



Occurrence and Sources of Aliphatic Hydrocarbons in Soils within the Vicinity of Hot Mix Asphalt Plants in Obigbo and Igwuruta Areas of Rivers State, Nigeria

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ABSTRACT: This study investigated the occurrence and sources of aliphatic hydrocarbons (AHCs) in soils within the vicinity of hot mix asphalt (HMA) plants. Soil samples were collected from two HMA plants and analysed with gas chromatography - flame ionisation detector (GC-FID). Sample collection was from both surface (0-15 cm) and subsurface (15-30 cm) soils at an increasing distance of 10 m from the HMA plants while the control samples at both depths were collected at 1 km away from the plants. The AHCs concentration (nC_9 - nC_{38}) in soils from both HMA plants ranged from 8.16 - 433.04 mg/kg and 5.91-177.83 mg/kg for surface and subsurface soils respectively while the concentration in the control samples ranged from 5.97 - 23.95 mg/kg and 2.52 - 13.31 for surface and subsurface soil respectively. The sources of the AHCs were determined using isoprenoid ratios, carbon preference index (CPI) and maximum carbon chain (C_{max}). The isoprenoid ratios and CPI values of the samples closer (< 20 m) to the HMA plants were < 1 and < 2 respectively indicating anthropogenic inputs. Samples > 20 m from the HMA plants showed mixture of both anthropogenic and biogenic sources. ©JASEM

<http://dx.doi.org/10.4314/jasem.v20i4.24>

Keywords: Asphalt Plants; Soil; Aliphatic hydrocarbons; Pristane; Phytane.

Hot mix asphalt (HMA) plant is an assemblage of mechanical equipment where aggregates or inert mineral materials such as sand, gravel, crushed stones, Slag, rock dust or powder are blended, heated, dried and mixed with bitumen in measured quantities (Mamlouk and Zaniewski, 2011). It can be constructed as a permanent plant, a skid-mounted (easily relocated) plant, or a portable plant (EPA, 2000). HMA plants can be a source of a number of basic environmental pollutants. These pollutants may issue from dryers, burner blowers, exhaust fans and dust collection systems (Rilwanu and Agbanure, 2010). Other activities like asphalt loading, use and disposal of petroleum products as well as routine vehicle and plant maintenance also contribute to environmental pollution sources within HMA plant vicinities (Ilechukwu, 2013).

Petroleum hydrocarbons ranging from light products like diesel to heavy residues such as bitumen are used in asphalt production process. These petroleum products have variable hydrocarbon composition and distribution that differ from each other (Wang *et al.*, 2004). For example, bitumen, a product of non-destructive distillation of crude oil consisting of aliphatic and cyclic alkanes, aromatic hydrocarbons, heterocyclic compounds as well as metals like nickel, vanadium and iron serves as the cement that binds the aggregate materials (NIOSH, 2001). These petroleum hydrocarbons may be released into the environment from spills, indiscriminate waste disposal, atmospheric depositions and vehicular emissions. Source determination of these hydrocarbons in environmental media makes it possible to identify,

differentiate, determine risk to health and environment, direct remedial efforts and assign blame where necessary (Yang *et al.*, 2011; Ziegler *et al.*, 2008; Zemo *et al.*, 2007; Kassim, 2005).

Aliphatic hydrocarbons (AHCs) are ubiquitous environmental contaminants. They consist of odd and even carbon numbers ranging up to 64 carbons with no alkyl branch or substitutes. They have been employed in source determination of hydrocarbon pollution especially in distinguishing biogenic hydrocarbons from petrogenic hydrocarbons. Wang *et al.*, (1995) reported that the biogenic hydrocarbons have characteristic chemical composition where the aliphatic hydrocarbons show a distribution pattern of odd-carbon-numbered aliphatics being much abundant than even carbon-numbered aliphatics in the range of nC_{21} - nC_{33} . The “even” carbon numbers are from anthropogenic sources while the “odd” carbons are usually derived from the biogenic sources especially from terrestrial vascular plants. (Sakari *et al.* 2008; Azevedo *et al.*, 2007). The objective of this study therefore, was to determine the occurrence and sources of aliphatic hydrocarbons in soils within the vicinity of HMA plants.

MATERIALS AND METHODS

The two HMA plants used for this study were located in Obigbo (HMA Plant A) and Igwuruta (HMA Plant B) areas of Rivers State, Nigeria. HMA Plant A is located between Latitude (4° 51' 0" and 4° 51' 55") N and longitudes (7° 04' 55" and 7° 05' 26") E while HMA Plant B is located between Latitude (4° 55' 04" and 4° 56' 30") N and longitudes (7° 02' 30" and

7° 03' 0" E. Both plants have been in operation for 12 years and are in a sparsely residential area surrounded by farmlands.

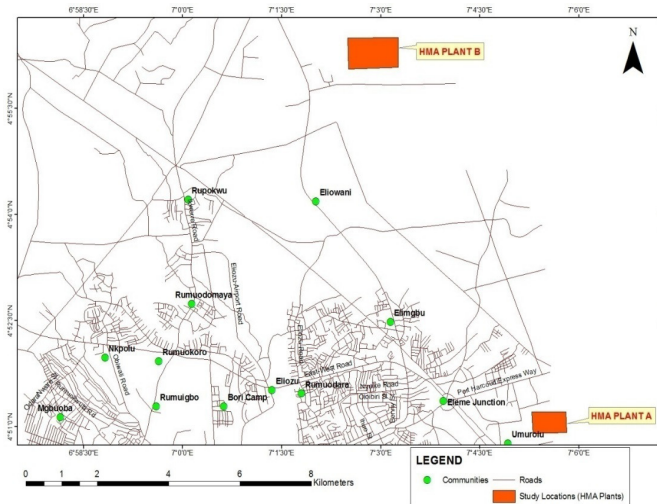


Fig. 1: Map of the Study Area indicating the HMA Plants

Soil samples were collected in March (dry season) and August (rainy season). Samples were collected at both surface (0-15cm) and subsurface (15-30cm) depths. They were randomly collected across the plant vicinities and blended to form a homogenous mix. This was done at an increasing distance of 10m from both plants terminating at 50 m and 40 m for Plant A and Plant B respectively. The control samples were collected at 1 km away from both plants.

Ten grams (10 g) of each soil sample was extracted in a soxhlet apparatus for 4 h with 200 ml of dichloromethane. The extracts were concentrated to 1 ml using a rotary evaporator. Each of the concentrated extract was fractionated using an activated silica gel column (100-200 mesh, 15 × 1 cm) topped with 0.5 g anhydrous sodium sulphate for water removal. The column was eluted with 20 ml of hexane to obtain the aliphatic fractions. Each of these fractions was concentrated to 1 ml using a rotary evaporator.

One microlitre (1µl) of each sample extract was analysed with AGILENT 6890 gas chromatography equipped with flame ionization detector (FID) under the following operational conditions: capillary column of length 25.0 m, diameter 320 µm, stationary phase; phenyl methylsiloxane, film thickness 0.17 µm. The column temperature was programmed from 40°C to 320°C at a rate of 6°C/min and held at 350°C for 15 minutes. Helium was used as the carrier gas.

The injector was maintained at 325°C and 1 µl of each of the sample extract was injected in splitless mode.

Quantification was determined by comparing the peak area of the internal standard perdeuterated n-tetracosane to those of the analytes. The total aliphatic hydrocarbons for each extract were quantified by GC/FID via total detector response.

RESULTS AND DISCUSSION

The concentration of aliphatic hydrocarbons in the soil samples from HMA Plant A is shown in Tables 1 and 2 for dry and rainy seasons respectively while that of HMA Plant B is shown in Tables 3 and 4 for dry and rainy seasons respectively.

The AHCs concentration in soils from HMA Plant A during the dry season ranged from 9.81 – 433.04 mg/kg and 6.76 – 177.83 mg/kg for surface and subsurface soils respectively while the concentration in the control samples was 5.97 mg/kg and 2.52 mg/kg for surface and subsurface soils respectively. In the rainy season, the concentration of the AHCs ranged from 8.16 – 82.85 mg/kg and 7.43 – 27.36 mg/kg for surface and subsurface soils respectively while the concentration in the control samples was 7.85 mg/kg and 5.86 mg/kg for surface and subsurface soils respectively.

Table 1: Aliphatic hydrocarbons concentration in HMA Plant A (Dry Season)

AHCs (mg/kg)	10m		20m		30m		40m		50m		1KM	
	S	SS	S	SS	S	SS	S	SS	S	SS	CS	CSS
C9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C11	0.00	5.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C12	11.36	5.60	0.00	0.00	0.00	1.13	1.32	0.00	0.00	0.00	0.00	0.00
C13	5.64	7.08	0.00	0.00	0.00	0.34	1.09	0.00	0.00	0.00	0.00	0.00
C14	11.45	8.37	1.44	0.00	1.12	0.74	1.54	0.00	0.00	0.00	0.00	0.00
C15	17.76	7.92	0.91	0.00	0.00	1.35	1.79	0.00	0.00	0.00	0.00	0.00
C16	33.88	15.66	2.65	2.14	0.00	1.45	13.90	0.00	0.00	0.00	0.00	0.00
C17	22.56	15.35	3.53	1.80	3.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pristane	13.25	8.82	1.41	1.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C18	21.74	8.07	6.18	1.74	1.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phytane	14.31	2.33	2.44	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C19	10.83	9.36	7.58	2.26	1.72	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C20	26.36	7.69	2.68	1.07	1.79	0.56	0.00	0.59	0.56	1.42	0.00	0.58
C21	18.86	9.47	1.72	0.47	1.40	0.55	0.43	0.58	1.56	0.00	0.00	0.56
C22	9.60	3.50	2.92	6.72	1.52	2.01	0.00	0.00	0.00	0.00	0.00	0.00
C23	9.37	7.89	3.91	0.67	1.65	1.70	0.00	0.00	1.46	0.00	0.00	0.00
C24	9.85	3.26	0.78	1.26	0.77	0.93	0.00	0.95	1.94	0.00	0.00	0.00
C25	9.09	2.58	1.00	0.85	0.88	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C26	2.96	4.30	1.52	0.94	1.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C27	14.82	5.11	1.66	1.08	1.54	1.35	0.00	1.41	4.29	1.41	0.00	1.38
C28	15.80	2.71	1.97	1.18	2.02	0.00	1.29	0.00	0.00	0.00	0.00	0.00
C29	12.84	3.97	1.91	1.50	1.71	0.00	1.37	1.02	0.00	0.00	1.39	0.00
C30	30.80	8.53	6.39	2.41	4.37	0.00	1.43	0.00	0.00	0.00	0.00	0.00
C31	27.26	5.02	2.10	1.55	1.96	0.00	0.00	0.00	0.00	0.00	2.22	0.00
C32	13.04	1.57	1.31	0.00	1.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C33	29.72	2.54	1.38	0.00	1.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C34	9.34	1.70	1.40	0.00	0.00	0.00	0.00	0.00	0.00	1.32	0.00	0.00
C35	5.26	3.55	1.97	2.13	3.19	3.49	1.95	2.27	0.00	2.61	2.36	0.00
C36	5.25	1.70	1.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C37	8.49	3.54	1.93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C38	11.55	4.91	2.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	433.04	177.83	66.64	31.45	34.46	15.60	26.11	6.82	9.81	6.76	5.97	2.52
Pri/Phy	0.93	3.79	0.58	4.99	nd	nd	nd	nd	nd	nd	nd	nd
CPI ₂₅₋₃₅	1.22	0.86	0.64	1.10	0.76	1.44	0.50	2.57	0.69	nd	0.52	nd
C _{max}	C16	C16	C19	C22	C30	C35	C16	C35	C27	C35	C35	C27
C17/Pri	1.70	1.74	2.50	1.29	nd	nd	nd	nd	nd	nd	nd	nd
C18/Phy	1.52	3.46	2.53	6.21	nd	nd	nd	nd	nd	nd	nd	nd

In HMA Plant B, the concentration of the AHCs in the dry season ranged from 99.02 - 389.84 mg/kg and 5.91 - 116.22 mg/kg for surface and subsurface soils respectively while the concentration in the control sample was 23.95 mg/kg and 9.14 mg/kg for surface and subsurface soils respectively. In the rainy season, the range was between 39.03 - 65.08 mg/kg and 8.69 - 33.34 mg/kg for surface and subsurface soils respectively while the concentration in the control samples was 14.76 mg/kg and 13.31 mg/kg for surface and subsurface soils respectively.

The AHCs concentration decreased with increase in distance from HMA Plant A, an indication that the plant is the dominant source of AHCs in the vicinity. The AHCs concentration in all the samples was higher than that of the control samples except subsurface sample 20 m in HMA Plant B which was lower than the corresponding control subsurface

sample in both seasons. Furthermore, the concentration of the AHCs in the surface soils was higher than that of the corresponding subsurface soils at all sampling location. This also indicates that the AHCs might be migrating downward the soil profile from the top soil. Unlike HMA Plant A, there was no steady decline in the concentration of AHCs in HMA Plant B as the distance from the Plant increases. This could be attributed to the fact that Plant B also serves as an equipment/heavy duty vehicle yard. The maintenance and repair of these equipment and vehicles also contributed to the hydrocarbon content of the soils within the HMA plant vicinity.

The general decrease in the AHCs concentration in the samples from both plants during the rainy season may be attributed to dissolutions and runoffs from rainfall as well as a significant decrease in asphalt production during the rainy season due to reduced construction activities.

Table 2: Aliphatic hydrocarbons concentration in HMA Plant A (Rainy Season)

AHCs (mg/kg)	10m		20m		30m		40m		50m		1KM	
	S	SS	S	SS	S	SS	S	SS	S	SS	CS	CSS
C9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C14	12.21	6.13	0.00	0.00	0.00	0.00	1.34	1.70	1.06	1.28	0.00	1.12
C15	0.00	0.00	1.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C16	1.15	0.00	1.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C17	3.61	0.00	1.39	1.60	1.68	0.00	0.00	0.00	0.00	0.00	1.86	0.00
Pristane	13.68	11.4	3.48	1.40	1.29	1.06	1.48	1.80	1.68	1.23	1.02	1.77
C18	6.65	0.00	1.51	1.08	0.62	1.10	3.16	0.00	3.62	0.00	0.84	0.00
Phytane	16.23	3.00	4.15	1.50	1.01	1.85	3.60	1.65	1.80	1.06	1.16	1.75
C19	9.51	1.21	0.00	0.00	0.00	1.69	0.00	0.00	0.00	1.13	1.14	0.00
C20	1.54	3.93	1.09	1.36	2.51	1.13	0.00	2.32	0.00	1.66	1.83	0.00
C21	0.00	0.00	0.00	1.71	0.99	1.32	1.96	0.00	0.00	0.00	0.00	1.22
C22	4.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C24	0.00	0.00	1.19	0.00	1.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C25	1.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C26	0.00	1.69	1.03	1.55	2.90	0.00	0.00	1.09	0.00	1.07	0.00	0.00
C27	1.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C28	4.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C29	1.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C32	0.00	0.00	0.00	1.04	2.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C33	0.00	0.00	0.00	1.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C34	0.00	0.00	0.00	1.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C35	0.00	0.00	0.00	1.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C36	0.00	0.00	0.00	0.00	1.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C37	4.18	0.00	0.00	0.00	1.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	82.58	27.36	16.96	15.21	17.32	8.15	11.54	8.56	8.16	7.43	7.85	5.86
Pri/Phy	0.84	3.80	0.84	0.93	1.28	0.57	0.41	1.09	0.93	1.16	0.88	1.01
CPI ₂₅₋₃₅	0.78	nd	nd	0.35	nd	nd	nd	nd	nd	nd	nd	nd
C _{max}	C14	C14	C16	C21	C26	C19	C18	C20	C18	C20	C17	C21
C17/Pri	0.26	nd	0.40	1.14	1.30	nd	nd	nd	nd	nd	1.82	nd
C18/Phy	0.41	nd	0.36	0.72	0.61	0.59	0.87	nd	2.01	nd	0.72	nd

The aliphatic hydrocarbons (AHCs) distribution in the samples was used to determine the hydrocarbon sources using isoprenoid (pristane/phytane) ratios, carbon preference index (CPI) and maximum carbon chain (C_{max}).

The isoprenoid ratios are often used to differentiate the origin of hydrocarbons in environmental samples based on the fact that they are generally <1 for crude oil contaminated samples and > 1 for uncontaminated samples (Wagener *et al.*, 2010; Jeng and Huh, 2006; Pavlova and Papazova, 2003). The pristane/phytane ratios obtained from these samples indicated that petroleum products contributed to the hydrocarbon content of the soils within the plant vicinities. In HMA plant A, the pristane/phytane ratios of subsurface samples 10 and 20 m in the dry season and 10 m in the rainy season were higher than unity. This

suggests a mixture of oil and terrestrial plant materials which may be attributed to the decayed vegetation in the subsurface soils since the vicinity has been previously used as farmstead (Osuji and Achugasim, 2007). Isoprenoids (pristane and phytane) were not detected in samples from distances beyond 30 m in HMA Plant A during the dry season. Their presence in all samples from both HMA plants in the rainy season may be attributed to dissolutions and runoffs associated with the rains. The *n*C₁₇/pristane and *n*C₁₈/phytane ratios showed values below or close to 1 in most samples during the rainy season and above 1 in most dry season samples. Degradation process is suggested by values of *n*C₁₇/pristane and *n*C₁₈/phytane ratios below or close to 1 (Massone *et al.*, 2013). This suggests that the rains enhance biodegradation of the hydrocarbons in the rainy season. The *n*C₁₇/pristane and

nC_{18} /phytane ratios of the control samples in the rainy season may be attributed to the diverse sources of hydrocarbons in the area probably from leaching and runoffs associated with the rains.

Table 3: Aliphatic hydrocarbons concentration in HMA Plant B (Dry Season)

AHCs (mg/kg)	10m		20m		30m		40m		1km	
	S	SS	S	SS	S	SS	S	SS	CS	CSS
C9	0.00	0.00	1.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C12	3.09	0.00	0.00	0.00	0.00	0.00	2.08	0.00	0.00	0.00
C13	6.47	0.00	0.00	0.00	0.00	3.13	2.46	0.00	0.00	0.00
C14	19.73	0.73	1.00	0.00	3.12	3.21	4.47	0.00	0.00	0.00
C15	27.29	1.81	2.60	0.00	2.13	1.82	7.42	0.00	0.00	0.00
C16	23.24	5.97	2.81	0.00	2.63	3.52	8.30	0.00	0.00	0.00
C17	9.71	14.84	3.43	0.00	5.19	1.75	7.73	2.56	0.00	0.00
Pristane	14.97	5.03	0.43	0.00	5.62	3.13	6.15	0.38	0.00	0.00
C18	30.38	10.29	4.25	0.00	6.04	3.46	10.36	2.41	0.00	0.00
Phytane	21.14	7.28	0.00	0.00	2.35	4.95	8.59	1.63	0.00	0.00
C19	53.27	11.53	5.63	0.00	14.54	3.63	13.31	0.78	0.00	0.00
C20	4.87	12.84	6.02	0.00	13.12	2.12	14.12	0.50	0.00	0.00
C21	10.98	6.76	5.94	0.42	3.13	1.46	12.49	0.40	0.43	0.00
C22	5.20	5.63	2.57	0.00	4.29	1.97	7.26	0.60	0.00	0.00
C23	12.44	1.38	2.12	0.00	4.18	3.01	7.42	0.64	0.00	0.00
C24	2.00	1.42	5.70	0.00	3.32	3.32	3.89	0.77	0.00	0.00
C25	8.64	1.16	5.92	0.00	2.60	5.10	18.26	0.84	0.00	0.00
C26	8.13	1.71	6.83	0.00	4.51	2.54	25.56	0.96	1.11	0.00
C27	4.04	1.75	9.49	1.13	4.59	1.15	13.71	1.10	1.25	1.16
C28	9.03	2.73	6.49	1.20	5.18	2.21	57.69	1.25	1.14	1.27
C29	41.28	3.85	4.42	1.37	5.92	1.67	15.81	2.00	1.70	1.61
C30	38.27	4.14	4.83	1.79	5.93	1.46	18.60	1.55	1.40	1.49
C31	4.61	1.40	2.22	0.00	1.38	3.37	17.47	1.42	1.36	0.00
C32	8.48	1.64	2.85	0.00	1.39	4.33	16.08	1.43	1.52	1.85
C33	5.77	2.13	1.99	0.00	0.00	3.35	20.53	2.11	1.38	1.76
C34	7.18	1.66	1.87	0.00	0.00	1.98	21.48	1.54	1.61	0.00
C35	1.89	1.77	1.38	0.00	0.00	1.31	5.09	1.22	1.68	0.00
C36	2.45	1.74	1.44	0.00	2.00	3.61	6.21	1.66	1.92	0.00
C37	2.18	2.12	2.73	0.00	3.26	3.93	7.27	2.04	3.33	0.00
C38	3.11	2.91	2.94	0.00	3.89	2.80	9.31	2.76	4.12	0.00
TOTAL	389.84	116.22	99.02	5.91	110.31	79.29	369.12	32.55	23.95	9.14
Pri/Phy	0.71	0.69	nd	nd	2.39	0.63	0.72	0.23	nd	nd
CPI ₂₅₋₃₅	0.93	0.83	0.87	0.84	0.71	1.06	0.65	0.99	0.97	0.98
C _{max}	C19	C17	C27	C30	C19	C25	C28	C38	C38	C32
C17/Pri	0.65	2.95	7.98	nd	0.92	0.56	1.26	6.74	nd	nd
C18/Phy	1.44	1.41	nd	nd	2.57	0.70	1.21	1.48	nd	nd

The carbon preference index (CPI) of AHCs is useful for determining the degree of biogenic versus petrogenic input. It expresses the ratio of odd-carbon numbered to even-carbon numbered aliphatics in a given sample and has been used to differentiate biogenic AHCs from those of petrogenic or anthropogenic sources. CPI values > 2 indicates predominant biogenic sources such as epicuticular waxes of terrestrial plants while CPI values of near unity signify the source as fossil fuels or incomplete combustion of petroleum products (Simoneit, 1984). The AHCs distribution of samples between nC_{24} – nC_{34} in both plants and both seasons showed that CPI values for both surface and subsurface soils were

mostly below or close to unity signifying fossil fuel input as a result of vehicular emission and other anthropogenic activities (Kavouras *et al.*, 1999). Subsurface sample 40 m from Plant A in the dry season has a CPI value of 2.57 which suggested multiple sources (petrogenic and biogenic) or a mixture of inputs (Bakhtiari *et al.*, 2009; Azevedo *et al.*, 2007). The CPI values of samples from both HMA plants indicate that inputs from anthropogenic activities were more significant than the input from biogenic sources (Didyk *et al.*, 2000; Kavouras *et al.*, 1999).

Table 4: Aliphatic hydrocarbons concentration in HMA Plant B (Rainy Season)

AHCs (mg/kg)	10m		20m		30m		40m		1KM	
	S	SS	S	SS	S	SS	S	SS	CS	CSS
C9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C10	0.00	0.00	0.00	0.00	8.08	1.74	0.00	0.00	0.00	0.00
C11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C12	0.00	0.00	0.00	0.00	0.00	0.00	2.05	0.00	0.00	0.00
C13	0.00	0.00	0.00	0.00	0.00	0.00	2.20	0.00	0.00	0.00
C14	3.76	1.98	4.78	0.00	3.29	4.20	10.9	3.83	0.00	1.34
C15	1.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C16	2.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C17	2.35	0.00	0.00	0.00	0.00	0.00	1.94	0.00	4.64	0.00
Pristane	4.61	3.76	3.01	1.20	3.78	7.69	10.40	3.48	1.06	2.48
C18	7.05	0.00	0.00	0.00	0.00	0.00	4.20	0.00	1.60	1.97
Phytane	11.52	8.39	7.46	1.94	9.22	9.37	6.54	5.93	1.48	4.67
C19	14.35	0.00	6.13	0.00	8.14	8.47	20.83	6.59	0.00	0.00
C20	1.05	1.89	4.02	2.07	3.83	0.00	0.00	6.48	4.85	0.00
C21	7.30	0.00	4.62	1.64	0.00	0.00	0.00	0.00	0.00	0.00
C22	2.04	0.00	7.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C23	0.00	0.00	1.92	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C24	0.00	1.68	0.00	0.00	1.35	1.87	0.00	2.31	0.00	1.83
C25	0.00	0.00	0.00	1.84	0.00	0.00	0.00	0.00	1.13	1.02
C26	0.00	7.26	0.00	0.00	3.17	0.00	1.32	0.00	0.00	0.00
C27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C28	0.00	0.00	0.00	0.00	0.00	0.00	2.52	0.00	0.00	0.00
C29	0.00	0.00	0.00	0.00	0.00	0.00	2.18	0.00	0.00	0.00
C30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C34	0.00	0.00	0.00	0.00	9.59	0.00	0.00	0.00	0.00	0.00
C35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	58.3	24.96	39.03	8.69	50.45	33.34	65.08	28.62	14.76	13.31
Pri/Phy	0.40	0.45	0.40	0.62	0.41	0.82	1.59	0.59	0.72	0.53
*CPI ₁₅₋₃₅	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C _{max}	C19	C26	C22	C20	C34	C19	C19	C19	C20	C18
C17/Pri	0.51	nd	nd	nd	nd	nd	0.19	nd	4.38	nd
C18/Phy	0.61	nd	nd	nd	nd	nd	0.64	nd	1.08	0.42

*CPI; Carbon Preference Index = $0.5 \times [(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}) / ((C_{24}+C_{26}+C_{28}+C_{30}+C_{32}) + [(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}) / (C_{24}+C_{26}+C_{28}+C_{30}+C_{32})])]$, S; surface sample, SS; subsurface sample, CS; control surface sample, CSS; control subsurface sample, **pri/phy**; pristane/phytane, **nd**; cannot be detected because of the zero value of the numerator and/or denominator

The CPI of the rainy season samples could not be calculated because $nC_{24}-nC_{34}$ was not detected in the samples except for surface sample 10 m and subsurface sample 20 m in Plant A. Thus the AHCs in the rainy season samples might have been dominated by the short carbon chain aliphatics due to runoffs and predominance of hydrocarbons from diesel and petrol. The maximum AHCs concentration (C_{max}) varied from $nC_{16}-nC_{35}$ in HMA Plant A in the dry season and from $nC_{14}-nC_{26}$ during the rainy season. In HMA Plant B, it varied from $nC_{19}-nC_{38}$ during the dry season and $nC_{19}-nC_{34}$ during the rainy season. This was largely due to variations in the relative contribution of anthropogenic and biogenic

sources. In the dry season, the samples closer to the asphalt plants peaked between $nC_{16}-nC_{19}$ indicating petrogenic input. The farther samples especially in Plant A were dominated by nC_{35} except for surface sample 50 m that peaked at nC_{27} . While this might be attributed to easy susceptibility of short chain aliphatics to weathering, it also suggests biological input because high concentration of aliphatics dominated by odd number peaks is an indication of significant biological input (Maioli *et al.*, 2011; Young and Wang, 2002).

The dry season samples in HMA Plant B also showed petrogenic sources more from lubricant use.

Simoneit, (1986) has reported that a profile peak dominated by nC_{19} is an indication of lubricant oil used in gasoline and diesel powered engines. This was not surprising as the Plant B vicinity also serves as a maintenance yard for heavy duty vehicles and equipment. The rainy season samples of both plants showed clear domination of petrogenic inputs though there was reduced asphalt production in the rainy season. This might be ascribed to runoffs and dissolutions during rains as short chain carbons are more susceptible to weathering and redistribution during rainfall especially to areas that might have been predominantly dominated by biogenic sources.

Conclusion: The soil samples under study were polluted by aliphatic hydrocarbons when compared with the control samples. The most polluted sites were closer to the HMA plants which suggest anthropogenic activities associated with asphalt production as the major source of the hydrocarbons.

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