Cogitation on Hydrocarbon Contaminants in Shallow Groundwater around Kaduna Refining and Petrochemical Company, Nigeria

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Study Area: Kaduna, Nigeria

Coordinates: 7°28'45" - 7°30'0" E; 10°24'0"-10°25'20"N.

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Abstract

Kaduna refinery is the third petroleum refinery in Nigeria which consists of the fuels, lubricants and petrochemical plants. An investigation was carried out on groundwater around the refinery to ascertain the presence of hydrocarbon contaminants. Twenty-six groundwater samples were collected in the dry and rainy seasons and analyzed for identification of aromatic compounds followed by the analysis of five selected samples for the individual compounds of benzene, toluene, ethylbenzene, and xylene (BTEX) determination. Only one sample out of the twenty-six indicated the presence of aromatic hydrocarbons. The sample was selected with four others for the GC-MS analysis. None of the samples confirmed the presence of BTEX in groundwater of the area. Benzene derivative compounds were however, found in one sample. Installation of properly designed monitoring wells around the refinery was recommended for continuous groundwater monitoring

Introduction:

Groundwater plays an important role in supporting human livelihood and ecological balance. Its quality is, however, threatened by numerous anthropogenic activities. The sources of groundwater contamination are as numerous and diverse as human activities (Zaporezec, 2002). In many parts of the world, groundwater quality has deteriorated and seems unfit for human consumption without prior treatment (Yidana *et al.*, 2010; Yerima *et al.*, 2008; Raja & Venkatesan, 2010; Mohammed *et al.*, 2008; Galadima *et al.*, 2011; Foster & Chilton, 2003; Foster *et al.*, 2002; Asadi *et al.*, 2007; Berg *et al.*, 2001; Castillejos, 2010; Singh *et al.*, 2010). The impacts of many human activities on groundwater resources and on the broader environment, therefore, need to be clearly understood in order to manage properly the system (Glasser *et al.*, 2007).

Typical contaminants concern are the different components of hydrocarbons which are indeed the principal constituents of petroleum and natural gas. Hydrocarbons are the simplest organic compounds composing only hydrogen and carbon. They can be straight chain, branched chain or cyclic molecules. They can be classified as either aliphatic or aromatics. Aliphatic is derived from chemical degradation of fats or oils, whereas aromatic is derived from degradation of certain pleasant-

smelling plant extracts. Aliphatic and aromatic hydrocarbons are likely the most frequent contaminants in the environment. They are part of different distillation products such as crude oils, gasoline, kerosene, diesel, heavy oils, or asphalts, and are used in a wide range of applications such as fuel or lubrication (Kralik *et al.*, 2004). One of the main sources of hydrocarbon contamination of groundwater includes production and refining of crude petroleum and leaking of underground storage tanks (USTs) from the petrol stations. Most components of hydrocarbons are hazardous to both human life and the environment, some are either known or suspected human carcinogens (benzene), some have an adverse impact on the nervous system (toluene), while some are known to cause cardiovascular damage (ethylbenzene), they are thus, subject to strictest regulation.

When hydrocarbon compounds are released, they undergo physical, chemical and biological changes (Williams *et al.*, 2006). Their degradations depend on the physical and chemical properties of the hydrocarbon. Once hydrocarbon enters into the soil, it migrates downward through the unsaturated zone under the influence of gravity (Abriola & Pinder, 1985). Hydrocarbon may occur in soil in four different phases, dissolved in water, sorbed on solid particles, comprising the soil gas and due to their

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limited solubility forming an individual liquid phase known as non-aqueous phase liquid (NAPL) (Konecny *et al.*, 2003; Bear & Cheng, 2009; Bear 1979) but it is more customarily encountered as a distinct no-aqueous phase (Abriola & Pinder, 1985). In the capillary zone, the NAPL infiltration may be retained by the capillary forces leading to lateral migration, and the vapour may extend beyond the main area of contamination as a result of volatilization of light components. Some of the contaminants especially in large spills reach the water table and the soluble components dissolved, forming a plume of contaminated water extending outward beyond the contamination zone as part of the groundwater. The NAPL may move on its own pressure gradient within the capillary fringe zone and eventually depress natural groundwater levels (Abriola & Pinder, 1985). Perhaps the NAPL an almost immiscible integrant in water, its small solubility is sufficient to cause groundwater contamination (Bear & Cheng, 2009). Benzene, toluene, ethyl benzene and xylene (BTEX) are the most common aromatic compounds in petroleum and also the most soluble with a lowest organic carbon partition coefficient (Koc). Benzene is the most toxic and mobile in groundwater, it is the main groundwater contaminant of concern at petroleum release sites (Williams *et al.*, 2006; Lovanh *et al.*, 2000) and it is, therefore, subject to the strictest clean up standard and thus, dictates the need for remedial action in many places (Lovanh *et al.*, 2000).

Petroleum refining process consists of a complex combination of interdependent operations which involves the separation of crude molecular constituents, molecular cracking, molecular rebuilding and solvent finishing (Department of Petroleum Resources (DPR, 2002). Petroleum hydrocarbons are of environmental concern due to their volatility, adverse effect through human and environmental toxicity, mobility from point of release (lighter ends), persistent in the environment (larger and branched chain), impairment of aesthetic value such as offensive odour, taste or appearance (Saskatchewan Ministry of Environment, 2008). In the processing of crude oil, several gaseous, liquid and solid hydrocarbon wastes are discharged into the environment which may find their ways into the atmosphere, surface water, soil, and groundwater. Contaminants may reach groundwater system due to localized spill incidence from piping, storage, processing, and loading of the products as well as poor handling of waste products.

Having discovered that the risk of groundwater contamination by hydrocarbons from the KRPC operations is at best, moderate (Ahmed, 2016), it is pertinent to investigate if the operations have impacted on the groundwater of the neighbouring areas. Several researches conducted in the neighbourhood of the refinery have indicated that, the surface water, soil, and groundwater were contaminated by heavy metals among other

contaminants (Amadi *et al.*, 2014; Al-Amin 2013, Lekwot *et al.*, 2012, Vivien *et al.*, 2012, Akpan *et al.*, 2008; Al-Amin, 2006). For obvious reason, this investigations focused on the hydrocarbon contaminants in the groundwater sources of the settlements located near the refinery. The settlements under review (Rido, Kpam, Railway quarters, and Chidunu), encircled the refinery and their choice reflected the radial pattern of groundwater flow in the area as well as proximity. Since it is an established fact that, the main contaminants of concern at a crude oil and petroleum products release site are benzene, toluene, ethylbenzene and xylene (BTEX) compounds, this research concentrated on ascertaining their presence in groundwater as a clear indication of hydrocarbon contamination from the refinery. BTEX in groundwater as opined by Fetter in Kralik *et al* (2004), is a diagnostic of the oil spill. Two analytical techniques, Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography/ Mass Spectrometry (GC-MS) were used in the investigation.

Methodology:

Study area: Kaduna Refining and Petrochemical Company (KRPC) is located at the outskirts of Kaduna metropolis. It was commissioned in 1980 with an initial capacity of 100,000 barrel per stream day (bpsd) which was increased to 110,000 bpsd by 1985. It was designed to process both Nigerian and imported crude oils into fuels and lubes products. A 30,000 metric tonnes per annum Linear Alkyl Benzene (LAB) plant was also commissioned in December 1988 in the complex. KRPC produces petrol/gasoline (Premium Motor Spirit; PMS), Dual Purpose Kerosene (DPK), diesel or Automotive Gas Oil (AGO), asphalt, Linear Alkyl Benzene (LAB), base oils, Liquefied Petroleum Gas (LPG) and fuel oil.

Sources of contaminated water which pose a serious threat to groundwater system include sour water stripper condensate, cooling tower blowdown, caustic wash water, desalter water, oily process area stormwater, oily cleaning water, and spent chemicals (DPR, 2002). Among other contaminants, BTEX compounds (benzene, toluene, ethylbenzene, and xylene), and Polycyclic Aromatic Hydrocarbons (PAHs), as well as heavy metals characterized the effluent (DPR, 2002). Sources of solid waste in the refinery include sludge from crude and product tanks, corrosion products, solid from cleaning and maintenance operation, spent catalyst, refuse, sludge from wastewater treatment plant, empty metals/plastic chemical containers. Oily sludge, heavy metals, organic constituents, residue, and rust characterized the waste (DPR, 2002).

A treatment plant for wastewater was constructed in the refinery to treat all the effluents into the acceptable level before it is finally discharged into the River Romi. Equally, some of the solid waste is designed to be incinerated and the end products are used in making

fertilizer. There is also an existing contractual agreement between the company and the Kaduna State Environmental Protection Agency (KEPA) to evacuate the solid wastes to a safe site.

Figure 1: Groundwater Flow Direction Around Kaduna Refinery (Modified from Center for Energy Research and Training, 1991)

Groundwater Sampling: for hydrocarbon analysis in the laboratory groundwater samples were collected from the communities surrounding the KRPC (Figure-1). Monitoring wells were selected perpendicular to the groundwater flow directions to trap the possible hydrocarbon plume movement. A control well was selected far away from the refinery (Unguwan Dosa) and away from possible hydrocarbon sources to serve as a control sample. A total of thirteen monitoring wells were selected for screening, which were later reduced to five. Out of the thirteen wells, only two were boreholes, the remaining were open wells. Samples were collected in the dry (February, 2015) and wet seasons (August, 2014 & August 2015) to detect any seasonal variation either due to recharge or rise in groundwater level. All samples were collected in sampling bottles prepared and obtained from the National Research Institute on Chemical Technology (NARICT) Zaria laboratory. The samples were stored in an ice-packed cooler to avoid the volatilization of hydrocarbon components due to temperature rise. Samples were immediately transferred to the laboratory for extraction and hydrocarbon analyses.

Laboratory Analysis : Hydrocarbon extractions were performed in the laboratory first before running the analysis. Analyses were conducted in the laboratory of NARICT, Zaria.

Determination of organic compound using Fourier Transform Infrared Spectroscopy (FTIR): the samples of about 1 ml were absorbed and poured into a cell. This cell was then compressed into a thin pellet for 5 min. The sample was then analyzed using Shimadzu 8300 spectrometer and the spectrum was recorded in a spectral range.

Determination of Hydrocarbons (BTEX) using Gas Chromatography-Mass Spectrometer (GC-MS): isolation and extractions were conducted using Liquid-Liquid extraction (LLE) methods. 20ml of an aqueous sample was placed in a 100ml beaker, petroleum-ether (20ml) extraction solvent which has good chromatographic behavior (good extraction properties for the compounds of interest) was then injected rapidly into the solution by use of a 1.00ml gastight syringe (Hamilton, USA) and the mixture was shaken gently. A cloudy solution (water sample, Pet-ether) was formed in the test tube. The solution was then put in an oven at 45°C for about 30 min. The mixture was then centrifuged using Centurion Scientific (UK) model 2010D for 2.0 min at 5,000 rpm, causing the dispersed fine droplets of the extraction phase to settle to the bottom of the tube; 0.50ml of the settled extraction phase was then collected using a 1.00ml microsyringe and injected for GC-FID analysis. Gas chromatography was performed with a Shimadzu GC 2010 instrument with splitless injection and a flame-ionization detector. Compounds were separated on a 9 mm capillary column coated with a 0.25 mm film of BP-5 (95% methyl, 5% phenyl copolymer; SGE). Ultra-pure helium (99.9999%), passed through a molecular sieve trap and an oxygen trap was used as carrier gas at a constant linear velocity of 30 cm^{s-1}. The injection port was held at high temperature and used in splitless mode with a splitless time 0.5 min. The oven temperature was held at about 300°C. The total time for one GC run was 15 min.

Results and Discussion:

Fourier Transform Infrared Spectroscopy (FTIR) analysis: a preliminary investigation of aromatic compounds, the functional group which BTEX belongs was conducted by analyzing a total of twenty-six groundwater samples in the NARICT laboratory using the SHIMADZU FTIR-8400S Fourier Transform Infrared Spectrophotometer. The recorded peaks were compared with the correlation charts (Table-1) to deduce the functional groups of each absorption peak. Since the study was basically concern with the aromatic hydrocarbons, a diagnosis guide for aromatic according to Coates (2000) was strictly adhered to, to avoid assigning wrong interpretation due to an inherent overlap of the absorption frequency (cm⁻¹). Following the guideline, aromatics were found in only one sample tagged Railway quarters 2 which is located opposite the railway station behind the refinery. The sample which was collected in February 2015, recorded a peak at

1528.64cm⁻¹, ordinarily, it might be assigned to the amides group but the presence of two other peaks at 672.21cm⁻¹ and 779.27cm⁻¹ indicated the presence of aromatics as opined by Coates (2000). Other samples that recorded peaks at around 1533-1560cm⁻¹ such as Railway quarters 3, Rido 2, Chidunu 1 & 2 could not be supported by other peaks which are indicators of the presence of aromatics, for this reason, they were interpreted as amides. Table- 2 summarizes the result and interpretations of the analysis. From the analyses, it is evident that only one sample out of the total samples of 26 (for both wet and dry seasons), has aromatic compounds and thus, expected to contain the BTEX compounds. Such sample and four others were subjected to more robust GC-MS analysis in order to unveil their real contents. Interestingly, the control sample collected at Unguwan Dosa, more than 20KM away from the refinery contains similar compounds (alkyl halides, amines, amides and the like) as obtained within the vicinity of the refinery. This is possible as FTIR is capable of capturing both organic and inorganic compounds (Coates, 2000).

Gas Chromatography-Mass Spectrometry (GC-MS) analysis: to detect the presence of BTEX compound, five water samples from the neighborhood of Kaduna refinery were collected and subjected to GC-MS analysis. Again none of the samples was found to have the individual compounds of benzene, toluene, ethylbenzene, and xylenes. The samples were found to have different types of hydrocarbons especially the acids and esters among others (Table- 3). In the sample collected from Kankwana water well (behind the refinery's effluent discharge point tagged as Sample A), the majority of the hydrocarbon constituents (over 70%) were acids of different types. Their carbon numbers ranged between C₁₁ and C₂₂. About 4% of the constituents were the esters (C₂₁-C₃₉) of some of the acids such as octadecanoic, oleic, hexadecanoic among others. Alcohol and aldehydes account for up to 11% of the hydrocarbon content in the sample, they were mostly within the range of C₁₁-C₁₉. About 9% of the hydrocarbon content in the sample was oxacyclotetradecan-2-one with the remaining percentage (about 4%) from relatively lower molecular compounds (C₉-C₁₀) of fluorine derivatives. BTEX compounds were not found in the sample.

The sample collected from Kpam water well (Sample B) indicated the presence of hydrocarbons with more than 96% comprising different forms of carboxylic acids. Ester of octadecanoic acid account for the remaining 4%. Again, the analysis failed to indicate the presence of BTEX in the sample.

About 87% of the hydrocarbon content in the sample collected from water well close to the tanker parking area of the depot (Sample-C) are also the carboxylic acid compounds with a carbon number between 11-22. Esters account for more than 5% in the sample while butane, 1, 3-dichloro-2-methyl- and oxacyclotetradecane-2, 11-dione,

13-methyl- (C₅ and C₁₄ respectively account for about 1% each. About 2% of the hydrocarbon content in the sample were benzene compounds derivatives: 2,6,2',6'-Tetramethylazobenzene (C₁₆H₁₈N₂O₂), Benzaldehyde, 2-hydroxy-4-methyl- (C₈H₈O₂), Benzenemethanol, 4-nitro- (C₇H₇NO₃) and Benzene, [(2, 2-dimethylcyclopropyl)methyl]- (C₁₂H₁₆) although no actual benzene (C₆) was detected. Carboxylic acid compounds (C₁₁₋₁₂) constituted about 65% of the hydrocarbon content in the groundwater sample collected from the Railway quarters (Sample D). About 9% each of the content were esters and aldehydes, 12% alcohols and 5% fluorine compounds. None of the BTEX compounds was detected.

Table 1: Characteristic IR Absorptions
m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Frequency, cm ⁻¹	Bond	Functional group
36403610 (s, sh)	OH stretch,	free hydroxyl alcohols, phenols
35003200 (s,b)	OH stretch,	Hbonded alcohols, phenols
34003250 (m)	NH stretch	1°, 2° amines, amides
33002500 (m)	OH stretch	carboxylic acids
33303270 (n, s)	C≡CH:CH str.	alkynes (terminal)
31003000 (s)	CH stretch	aromatics
31003000 (m)	=CH stretch	alkenes
30002850 (m)	CH stretch	alkanes
28302695 (m)	HC=O: CH str.	aldehydes
22602210 (v)	C≡N stretch	nitriles
22602100 (w)	C≡C stretch	alkynes
17601665 (s)	C=O stretch	carbonyls (general)
17601690 (s)	C=O stretch	carboxylic acids
17501735 (s)	C=O stretch	esters, saturated aliphatic
17401720 (s)	C=O stretch	aldehydes, saturated aliphatic
17301715 (s)	C=O str. α, β	unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
17101665 (s)	C=O str. α, β	unsaturated aldehydes, ketones
16801640 (m)	C=C stretch	alkenes
16501580 (m)	NH bend 1°	amines
16001585 (m)	CC str. (inring)	aromatics
15501475 (s)	NO asym. str.	nitro compounds
15001400 (m)	CC str. (inring)	aromatics
14701450 (m)	CH bend	alkanes
13701350 (m)	CH rock	alkanes
13601290 (m)	NO sym. str.	nitro compounds
13351250 (s)	CN stretch	aromatic amines
13201000 (s)	CO stretch	alcohols, carboxylic acids, esters, ethers
13001150 (m)	CH wag (CH ₃ X)	alkyl halides
12501020 (m)	CN stretch	aliphatic amines
1000650 (s)	=CH bend	alkenes
950910 (m)	OH bend	carboxylic acids
910665 (s, b)	NH wag 1°, 2°	amines
900675 (s)	CH "oop"	aromatics
850550 (m)	CCl stretch	alkyl halides
725720 (m)	CH rock	alkanes
700610 (b, s)	C≡CH: CH	bendalkynes
690515 (m)	CBr stretch	alkyl halides

str.=stretch; sym.=symmetric; asym=asymmetric

Hydrocarbon content in the groundwater sample

collected from Rido revealed that about 90% were from different acid compounds (C_9 , C_{14} - C_{22}) with esters accounting for over 6%. Other compounds present in the sample include alcohols, aldehydes among others. Again, none of the BTEX compounds was discovered in the sample.

Table-2: FTIR interpretation

Table-2 a): RIDO 1 (Gidan Hassan)			
August 2014		February 2015	
Peak	Interpretation	Peak	Interpretation
470.65	Alkyl halides	401.21	Alkyl halides
1273.06	Alkyl halides	517.9	Alkyl halides
1643.41	Amides/alkenes	1016.52	Alkyl halides
2088.98	(All four)**	1640.51	Amides
3433.41	Amides	2061.01	(All four)**
		2342.62	
		3444.02	Amides
		3850.04	Amines

Table 2b): RIDO 2 (Gidan Dagaci)			
August 2014		February 2015	
455.22	Alkyl halides	406.3	Alkyl halides
1642.44	Amides/alkenes	515.98	Alkyl halides
2090.91	(All four)**	667.39	Alkyl halides
3443.05	Amides	1038.7	Alkyl halides
		1533.46	Amides
		1641.48	Amides/alkenes
		2071.62	(All four)**
		3440.16	Amides

Table 2c: RIDO 3 (Gidan Fati Maiwaina)			
August 2014		February, 2015	
Peak	Interpretation	Peak	Interpretation
476.3	Alkyl halides	409.89	Alkyl halides
516.94	Alkyl halides	542.98	Alkyl halides
1644.37	Amides/alkenes	1023.27	Alkyl halides
2087.05	(All four)**	1183.37	Alkyl halides
3347.57	Amides/alcohols	1455.34	Alkanes & alkyls
3430.51	Amides	1639.55	Amides
3520.21	Amines	2061.01	(All four)**
		3445.94	Amides

Table 2d: RIDO 4 (Mosque)			
August, 2014		February, 2015	
479.33	Alkyl halides	419.53	Alkyl halides
1272.1	Alkyl halides	501.51	Alkyl halides
1643.41	Amides/alkenes	592.17	Alkyl halides
2089.94	(All four)**	667.39	Alkyl halides
3439.19	Amides	1159.26	Alkyl halides
		1448.59	
		1640.51	Amides/alkenes
		2065.83	(All four)**
		2947.33	Alkanes & alkyls/ carboxylic acid
		3446.91	Amides

Table 2e: Railway quarters 1			
August, 2014		February, 2015	
481.26	Alkyl halides	531.41	Alkyl halides
1643.41	Amides/alkenes	1165.04	Alkyl halides

2088.98	(All four)**	1639.55	Amides
3433.41	Amides	2074.51	(All four)**
		2346.48	
		3444.02	Amides
		3862.58	Amides

Table 2f: Railway quarters 2			
August 2014		February, 2015	
453.29	Alkyl halides	407.96	Alkyl halides
1643.41	Amides/alkenes	510.19	Alkyl halides
2090.91	(All four)**	672.21	Aromatics
3427.62	Amides	779.27	Aromatics
		1052.2	Alkyl halides
		1528.64	Aromatics
		1646.3	Amides/alkenes
		2033.04	(All four)**
		2947.33	Alkanes & alkyls
		3443.05	Amides
		3721.77	Amines

Table 2g: Railway quarters 3			
August, 2014		February, 2015	
473.54	Alkyl halides	404.1	Alkyl halides
1643.41	Amides/alkenes	544.91	Alkyl halides
2089.94	(All four)**	1037.74	Alkyl halides
3441.12	Amides	1161.19	Alkyl halides
		1251.84	Alkyl halides
		1542.14	Amides
		1559.5	Amides
		1642.44	Amides/amines/alkenes
		2064.87	(All four)**
		3444.02	Amides

Table 2h: Railway quarters 4			
August, 2014		February, 2015	
501.51	Alkyl halides	384.81	Alkyl halides
1642.44	Amides/alkenes	1026.16	Alkyl halides
2088.98	(All four)**	1639.55	Amides
3318.64	Amides	2072.58	(All four)**
3382.29	Amides	2336.84	
3507.67	Amines	3444.02	Amides
		3851.97	Amines

Table 2i: kan-kwana			
August, 2014		February, 2015	
422.42	Alkyl halides	379.02	Alkyl halides
457.14	Alkyl halides	1021.34	Alkyl halides
1644.37	Amides/alkenes	1639.55	Amides
2092.83	(All four)**	2070.65	(All four)**
3446.91	Amides	2344.55	
		3444.02	Amides
		3854.87	Amines

Table 2j: kpam 1			
August, 2014		February, 2015	
496.69	Alkyl halides	415.67	Alkyl halides
1644.37	Amides/alkenes	549.73	Alkyl halides
2089.94	(All four)**	1638.58	Amides
3349.5	Amides/alcohols	2062.94	(All four)**
3457.52	Amides	3414.12	Amides
3558.78	Amines	3570.36	Amides

Table 2k: kpmam 2

August, 2014	February, 2015 (no data)
440.75 Alkyl halides	
1644.37 Amides/alkenes	
2088.01 (All four)**	
3443.05 Amides	

Table 2l: chidunu 1

August, 2014	February, 2015
557.45 Alkyl halides	405.06 Alkyl halides
1374.33 Alkanes & alkyls	650.03 Alkyl halides
1643.41 Amides/alkenes	1189.15 Alkyl halides
2094.76 (All four)**	1538.28 Amides
2388.92	1640.51 Amides
3468.13 Amides	2063.9 (All four)**
3851.97 Amines	3438.23 Amides

Table 2m: Chidunu 2

Chidunu 2- Gidan Ayuba (Aug '14)	February, 2015
497.65 Alkyl halides	390.6 Alkyl halides
1254.74 Alkyl halides	468.72 Alkyl halides
1641.48 Amides/alkenes	654.85 Alkyl halides
2088.01 (All four)**	1539.25 Amides
3444.02 Amides	1639.25 Amides
	2071.62 (All four)**
	3440.16 Amides

Table 2n: Unguwan Dosa

February, 2015	
339.48 Alkyl halides	1031.95 Alkyl halides
1454.38 Alkenes & alkyls	1638.58 Amines/amines
2074.51 (All four)**	3443.05 Amides
3854.87 Amines	

(All four)**=Allenes, ketenes, isocyanates, isothiocyanates

Table 3: Results of gc-ms analysis

Table 3a: Kankwana (Sample A)

Compound	Mol. For.	%
Undecanoic acid	C ₁₁ H ₂₂ O ₂	0.658
Dodecanoic acid	C ₁₂ H ₂₄ O ₂	0.658
Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	9.14
Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	5.372
Pentadecanoic acid	C ₁₅ H ₃₀ O ₂	5.372
Octadecanoic acid	C ₁₈ H ₃₆ O ₂	6.288
Heptadecanoic acid	C ₁₇ H ₃₄ O ₂	2.52
Oleic Acid	C ₁₈ H ₃₄ O ₂	9.112
Erucic acid	C ₂₂ H ₄₂ O ₂	9.112
Hexadecenoic acid,	C ₁₆ H ₃₀ O ₂	18.224
n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	3.148
(E)-13-Docosenoic acid	C ₂₂ H ₄₂ O ₂	0.378
9-Octadecenoic acid (Z)-,	C ₂₁ H ₄₀ O ₄	0.378
Octadecanoic acid, 2-(2-hydroxyethoxy)		
ethyl ester	C ₂₂ H ₄₄ O ₄	1.574
Oleic acid, 3-hydroxypropyl ester	C ₂₁ H ₄₀ O ₃	0.378
Oxacyclotetradecan-2-one	C ₁₄ H ₂₆ O ₂	9.112
Hexadecanoic acid, 1-[[[(2-aminoethoxy)hydroxyphosphinyl]oxy]methyl]-1,2-ethanediyl ester	C ₃₇ H ₇₄ NO ₈ P	1.432
Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester	C ₃₅ H ₆₈ O ₅	1.432

Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester

9-Octadecenal	C ₁₈ H ₃₄ O	2.032
10-Undecenal	C ₁₁ H ₂₀ O	2.032
9-Hexadecenal	C ₁₆ H ₃₀ O	0.378
9-Tetradecenal	C ₁₄ H ₂₆ O	2.032
11-Tridecen-1-ol	C ₁₃ H ₂₆ O	2.032
2-Octadecadecan-1-ol	C ₁₈ H ₃₆ O	2.032
12-Methyl-E,E-2,13-octadecadien-1-ol	C ₁₉ H ₃₆ O	0.378
1-Fluorodecane	C ₁₀ H ₂₁ F	1.628
1-Fluorononane	C ₉ H ₁₉ F	1.628
1-Propoxyheptane	C ₁₀ H ₂₂ O	0.814

Table 3b: Kpmam (Sample B)

Compound	Mol. For.	%
Eicosanoic acid	C ₂₀ H ₄₀ O ₂	7.662
Nonanoic acid	C ₉ H ₁₈ O ₂	0.506
n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	17.996
Octadecanoic acid	C ₁₈ H ₃₆ O ₂	16.732
Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	7.662
Oleic Acid	C ₁₈ H ₃₄ O ₂	8.608
Erucic acid	C ₂₂ H ₄₂ O ₂	8.608
E-9-Tetradecenoic acid	C ₁₄ H ₂₆ O ₂	8.608
Hexadecenoic acid, Z-11-	C ₁₆ H ₃₀ O ₂	8.608
9-Hexadecenoic acid	C ₁₆ H ₃₀ O ₂	8.608
Heptadecanoic acid	C ₁₇ H ₃₄ O ₂	2.672
Octadecanoic acid, 2-(2-hydroxyethoxy)		
ethyl ester	C ₂₂ H ₄₄ O ₄	3.73

Table 3c: Depot (Trailer parking area (Sample C)

Compound	Mol. For.	%
2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂	0.328
6-Methyl-3-phenethylsulfanyl-[1,2,4] triazin-5-ol	C ₁₂ H ₁₃ N ₃ OS	1.02
cis-Z-11,12-Epoxytetradecan-1-ol	C ₁₄ H ₂₈ O ₂	0.26
6,11-Dimethyl-2,6,10-dodecatrien-1-ol	C ₁₄ H ₂₄ O	0.156
2,7-Dioxa-tricyclo[4.4.0.0(3,8)]deca-4,9-diene	C ₈ H ₈ O ₂	0.328
Farnesol isomer a	C ₁₅ H ₂₆ O	0.156
2,6,2',6'-Tetramethylazobenzene	C ₁₆ H ₁₈ N ₂ O ₂	0.328
Benzaldehyde, 2-hydroxy-4-methyl-	C ₈ H ₈ O ₂	0.328
Benzenemethanol, 4-nitro-	C ₇ H ₇ NO ₃	0.328
Benzene,[(2,2-dimethylcyclopropyl)methyl]	C ₁₂ H ₁₆	1.02
Oxacyclododecan-2-one	C ₁₁ H ₂₀ O ₂	0.982
Cyclopropanecarboxylic acid, benzyl ester	C ₁₁ H ₁₂ O ₂	2.04
Octadecanoic acid, 2-(2-hydroxyethoxy)		
ethyl ester	C ₂₂ H ₄₄ O ₄	3.03
Butane, 1,3-dichloro-2-methyl-	C ₅ H ₁₀ Cl ₂	1.02
Oxacyclotetradecane-2,11-dione, 13-methyl-	C ₁₄ H ₂₄ O ₃	0.982
Undecanoic acid	C ₁₁ H ₂₂ O ₂	0.874
Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	2.23
n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	16.812
Dodecanoic acid	C ₁₂ H ₂₄ O ₂	0.874
Pentadecanoic acid	C ₁₅ H ₃₀ O ₂	7.516
Octadecanoic acid	C ₁₈ H ₃₆ O ₂	13.004
Oleic Acid	C ₁₈ H ₃₄ O ₂	7.39
9-Hexadecenoic acid	C ₁₆ H ₃₀ O ₂	7.39
Z-11-Tetradecenoic acid	C ₁₄ H ₂₆ O ₂	0.982
Heptadecanoic acid	C ₁₇ H ₃₄ O ₂	8.994

Erucic acid	$C_{22}H_{42}O_2$	6.408
Hexadecenoic acid, Z-11-	$C_{16}H_{30}O_2$	7.342
E-9-Tetradecenoic acid	$C_{14}H_{26}O_2$	5.474
9,12-Octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$	0.26
9-Octadecynoic acid	$C_{18}H_{32}O_2$	0.26
Undec-10-ynoic acid	$C_{11}H_{18}O_2$	0.26
Eicosanoic acid	$C_{20}H_{40}O_2$	0.906
1,5,9-Undecatriene, 2,6,10-trimethyl-, (Z)-	$C_{14}H_{247}$	0.156
Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, [1R-(1.alpha.,2.beta.,5.alpha.)]-	$C_{10}H_{18}$	0.26
Squalene	$C_{30}H_{50}$	0.156
4,4,8-Trimethyl-non-5-enal	$C_{12}H_{22}O$	0.156

Table 3d: Railway Quarters (Sample D)

Compound	Mol. For.	%
Undecanoic acid	$C_{11}H_{22}O_2$	0.78
Dodecanoic acid	$C_{12}H_{24}O_2$	0.78
Tetradecanoic acid	$C_{14}H_{28}O_2$	5.584
n-Hexadecanoic acid	$C_{16}H_{32}O_2$	4.844
Pentadecanoic acid	$C_{15}H_{30}O_2$	6.122
Octadecanoic acid	$C_{18}H_{36}O_2$	5.342
Heptadecanoic acid	$C_{17}H_{34}O_2$	4.602
Oleic Acid	$C_{18}H_{34}O_2$	6.964
Erucic acid	$C_{22}H_{42}O_2$	6.964
Hexadecenoic acid, Z-11-	$C_{16}H_{30}O_2$	6.964
9-Hexadecenoic acid	$C_{16}H_{30}O_2$	6.964
E-9-Tetradecenoic acid	$C_{14}H_{26}O_2$	8.242
n-Hexadecanoic acid	$C_{16}H_{32}O_2$	0
(E)-13-Docosenoic acid	$C_{22}H_{42}O_2$	0.494
Decane, 1-fluoro-	$C_{10}H_{21}F$	3.876
1-Fluorononane	$C_9H_{19}F$	1.058
Hexadecanoic acid, 2,3-dihydroxypropyl ester, (+/-)-	$C_{19}H_{38}O_4$	1.38
Pentafluoropropionic acid, tridecyl ester	$C_{16}H_{27}F_5O_2$	1.058
Hexadecanoic acid, 1-[[[(2-aminoethoxy)hydroxy-phosphinyl]oxy]methyl]-1,2-ethanediyl ester	$C_{37}H_{74}NO_8P$	1.57
Octadecanoic acid, 2-(2-hydroxyethoxy) ethyl ester	$C_{22}H_{44}O_4$	1.278
Hexadecanoic acid, 2,3-dihydroxypropyl ester	$C_{19}H_{38}O_4$	2.76
Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester	$C_{39}H_{76}O_5$	1.058
Dodecanoyl chloride	$C_{12}H_{23}Cl$	0.19
Decanoyl chloride	$C_{10}H_{19}Cl$	0.19
2-Methyl-Z,Z-3,13-octadecadienol	$C_{19}H_{36}O$	3.79
9-Octadecenal	$C_{18}H_{34}O$	3.79
10-Undecenal	$C_{11}H_{20}O$	3.79
E-9-Tetradecenal	$C_{14}H_{26}O$	0.494
2-Tridecenal, (E)-	$C_{13}H_{24}O$	0.494
2-Dodecenal, (E)-	$C_{12}H_{22}O$	0.494
3,11-Tetradecadien-1-ol	$C_{14}H_{26}O$	0.494
E-2-Octadecadecen-1-ol	$C_{18}H_{36}O$	3.79
3,11-Tetradecadien-1-ol	$C_{14}H_{26}O$	3.79

Table 3e: Rido (Sample E)

Compound	Mol. For.	%
1-Decene	$C_{10}H_{20}$	0.222
1-Undecene	$C_{11}H_{22}$	0.222
3-Decene	$C_{10}H_{20}$	0.222

1-Dodecene	$C_{12}H_{24}$	0.222
1,6,10-Dodecatrien-3-ol, 3,7,11-trimethyl-,	$C_{15}H_{26}O$	0.158
7-Thiabicyclo[4.1.0]heptane, 1-methyl-	$C_7H_{12}S$	0.21
Cyclopropane, 1-(1'-propenyl)-2-hydroxymethyl-	$C_7H_{12}O$	0.21
2-Oxabicyclo[2.2.1]heptan-3-one, 1,7,7-trimethyl	$C_9H_{14}O_2$	0.21
1-Heptanol, 6-methyl-	$C_8H_{18}O$	0.416
9-Hexadecenoic acid	$C_{16}H_{30}O_2$	9.012
Hexadecenoic acid, Z-11-	$C_{16}H_{30}O_2$	18.024
Pentadecanoic acid	$C_{15}H_{30}O_2$	5.216
Tetradecanoic acid	$C_{14}H_{28}O_2$	9.822
Octadecanoic acid	$C_{18}H_{36}O_2$	9.822
n-Hexadecanoic acid	$C_{16}H_{32}O_2$	14.918
Heptadecanoic acid	$C_{17}H_{34}O_2$	4.726
7-Hydroxy-6-methyl-oct-3-enoic acid	$C_9H_{16}O_3$	0.21
Oleic Acid	$C_{18}H_{34}O_2$	9.012
Erucic acid	$C_{22}H_{42}O_2$	9.012
Butanoic acid, 4-chloro-, methyl ester	$C_5H_9ClO_2$	0.48
Hexanoic acid, 5-methyl-, methyl ester	$C_8H_{16}O_2$	0.16
4-Nonenoic acid, methyl ester	$C_{10}H_{18}O_2$	0.37
Octadecanoic acid, 2-(2-hydroxyethoxy) ethyl ester	$C_{22}H_{44}O_4$	4.606
Valeric acid, 2-pentadecyl ester	$C_{20}H_{40}O_2$	0.416
4-Tridecene, (Z)-	$C_{13}H_{26}$	0.416
1-Nonanol	$C_9H_{20}O$	0.222
Isooctanol	$C_8H_{18}O$	0.416
2-Undecenal	$C_{11}H_{20}O$	0.416
1,1-Cyclopropanedicarbonitrile, 2-methyl-2-pentyl-	$C_{11}H_{16}N_2$	0.158
9-Oxabicyclo[6.1.0]nonane, 1-methyl-, cis-	$C_9H_{16}O$	0.158
8-Decen-2-one, 9-methyl-5-methylene-	$C_{12}H_{20}O$	0.158
3-Ethyl-6-heptafluorobutyryloxyoctane	$C_{14}H_{21}F_7O_2$	0.158

Mol.For = Molecular formula

Conclusion:

Although the risk from the refinery appears to be moderate, traces of benzene compounds (C_7 , C_8 , C_{12} , and C_{16}) were found in the groundwater sample collected around the refinery's access gate by trailer parking area (Sample C) in the GC-MS analysis. Also, the presence of aromatic compounds was discovered in one of the groundwater samples collected at railway quarters in the FTIR analysis. The two samples were both taken from open wells with poor casings and cover. Facts deduced from these occurrences are, either, the concentrations of the BTEX compounds especially benzene were higher in the groundwater than the observed content, or the contaminants were introduced via other pathways or both. Considering the volatility of the compounds, it could be stated that, most of the lighter hydrocarbon components especially benzene (C_6) have volatilized into the air leaving the heavier ones in the groundwater as observed in Sample C. The result could be different if the samples were from properly designed monitoring wells. It is therefore evident that only a properly designed monitoring well network can reveal the extent of hydrocarbon content in the groundwater system around the refinery. It is

recommended that properly designed monitoring wells surrounding the refinery should be drilled for continuous groundwater monitoring. Completion of the sludge pit remediation program in the refinery and rehabilitation of the wastewater treatment plant is highly recommended. On the part of the communities, proper casing and cover of the water wells to avoid hydrocarbon contaminants influx should be strictly adhered to. This practice will help safeguard the safety of groundwater in the area.

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