Journal of Applied Sciences

ISSN 1812-5654

science alert

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OPEN ACCESS Journal of Applied Sciences

ISSN 1812-5654
DOI: 10.3923/jas.2019.624.628

Research Article
Sources and Variations of Aliphatic Hydrocarbons in Petroleum Products Contaminated Soils

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Abstract
Background and Objective: Aliphatic hydrocarbons are carcinogenic at high concentrations and can be hazardous to biological system. This study aimed to examine the aliphatic hydrocarbon variations in soils from the vicinity of mechanic workshops. **Materials and Methods:** The aliphatic hydrocarbons (AHCs) in soil samples collected from auto-mechanic workshops in Nnewi, Anambra state, Nigeria, were analyzed with gas chromatography-flame ionization detector (GC-FID) to determine their sources and examine the variations in their composition. Petroleum products contribution to the hydrocarbons in the soil samples were estimated from composition of n-alkanes. **Results:** The GC-FID resolved aliphatic hydrocarbons (AHCs) in the samples were composed of C_8, C_{10}, C_{16}-C_{35}, C_{16}, C_{25}, C_{28}, C_{30}-C_{36}, C_{16} - C_{18}, C_{21}-C_{36} n-alkanes with unresolved complex mixture (UCM) of hydrocarbons from C_{22}-C_{36} in one of the samples. These n-alkanes carbon number ranges suggest gasoline, diesel, lube oil and grease as the source of petroleum hydrocarbon contamination in the samples. The kerosene range n-alkanes (C_{10}-C_{15}) were not detected in any of the samples. **Conclusion:** The chemical composition features showed grease as the dominant source of petroleum products in the soils with varying inputs from gasoline, diesel and lube oil. The presence of UCM of hydrocarbons in one of the samples indicated the aliphatic hydrocarbons in the soil had undergone degradation.

Key words: Mechanic workshop, lube oil, petroleum products, aliphatic hydrocarbons, n-alkanes, petroleum products, soil, contamination

Received: January 09, 2019 Accepted: March 02, 2019 Published: May 15, 2019

Citation: Ifenna Ilechukwu, Mark Obinna Onyema and Grace Imperial Tejano, 2019. Sources and variations of aliphatic hydrocarbons in petroleum products contaminated soils. J. Applied Sci., 19: 624-628.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In the past few decades there has been increased concern about petroleum contamination of the environment[1,2]. The source and fate of petroleum products released into the environment, either intentionally or accidentally are frequently investigated[3-5]. For environmental impact assessment of petroleum contaminated sites, it is important to unambiguously characterize the chemical compositions of samples and identify the contamination source. This is mostly achieved by the use of chromatographic techniques such as high-performance liquid chromatography (HPLC), gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS) to obtain detailed petroleum hydrocarbon composition of the contaminated environment[6]. Petroleum hydrocarbon components frequently utilized in environmental studies include aliphatic hydrocarbons (AHCs), biomarkers (e.g., triterpanes and steranes) and polycyclic aromatic hydrocarbons (PAHs), 2-6 fused ring aromatic compounds[7-10]. The saturate AHC component constitutes the most abundant hydrocarbons in non-degraded crude oils and refined petroleum products. The AHC compositions and distribution are used for characterization, identification and correlation of oils especially between spilled oils and source oil[11,12]. Environmental geochemists appraise AHCs from quantitative chromatographic analyses by compiling histogram distribution and diagnostic ratios of source-specific compounds for visual and statistical comparisons of samples[13-15].

The concentrations of aliphatic hydrocarbons analyzed by gas chromatography are used to evaluate petroleum contamination of the environment and identify their sources[16,17]. The comparison of AHC compositions of mixtures of 2 oil types was used by Ho *et al.*[18] to evaluate weathering rate as well as estimate the mixing proportions of the oils. Aliphatic hydrocarbons are carcinogenic at high concentrations and can be hazardous to biological receptors due to formation of toxic metabolites during biodegradation. However, most studies focus on aromatic hydrocarbons[19]. Nnewi is the second largest city in Anambra state, south east Nigeria. The city falls within the tropical rain forest region of Nigeria and thus rich in agricultural produce. The city is also highly industrialized with majority of the residents dealing on motor and motorcycle spare parts. These spare parts are traded at Nkwo Nnewi market, the major import and wholesale point for auto spare parts in Nigeria and the largest in west Africa[20]. Mechanic workshops are widely distributed in Nnewi for the repair of these vehicles and their spare parts. This study therefore, was aimed to investigate the aliphatic hydrocarbon variations in soils from the vicinity of mechanic workshops.

MATERIALS AND METHODS

Sampling: Oil contaminated soil samples were collected at 0-5 cm depth from 3 auto mechanic workshops in Nnewi, Anambra state, Nigeria. Samples were collected in March, 2017. The sampling locations of the auto mechanic workshops are Sample-1 6.0223° N and 6.9141° E, Sample-2 6.0214° N and 6.9154° E, Sample-3 6.0213° N and 6.9154° E. At each sampling location, soil samples were collected from 4 points and thoroughly mixed to form a composite sample. The samples were collected using a stainless steel scoop, packed in pre-cleaned glass jars, labelled appropriately and preserved at a temperature of 4°C prior to analysis.

Petroleum hydrocarbon extraction and clean up: About 5 g of each soil sample was separately weighed into glass bottles and 20 mL hexane was added for extraction. Glass bottles with contents were placed in an ultrasonic shaker for 1 h. The process was repeated twice after which the extracts were pooled and concentrated to 2 mL using a rotary evaporator. The concentrated extract was transferred to the top of a glass column (50×1 cm) packed with activated silica (mesh 100-200) and stuffed with glass wool at the base. About 10 mL of hexane was used to elute the saturate fraction, which contains aliphatic hydrocarbons. The eluent was evaporated to less than 2 mL under a gentle stream of nitrogen.

Gas chromatographic analysis: Analysis of AHCs was performed on a Hewlett Packard (HP) 6890 gas chromatography (GC) system fitted to a DB-5 silica capillary column (30×0.25 mm ID and 0.25 µm film thickness, J and W scientific Co., Ltd., USA) and equipped with a flame ionization detector (FID). About 1 µL of the concentrated saturate fraction was injected into the GC column with the aid of an auto sampler using the splitless injection mode. Oven temperature was programmed from 40-320°C at 5°C min^{-1} with a 5 min hold at 40°C and 20 min hold at 320°C. The AHCs were identified by their relative retention times in comparison with internal standard and quantification acquired by area integration of each identified compound peak, which was processed by HP Chemstation software.

RESULTS AND DISCUSSION

Distribution of aliphatic hydrocarbons: The GC-FID fingerprints from analysis of soil samples from the auto mechanic workshops showed the presence of aliphatic hydrocarbons (AHCs) in all the samples (Fig. 1a-c). The GC-FID

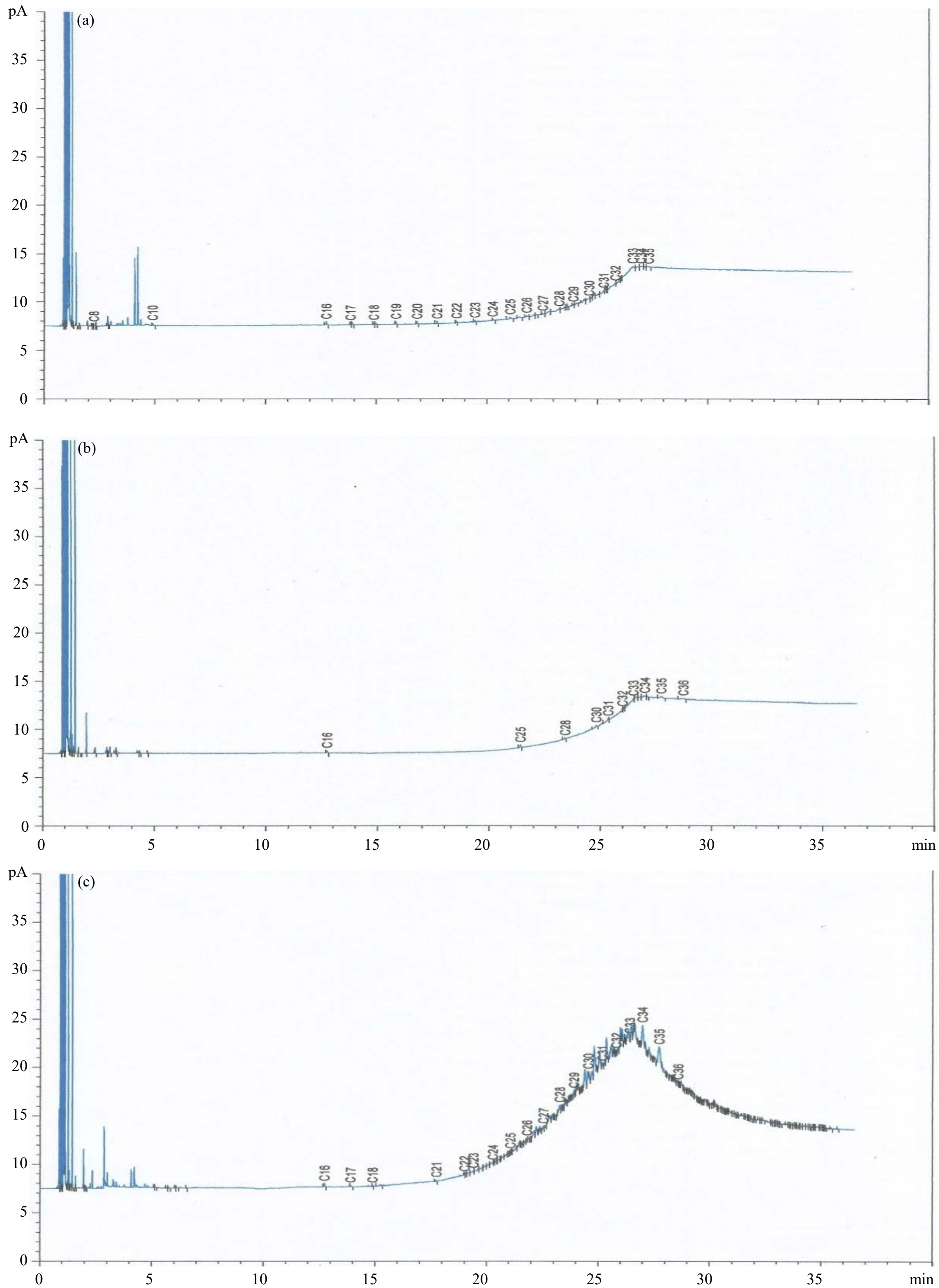

Fig. 1(a-c): Gas chromatogram of aliphatic hydrocarbons (AHCs) for sample (a) 1, (b) 2 and (c) 3

chromatogram provides a descriptive picture of hydrocarbons present in a sample as well as information used for characterization of spilled petroleum products[11,13-15]. The GC chromatograms showed AHCs which were resolved and composed mainly of n-alkanes (Fig. 1a-c).

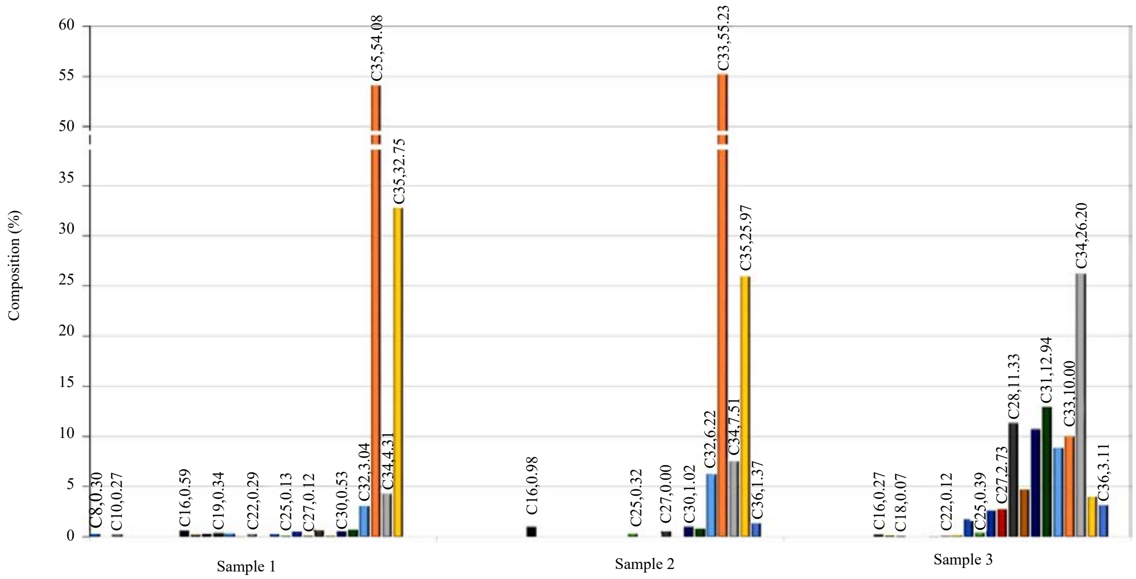

Fig. 2: Composition (%) of n-alkanes in the oil-contaminated soil samples

Carbon number distribution of n-alkanes were C_8, C_{10}, C_{16}-C_{35} and C_{16}, C_{25}, C_{28}, C_{30}-C_{36} for sample 1 and 2, respectively (Fig. 1a, b). The n-alkane carbon number distribution in sample 3 was from C_{16}-C_{18} and C_{21}-C_{36}, with a noticeable hump (Fig. 1c). The hump, which represents unresolved complex mixture (UCM) of hydrocarbons was nearly symmetrical with carbon number distribution from C_{22}-C_{36}, maximizing at C_{33}. Crude oil and its refined products are often identified by their GC profile carbon number distribution, especially during the early stages of an oil spill[21,17]. The n-alkane carbon number distributions of the samples were narrower than C_8-C_{40} range of crude oil but within range of some refined petroleum products. The AHC distribution suggested gasoline, diesel, lube oil and grease sources for petroleum contamination of sample 1 soils, diesel and grease sources for contamination of sample 2 soils and diesel, lube oil and grease sources for contamination[18] of sample 3. The kerosene carbon range C_{10}-C_{15} n-alkanes was not detected in any of the samples. This is expected for auto mechanic workshops since kerosene plays no part as auto fuels in this region. The presence of UCM is attributed to degradation of petroleum hydrocarbons[22].

Composition of n-alkanes: Percentage n-alkane compositions of the soil samples showed nearly identical distribution pattern for samples 1 and 2 particularly for n-alkanes greater than C_{26}. But, sample-3 showed difference in n-alkane percentage [H1] composition distribution pattern (Fig. 2). Petroleum products contribution to the hydrocarbon mix in each soil sample was estimated from their compositions of n-alkane. The n-alkane composition features indicated the major contamination source for sample 1 soils was grease, with minor inputs from gasoline, diesel and lube oil, for sample 2 soils, major contaminant was also grease with [H2] minor input from diesel, while sample 3 soils were contaminated with lube oil and grease with minor input from diesel.

CONCLUSION

The GC analysis of soil samples from these auto mechanic workshops revealed presence of aliphatic hydrocarbons which were composed of n-alkanes. The n-alkane carbon number distributions were C_8, C_{10} and C_{16}-C_{35} for sample 1, C_{16}, C_{25}, C_{28} and C_{30}-C_{36} for sample 2 and C_{16}-C_{18} and C_{21}-C_{36} for sample 3. These n-alkane compositions suggest grease as the dominant source of contamination contributing to the hydrocarbon mix in the soils with varying inputs from gasoline, diesel and lube oil. The kerosene range C_{10}-C_{15} n-alkanes were not detected in any of the samples. This is typical for auto mechanic workshops. The presence of UCM in sample 3 soils from C_{22}-C_{36} and maximizing at C_{33} indicated petroleum hydrocarbons had undergone degradation.

SIGNIFICANCE STATEMENT

The study showed the sources of aliphatic hydrocarbons in soils from mechanic workshops. The GC-FID analysis and the fingerprinting procedures that were employed showed grease was the dominant source of aliphatic hydrocarbons in the studied samples.

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