capability of SOM in the vadose zone. This may increase groundwater contamination with gasoline compounds.

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