Unexpected malformations in
Xenopus tropicalis

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Sorption and phase distribution of ethanol and butanol blended gasoline vapours in the vadose zone after release

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A B S T R A C T

The sorption and phase distribution of 20% ethanol and butanol blended gasoline (E20 and B20) vapours have been examined in soils with varying soil organic matter (SOM) and water contents via laboratory microcosm experiments. The presence of 20% alcohol reduced the sorption of gasoline compounds by soil as well as the mass distribution of the compounds to soil solids. This effect was greater for ethanol than butanol. Compared with the sorption coefficient (K_d) of unblended gasoline compounds, the K_d of E20 gasoline compounds decreased by 54% for pentane, 54% for methylcyclopentane (MCP) and 63% for benzene, while the K_d of B20 gasoline compounds decreased by 39% for pentane, 38% for MCP and 49% for benzene. The retardation factor (R) of E20 gasoline compounds decreased by 53% for pentane, 53% for MCP and 48% for benzene, while the R of B20 gasoline compounds decreased by 39% for pentane, 37% for MCP and 38% for benzene. For all SOM and water contents tested, the K_d and R of all gasoline compounds were in the order of unblended gasoline > B20 > E20, indicating that the use of high ethanol volume in gasoline to combat climate change could put the groundwater at greater risk of contamination.

Introduction

Groundwater contamination by alcohol-blended gasoline is a rising concern associated with the increased use of alcohol in gasoline to meet the Clean Air Act requirements (Powers et al., 2001). Presently, ethanol is the most commonly used gasoline oxygenate in the UK and other countries of the world, including United States and Brazil (Hahn-Häerdal et al., 2006). However, the interest in butanol has grown recently due to its 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; US EPA, 2005). Thus, knowing the effect of each alcohol on the sorption and phase distribution of gasoline compounds in the vadose zone is vital in making informed decision on which alcohol to adopt as future gasoline oxygenate.

Alcohol is being considered a suitable fuel oxygenate since it addresses air quality objectives without seriously deteriorating groundwater quality compared to methyl tertiary butyl ether (Beller et al., 2001). As ethanol has been in the fuel market for decades, several studies on its impact on the sorption and distribution of gasoline compounds in the vadose zone have been published (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; Ugwoha and Andresen, 2012; Yu et al., 2009). These studies have shown that ethanol affects the infiltration, distribution and sorption of gasoline compounds. 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.

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Consequently, these processes alter the overall interactions between gasoline, soil water and soil particles. In contrast, since butanol is still new in the fuel market, little is known about its potential impact on the sorption and distribution of gasoline compounds in the vadose zone. The few studies on butanol-blended gasoline have focused on the effect of butanol on the biodegradation of gasoline compounds (Gomez and Alvarez, 2010; Mariano et al., 2009).

A good knowledge of the sorption and phase distribution of alcohol-blended gasoline in the vadose zone could provide a significant insight on its groundwater contamination risk. When released in the vadose zone, alcohol-blended gasoline, like other organic contaminants, is expected to gradually partition into the vadose zone phases, i.e. soil, water and air. This distribution between phases will depend on the physicochemical properties of the gasoline blend 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). Two vital characteristics of the geologic media that have been studied that can affect sorption and phase distribution are soil organic matter (SOM) and soil water content. Previous studies have shown that SOM 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), and that the removal of SOM from soils could decrease sorption significantly (Shi et al., 2010). However, these studies were conducted mainly with single hydrophobic organic compounds, which lacks the intermolecular interactions that exists amongst gasoline compounds (Lawrence et al., 2009), hence may not be applicable to gasoline blends. Consequently, it is still unclear how SOM will affect the distribution of alcohol-blended gasoline compounds between the vadose zone phases.

Studies on the effect of soil water content on the fate of released contaminants have shown that the water content of a soil can affect the sorption and transport of organic contaminants in the vadose zone (Acher et al., 1989; Johnson and Perrott, 1991; Ong and Lion, 1991; Serrano and Gallego, 2006; Site, 2001; Smith et al., 1990; Steinberg and Kreamer, 1993). These studies argued that the increase in the water content of a soil could reduce the available surface area of the soil by filling some of the pores. Because water can substantially reduce the surface activities of inorganic surfaces by occupying the high-energy sites (Site, 2001), it is possible that increasing the water content of a soil could also decrease the SOM sorptive capability. Understanding the degree of this impact will be useful in predicting the behaviour of alcohol-blended gasoline in the soil during dry summer and wet winter.

In this study, a number of laboratory microcosm experiments were performed. The soils used consisted of uncontaminated sand with approximately 0, 1%, 3% and 5% SOM. The soil water contents tested were 0, 4.5%

and 9% (W/W). Contamination involved a vapour phase injection of synthetic gasoline alone and blended with 20% ethanol or butanol into the headspace of microcosms and allowing sorption and phase distribution within the soils. The aim of the study was to investigate the impact of the different alcohols on the sorption and phase distribution of gasoline compounds in vadose zones with varying SOM and water contents. The data obtained showed that ethanol would have a greater adverse impact on the sorption and phase distribution of gasoline compounds in the vadose zone than butanol.

1 Materials and methods

1.1 Alcohol-blended gasoline composition

The alcohol-blended gasoline used in this study was a synthetic gasoline blended with 20% ethanol and butanol individually, referred to as E20 and B20, respectively (**Table 1**). The ethanol (> 99.5%) and butanol (99.8%) were purchased from Sigma-Aldrich Chemical Company, UK. The synthetic gasoline, referred to as unblended gasoline (UG), was prepared from six typical fuel compounds. The synthetic gasoline and its components are described elsewhere (Ugwoha and Andresen, 2012). All experiments were performed with vapours coming from the mixture of the compositions as given in **Table 1**.

The concentration of each gasoline compound in the gas phase for the alcohol-blended fuels used was calculated based on the initial mole fraction and vapour pressure governed by Raoult's law as expressed in Eq. (1) (Höhener et al., 2003; Pasteris et al., 2002):

$$C_g = \frac{P^\circ X}{RT} \times \text{MW} \tag{1}$$

where, C_g (g/m^3) is the concentration in gas phase, P° (atm) is the vapour pressure, X is the mole fraction, R (8.21×10^{-5} (m^3·atm)/(K·mol)) is the universal gas constant, T (K) is the temperature, and MW (g/mol) is the molecular weight. The C_g was converted to the desired unit of g/mL by dividing result in g/m^3 by 10^6.

1.2 Soil description

The soils used were fully described in our previous work (Ugwoha and Andresen, 2012). Briefly, the soils comprised a mixture of sand and peat as the source of SOM. The sand contained negligible amount of SOM (< 0.1%), and had a particle size distribution of coarse (20%), medium (53%) and fine (27%). The peat contained about 96% SOM in its dry state. The sand and peat were mixed to obtain soils 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 porosities of the dry soils were 0.51, 0.52, 0.53 and 0.54 while the surface areas were

Table 1	Ethanol and butanol blended gasoline composition						
Fuel compound	Weight in mix (%)	Volume (mL)	ρ at 25°C [a] (g/mL)	Vapour pressure at 25°C [a] (Pa)	Solubility at 25°C [c] (g/L)	H [c]	K_{ow} [c]
Pentane	9.6	15.3	0.626	57900	0.04	51.4	2818.4
Octane	25.8	36.7	0.703	1470	0.0004	211	141253.8
MCP	19.5	26.0	0.75	17732[b]	0.4	14.7	2344.2
MCH	32.3	41.9	0.77	4930	0.01	17.5	7585.8
Benzene	3.2	3.7	0.874	9950	1.76	2.26E-01	134.9
Toluene	3.2	11.1	0.865	2910	0.54	2.65E-01	537.0
			Fuel oxygenate				
Ethanol	–	0–20%	0.789	5950	Total	2.94E-04	0.5
Butanol	–	0–20%	0.81	500	80.61	4.99E-04	6.9

MCP: methylcyclopentane; MCH: methylcyclohexane; H: Henry's law constant; K_{ow}: octanol-water partition coefficient.
[a] values obtained from Sigma Aldrich Material Safety Data Sheet; [b] value obtained from Pasteris et al. (2002) Supporting Information; [c] values obtained from Yaws (2008).

0.82, 1.04, 1.47 and 1.91 m^2/g for 0%f_{om}, 1%f_{om}, 3%f_{om} and 5%f_{om}, respectively.

1.3 Microcosm experiments

All microcosm experiments were performed using glass vials of 60 mL as described in a previous publication (Ugwoha and Andresen, 2012). The SOM impact experiments were conducted with 0%f_{om}, 1%f_{om}, 3%f_{om} and 5%f_{om} soils, autoclaved and wetted to 9% (W/W). About 65 g of the soils were packed individually into the microcosm and compacted to a stable height. The porosities of the soils in the glass vials 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 microcosms and their contents were stored in a Thermostatic bath set at 25°C to maintain a stable temperature throughout the duration of the experiment. Each microcosm was contaminated by injecting a 10 mL gas volume of the gasoline mixture into it using a 10 mL gas-tight syringe following the extraction of a 10 mL air from the microcosm. The mass of each gasoline compound in the 10 mL gas volume for the different gasoline blends, obtained by multiplying the gas phase concentration with the extracted gas volume, is summarized in **Table 2**. The decrease in concentrations of the gasoline compounds in the headspace of each microcosm was monitored daily for up to 15 days by Gas Chromatography (GC) measurements. The extraction of the vapour phase samples as well as the GC type and operating conditions are described elsewhere (Ugwoha and Andresen, 2012). The increase in sorption resulting from SOM was calculated as the difference between the average sorption in SOM-containing soils and the average sorption in the 0%f_{om} soil. All experiments were performed in triplicates.

The effect of water content on the sorptive capacity of SOM was investigated with 5%f_{om} wetted to 0, 4.5% and 9% (W/W). Microcosms were similarly treated as described for the SOM impact experiments. For the 0 and 4.5% (W/W) experiments, the porosities of the soils were

Table 2	Mass of gasoline compounds injected into microcosm		
Fuel compound	Mass injected (g)		
	UG	E20	B20
Pentane	2.43E-03	1.58E-03	1.81E-03
Octane	1.87E-04	1.21E-04	1.38E-04
MCP	1.29E-03	8.39E-04	9.62E-04
MCH	6.61E-04	4.29E-04	4.91E-04
Benzene	1.53E-04	9.84E-05	1.13E-04
Toluene	1.31E-04	8.51E-05	9.75E-05

0.46 and 0.48, respectively, while the porosity of the soil for 9% (W/W) experiment was as described for the SOM impact experiment. The average sorption of the UG, E20 and B20 gasoline compounds by the soil was compared for the different water contents.

1.4 Estimation of mass distribution, sorption coefficient and retardation factor

All calculations were performed with the vapour phase concentrations of compounds measured from the microcosm experiments. The mass of gasoline compounds that partitioned to the soil air (M_a), soil water (M_w) and soil solid (M_s) phases of the vadose zone were estimated using Eqs. (2), (3) and (4), respectively (Kerfoot, 1991; Ugwoha and Andresen, 2012). Sorption coefficient (K_d), the ratio of the concentration of gasoline compound on the soil (C_s) to the concentration in the water (C_w), was estimated using Eq. (5) (Kerfoot, 1991; Vallero, 2004). Retardation factor (R) which relates to the extent that the migration of a gasoline compound in the vadose zone is retarded as a result of sorption was estimated using Eq. (6) (Hemond and Fechner-Levy, 2000; Logan, 2012; Mehran et al., 1987; Myrand et al., 1992; Rivett et al., 2001; Site, 2001):

$$M_a = C_a \times V_a \tag{2}$$

$$M_w = \frac{C_a}{H} \times V_w \tag{3}$$

$$M_s = M_t - C_a\left(V_a + \frac{V_w}{H}\right) - M_L \tag{4}$$

$$K_d = \frac{C_s}{C_w} = \frac{H}{C_a M_{ts}}\left(M_t - C_a V_a - \frac{C_a V_w}{H} - M_L\right) \tag{5}$$

$$R = 1 + \left(\frac{\rho}{n}\right) K_d \tag{6}$$

where, M_t (g) is the total mass of gasoline compound injected into the microcosm, C_a (g/mL) is the vapour phase concentration of gasoline compound measured at the headspace of microcosm, V_a (mL) and V_w (mL) are the volumes of air and water in the microcosm, respectively, H is the dimensionless Henry's law constant, M_L (g) is the mass of gasoline compound lost via sampling, M_{ts} (g) is the total soil mass in microcosm, and ρ (kg/L) and n are the bulk density and porosity of the soil in the microcosm, respectively.

2 Results and discussion

2.1 SOM impact on the sorption and phase distribution of UG, E20 and B20

2.1.1 Sorption of gasoline compounds

The headspace concentrations of selected gasoline compounds for UG, E20 and B20 with increasing SOM fractions of the soil were compared (**Fig. 1**). The selected three gasoline compounds are good representatives of the three hydrocarbon groups constituting the synthetic gasoline mixture. Selection of the representative gasoline compounds was necessary to reduce congestion of figure, and was based on volatility. The behaviours of the unshown compounds followed the same trend as their representative compounds. The headspace concentrations of all gasoline compounds decreased with time, signifying the increase in sorption to the soil. The addition of 20% alcohol by volume to gasoline reduced the sorption of all gasoline compounds due to the early high alcohol sorption and the associated blockage of the soil surface. This reduction was greater on day 1 and affected the E20 gasoline compounds to a greater extent compared to the B20 gasoline compounds. According to Yu (1995), such reduction in sorption denotes increase in the amount of gasoline compounds in the mobile air phase, which represents increased risk of groundwater contamination. Consequently, **Fig. 1** suggests that E20 could result in greater risk of groundwater contamination with gasoline compounds than B20, and that the difference is likely to be greatest on the first day of spill. Similar observation has been reported for E26 gasoline compounds, where it was noted that the presence of ethanol would have a significant effect on gasoline compounds only at very early leaching times when ethanol still persist and thereafter would have insignificant effect due to ethanol wash out (Reckhorn et al., 2001). In this study, the effects of the alcohols on the sorption of the gasoline compounds were significant between day 1 and 6 as the alcohols persisted in the headspace, but insignificant between day 6 and 15 due to the partitioning of the alcohols to the soil water. Compared with the sorption of the UG gasoline compounds by the $0\% f_{om}$ soil on day 1, the reductions in the sorption of the E20 gasoline compounds were 28% for pentane, 25% for MCP and 91% for benzene, while the reductions in the sorption of the B20 gasoline compounds were 7% for pentane, 7% for MCP and 96% for benzene. Although the sorption of benzene from B20 seemed to be reduced to a greater extent than the benzene from E20 on day 1, the reductions on the subsequent experimental days, when equilibrium had been attained, were clearly higher for E20. For example, on day 8 the reduction was 38% for E20 and
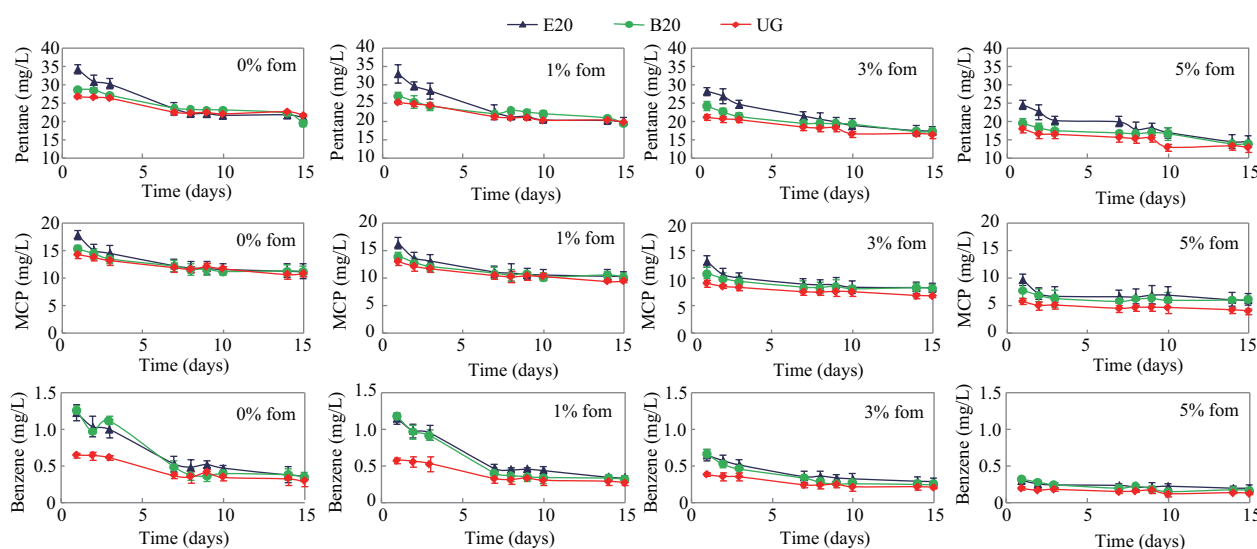

Fig. 1 Headspace concentrations of gasoline compounds with increasing SOM fraction (f_{om}) of soils as a function of gasoline composition.

7% for B20, and on day 15 it was 25% for E20 and 20% for B20.

The increase in the SOM fraction of soils resulted in a rapid and greater sorption for all the gasoline compounds. This impact varied with gasoline composition. SOM promoted the sorption of the B20 gasoline compounds to a greater extent compared to those of the E20 gasoline compounds. This implies that the increase in the SOM content of soils may reduce the groundwater contamination with B20 gasoline compounds to a greater extent than that with E20 gasoline compounds. On Day 1 after contamination, when the effect of SOM on sorption was generally greatest, the sorption of B20 gasoline compounds was increased by 32% for pentane, 50% for MCP and 75% for benzene, while the sorption of E20 gasoline compounds was increased by 29% for pentane, 46% for MCP and 76% for benzene, for 5% increase in the SOM fraction of a sand. The similar increase in the sorption of benzene by SOM suggests that butanol and ethanol may have similar cosolvent effect on benzene.

Overall, the data show that the addition of 20% alcohol by volume to gasoline in attempts to reduce vehicular emissions to the atmosphere could reduce the sorption of gasoline compounds by soils and thus increase the risk of groundwater contamination with gasoline compounds. This impact is likely to be greater for ethanol than butanol. Although soils with high SOM content could significantly reduce the degree of groundwater contamination, the difference in groundwater contamination risk between ethanol-blended gasoline and butanol-blended gasoline is unlikely to be eliminated.

2.1.2 Soil-water interaction of gasoline compounds

Figure 2 shows the effect of SOM on the average sorption coefficient (K_d) of gasoline compounds as a function of gasoline composition. The addition of alcohol to gasoline reduced the K_d of all gasoline compounds, suggesting a decrease in the adsorption of gasoline compounds on the soil and/or increase in the dissolution of gasoline compounds into the water. This impact was greater for the E20 gasoline compounds than for the B20 gasoline

compounds, implying that the E20 gasoline compounds will have a higher percentage in the mobile water phase which in turn will result in greater risk of groundwater contamination (Yu, 1995). Compared with the K_d of UG gasoline compounds in 0% f_{om}, the K_d of B20 gasoline compounds were reduced by 39% for pentane, 38% for MCP and 49% for benzene, while the K_d of E20 gasoline compounds decreased by 54% for pentane, 54% for MCP and 63% for benzene.

The K_d of all the gasoline compounds increased with increasing SOM fraction (f_{om}) of the soil, suggesting an increase in the adsorption of all gasoline compounds on the soil and/or decrease in the dissolution of all gasoline compounds into the water. Although the K_d of E20 and B20 gasoline compounds were similarly increased by 7 times for aromatics, 4 times for cycloalkanes and 2 times for alkanes, for 0 to 5% increase in f_{om}, the K_d of the B20 gasoline compounds were generally greater than those of the E20 gasoline compounds for all the SOM fractions tested. More so, when compared with the K_d of UG gasoline compounds, the K_d of B20 and E20 gasoline compounds in 1% f_{om}, 3% f_{om} and 5% f_{om} were generally reduced with a trend similar to the reduction for the 0% f_{om} soil as stated in the preceding paragraph. This may have two implications. First, it suggests that the risk of groundwater contamination with gasoline compounds will always be higher for alcohol-blended gasoline than for alcohol-free gasoline regardless of the SOM content of soils. Second, it strengthened the observation in Section 2.1.1 that the difference in groundwater contamination risk between B20 and E20 cannot be eliminated by SOM.

2.1.3 Retardation of the migration of gasoline compounds

The impact of SOM on the retardation of the migration of gasoline compounds quantified by the retardation factor (R) for different gasoline blends is presented in **Fig. 3**. As expected, the addition of alcohol to gasoline caused a reduction in the R values for all gasoline compounds. This reduction was greater for the E20 gasoline compounds than for the B20 gasoline compounds, suggesting that the
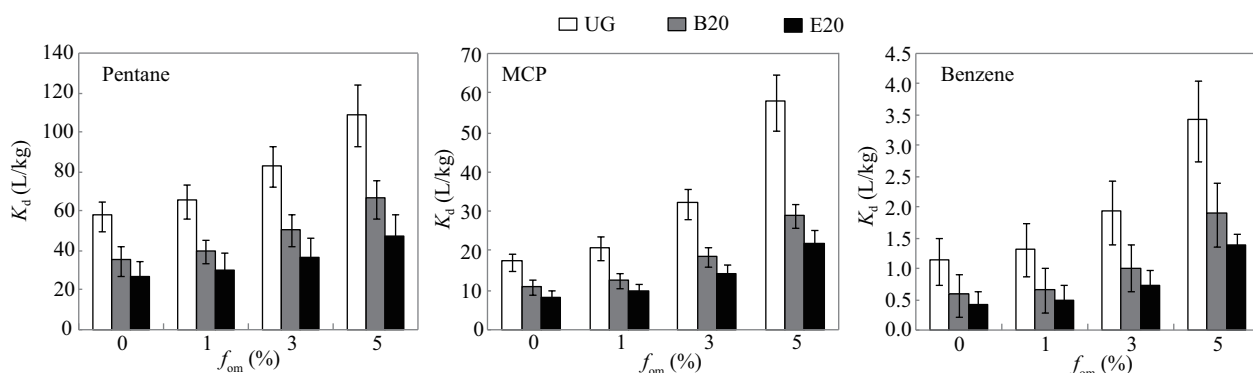

Fig. 2　Average sorption coefficient (K_d) of gasoline compounds with increasing SOM fraction (f_{om}) of soils as a function of gasoline composition.
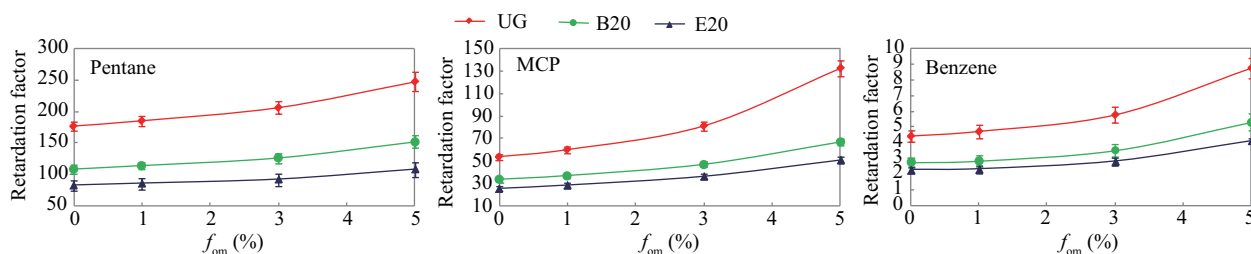
Fig. 3   Retardation factor (R) of gasoline compounds with increasing SOM fraction (f_{om}) of soils as a function of gasoline composition.

migration of the E20 gasoline compounds in the vadose zone would be retarded lesser than the migration of the B20 gasoline compounds after spills. The addition of alcohol to gasoline reduced the R values for B20 gasoline compounds in 0% f_{om} by 39% for pentane, 37% for MCP and 38% for benzene, while it reduced the R values for E20 gasoline compounds by 53% for pentane, 53% for MCP and 48% for benzene.

The increase in the SOM fraction of soils increased the R values for all the gasoline compounds, implying a reduction in the migration of gasoline compounds in the vadose zone. Similar to R values in 0% f_{om}, the R values for all gasoline compounds in 1% f_{om}, 3% f_{om} and 5% f_{om} were in the order of UG > B20 > E20, indicating that the migration of E20 gasoline compounds would be retarded the least regardless of the SOM content of the soil.

2.1.4 Mass distribution of gasoline compounds between vadose zone phases

The mass of a representative gasoline compound in the water, air and soil with increasing SOM fraction of soils as a function of gasoline composition is presented in **Table 3**. The mass distribution of pentane in 0% f_{om} and 5% f_{om} has been chosen to reduce complexity. The behaviours of the other representative gasoline compounds followed similar trend as the pentane presented here. The addition of alcohol to gasoline caused an increase in the mass of pentane distributed to the mobile phases (air and water), but reduced the mass distributed to the immobile soil phase. Although this effect was observed throughout the experimental duration, it was greatest on day 1 and affected the E20 gasoline compounds to a greater extent than the

B20 gasoline compounds.

The increase in the SOM fraction of soils generally promoted the adsorption of pentane on the soil, but reduced its concentrations in the water and air. This effect was greatest on day 1 and affected the E20 gasoline compounds to a greater extent compared with the B20 gasoline compounds. However, despite such higher effect on E20, the order of adsorption for the 5% f_{om} soil was still the same as with 0% f_{om}, UG > B20 > E20. This observation indicates that SOM is unlikely to change the order of mass distribution to the vadose zone phases for different gasoline blends. This further implies that the risk of groundwater contamination with gasoline compounds will always be higher for E20 than B20 regardless of the SOM content of the soil.

2.2 Soil water content impact on SOM sorptive capability for UG, E20 and B20

2.2.1 Sorption of gasoline compounds

Figure 4 compares the headspace vapour concentrations of UG, B20 and E20 representative gasoline compounds for 0, 4.5% and 9% W/W water contents for a 5% f_{om} soil. The increase in the soil water content increased the headspace concentrations of all compounds, indicating a general decrease in the sorption of all compounds by the soil. This decrease in sorption has been interpreted to be due to the blockage of some of the sorption sites of the soils (Ong and Lion, 1991; Serrano and Gallego, 2006; Smith et al., 1990; Steinberg and Kreamer, 1993). The addition of alcohol to gasoline resulted in a decreased sorption of the gasoline compounds for all soil water contents tested.

Table 3   Mass distribution of pentane between vadose zone phases with increasing SOM fraction (f_{om}) of soils as a function of gasoline composition

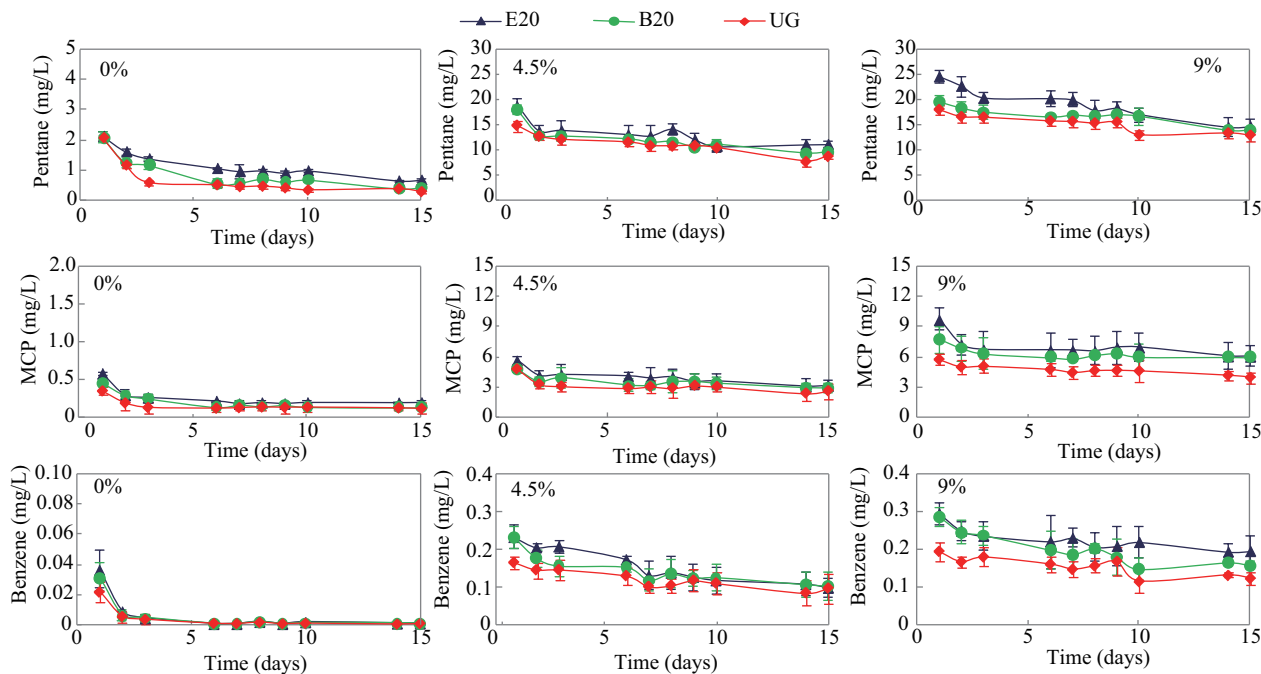| Day	UG			B20			E20		
	Solid (%)	Air (%)	Water (%)	Solid (%)	Air (%)	Water (%)	Solid (%)	Air (%)	Water (%)
For 0% f_{om}									
1	66.3	33.6	0.1	51.6	48.3	0.2	33.6	66.2	0.3
8	71.7	28.1	0.1	58.7	40.8	0.2	56.7	42.8	0.2
15	72.5	27.0	0.1	66.6	32.8	0.1	58.6	40.6	0.2
For 5% f_{om}									
1	80.7	19.2	0.1	71.9	28.0	0.1	59.5	40.4	0.2
8	83.5	16.3	0.1	75.9	23.8	0.1	70.3	29.3	0.1
15	86.1	13.7	0.1	79.6	19.9	0.1	75.4	24.0	0.1

Fig. 4 Impact of soil water content on the headspace vapour concentrations of gasoline compounds as a function of gasoline composition.

Among the alcohols, ethanol caused a greater decrease in sorption than butanol. Consequently, the E20 gasoline compounds were generally sorbed to a lesser extent by the soil compared with the B20 gasoline compounds for all soil water contents. This suggests that the sorption of gasoline compounds by soils after spills is likely to be lesser for the E20 than B20 at all soil water contents. The difference in sorption between the E20 and B20 gasoline compounds for the different soil water contents on day 8, when sorption equilibrium can reasonably be assumed, ranged from 13% for aromatics to 58% for alkanes at 0% (W/W) water content, from 3% for aromatics to 23% for alkanes at 4.5% (W/W) water content, and from 2% for aromatics to 8% for alkanes at 9% (W/W) water content. Therefore, the data show that the increase in soil water content is likely to have greater adverse impact on the sorption of the ethanol-blended gasoline compounds than

on the sorption of the butanol-blended gasoline compounds after spills.

2.2.2 Soil-water interaction of gasoline compounds

Figure 5 shows the average sorption coefficient (K_d) values for the UG, B20 and E20 gasoline compounds in 5%f_{om} at 4.5 and 9% (W/W) water addition. The K_d of all compounds decreased with increasing soil water content, implying a general decrease in the adsorption of the gasoline compounds on the soil or increase in dissolution into the water. The addition of alcohol to gasoline resulted in further reductions of the K_d values for all gasoline compounds. This impact was generally greater for ethanol than butanol. Accordingly, K_d values for gasoline compounds were generally in the order of UG > B20 > E20 for all the soil water contents tested. For soil water content increase from 4.5% to 9%, the K_d of B20
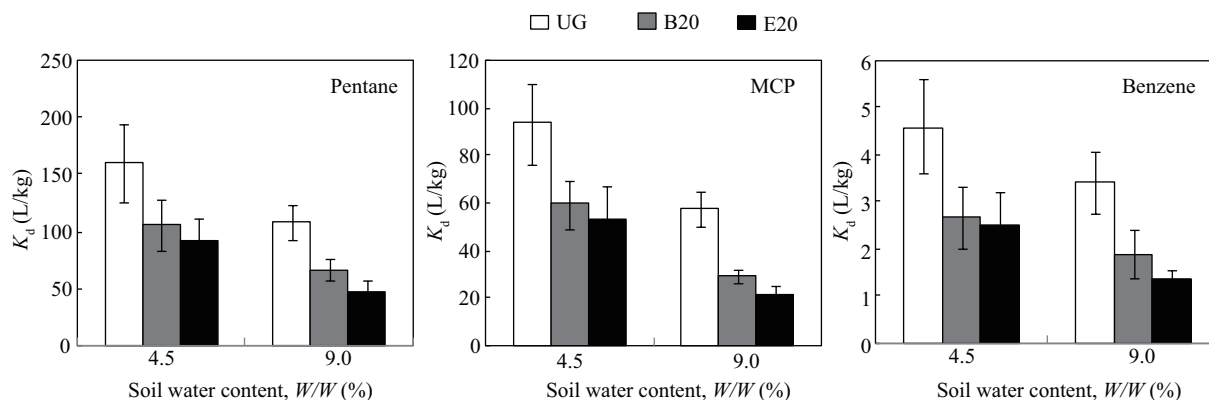

Fig. 5 Average sorption coefficient (K_d) of gasoline compounds with increasing soil water content as a function of gasoline composition.

Table 4   Mass distribution of pentane between vadose zone phases with increasing soil water content as a function of gasoline composition

Day	UG			B20			E20		
	Soil (%)	Air (%)	Water (%)	Soil (%)	Air (%)	Water (%)	Soil (%)	Air (%)	Water (%)
0% water content									
1	97.58	2.42	0.00	96.72	3.28	0.00	96.80	3.20	0.00
8	99.48	0.51	0.00	98.90	1.09	0.00	98.65	1.33	0.00
15	99.69	0.30	0.00	99.34	0.64	0.00	98.84	1.13	0.00
4.5% water content									
1	83.46	16.50	0.03	72.93	27.01	0.06	73.04	26.91	0.06
8	87.91	11.95	0.02	82.48	17.32	0.04	80.97	18.80	0.04
15	90.51	9.69	0.02	85.56	14.16	0.03	82.40	17.28	0.04
9% water content									
1	80.71	19.20	0.08	71.90	27.98	0.12	59.46	40.36	0.18
8	83.48	16.32	0.07	75.87	23.80	0.10	70.28	29.27	0.13
15	86.04	13.68	0.06	79.66	19.90	0.09	75.46	23.96	0.10

gasoline compounds decreased from 106.3 to 66.8 L/kg for alkanes, 59.6 to 29.1 L/kg for cycloalkanes and 2.7 to 1.9 L/kg for aromatics. In contrast, the K_d of E20 gasoline compounds decreased from 91.0 to 47.3 L/kg for alkanes, 52.8 to 22.0 L/kg for cycloalkanes and 2.5 to 1.4 L/kg for aromatics. Overall, the data indicate that an increase in soil water content could reduce the sorptive capability of SOM for gasoline compounds. At all soil water contents, ethanol-blended fuels are likely to be adsorbed less than butanol-blended fuels.

2.2.3 Mass distribution of gasoline compounds between vadose zone phases

Table 4 lists the mass percentages of pentane in the soil, air and water of a 5% f_{om} soil with increasing water content as a function of gasoline composition. The increase in soil water content generally reduced the adsorption of pentane for all blends on the soil but increased their partitioning to the air and water. This reduction was greater in the presence of alcohol. Among the alcohols, the reduction was greater in the presence of ethanol than butanol. The mass distribution trend of E20-pentane and B20-pentane at the different soil water contents shows that at very low soil water content (0–4.5%, W/W) the distribution of the ethanol-blended and butanol-blended gasoline compounds between the vadose zone phases could be relatively similar, but could vary greatly as soil water content increases. Soil water contents of 9% and higher are more realistic in nature than those of 0–4.5%, suggesting that a great difference is likely to exist between the phase distributions of ethanol-blended and butanol-blended gasoline in natural vadose zone. Thus, implying greater risk of groundwater contamination with ethanol-blended gasoline compounds compared with butanol-blended gasoline compounds after spills to natural vadose zone.

3 Conclusions

The effect of ethanol and butanol on the sorption and phase distribution of gasoline compounds in the vadose zone has been compared. The comparison is vital in making informed decision on which alcohol to adopt as future gasoline oxygenate. The results obtained, at varying soil organic matter and water contents, indicated that the use of ethanol-blended gasoline as transportation fuel could result in greater risk of groundwater contamination with gasoline compounds after spills than the use of butanol-blended gasoline.

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