The Fate of Diesel in Soil Samples with Different Amount of Soil Organic Matter

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Abstract

The interaction/binding between components of soil organic matter and most anthropogenic organic compounds such as polynuclear aromatic compounds has long been established [Khol S. and Rice J. A. and Khan S. U. 1982]. Kerosene is also recently found to bind with soil organic matter [Beke M. 2012]. This work studies the fate of diesel in soil samples containing different amounts of soil organic matter. Soil samples containing different amounts of soil organic matter and three different concentrations of diesel were used in this research. A given amount of a concentrate of diesel in petroleum spirit was used to spike a set of soil samples containing different amount of soil organic matter. This was then left in a fume hood for 48 hours for the petroleum spirit to dry off. Dichloromethane solution containing an internal standard was then used to extract the diesel from the spiked soil sample by vortex method. The extracts were then analysed by GCMS for the amount of diesel. The results show a gradual reduction of the amount of diesel in the extracts as the amount of soil organic matter in the soil sample increases. For the highest concentration of diesel (50,000mg/l) and at 50% soil organic matter, the amount of diesel extracted was 28.3±3.1% of the initial amount of diesel used in spiking the soil sample; this implies that as much as 71.7% of diesel was held back.

Key Words: Soil Organic Matter, Diesel, Soil Sample, Concentration.

Introduction

Research has shown that hydrocarbons contaminants introduced into the soil becomes quickly and often irreversibly bound to components of soil organic matter. Soil organic matter can be categorised as humic and non-humic substances. Humic substances are polyelectrolytes formed from non-humic substances while non-humic substances are hydrocarbons that belong to classes of recognizable compounds, such as fatty acids, proteins and carbohydrates [Khol S. and Rice J. A]. Soil organic matter is generally divided into three component fractions based on its solubility as a function of its pH;

These are humic acid, humin and fulvic acid. Each component has been shown to significantly affect the fate of hydrophobic organic matter introduced into the environment. The humin components of humic substances usually make up the bulk of organic materials found in soil and sediments [Khol S. et al and Laplante M. 1998]. Most anthropogenic organic substances such as polynuclear aromatic hydrocarbon (PAH), polychlorinated biphenyls (PCB), herbicides and pesticides are known to rapidly bind to humin [Laplante M. et al, 1998, Stevenson F. J., 1982, Fuhr F. 1987.]. A research on kerosene [Beke M., 2012], a fraction of crude oil was found to hold back as much as 95% of the kerosene in soil samples containing SS50% organic matter when spiked with 50,000mg/l concentration of kerosene. In furtherance of the work on kerosene, this work considers a higher fraction of crude oil, diesel, and studies the fate of diesel in diesel spiked soil containing different amounts of soil organic matter. In Nigeria, contamination of the environment with petroleum hydrocarbon is rampant and diesel which is used to fuel most power plants is a common contaminant of the environment. If soil organic matter can equally be bind with diesel to a significant measure, then it may be used as a tool of remediation of diesel contaminated soil. This can be used to trap diesel in the soil before it gets to ground water as illustrated in figure 1.

IMPACT OF PETROLEUM HYDROCARBONSPILL ON SOIL

Petroleum hydrocarbon makes contact with the environment either naturally or by human activities. When petroleum hydrocarbon is spilled on soil, some of the volatile components are likely to first evaporate off, a fraction will remain at the surface while others will pass through different layers of the soil into the groundwater. In the soil, some of the petroleum hydrocarbon will interact with organic matter present in it; while the soil itself will accommodate a part of the petroleum hydrocarbon [Khol S. and Rice J. A], various methods of protecting the environment from petroleum hydrocarbon contamination have been adopted, these include; the use of sorbent materials, chemical dispersants and burning [Aiken, G. R. et al 1985.]. Most of these methods have been found to have negative ecological effects on the environment [Aiken, G. R. et al 1985.]. Therefore protecting the environment with safer alternative material has become necessary [Aiken, G. R. et al 1985.]. If soil organic matter can bind/interact strongly with diesel as it was established with kerosene and other organic compounds such as polynuclear aromatic hydrocarbons, herbicides and pesticides [Khol S. and Rice J. A, Khan S. U. 1982], then it can be considered as a tool for remediation of petroleum hydrocarbon contaminated soil.

MATERIALS AND METHODS

The materials used are bought from business outlets in Bangor, North Wales in the United Kingdom, while the soil samples were collected from a farmland in Bangor. Three concentrates of diesel were prepared (10,000mg/l, 25,000mg/l and 50,000mg/l) for spiking soil samples. These were prepared by dissolving a measured amount of diesel into petroleum spirit solvent. Commercial compost was used as a source of soil organic matter and this was purchased from B&Q Company. Soil samples of 10g each were prepared in sets of six, with added compost/soil organic matter content ranging from 0% to 50%.

PREPARATION OF DIESEL SOLUTION (10,000mg/l)

Density of diesel = 832mg/l, mass of diesel = 10,000mg, volume of diesel =?

But density = mass / volume, and volume = mass / density

Volume of diesel required = 10,000 / 832 = 12.0ml

12.0ml of diesel is dissolved in petroleum spirit solvent in a 1000ml volumetric flask and made up to the mark with the solvent.

The same method was used to prepare 25,000mg/l and 50,000mg/l concentrations of diesel.

LOSS ON IGNITION TEST FOR SOIL AND COMPOST

This test was done in triplicate for the soil and compost used for the experiment. Six crucibles were weighed and then oven dried for two (2) hours at 105^0C, the crucibles were weighed again to determine any change of mass. The mass of the dry crucibles are used for all calculation with regards to loss on ignition test. 10g of soil samples were then measured in triplicate and transferred into three crucibles labeled A1, A2 and A3. This is also done for compost and labeled B1, B2 and B3. The samples in the crucible were then oven dried twice at 105^0C and 450^0C for two hours each time.

METHOD OF PREPARATION OF SOIL SAMPLES

The soil samples were prepared in sets of six, each containing different amount of compost. A sample of the soil without compost is also included in each set to show the actual effect of compost on the diesel spiked soil samples. Each soil sample weighs 10g with compost content ranging from 0% to 50%. The table 1, shows the composition of a set of soil sample.

SPIKING OF SOIL SAMPLES

100ml of each a concentrate of a diesel is used to spike each 10g component of a set of soil sample. The spiking was done by adding the 100ml portion of the diesel solution into each 10g component of a set of soil sample; these were then left in the fume-hood for 48hours for the spiking solvent to evaporate off completely.

PREPARATION OF EXTRACTING SOLVENT

Dichloromethane is used as the extracting solvent. The internal standard used for quantitative analysis (peak area ratio) of the petroleum hydrocarbon was added to the extracting solvent before extracting the diesel from the soil sample. The internal standard used is; 1, 3, 5-trichlorobenzene.

100mg portion of the internal standard was measured and transferred into a 1000ml volumetric flask; dichloromethane is then added up to the 1000ml mark

EXTRACTION OF DIESEL FROM SPIKED SOIL SAMPLES

100ml of the extracting solvent was added to a 10g portion of spiked soil sample already in a 250ml conical flask. This was then stirred for thirty (30) minutes with a magnetic stirrer. The soil sample and the filtrate were then separated by filtration.

GCMS ANALYSIS OF EXTRACTED DIESEL FROM SPIKED SOIL SAMPLES

1ml portion of the extract, containing the diesel was transferred into a 1ml GCMS vial and analysed with an (hp) Hewlett Packard 5890 Series II GC machine with a 5971 mass spectrometer. The column of the machine is DB5 wax lined, 0.25micron by 30M. The operating condition of the GC component of the machine is;

- Initial temperature: 40^{o}C
- Initial time: 2 minutes
- Ramp rate: 5^{o}C/minute
- Final temperature: 220^{o}C
- Final time: 5 minutes
- There is also a 3 minutes solvent delay

RESULTS AND DISCUSSIONS

Diesel is a semi volatile hydrocarbon and consists basically of, C_{10} to C_{32} hydrocarbons. A GCMS trace of diesel is shown in figure 1.

The individual petroleum hydrocarbons (C_{11} to C_{15}) were identified by studying the ions of the peaks in each of the chromatogram and cross checking it with the data in the library. The ions observed for C_{11} to C_{15} in the GCMS trace are given in table 2.

RESULTS OFSOIL AND COMPOST ANALYSIS

The results of the organic matter content analysis in the laboratory for the soil and compost by loss on ignition shows that the organic matter content of the soil and compost are, 11.54 + 0.04 % and 90.1 + 0.37 % respectively.

LOADING / RECOVERY OF DIESEL FROM SAMPLES

For the 10,000mg/l of diesel, 12ml of the diesel was dissolved in a 1000ml volumetric flask and made up to the mark with petroleum spirit. 100ml portion of it was then loaded to a 10g portion of soil sample. This implies that for each 10,000mg/l concentration of diesel, the amount of diesel in each 100ml of the solution will be 1.2ml of diesel. Similarly, 25,000mg/l and 50,000mg/l spiked soil samples will contain; 3.0ml/10g and 6.0ml/10g respectively. Dichloromethane was used as the extracting solvent. 1000ml of the extracting solvent contains 100mg of the internal standard (1, 3, 5 – Trichlorobenzene) used for the diesel chromatogram peak area ratio analysis.

A graphical result of the experiment on petroleum hydrocarbon is provided in figures 2 and 3, these show the peak area ratios of C_{11} to C_{15} of diesel recovered.

The hydrocarbons generally decrease with an increase in the amount of compost when compared with the initial peaks of the spiking solution. The result show that at 50% compost and 50,000mg/l (6ml/100ml) diesel solution, the largest amount of hydrocarbon (C_{15}) recovered has a peak ratio of 8.1, which is 34% of the initial peak before spiking the soil sample; this implies as much as 66% of it was trapped in the soil sample. This again shows the effect of organic matter on the amount of diesel that can be extracted from contaminated soil samples.

This clearly shows that soil organic matter has a significant limiting effect on the amount of diesel that can be extracted from contaminated soil samples. Table 3 below gives the results of the amount of diesel recovered by extraction from spiked soil samples at 50% compost and 50,000mg/l (6ml/100ml) concentration diesel.

The results show that hydrocarbons of diesel can equally bind with soil organic matter as well as other anthropogenic organic compounds such as polynuclear aromatic hydrocarbons, herbicides and pesticides.

CONCLUSION

The results show a gradual reduction in the amount of diesel recovered from 81.3$\pm$2.3% at 0% compost to 28.3+3.1% in 50% compost at 50,000mg/l (6.0ml/100ml) diesel in petroleum spirit. This gradual decrease in the amount of diesel recovered from the spiked soil samples as the amount of added organic matter increases is a reflection of the impact of soil organic matter on diesel in contaminated soil. Considering the method of extraction of the diesel from the spiked soil samples and the strength of dichlomethane as an extracting solvent, this suggests that the bond/interaction between the hydrocarbons of the diesel and the particles of the soil organic matter should be very strong. This also suggests that petroleum hydrocarbon can bind with soil organic matter just as other anthropogenic hydrocarbon. Although a lot of work still need to be done especially with regards to the particular component of soil organic matter that binds with the diesel hydrocarbons. The results of this research work presents hope for the use of soil organic matter as a tool for petroleum hydrocarbon contaminated soil remediation. By advancing our study and knowledge on soil organic matter and its interaction with other petroleum hydrocarbon, it may be possible to predict its fate in soil and by implication the environment.

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RESULT TABLES AND FIGURES

Sample Composition (%)	Amount of Compost (g)	Amount of Soil (g)
0% Soil Sample (A)	0g Compost	10g Soil
10% Soil Sample (B)	1g Compost	9g Soil
20% Soil Sample (C)	2g Compost	8g Soil
30% Soil Sample (D)	3g Compost	7g Soil
40% Soil Sample (E)	4g Compost	6g Soil
50% Soil Sample (F)	5g Compost	5g Soil

Table 1; Showing a set of soil sample compost / soil composition

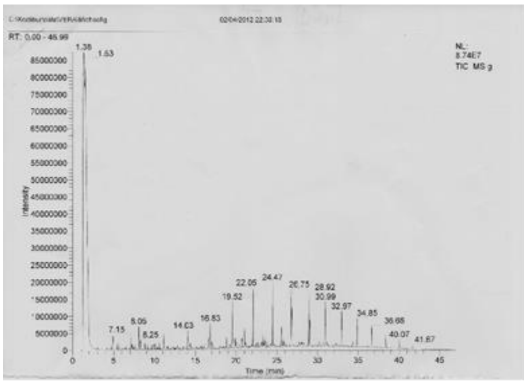

Figure1, Chromatogram of diesel

Hydrocarbons	Ions Observed
C_{11}	156
C_{12}	170
C_{13}	184
C_{14}	198
C_{15}	212

Table 2, Hydrocarbons and their ions

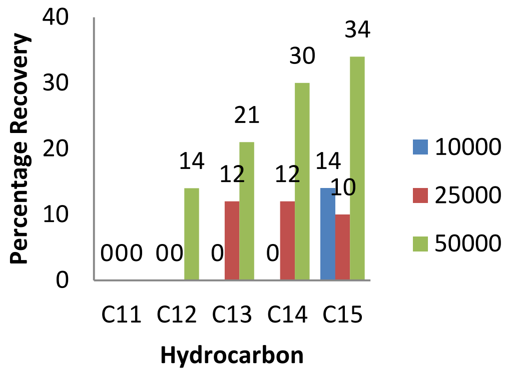

Figure 2, Hydrocarbons of Diesel Recovered

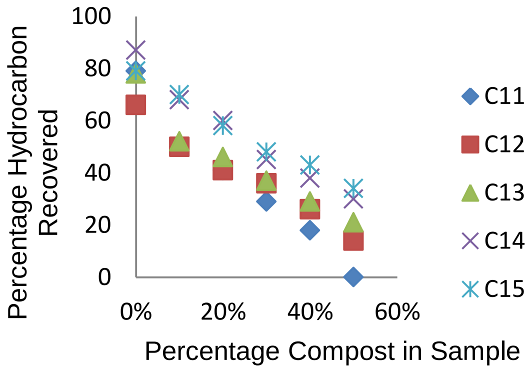

Figure 3, Graph of Hydrocarbons of Diesel Recovered

50,000mg/l (6.0ml/100ml) Diesel/Petroleum Spirit Solution Results

Amount of Compost	C13	C14	C15	Mean	Standard Deviation	Results
0% Compost	78%	87%	79%	81.3	4.0	81.3±2.3%
10% Compost	52%	68%	70%	63.3	8.1	63.3±4.7%
20% Compost	46%	60%	58%	54.7	6.2	54.7±3.6%
30% Compost	37%	45%	48%	43.3	4.7	43.3±2.7%
40% Compost	29%	38%	43%	36.7	10.0	36.7±5.8%
50% Compost	21%	30%	34%	28.3	5.4	28.3±3.1%

Table 3, Percentages of hydrocarbons recovered (50,000mg/l diesel)