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Effect of alcohol addition on the movement of petroleum hydrocarbon fuels in soil

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Abstract

Groundwater contamination by fuel spills from aboveground and underground storage tanks has been of growing concern in recent years. This problem has been magnified by the addition of oxygenates, such as ethanol and methyl-tertiary-butyl ether (MTBE) to fuels to reduce vehicular emissions to the atmosphere. These additives, although beneficial in reducing atmospheric pollution, may, however, increase groundwater contamination due to the co-solvency of petroleum hydrocarbons and by the provision of a preferential substrate for microbial utilisation. With the introduction of ethanol to diesel fuel imminent and the move away from MTBE use in many states of the USA, the environmental implications associated with ethanol additive fuels must be thoroughly investigated. Diesel fuel movement was followed in a 1-m soil column and the effect of ethanol addition to diesel fuel on this movement determined. The addition of 5% ethanol to diesel fuel was found to enhance the downward migration of the diesel fuel components, thus increasing the risk of groundwater contamination. A novel method using soil packed HPLC columns allowed the influence of ethanol on individual aromatic hydrocarbon movement to be studied. The levels of ethanol addition investigated were at the current additive level (approx. 25%) for ethanol additive fuels in Brazil and values above (50%) and below (10%) this level. An aqueous ethanol concentration above 10% was required for any movement to occur. At 25% aqueous ethanol, the majority of hydrocarbons were mobilised and the retention behaviour of the soil column lessened. At 50% aqueous ethanol, all the hydrocarbons were found to move unimpeded through the columns. The retention behaviour of the soil was found to change significantly when both organic matter content and silt clay content was reduced. Unexpectedly, sandy soil with low organic matter and low silt clay was found to have a retentive behaviour similar to sandy subsoil with moderate silt clay, but little organic matter. It was concluded that sand grains might have a more important role in the adsorption of petroleum hydrocarbons than first realised. This method has shown that soil packed HPLC columns can be used to provide a quick estimate of petroleum hydrocarbon, and possibly other organic contaminant, movement in a variety of different soil types.

1. Introduction

Since the petroleum crisis of the early 1970s, Brazil is the only country that has attempted a large scale programme to substitute a non-renewable fuel source by an entirely renewable one i.e. hydrated ethanol (Massad et al., 1993). Brazil, a country rich in potential to produce vast quantities of biomass, has been a leader in the manufacture of ethanol for fuel use. A large proportion of cars are fuelled exclusively by ethanol and the remaining gasoline sold in petrol stations contains 24% ethanol. Like any other large-scale energy programme, the advantages and disadvantages of ethanol fuel usage have been investigated. Brazil has the land area required to support large-scale biomass production which reduces the need for crude oil importation, has an abundant water supply which is an essential component of ethanol production, and receives a large percentage of the solar radiation that reaches earth. As well as the inherent economic advantages, ethanol addition to fuel is environmentally appealing as it is one of the oxygenates, along with methyl-tertiary-butyl ether (MTBE), used to reduce vehicular emissions of carbon monoxide and ozone precursors to the atmosphere.

The demand for oxygen additives in the USA has largely been driven by regulations imposed by the 1990 Clean Air Act which committed retailers in certain states in the USA with poor air quality to sell petroleum containing at least 2.7% oxygen (Environment Agency, 1999). This led to approximately 80% of the world's production of MTBE being used in the USA. Although MTBE use is relatively low in the UK at the moment, this could change with the new European Union (EU) directive on fuel quality and vehicle emissions (Environment Agency, 1999). However, recent problems of groundwater contamination both in the USA and the UK have shown MTBE to be persistent in subsurface systems and to create taste and odour problems. Oil companies in the USA unanimously supported the use of MTBE until 1997 when Tosco, the largest independent oil refiner in the USA asked the Californian Air Resources Board to 'move away from MTBE use' as extensive contamination would result in huge costs to restore the state's drinking water. In March 1999, California announced plans to phase out MTBE use by 2003 following a number of incidents involving the loss of groundwater supplies due to MTBE pollution (Environment Agency, 1999). In May this year, Senator Tom Harkin (Washington DC) introduced legislation to support ethanol addition to fuel and ban alternatives to ethanol as other fuel additives, such as MTBE, were highly polluting. Harkin's Bill would phase out MTBE use over the next 3 years (YellowBrix, Inc., 2001). It is clear that a decision must be taken on the future use of MTBE based on sound scientific information and the lessons learned from experiences in the USA. The shift towards ethanol use as the common oxygenate added to fuels seems inevitable.

Several studies have been carried out on gasoline-ethanol fuels, but little work has been done on other fuels. With the introduction of 3% ethanol to diesel fuel, which is currently under revision by the Brazilian authorities, and the move away from MTBE use in many states in the USA, the environmental implications associated with ethanol additive fuels must be thoroughly investigated.

Theoretically, the addition of ethanol to gasoline should enhance the downward migration of this contaminant in soil due to increased solubilisation of gasoline components in ethanol and thewetting effect of ethanol on the more hydrophobic soil components. If this is true, then the risk of contamination of groundwater by gasoline is greatly increased when ethanol is present. Gasoline comprises low molecular weight alkanes (C5-C10) and aromatics (mainly benzenes and naphthalenes) with very little polyaromatic hydrocarbons(PAHs). A large proportion of gasoline is made up of BTEX (benzene, toluene, ethylbenzene and *m*-, *o*- and *p*-xylene) components, which are relatively soluble and would degrade readily under the right environmental conditions. The presence of ethanol along with gasoline may, however, retard the degradation of gasoline components, with micro-organisms preferentially utilising

ethanol over gasoline (personal communication). This increases the residence time of gasoline in the soil, which may cause further groundwater contamination problems.

A blend of ethanol with other additives was developed for use with diesel engines. The above implications can be implied for the diesel-additive ethanol situation. Diesel, however, contains a higher percentage of aromatics, which can include up to 3% PAHs. PAHs are of specific concern as they are more persistent in the environment and some PAHs have adverse health effects. Action levels for PAHs in groundwater are very low and contamination by diesel fuel components would pose a serious threat to groundwater quality. The higher concentration of aromatics in diesel may prevent the downward migration of the contaminant due to lower solubility of the aromatics and increased adsorption of the aromatics on soil components. However, the possibility of movement into groundwater must be investigated.

A laboratory study was undertaken to investigate the movement of diesel fuel and various aromatic compounds found commonly in gasoline (toluene, naphthalene) and diesel fuel (naphthalene, 1-ethyl naphthalene, 2,5 dimethylnaphthalene, phenanthrene, anthracene, pyrene and chrysene) through a soil column and to determine if the movement of these compounds is enhanced by ethanol. The effect of soil components on contaminant movement was also investigated.

2. Materials and methods

2.1. Movement of diesel fuel through soil column

2.1.1. Leaching column set up

Polythene drain pipe was cut into sections (length 10 cm i.d. 4 cm). The sections were sealed together using waterproof tape to provide an airtight seal at the joins. Ten sections were fitted together to create a column 1 m in length. As the sections were fitted together, the column filled with John Innes compost No. 2 by tapping the soil into each section to create an evenly packed column. John Innes Compost No. 2 was chosen as a substitute soil as it is prepared from sterilised loam which provided a low microbial activity soil (Adam and Duncan, 2001) with similar textural properties (textural class: sand, 89.8% sand, 4.9% silt, 8.4% clay and 10.2% organic matter (LOI) content) to the natural soil used later in this study. The column was built up, section by section, in this way. The bottom section of the column had a fine Nylon mesh covering the lower end to prevent the soil from escaping, but allowing the leachate to freely drain away. An extra section was placed on the top of the column to provide a collar for the water reservoir. The column was run at a temperature of approximately 15°C to reduce microbial activity in the column. The complete set up of the column is illustrated in Fig. 1.

2.1.2. Procedure

Ten millilitres of diesel fuel oil was added, using a 50-ml syringe, to the top of the column. The diesel fuel was allowed to penetrate into the soil for approximately 30 min. After this time, 50 ml of deionised water was poured in to wet the column, then 2 l of deionised water was added by inverting a 2.5-l plastic bottle into the top of the column. This acted as a reservoir allowing a constant supply of water to leach through the column. The flow rate depended entirely on gravity flow and the density of the soil packed column. It took

approximately 24 h for 2 l of deionised water to leach through the column; therefore, a fresh 2-l reservoir was set up each day. This process was continued for 5 days and provided a total of 10 l of water leached through the column.
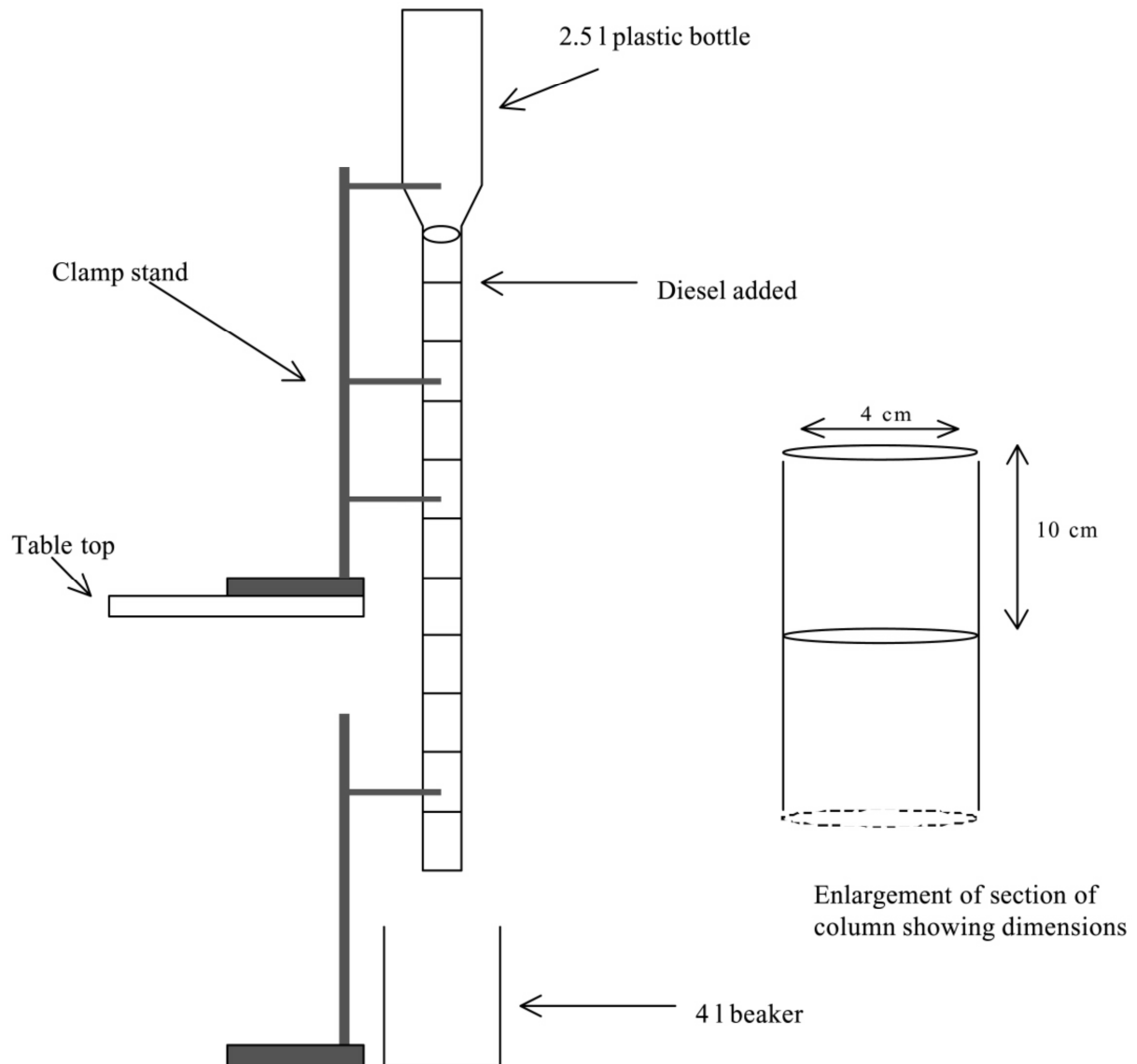

Figure 1. Diagrammatic representation of the leaching column set up. The column consists of 11 sections (one extra section on top of the column to act as a collar for the reservoir) supported by clamp stands. The reservoir is a 2.5-l plastic bottle containing 2 l of water. A 4-l beaker collects the leachate beneath the column.

The column was dismantled one section at a time and a 40-g subsample was taken from each section. The samples were then extracted separately to determine the amount of diesel fuel present in each section. This procedure was repeated using 10 ml of diesel fuel oil

with 5% ethanol additive. Ten litres of water was again leached through the column and the sections dismantled for diesel analysis as above.

2.1.3. Diesel fuel extraction

Due to the short residence time of diesel fuel in the soil column, a method of extraction was developed that allowed the volatile, lighter fuel components to be removed effectively, followed by extraction of the heavier fuel components. A cold shaking extraction method was developed from the mechanical shaking method of Schwab et al. (1999). Fresh soil (40 g; sieved <2 mm) was extracted for 30 min in 100 ml 1:1 acetone:dichloromethane in an orbital incubator (15°C, 200 rev min^{-1}). The extract was filtered (Whatman, No. 2) into a 100-ml volumetric flask and the volume made up with 1:1 acetone:dichloromethane. This extract was analysed by GC-FID using the conditions described below and the total petroleum hydrocarbon (TPH) value calculated.

The 40-g soil sample was left to air dry overnight and was then transferred to a cellulose thimble for Soxhlet extraction. The Soxhlet method was modified from the US EPA method 3540C for non-volatile and semi volatile organic compounds and the method of Song et al. (1990). Anhydrous sodium sulfate (5 g) was added to the bottom of a cellulose extraction thimble, then the air-dried soil sample was added. The thimble was plugged with glass wool, then placed into the Soxhlet apparatus. One hundred ml of 1:1 acetone:dichloromethane was added and the sample extracted for 6 h. Once cool, the extract was transferred, with washings, to a 100-ml volumetric flask and the volume made up to 100 ml with 1:1 acetone:dichloromethane. The extract was analysed by GC-FID as described below and the residual TPH value calculated. The TPH values obtained for each step of the extraction were summed to provide a total TPH value for the sample. Dilution of the original diesel fuel in dichloromethane served as a quantitative analytical standard.

2.1.4. Diesel fuel analysis by GC-FID

The method for diesel fuel analysis by capillary GC-FID was modified from the US EPA method 8100 for the analysis of polynuclear aromatic hydrocarbons (US EPA, 1986). The chromatographic conditions were as follows. Analyses were carried out with a Hewlett-Packard 5890A gas chromatograph and flame ionisation detector (FID). The GC was interfaced with a Hewlett-Packard Chemstation data system. Helium carrier gas was adjusted to the recommended linear flow velocity of 20 cm s^{-1} using the non-retained compound butane. Separations were performed on a SGE BPX 5 polysilphenylene-siloxane capillary column (25 m, 0.32 mm i.d., 0.5 m). A 0.5 µl sample was injected at 35°C with a temperature hold of 3 min. The temperature increased 5°C min^{-1} up to 250°C with a 10-min hold at the end of the run. The injector temperature was 260°C and the detector temperature was 270°C.

2.1.5. Statistical analysis

Triplicate injections of each extract with no more than a 5% difference in total peak area were obtained for each sample. Retention times and peak areas of each replicate injection were tabulated using Microsoft Excel to allow comparison of individual diesel fuel components. Ten assigned peaks were used for verification of acceptable replicate analysis. The average total peak area from the three replicates was calculated and used to work out the total TPH content of that section.

2.2. Movement of individual aromatic hydrocarbons through HPLC column

2.2.1. Preparation of column packing material

The packing materials used in the study were prepared by sieving the initial samples to <150 µm. This provided material, with an acceptable particle size range and narrower particle size distribution, for packing into a HPLC column that would give constant back pressure values and good chromatographic conditions.

The soil used throughout this part of the study was Barassie soil which was collected from Ayrshire, Scotland and has developed from raised beach deposits. The soil has been classed as a freely drained forest soil according to soil series using the soil memoirs and soil maps for the area (Grant et al., 1962). Textural class has been determined as sand from the texture charts prepared by the Soil Survey of England and Wales (Hodgson, 1976). Column G-01 packing material was prepared entirely from sieved Barassie soil (40.5% sand, 21.5% silt, 25.9% clay and 16.7% organic matter (LOI) content). Column G-05 material is the sieved subsoil from the Barassie series. This provides the same soil matrix with lower organic matter, silt and clay content. Column G-05F material is Barassie soil that has been placed in a furnace at 500°C for 6 h to burn off all the organic matter. For control purposes, a column packed with acid washed quartz sand (G-06) and unbonded silica gel columns (G-07 and G-08) was included.

Particle size analysis for the determination of size distribution was carried out by mechanical analysis as described by the modified method of Khan (Ph.D. thesis, University of Glasgow, 1987) from ADAS Method 57 (1986). Organic matter content was assessed by loss on ignition (LOI). A 5-g soil sample was weighed, in triplicate, into silica basins and dried overnight at 105°C. The soils were weighed to obtain the oven dry soil weight. The soils were then placed in a muffle furnace and ignited at 500°C for 6 h. The samples were re-weighed and the weight of ignited soils calculated. The percentage of organic matter by loss on ignition was calculated by subtracting the weight of ignited soil from the weight of oven dry soil. This value was then divided by the weight of oven dry soil and the resulting value multiplied by 100 to obtain the percentage LOI. Table 1 shows the physical characteristics of the six packing materials used in the study.

2.2.2. Column preparation

The prepared material was packed into an empty stainless steel HPLC column (length 100 Mm, i.d. 4.6 mm) by dry tapping. The packed column was attached to a HPLC pump and 50% aqueous ethanol flowed through (0.1-1.5 ml min-1) as a packing solvent. After 30 min, a small portion of soil, saturated in 50% aqueous ethanol, was added to the column head to fill up the crack left by the material shifting during packing. Once the column was successfully packed, 50% aqueous ethanol was run through overnight at 0.1 ml min^{-1}. Acetone was used to measure the void volume.

2.2.3. Petroleum hydrocarbon standards

One hundred mg l^{-1} solutions of toluene (Fisher Scientific International Company, UK., 99+% Analar), naphthalene, 1-ethylnaphthalene, 2,5-dimethylnaphthalene, anthracene, phenanthrene, pyrene and chrysene (Sigma-Aldrich Co. Ltd., UK, 99+%. were prepared in acetone (Riedel-de Häen, Sigma-Aldrich Co. Ltd., UK, Analar).

Table 1 Physical characteristics of the packing materials used in this study

Column	Description	Organic matter LOI %	Particle size distribution			
			Coarse + medium sand %	Fine sand %	Silt %	Clay %
G – 01	Sandy soil	16.68	1.68	38.86	21.56	24.78
G – 05	Sandy subsoil	5.01	36.00	45.33	10.17	6.97
G – 01F	Sandy soil (OM removed)	0.00	1.95	44.75	24.80	28.50
G – 06	acid washed sand (Fisher Scientific Chemicals)	0.00	←—— 100 ——→		0.00	0.00
G – 07	Matrex silica 60 (Fisher Scientific Chemicals)			←—— 100 ——→ (0.070 - 0.0035 mm)		
G – 08	Silica Gel 60H (Merck BDH)				100 ←—→ (0.0015mm)	

Percentage sand values are based on one replicate measurement and percentage silt and clay are based on duplicate measurements. Mechanical analysis recoveries for G – 01 and G – 05 were 103.56 % and 103.48 % respectively. Particle size measurements are based on : coarse sand > 0.18 mm, fine sand 0.18 – 0.05 mm, silt 0.05 – 0.002 mm, clay < 0.002 mm.

2.2.4. Procedure

Each petroleum hydrocarbon standard was added to the selected column individually and varying percentage aqueous ethanol concentrations used as the mobile phase with isocratic elution. The hydrocarbon standards were injected into the column at 1.6 ml min^{-1} and detected by UV at 254, 285 and 335 nm. The flow rate was set for each column at a rate that provided constant back pressure. The chromatographic conditions used for each column are outlined in Table 2. The trend of retention of the hydrocarbons on each column showed good linearity with carbon number, suggesting the column was performing successfully. A good recovery of the petroleum hydrocarbon analytes from each column under these conditions was achieved when the absorbance of the eluent from each column was measured by UV spectrophotometry and compared to the corresponding standard solution. The recoveries for mono- and di-aromatic analytes were ~99% and ~94% for polyaromatic analytes.

Table 2 Chromatographic conditions used for individual packed columns

	Mobile phase					
	25 % aqueous ethanol				water	
Column	G-01	G-05	G-01F	G-06	Silica A	Silica B
Packing weight g^{-1}	1.6	2.6	2.4	2.2	1.2	0.85
Flow ml min^{-1}	1.6	1.6	1.6	1.6	0.8	1.2
Pressure psi	90	600	110	20	100	2000

Pressure measured in lb/in^2 (psi). Metric conversion – 1 psi ~ 7 kPa.

3. Results

3.1. Vertical movement of diesel fuel through a soil column

The results from the 1-m soil columns suggested that the downward migration of diesel fuel in the soil profile was enhanced by ethanol addition. Fig. 2 shows the percentage distribution of diesel fuel in 1-m soil columns leached with 10 l of water, where only diesel fuel had been added and where diesel fuel with 5% ethanol had been added. Little movement of diesel fuel was observed in the diesel fuel only column with diesel fuel distribution decreasing evenly from the top of the column (section 1) to a depth of 30 cm (section 3). Negligible amounts of diesel fuel were found below this depth. Diesel fuel with 5% ethanol, on the other hand, was seen to migrate to a depth of 40 cm and the pattern of diesel fuel distribution in the soil profile was very different from that seen in the diesel fuel only column. Again, the largest percentage of diesel fuel was found in the top 10 cm (section 1). The percentage of diesel fuel in section 2 and 3 decreased, as before, to 22.5% and 13.8%. However, the percentage of diesel fuel in section 4 rose to 24.1% of the total diesel fuel added. No diesel fuel was found in sections below this depth.
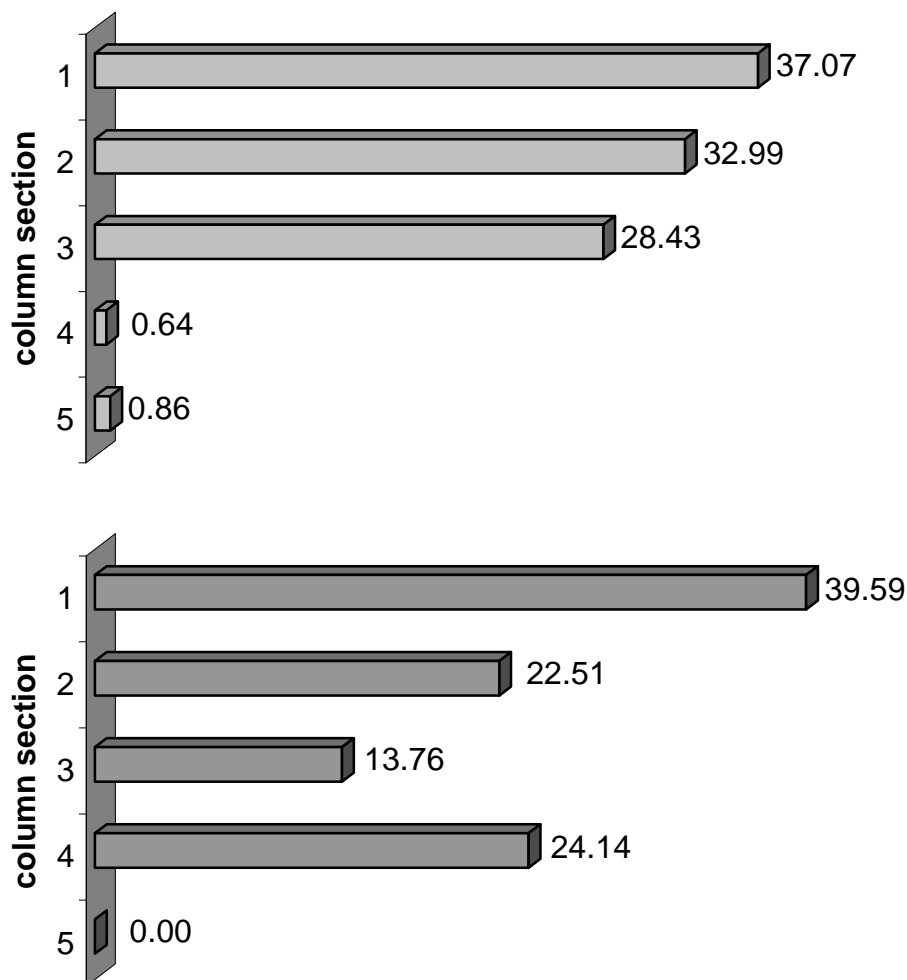
Figure 2. Percentage distribution of diesel in 1-m soil columns for diesel only (top) and diesel plus 5% ethanol (bottom). Only sections 1-5 are shown as no diesel was found in the lower sections of the column (sections 6-10).

3.2. Effect of ethanol on aromatic hydrocarbon movement in surface soil

The concentrations of ethanol required to enhance movement of aromatic hydrocarbons into the subsurface was investigated by a novel method using soil packed HPLC columns. A soil (Barassie: 40.5% sand, 21.5% silt and 25.0% clay) with an average organic matter content (16.7%) was assessed. The Barassie soil was used throughout this investigation as it provided a sandy soil commonly found around the coastal areas of Scotland. A soil with sandy texture was assessed as it provided a fragile soil system which would illustrate the worst case scenario on the environmental impact of ethanol additive fuels on Scottish soils. Aqueous ethanol concentrations ranging from 0-50% ethanol were used as the mobile phase in this column (G-01). An aqueous ethanol concentration of above 10% was required before any movement of aromatic hydrocarbons was observed. At a 25% aqueous ethanol concentration,

the lighter, more soluble aromatic hydrocarbons eluted slowly from the column whereas the larger aromatics (1,5 dimethyl naphthalene, phenanthrene, anthracene, pyrene, chrysene) were retained on the column (Table 3). Toluene, naphthalene and 1-ethyl naphthalene had retention times of 2.49, 9.86 and 28.00 min, respectively. The length of time taken for these hydrocarbons to be eluted from column G-01 suggests the soil packing has hydrophobic sites capable of retaining aromatic hydrocarbons but the adsorption of the lighter hydrocarbons on these sites can be overcome by 25% aqueous ethanol. When the aqueous ethanol concentration of the mobile phase was raised further to 50% ethanol, all the aromatic hydrocarbons added could be eluted from the column and the time taken for elution was much less than with 25% ethanol. This implies that increasing concentrations of ethanol lessened the retentive behaviour of the soil column. This result is not unexpected, as ethanol breaks the surface tension of repellent soil, allowing increased penetration (King, 1981). Table 3 shows the retention time (t_R) and capacity factor (k') of hydrocarbons on the sandy soil column (G-01) using different ethanol mobile phase concentrations. Capacity factors are included as, although a peak can be identified by its retention time, this varies with column length and mobile phase flow rate (Lindsay, 1992). The same column lengths are used throughout this experiment, but the mobile phase flow rates differ. By using capacity factors instead of retention times, a direct comparison can be drawn between different column results. The results clearly show that ethanol enhances hydrocarbon mobility and increasing ethanol concentration, in turn, increases the mobility of the hydrocarbons.

3.3. Influence of soil components on aromatic hydrocarbon movement

To determine what effect various soil components had on the adsorption of aromatic hydrocarbons, a series of soil columns were prepared with varying ratios of organic matter, sand, silt and clay. Column G-05 was prepared from the subsurface soil of the Barassie series used in column G-01. This subsurface soil consisted of a very large proportion of sand (approx. 81%) with low organic matter content (approx. 5%), silt (approx. 10%) and clay (approx. 7%). Column G-01F was packed from the Barassie soil used in column G-01 that had been ignited for 6 h in a 500°C furnace to remove all the organic matter. Column G-06 is a manufactured quartz sand (Fisher Scientific Chemicals, 40-100 mesh) which provided a measure for the mineral fraction of soil and, finally, columns G-07 and G-08, which are packed with unbonded silica of varying particle size. Column G-07 contains particles in the fine sand to silt range, whereas column G-08 contains only silt sized particles. Fig. 3 shows the trend in retention of hydrocarbons on various soil columns. Ethanol (25%) was used as the mobile phase as it was found to enhance hydrocarbon mobility in the original soil column (G-01) and has an important environmental value, as fuel in Brazil and many states in the USA contain 24% ethanol (Massad et al., 1993).

The original soil column (G-01) which contained average organic matter, sand, silt and clay contents had the highest adsorptive capacity for petroleum hydrocarbons. This is shown in Fig. 3 by the trend in retention lying above all the other column values as increasing ln k' values indicate increased retention of hydrocarbons due to increased adsorption to soil sites.

The sandy subsoil (column G-05), which contained high levels of sand but low levels of organic matter, silt and clay, had the next highest adsorptive capacity. The presence of organic matter appeared to be the most important factor in the adsorption of petroleum hydrocarbons because when all the organic matter was removed, as in column G-01F, the retentive behaviour of the soil column was drastically reduced. Petroleum hydrocarbons with a carbon number below 14 were not retained at all on the column but eluted along with the solvent front. However, some retention of the larger petroleum hydrocarbons, such as

phenanthrene, was observed suggesting other factors were involved in retaining hydrocarbons on soil. Column G-06, which is a manufactured sand of narrow particle size range, also showed signs of retaining larger aromatic hydrocarbons suggesting sand particles themselves have some retentive behaviour.

Table 3. Retention time (t_R) and capacity factor (k') of hydrocarbons on the Barassie soil column (G-01) using different ethanol mobile phase concentrations.

	Mobile phase			
	25% EtOH		50% EtOH	
Hydrocarbon	t_R	k'	t_R	k'
Acetone,	$t_o = 0.78$		$t_o = 0.78$	
toluene	2.49	2.19	1.40	0.79
Naphthalene	9.86	11.64	1.45	0.86
1 ethyl naphthalene	28.00	34.89	2.35	2.01
1, 5 dimethyl naphthalene	-	-	2.61	2.35
phenanthrene	-	-	4.28	4.49
anthracene	-	-	4.55	4.83
pyrene	-	-	6.69	7.58
chrysene			18.00	22.08

Capacity factor k' = t_R - t_o where t_R is the analyte peak retention time and t_o is the peak of the unretained solvent front.
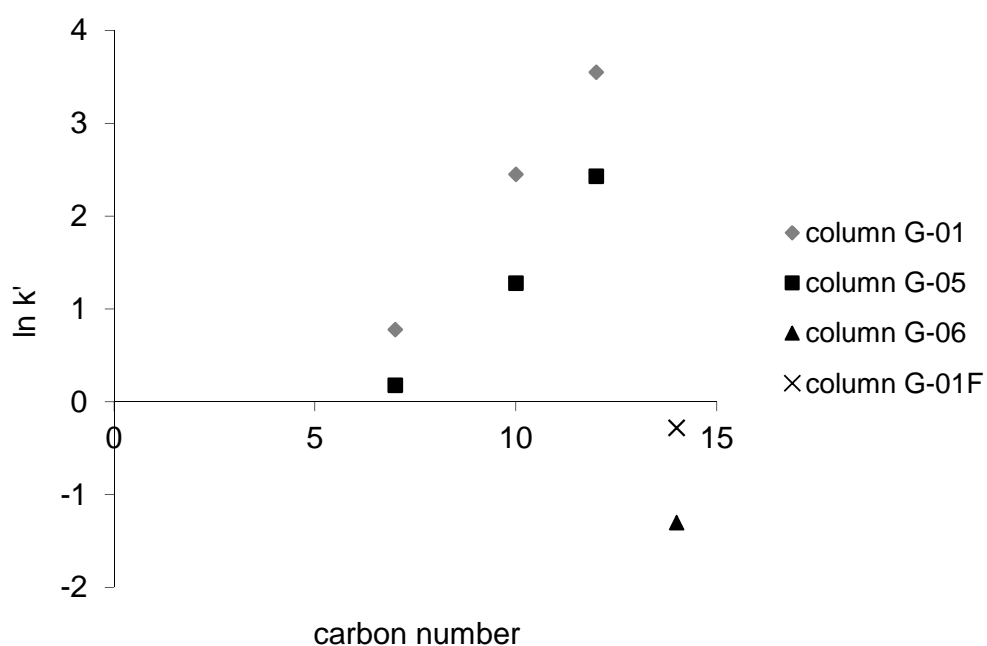
Figure 3. Trend in retention of hydrocarbons on various soil columns. Carbon number relates to : C7 – toluene, C10 – naphthalene, C12 – 1 ethyl naphthalene and 1, 5 dimethyl naphthalene, C14 – phenanthrene and anthracene, C16 – pyrene and C18 – chrysene.

3.4. Influence of sand particle size on aromatic hydrocarbon movement

Two silica columns were tested to distinguish between the influence of particle size on hydrocarbon retention. The results are given in Table 4. The silica used as packing material in these columns (G-07 and G-08) had no surface coatings hence, they had little adsorptive capacity. Because of this water was used as the mobile phase. Column G-07 had a larger particle size distribution (diameter ranging from 0.0035 to 0.70 mm) than column G-08 (0.0015-mm particle size diameter). This was reflected by the capacity factors of the aromatic hydrocarbons on each column. The time taken for elution of each hydrocarbon was almost double on column G-08 compared with column G-07. These results show that mineral particles such as sand, may influence the adsorption of hydrocarbons even when they are not coated with organic matter or other active functional groupings.

Table 4. Retention times and capacity factors for petroleum hydrocarbons on silica columns with varying particle size ranges

	Mobile phase : water			
	Column G-07		Column G-08	
Hydrocarbon	t_R	k'	t_R	k'
Acetone,	$t_o = 1.47$		$t_o = 2.86$	
toluene	2.10	0.42	4.81	0.68
Naphthalene	3.81	1.19	7.83	1.73
1 ethyl naphthalene	5.97	2.43	15.72	4.49
phenanthrene	6.17	2.54	18.95	5.62

4. Discussion

An important factor on diesel fuel entering a soil system is its subsequent movement, both lateral and vertical, in the soil profile. Rainfall can encourage contaminant leaching through the soil profile which can lead to surface water and groundwater contamination. Diesel fuel, due to its hydrophobic character, should not move far in the soil profile. However, this statement is highly dependent on the characteristics of the soil that the diesel fuel is contaminating and whether diesel fuel is contaminating from an aboveground or underground source. The difference in the surface and subsurface soil characteristics allow diesel fuel, on entering these systems, to behave very differently.

The pattern of diesel fuel distribution in the 1-m soil column clearly showed the enhancement of diesel fuel movement through the soil column due to a 5% ethanol addition. This finding is significant as the 5% additive value used is close to the 3% additive value proposed by the Brazilian authorities for addition to diesel fuel. Gas chromatographic analysis of diesel fuel extracted from each soil section resulted in traces whose pattern of hydrocarbon distribution was very similar. There was no indication that specific components or fractions of the diesel fuel were being mobilised and moving further down the soil profile than other components or fractions of the diesel fuel. This implies that the effect ethanol has on enhancing diesel fuel movement in the soil may be due to the 'wetting' effect of ethanol on the soil components allowing mass movement of diesel fuel. Hydrophobic, soil organic matter components such as humic, fulvic and fatty acids, impart a water repellent character to a soil (Anderson et al., 1995). Ethanol has been used in many studies on water repellent soils (King, 1981; Roy and McGill, 1997) as it can break the surface tension of repellent soil, allowing increased infiltration. Ethanol present within diesel fuel would, therefore, enhance infiltration of diesel fuel into the soil profile by lessening the adsorptive capacity of the hydrophobic sites of soil organic matter components. This allows diesel fuel to move further down the soil profile. By further increasing the concentration of ethanol in diesel fuel, enhanced movement of diesel fuel into the subsurface would be observed. This conclusion was verified by the results from the soil packed HPLC columns. Individual petroleum hydrocarbon movement was seen to increase with increasing ethanol content.

The characteristics of the contaminated soil were also important in influencing the movement of petroleum hydrocarbons. The percentage organic matter present was extremely important in retaining hydrocarbons. Organic matter is found at high levels in the surface soil and decreases to small amounts in subsurface soils. Therefore, petroleum hydrocarbons contaminating from an aboveground source would not migrate far in the soil profile due to adsorption by organic matter. If petroleum hydrocarbons were contaminating from an underground source, the amount of organic matter in subsurface soils is minimal; therefore, increased movement of contaminants would be expected. This theory was verified by the results obtained from the subsurface soil column (G-05) and the column with no organic matter (G-01F). However, the results obtained during this investigation using various sandy soils and surrogate sand columns indicate that other factors may be involved in the adsorption of petroleum hydrocarbons. Other authors have found that sandy soil can bind hydrocarbons adsorptively, although neither silty material nor significant amounts of organic matter were present. Loser et al. (1999) proposed that soil particles were covered with micropores, which enlarge the soil surface area in comparison with the macroscopic surface area. The authors found the microscopic surface of the model soil, estimated by the Brunauer Emmett Teller (BET) method, to be 120 times larger than the macroscopic surface, measured as the specific surface area. This microporosity is the reason for hydrocarbons being more strongly adsorbed to sandy soils than expected (Loser et al., 1999). This theory seems a likely explanation for the slightly retentive behaviour of both the silica columns tested (G-07 and G-08) and the sandy soil column with no organic matter present (column G-01F).

5. Conclusion

These results suggest a greater possibility of groundwater contamination by petroleum hydrocarbons in ethanol additive petrol and diesel fuel spills occurring from both underground storage tanks and aboveground spills. Surface soil components such as soil organic matter, as well as silt and clay, play an extremely important role in retaining petroleum hydrocarbons near the soil surface. However, ethanol was shown to enhance the

movement of both individual aromatic hydrocarbons and diesel fuel by lessening the adsorptive capacity of the surface soil components. If these petroleum hydrocarbons reach the subsurface level, the low organic matter content and lower silt and clay content will allow hydrocarbon migration to occur more freely. In addition, an underground petroleum hydrocarbon spill, which would normally migrate and contaminate groundwater quite readily, would be further enhanced by the addition of ethanol.

This work has shown the benefits of using soil packed HPLC columns to better understand the role of soil components in determining movement of petroleum hydrocarbons. The method could be used to provide a quick estimate of petroleum hydrocarbon and other organic contaminant movement in a variety of differing soil types.

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