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The use of biofuels has the potential to decrease greenhouse gas emissions. The potential for environmental risk should be accounted for. A labortory study was undertsken for predicting the fate and transport of hydrophobic organic compounds in the subsurface in the event of a biofuel spill. The spill scenarios generated can assist in the assessment of biofuel-contaminated sites.

Assessing Soil and Groundwater Contamination from Biofuel Spills

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Abstract

Future modifications of fuels should include evaluations of the proposed constituents for their potential to damage environmental resources such as the subsurface environment. Batch and column experiments were designed to simulate biofuel spills in the subsurface environment and to evaluate the sorption and desorption behavior of target fuel constituents (i.e., monoaromatic and polyaromatic hydrocarbons) in soil. The extent and reversibility of the sorption of aromatic biofuel constituents onto soil were determined. When the ethanol content in ethanol-blended gasoline exceeded 25%, enhanced desorption of the aromatic constituents to water was observed. However, when biodiesel was added to diesel fuel, the sorption of target compounds was not affected. In addition, when the organic carbon content of the soil was higher, the desorption of target compounds into water was lower. The empirical relationships between the organic-carbon normalized sorption coefficient (K_{oc}) and water solubility and between K_{oc} and the octanol-water partition coefficient (K_{ow}) were established. Column experiments were carried out for the comparison of column effluent concentration/mass from biofuel-contaminated soil. The dissolution of target components depended on chemical properties such as hydrophobicity and total mass of biofuel. This study provides a basis for predicting the fate and transport of hydrophobic organic compounds in the event of a biofuel spill. The spill scenarios generated can assist in the assessment of biofuel-contaminated sites.

Keywords: sorption, cosolvent effect, ethanol-blended gasoline, biodiesel

1. Introduction

In the present energetic context, diversifying fuel sources has become essential for meeting the growing world energy demand in a sustainable way. Biofuels derived from renewable resources represent an attractive source of energy because they generate a smaller greenhouse effect than fossil fuels. Such an objective implies the conversion of biomass into biofuels. The biofuels that are currently available are ethanol and ethyl tert-butyl ether (ETBE) for gasoline engines and biodiesel for diesel applications, which is produced from the trans-esterification of vegetable oils. Ethanol can be mixed with conventional gasoline and biodiesel with fossil diesel to different concentrations.

As biofuels are becoming widely used, their fate in the subsurface environment is an area of concern. For instance, ethanol is blended into gasoline to add octane and oxygen, and it may help reduce certain types of emissions. However, ethanol is water miscible; once ethanol-blended gasoline spills occur, ethanol will be at the front of the contaminant plume.[1-4] Therefore, ethanol tends to be attenuated in the unsaturated zone and in groundwater.[2,3] Previous batch equilibrium experiments have indicated that the concentrations of benzene, toluene, xylene and other hydrocarbons can be significantly enhanced when the ethanol concentration in the aqueous phase is greater than 10% (v/v).[5-8] Benzene was enhanced by a factor of 1.2 at 10 vol% ethanol.[5] Enhancements increased in proportion to the ethanol concentration, and enhancements were much greater for lower solubility compounds (e.g., enhancement for 1,2,4-trimethylbenzene >> benzene).[5-8] Additionally, ethanol may reduce the biodegradation rates of aromatic fuel components in the subsurface in both transient and near steady-state conditions.[9-12]

Variability in the biofuel-water partitioning of major aromatic constituents (i.e., benzene, toluene, ethylbenzene, and xylene (BTEX)) and methyl tert-butyl ether (MTBE) have been examined for ethanol-blended gasoline.[8] Ethanol at low percentages (below 5%),

was shown to have minimal or negligible cosolvent effects on hydrocarbon partitioning.[6] In the case of high fuel-to-water ratios (e.g., 1:1) or near the contaminant source zone, the cosolvent effect of gasoline with high ethanol content (e.g., 85%) is environmentally significant.[5,7,8]

Biodiesel is used to formulate a range of mixtures from 1% biodiesel blended with 99% fossil diesel to pure FAME (100% biodiesel), and is known by the percentage of biodiesel with a B-prefix. Since current blends typically range from 1% (B1) to 20% (B20) biodiesel, the partition coefficients of polynuclear aromatic hydrocarbons (PAHs) between biodiesel fuel mixtures (i.e., B1, B5, and B20) and water were determined.[13] Models were derived using the Raoult's law convention for the activity coefficients and the liquid solubility. The observed inverse, log-log linear dependence of the biodiesel-water partition coefficients of target compounds on the aqueous solubility were well predicted by assuming biodiesel to be an ideal solvent mixture.[13] The experimental partition coefficients were compared with calculations by polyparameter linear free energy relationship (PP-LFER) approaches. The experimental partition coefficients were generally well reproduced by PP-LFER.[13]

The chemical composition of biofuel products is complex and may change over time following release into the environment. Biofuel components might contaminate drinking water resources as a result of transfer from released constituents to groundwater followed by advective transport to a public or private well. However, most biofuel constituents are only weakly soluble in water and highly sorptive to aquifer solids. Therefore they are retarded with respect to groundwater flow or substantially biodegraded in the subsurface before migration to drinking water wells.

Risk-based analyses of biofuel-contaminated sites is hampered by a lack of readily available knowledge describing the fate and transport of biofuel products in the subsurface environment. This problem is magnified by biofuel additives. A thorough understanding

of the environmental behavior of biofuels and the influence that biofuel additives may have on the fate of other fuel constituents is needed. Thus, the objectives of this study were to (1) investigate the desorption of aromatic constituents from biofuel-contaminated soils, (2) assess any cosolvent effects of ethanol on the sorption of major components when a biofuel spill occurs, and (3) evaluate the leaching pattern of contaminants from biofuel-contaminated soil in the subsurface environment.

Materials and Methods

Biofuel products

The biofuels investigated in this study were ethanol-blended gasoline and biodiesel fuel. The E3 (gasoline with 3% ethanol), regular gasoline (research octane number 95), and B1 (1% biodiesel blended with 99% fossil diesel) were obtained from a major supplier (i.e., Chinese Petroleum Corporation (CPC)) in Kaohsiung, Taiwan. Ethanol-blended gasoline containing 10, 25, and 85% ethanol, respectively, was prepared by mixing regular gasoline (research octane number 95, CPC 95) and ethanol in the laboratory. B100 biodiesel was obtained from a production plant in southern Taiwan. B5 and B20 biodiesel were prepared by mixing the proper volumes of diesel and biodiesel fuels in the laboratory. The fuel products were transferred to different glass containers with Teflon-lined caps and stored in the dark at 4°C.

Biofuel-contaminated soils

The soil samples used in this study were collected in Kaohsiung, Taiwan. Upon receipt, the samples were wet-sieved through a 2 mm sieve, homogenized, and stored at 4°C in glass bottles with Teflon® lined caps. The samples were labeled S-1, S-2, and S-3. The physical and chemical properties of the soil samples were determined prior to initiation of the

experiments. The moisture content of the soil samples was determined by weighing approximately 10 g of soil before and after oven drying at 105°C for 24 hours. For the soils used, the moisture contents were 1, 3, and 12%, respectively (dry weight basis). Soil particle size distribution was determined using the hydrometer method.[14] Soil S1 contained 77% sand, 16% silt, and 7% clay. Soil S2 consisted of 70% sand, 21% silt, and 9% clay. Soil S3 was composed of 66% sand, 22% silt, and 12% clay. All the soil texture fell into sandy loam. Organic carbon was determined by the Walkley-Black procedure with manual titrimetric quantitation. The three soil samples (S-1, S-2, and S-3) with organic carbon contents of 2.6, 4.5, and 10% were prepared for sorption studies.

To ensure that sorption reached equilibrium in a reasonable time, a preliminary study was conducted to determine the proper equilibration time when biofuels contact soil. It was found that 24 hours was suitable for the constituents of ethanol-blended gasoline and biodiesel to reach equilibrium with soil. Ethanol-blended gasoline-contaminated soil was prepared by mixing 0.1, 0.5, or 1 mL of ethanol-blended gasoline with 10 g of soil and shaking for 24 hours in the dark at a constant temperature (20°C) to represent different contamination levels. Headspace in the vials was kept to a minimum. Biodiesel-contaminated soil was prepared by mixing 2, 4, or 6 mL of biodiesel with approximately 10 g of soil and shaking for 24 hours in the dark at constant temperature (20°C).

Batch sorption experiments

The equilibrium concentrations of aromatics in soil/water systems were determined by batch sorption experiments. The target aromatic compounds were BTEX and PAHs. The experimental setup was run in six replicates. Approximately ten grams of biofuel-contaminated soil was placed in a reaction vial containing 10 mL of deionized (D.I.)

water with 0.01 N calcium chloride to equilibrate for 24 hours on a shaker at room temperature (22±2°C). The calcium chloride was used to improve soil particle coagulation and settling after attaining equilibrium. After shaking, the aqueous and soil phases were separated by centrifugation. Prior to analysis, the aqueous samples in ethanol-blended gasoline/soil experiment were filtered with a 0.45 μm PTFE filter, and 2 gram of soil sample was extracted by adding 10 mL of methanol.

Soils from the biodiesel/soil experiment were extracted in triplicate using a batch extraction method developed in earlier study.[15] Approximately 5 g of soil was placed in a 35-mL Kimax tube and sequentially extracted with 1:1 v/v methanol-methylene chloride in the biodiesel/soil experiment. The aqueous sample in the biodiesel/soil experiment was extracted three times with 10 mL of methylene chloride. A sorption coefficient (K_p) that expresses the relationship between a component's concentration in soil (C_s) and the aqueous phase (C_w) was calculated for the target compounds:

$$K_p = C_s/C_w \quad (1)$$

Column experiments

Spills of biofuel in the contaminated subsurface environment were simulated by column experiments. The miscible displacement technique was adopted for all experiments.[16,17] This technique involves the displacement of a solution through a column packed with a material of interest.[17] In the spill experiments with ethanol-blended gasoline, stainless columns (1.5 cm i.d., 6 cm in length) packed with soil were employed to simulate spills of ethanol-blended gasoline in the subsurface environment. Each column was used for only one spill experiment. The column was saturated by flushing with an aqueous 0.01 N $CaCl_2$ solution for three hours (approximately 20 to 25 pore volumes) under continuous flow conditions with a flow rate of 0.576 mL/min. Once the soil was saturated, the column was

placed in a horizontal position to minimize density-driven flow patterns. An injection of 1 mL of ethanol-blended gasoline was applied to represent an ethanol-blended gasoline leak to the subsurface environment. After stopping the injection of ethanol-blended gasoline, the column was allowed to saturate for 48 hours. Water (containing 0.01 N $CaCl_2$) was pumped through the column at a flow rate of 0.96 mL/min for three hours (approximately 43 to 45 pore volumes). The effluent from the soil columns was collected continuously. The effluents were stored in 5 mL glass vials with Teflon® lined septa at 4°C before headspace GC/FID analysis.

Glass columns (4.8 cm i.d., 15 cm in length) (Kontes Scientific Glassware, New Jersey) packed with soil were employed to simulate spills of biodiesel in the subsurface environment. The columns had Teflon® endplate fittings that were held in place by screw caps. The column was saturated by flushing with an aqueous 0.01 N $CaCl_2$ solution for four hours under continuous flow conditions with a flow rate of 0.576 mL/min. A continuous injection of biodiesel was applied to represent a biodiesel spill in the subsurface environment. Biodiesel was injected into the column at a flow rate of 0.576 mL/min for seventy minutes (approximately 40 mL of biodiesel). After stopping the injection of biodiesel, the column was allowed to saturate for 48 hours. Then, water (containing 0.01 N $CaCl_2$) was pumped through the column at a flow rate of 0.96 mL/min for three hours. This represents groundwater flow past the biodiesel spill site after biofuel leakage/spillage had stopped. The effluent from the soil columns was collected continuously every 30 mL. The effluents were stored in 40 mL glass vials with Teflon® lined septa at 4°C before PAH analysis. To assess the elution profile, zero moment analysis was conducted to calculate the mass of hydrophobic organic compounds (HOCs) mobilized by groundwater.

Analysis of target compounds

The aqueous and soil samples from the sorption and column studies of ethanol-blended

gasoline were analyzed by an Agilent 6850 gas chromatograph/flame ionization detector (GC/FID) equipped with a Teledyne Tekmar HT3 static/dynamic headspace system (Teledyne Tekmar, USA). The individual vials were heated to 85°C and allowed to equilibrate for 50 min. Each sample was mixed by mechanical vibration for 5 min during this equilibration period. Each vial was pressurized with helium carrier gas to a pressure of 10 psi. The transfer line temperature was 150°C. The total run time including pressurized equilibration time, loop fill pressurization, and stabilization time was 55.2 min.

The aqueous samples from the sorption and column experiments with biodiesel were filtered with a 0.45 μm PTFE filter and extracted three times with 10 mL of methylene chloride. The extract was dried by passing it through a sodium sulfate column to remove residual water, and the extract volume was concentrated to 3-5 mL using a rotary evaporator. The extract volume was further reduced under a gentle stream of nitrogen to 1 mL. The extracts were transferred to 1 mL crimp-seal vials and refrigerated (4°C) until analysis.

Biodiesel-contaminated soil samples from both experimental settings were extracted in triplicate using a batch extraction method as described in the batch sorption experiment section. A portion of each contaminated soil sample was spiked with a 0.5 mL solution of surrogate compounds two hours prior to extraction as a quality control. The surrogate spiking solution contained naphthalene-d_8, anthracene-d_{10}, perylene-d_{12}, 2-fluorobiphenyl, and p-terphenyl-d_{14}. Each chemical was spiked into the soil at a level of 20 mg/kg. The subset of soil samples spiked included one for each biodiesel sorption experiment.

The extracts were analyzed for PAHs by an Agilent 6890/5973 GC/MS. Analytical separation was achieved with a 0.32 mm i.d., 30 meter, fused silica HP-5MS (5% phenyl-95% di-methylpoly siloxane) column with a 0.25 μm film thickness (Agilent J & W, USA). The temperature program included a 2 min hold time at 50°C, temperature ramping at 20°C/min to 130°C followed by 3 min hold time, then temperature ramping at 12°C/min to

180°C, ramping at 7°C/min to 275°C, with a final ramp at 5°C to 300°C with 4 min hold time. Helium was the carrier gas at a flow rate of approximately 1.0 mL/min. Both injector and detector temperatures were maintained at 250°C. The acquisition parameters for the MSD were as follows: mass range 50-400 amu, scan rate 5.46 s, acquisition time 35.74 min, filament delay 180 sec, mass defect 100 amu/100 amu, background mass 45 amu, electron energy 70 eV, electron multiplier voltage 1694 eV, and transfer line temperature 250°C. Internal standard calibration was performed during GC/MS analyses. The internal standards included naphthalene-d_8, acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}.

Results and Discussion

Batch sorption experiments

The results in Table 1 indicate that the BTEX and MTBE in ethanol-blended gasoline were not sorbed to the soil matrix as strongly as the aliphatic components, and they were more likely to contaminate larger water volumes. The sorption of HOCs is controlled by contaminant characteristics such as solubility, polarity and the octanol-water partition coefficient (K_{ow}).[18,19] In addition, sorption is influenced by the characteristics of the fluid medium and the organic matter content of the soil.[19] Overall, the sorption coefficients of the HOCs paralleled their hydrophobicity. The sorption coefficient of MTBE was the lowest among the compounds investigated as anticipated. However, it should be noted that MTBE is typically absent in ethanol-enriched fuels (i.e., E25 or E85). In most cases, the sorption coefficients of the target compounds in regular gasoline onto soil were the highest in the near-source zone (i.e., biofuel/soil/water ratio=1:1:1) due to its maximal content of target compounds.

Previous studies indicated that ethanol-enriched gasoline has a greater impact on soil

and groundwater than regular gasoline due to a variety of effects.[1,8,20] Ethanol-blended gasoline also undergoes a phase separation on contact with water, with ethanol reverting to the aqueous phase, increasing its volume. The effect of ethanol on sorption was more observable at the higher fuel/soil/water ratios in this study. The K_p values decreased with increasing levels of ethanol in the ethanol-blended gasoline. However, at the low biofuel/soil/water ratio (1:10:10) representing residual ethanol-blended gasoline contamination, the K_p values displayed greater variation than under near-source contamination. The non-parametric Mann-Whitney U test (Wilcoxon Rank Sum W test) and Kruskal-Wallis one-way ANOVA were generally used to compare outcomes between two and more than two independent groups, respectively. Thus, these two tests were used to analyze the difference in the sorption coefficients of the target compounds in the various gasoline products ($p<0.05$ as a significance level). A significant difference was found between ethanol content and the sorption coefficients of target compounds ($p<0.05$). Overall it was observed that the addition of ethanol led to reduced sorption of target compounds by soil, and therefore it may increase the spreading groundwater contamination.

The addition of cosolvents has been shown to increase the mass transfer rate in sorption.[21-24] It is anticipated that ethanol will decrease the retardation and sorption coefficients of target compounds in biofuels. For the sorption of HOCs from aqueous-organic binary solvent mixtures, the sorption coefficient is predicted to decrease exponentially as the fraction of organic solvent increases. A log-linear cosolvency model has been established to relate the equilibrium sorption coefficient (K_p) to the volume fraction of cosolvent in a binary mixed solvent.[25,26] The equation is expressed as:

$$\log K_{p,b} = \log K_{p,w} - \alpha\beta\sigma f_c \qquad (2)$$

where $K_{p,b}$ and $K_{p,w}$ are the equilibrium sorption constants for binary solvent and aqueous systems, respectively, α is a nonideality coefficient that accounts for cosolvent-sorbent

interactions, β accounts for water-cosolvent interaction, and σ is the cosolvency power of the cosolvent.

The cosolvent effect of ethanol was evaluated by calculating cosolvency powers for three soils. The cosolvent effect of ethanol on the sorption of MTBE was the smallest ($\alpha\beta\sigma$=0.92, 1.03, and 2.51, respectively, in the three soil samples) for the sorption of ethanol-blended gasoline onto soil. The reduction in the $K_{p,b}$ of benzene under the influence of ethanol was the highest ($\alpha\beta\sigma$=2.82, 3.13, and 4.22, respectively, in the three soil samples). Due to the high affinity of HOCs for the organic carbon in soil, cosolvent-induced inhibition of HOC sorption was more pronounced in soil with higher organic carbon content (i.e., S-3 in contrast to S-1).

The sorption coefficients of PAHs increased with higher organic carbon content in batch soil-water systems as illustrated in Table 2. The sorption coefficients of phenanthrene and fluoranthene were the highest among the PAHs investigated. For the same PAH compound, a reduction in PAH sorption from B1 to B20 was anticipated due to the lower PAH content of biodiesel. On the other hand, with the addition of more biodiesel, the increased viscosity of the biodiesel may inhibit the partitioning of PAHs from the soil phase into water. Previous studies have indicated that viscosity affects the partitioning of PAHs from motor oil to the water phase.[27] The influence of viscosity on rate may reflect the slower diffusion of aromatic substrates in more viscous oils and their subsequent slower mass transfer to water. Viscosity could also affect the rate of microbial utilization of petroleum hydrocarbons. The rate and extent of biodegradation decrease with increasingly viscous nontoxic nonaqueous phase liquids (NAPLs).[28] Given the combined effect of these two factors, the K_p values showed a greater variation than those of ethanol-blended gasoline. Additionally, this variation may depend on the composition of the soil's organic matter.[29-31] For the highly hydrophobic PAHs, their concentration in solution is often relatively low. Thus, the

measured sorption coefficients risk being analytical artifacts, in particular, the measurements of PAHs in aqueous phase. This may be the cause of low sorption coefficients for fluoranthene and pyrene in S-1 observed in this study.

The sorption of a target compound is related to the organic carbon content of the soil.[19] Examining the normalized sorption coefficients (K_{oc}) of BTEX and MTBE derived from K_p in this study, the addition of ethanol leads to a decrease in K_{oc} (Table 3). Generally the K_{oc} value correlates with the K_{ow} of target compounds. Careful determinations of nonionic organic compound sorption from regular gasoline into natural organic matter appear to yield log K_{oc} values that differ from previously reported values by approximately 0.37 to 0.96 log units. The log K_{oc} value for MTBE indicates a low potential for sorption onto aquifer material. The K_{oc} for BTEX in E85 was approximately 1.3 to 1.5 log units lower compared to regular gasoline.

The sorption of PAHs in biodiesel onto soil is stronger comparing to BTEX and MTBE. The sorption of HOCs from biodiesel is directly related to the organic carbon content of different soils. It was observed that PAH sorption was approximately 3 to 5 times higher with S-3 than S-1 (Table 2). The K_{oc} values for phenanthrene, fluoranthene, and pyrene were the highest, whereas that for naphthalene was the lowest as anticipated (Table 3). In Figure 1, the measured K_{oc} values are plotted versus the predicted values. Substantial evidence has indicated that the equilibrium partitioning model may not be sufficient to describe the sorption of HOCs in soil because organic matter is heterogeneous and sorption is governed by nonequilibrium processes.[30,31,33] K_{oc} values were found to vary up to a factor of 100 between different soils and/or sediments.[31] Therefore, the correspondence between the measured and predicted K_{oc} values was considered to be acceptable. The empirical relationship between K_{oc} and water solubility (S) and between K_{oc} and K_{ow} were established as follows:

$$\log K_{oc} = 0.6212 \log K_{ow} + 0.7919 \qquad r^2 = 0.915 \qquad (3)$$

$$\log K_{oc} = -0.4172 \log S + 3.5475 \qquad r^2 = 0.926 \qquad (4)$$

These empirical equations will enable the sorption behavior of biofuel contaminants to be quantitatively estimated in the event of a biofuel spill.

Column experiments

Liquid samples from the column effluent that interacted with biofuel-contaminated soil were analyzed for target HOCs. In the case of a biofuel spill in the subsurface environment, the aquifer may be contaminated with hydrophobic fuel constituents (e.g., aromatic compounds). The initial residual biofuel saturation was calculated for each soil sample from the entrapped volume of biofuel divided by the void volume of the column. This value ranged from 0.19 to 0.27 within columns contaminated with ethanol-blended gasoline, and from 0.38 to 0.41 within columns contaminated with biodiesel. It was found that the dissolution rate of biofuel in the column experiments depends on the effective solubilities and diffusivities of the target compounds, the physical distribution of the HOC in the porous medium, and the rate of water flow through and around the biofuel. The rate of mass transfer determines the dissolved-phase concentrations in the effluent water as well as the persistence of residual biofuel constituents in the column. Higher water velocities may result in a reduction in the dissolved concentrations.

In the case of dissolution from the residual phase, the local equilibrium concentration is reached after short flow distances through the NAPL zone if the residual NAPL saturation is high. Examining the breakthrough curves of the ethanol-blended gasoline constituents, MTBE eluted in the first five pore volumes (PV) due to its partially miscible nature in groundwater. The concentration of each constituent increased sharply over the first few pore volumes as groundwater progressed through the column. In terms of eluted mass (concentration), the

difference was obvious for compounds such as MTBE and xylenes (Figure 2). Continuous desorption of contaminants such as BTEX was observed until 50 PV in the ethanol-blended gasoline spill site. Notably, elution times were longer for more hydrophobic contaminants.

The addition of ethanol enables gasoline constituents to enter smaller pore spaces and to infiltrate more easily through the vadose zone to the water table. This effect is complicated by strong ethanol partitioning to vadose-zone water, which significantly reduces ethanol transport to the water table. Previous small-scale experiments have indicated that the loss of ethanol before ethanol-blended gasoline reaches the water table does not significantly change NAPL spreading on the capillary fringe or water table.[34] However, a large-volume spill of E25 or E85 could overcome this effect and reach the water table, increasing the spreading of NAPL. Our study indicated that the decreased sorption of hydrophobic contaminants causes NAPL spreading, thereby increasing the extent of the dissolved contaminant plume and contaminated area. In soil-water systems, the time to reach near-equilibrium conditions may be on the scale of several days, particularly in desorption experiments. The breakthrough concentration profile for each biofuel constituent was integrated over the cumulative effluent volume (i.e., the zeroth moment) to determine the total HOC mass removed during the experiment. Several parameters are necessary to allow such an evaluation: (1) the target compound concentrations in the biofuel, which allows the amounts of MTBE, BTEX, and PAHs that the biofuel puts in to the soil column to be estimated; (2) the amount of HOCs in the effluent by using zero moment analysis on the elution profiles as illustrated in Figures 2 and 3 (using effluent concentration measurements of sixty pore volumes for ethanol-blended gasoline 12 pore volumes for biodiesel). With these parameters, the net HOCs eluted can be estimated with the following equation:

$$\text{Eluted mass (\%)} = HOC_E/HOC_S \qquad (5)$$

where HOC_E is the amount of HOCs in the effluent by using zero moment analysis on the elution profiles as illustrated in Figures 2 and 3, and HOC_S is the original mass of HOCs in the contaminated soil.

The moment analysis indicated that more desorbed target compounds were observed in the effluent of E-85 than in regular gasoline. An effect of ethanol on the desorption of xylenes was observed in the elution profiles of E-25 and E-85. The mass of xylenes desorbed was greater in both E-85 and E-25 than in gasoline. Overall, the ethanol-induced desorption of target compounds in high-ethanol content gasoline has the potential to increase both the extent of contamination and the difficulty of remediation.

When groundwater encounters biodiesel-contaminated soil or aquifer material, the aqueous concentrations of PAHs that previously sorbed onto the soil desorb according to their dissolution rate. The effluent concentration increased and reached its maximum in the elution profile during the first pore volume (Figure 3). Naphthalene and phenanthrene were selected to show representative elution profiles. While groundwater was in contact with pure phase NAPL, the NAPL in the pore space was displaced by groundwater flowing in. Therefore, spikes in target compound concentrations were observed in the effluent as illustrated in Figure 3. Our study indicated that the leaching of PAHs in column experiments appears to be controlled by two major processes: the dissolution of PAHs from residual biodiesel and desorption of PAHs from contaminated soil. Examining the elution profiles of biodiesel in Figure 3, the elution of PAHs goes back to the normal dissolution rate after the first few pore volumes. However, these biodiesel constituents will continuously contaminate groundwater as long as groundwater passes through. The desorption of PAHs from soil with higher organic carbon content tends to be slower (S-3<S-1). Tailing of elution was observed while residual biofuel existed in the subsurface environment. It should be noted that the spill simulation conducted here only represents the scenario near the spill site. The effluent

measured is composed of PAHs from the dissolution of biofuel constituents from contaminated soil. The dissolution of PAH components depends on chemical properties such as hydrophobicity and total mass of biodiesel. Overall, the less-hydrophobic compounds elute first, while the opposite is true for more-hydrophobic compounds.

Conclusions

Proposals for the modification of current fuels should include evaluations of the constituents for their potential to damage environmental resources. The potential for chemicals of concern to leach from biofuel-impacted soil must be understood to assess the risk to groundwater. Knowledge of the sorption behavior of biofuel constituents is required to ensure that the proper fate and transport of such contaminants is understood at biofuel-contaminated sites.

Interactions such as sorption and desorption between dissolved organic species and solids in the aquifer or soil depend on the physico-chemical parameters of the contaminant as well as of those of the aquifer material. In this study, batch and column experiments were designed to simulate biofuel spills in the subsurface environment and to evaluate the sorption behavior of biofuel HOCs in soil. This study provides a rapid means of estimating the potential for contamination from target compounds (i.e., monoaromatic and polyaromatic hydrocarbons) and other organic contaminants from biofuels in various types of soil. The extent and reversibility of the sorption of major components from biofuels onto major soil types and groundwater were determined. The results showed that as the proportion of ethanol in gasoline increased, the desorption of pollutants to water occurred more readily, an effect that was obvious when the ethanol content exceeded 25%. However, if more biodiesel was added to diesel fuel, the sorption of HOCs was not affected. In addition, when the soil's organic carbon was higher, the desorption of target compounds was lower.

The empirical relationships between K_{oc} and both water solubility (S) and K_{ow} were established. These empirical equations will allow the sorption behavior of biofuel contaminants to be estimated in the event of a biofuel spill. The implication of this experiment is that determining the sorption behavior and leaching patterns of major biofuel constituents is important for future assessments of the impacts of biofuels. The spill scenarios generated may assist in the assessment of biofuel-contaminated sites.

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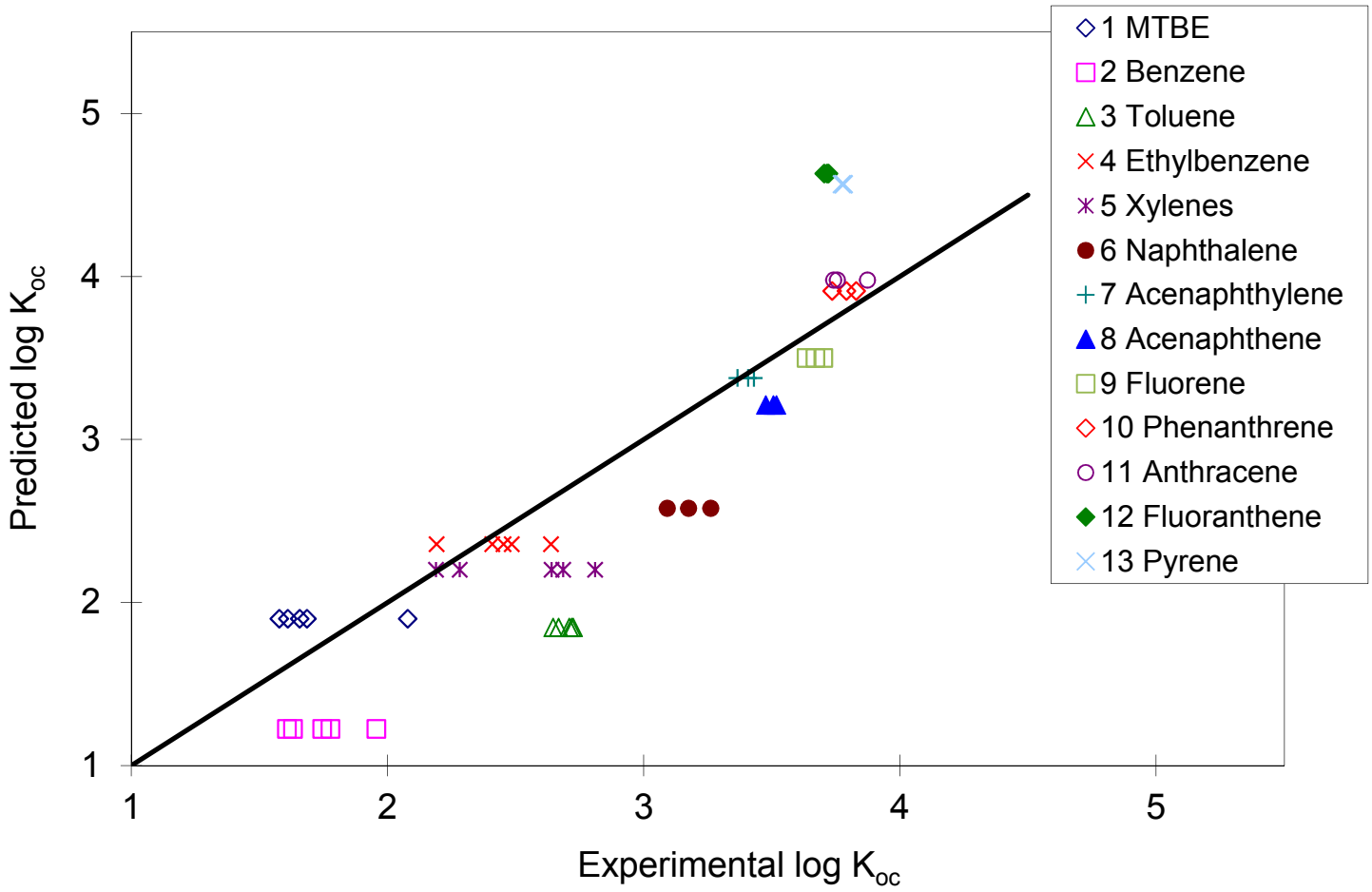

Figure 1. Experimental vs. predicted logK_{oc} values for target compounds in biofuel.

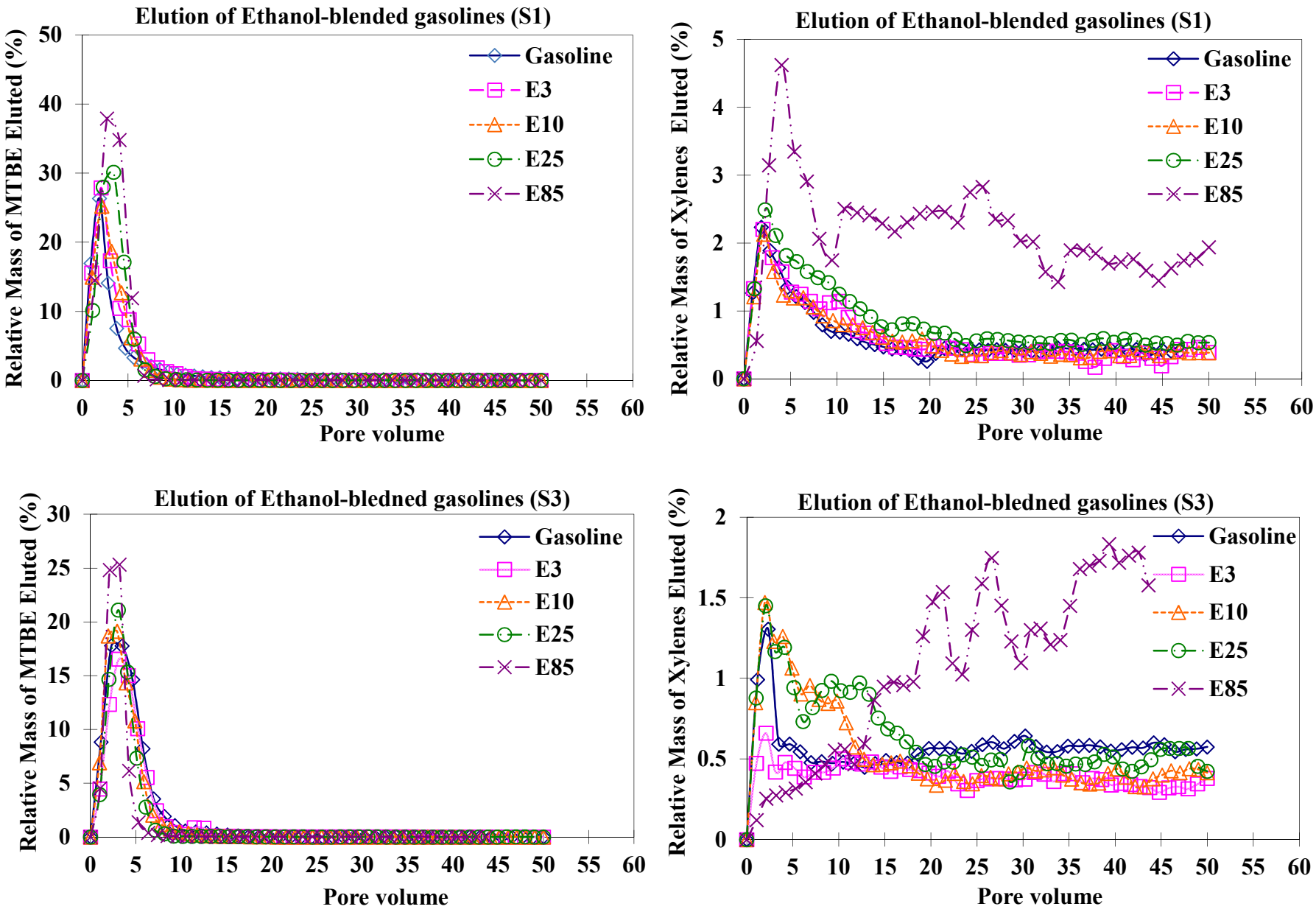

Figure 2. The elution profile of MTBE and xylenes in various gasoline products.

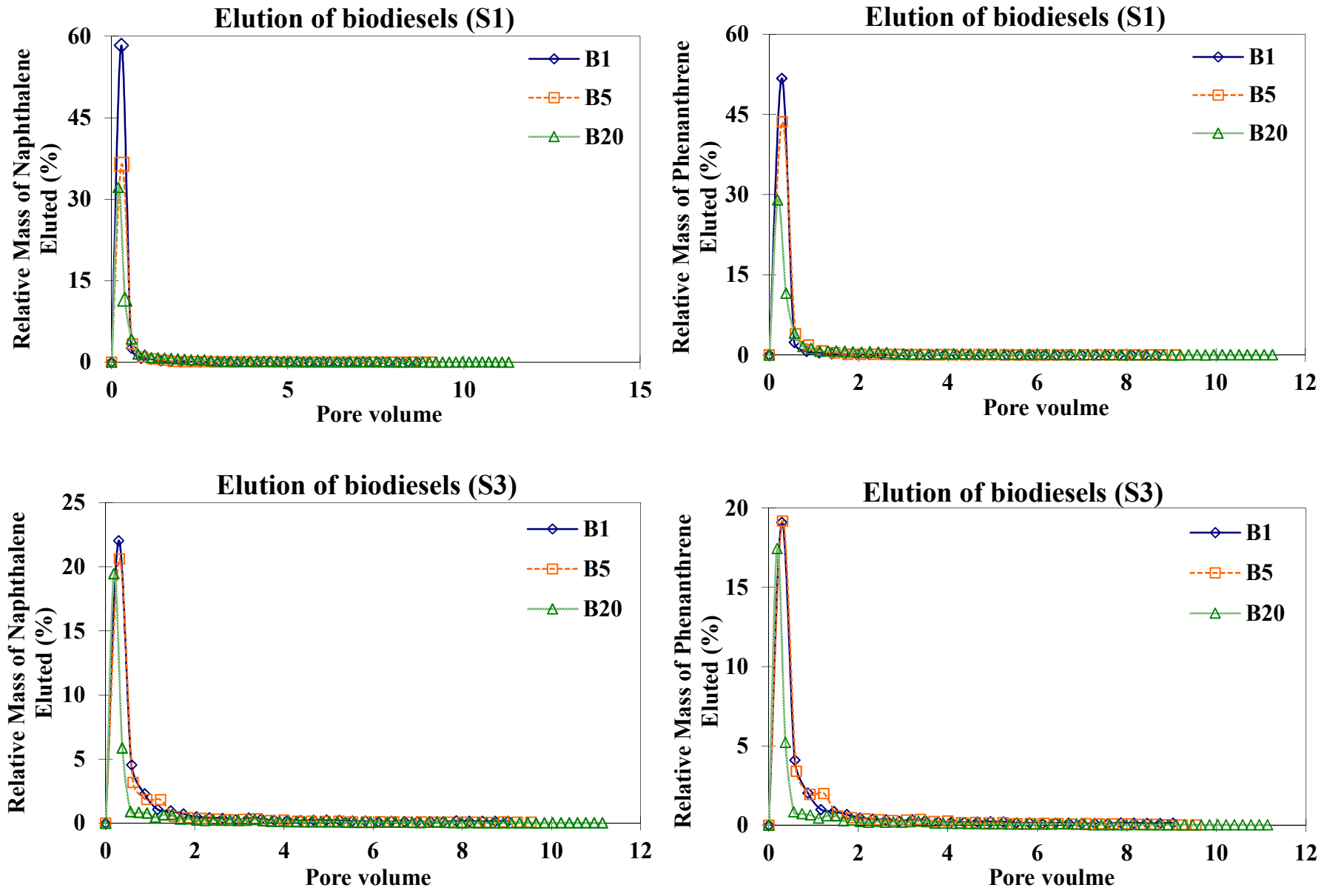

Figure 3. The elution profile of naphthalene and phenanthrene in various soils.

Table 1. The sorption coefficients (K_p) of target compounds in the ethanol-blended gasoline contaminated soil-water system.

Compound	S1 (f_{oc}=2.6%) (Fuel/soil=1:10)					S1 (f_{oc}=2.6%) (Fuel/soil=1:1)				
Fuel	MTBE	Benzene	Toluene	Ethylbenzene	Xylenes	MTBE	Benzene	Toluene	Ethylbenzene	Xylenes
CPC95	7.93	45.8	70.7	45.8	74.9	0.676	12.6	10.9	15.9	14.7
E3	12.7	43.0	63.1	37.0	49.9	0.542	10.0	9.65	13.7	12.2
E10	9.08	37.7	92.8	40.9	60.3	0.521	7.35	5.20	10.4	6.94
E25	5.54	39.2	80.7	69.9	83.6	0.390	1.55	2.36	3.47	2.24
E85	4.16	42.1	21.1	42.6	30.9	0.346	1.04	1.02	2.02	1.98
	S2 (f_{oc}=4.5%)					S2 (f_{oc}=4.5%)				
CPC95	15.	53.5	81.5	52.4	74.8	0.721	22.7	23.5	45.0	39.5
E3	24.0	45.8	106	44.1	68.8	0.708	15.1	11.6	9.91	10.7
E10	11.4	37.8	154	43.0	62.6	0.661	14.2	8.06	16.1	12.1
E25	7.25	39.1	110	67.5	91.8	0.303	1.27	1.71	4.07	3.24
E85	7.57	42.9	25.4	60.9	58.6	0.208	0.671	0.732	1.72	1.41
	S3 (f_{oc}=10.0%)					S3 (f_{oc}=10.0%)				
CPC95	18.3	51.8	110	58.3	88.0	4.24	70.0	95.4	100	123
E3	18.6	47.9	110	56.6	85.2	4.15	65.3	90.3	90.2	122
E10	12.8	40.7	142	62.5	94.3	3.51	31.4	32.1	39.4	36.2
E25	8.62	41.9	119	88.7	96.5	1.63	6.80	14.9	23.8	25.9
E85	8.44	48.5	58.3	77.5	83.0	0.245	0.791	0.798	0.912	1.24

Table 2. The sorption coefficients (K_p) of target compounds in the biodiesel contaminated soil-water system.

Compound / Biodiesel	S1 (f_{oc}=2.6%)							
	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
B1	25.11	70.87	89.84	80.13	183.7	117.5	195.7	141.6
B5	27.46	81.67	115.7	116.1	180.8	127.0	169.1	132.2
B20	43.51	91.42	116.6	94.13	156.7	113.2	197.9	139.3

Compound / Biodiesel	S2 (f_{oc}=4.5%)							
	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
B1	89.04	81.85	96.01	157.4	210.6	165.9	272.4	189.0
B5	85.57	128.5	129.6	175.9	213.7	157.1	363.2	157.0
B20	83.86	113.0	150.6	153.7	293.2	192.7	269.4	183.0

Compound / Biodiesel	S3 (f_{oc}=10.0%)							
	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
B1	145.8	211.8	264.8	423.0	555.3	522.8	386.2	535.3
B5	128.5	288.8	281.3	435.6	514.7	547.9	388.3	447.2
B20	140.3	213.1	352.8	434.6	440.8	513.7	373.0	440.8

Table 3. The K_{oc} values of target compounds in biofuels.

A. Ethanol-blended gasoline

Compound \ Biofuel	CPC95		E3		E10		E25		E85		Previous studies[a]
	K_{oc}	log K_{oc}	K_{oc}	log K_{oc}	K_{oc}	log K_{oc}	K_{oc}	log K_{oc}	K_{oc}	log K_{oc}	log K_{oc}
MTBE	28.2	1.45	26.0	1.42	23.3	1.37	12.7	1.10	6.11	0.791	1.08
Benzene	563	2.75	458	2.66	304	2.48	52.0	1.72	19.6	1.29	2.00
Toluene	632	2.80	511	2.71	234	2.37	92.6	1.97	20.8	1.32	2.06
Ethylbenzene	870	2.94	595	2.77	315	2.50	154	2.19	40.6	1.61	1.98, 2.41
Xylenes	890	2.95	654	2.82	299	2.48	152	2.18	44.2	1.65	2.11, 2.31

a From [32].

B. Biodiesel

Biofuel / Compound	B1		B5		B20		Previous Studies[a]
	K_{oc}	log K_{oc}	K_{oc}	log K_{oc}	K_{oc}	log K_{oc}	log K_{oc}
Naphthalene	1497	3.18	1235	3.09	1827	3.26	3.11
Acenaphthylene	2694	3.43	2324	3.37	2557	3.41	3.40
Acenaphthene	3209	3.51	3299	3.52	2999	3.48	3.66
Fluorene	4677	3.67	4326	3.64	5029	3.70	3.70, 3.86
Phenanthrene	6756	3.83	6182	3.79	5443	3.74	4.15, 4.36
Anthracene	5703	3.76	7460	3.87	5507	3.74	4.15, 4.27
Fluoranthene	5267	3.72	5195	3.72	5065	3.70	4.58, 4.62
Pyrene	6016	3.78	5828	3.77	6040	3.78	4.58, 4.81

a From [32].