International Journal of Environmental Protection and Policy
2020; 8(2): 36-43
http://www.sciencepublishinggroup.com/j/ijepp
doi: 10.11648/j.ijepp.20200802.11
ISSN: 2330-7528 (Print); ISSN: 2330-7536 (Online)

Characterized Organic Pollutants and Their Health Effects in Sampled Groundwater Around Ilorin Metropolis

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To cite this article:

Oluwaseun Emmanuel Odipe, Henry Olawale Sawyerr, Solomon Olayinka Adewoye. Characterized Organic Pollutants and Their Health Effects in Sampled Groundwater Around Ilorin Metropolis. *International Journal of Environmental Protection and Policy*. Vol. 8, No. 2, 2020, pp. 36-43. doi: 10.11648/j.ijepp.20200802.11

Received: March 6, 2020; **Accepted**: March 23, 2020; **Published**: April 30, 2020

Abstract: The study was aimed at determining the possible volatile organic compounds present in groundwater from hand-dug wells within and around filling stations across Ilorin metropolis as well as to ascertain the possible sources of the contaminants and their health effects. Water samples were obtained from twenty-six (26) wells that were found within the scope of stations above the age of 15 years and functioning with underground storage tank capacities of over 33,000 L each for different petroleum products stored above the water level. Laboratory analysis to determine volatile organic compounds and their concentrations were carried out using the gas chromatography- mass spectrophotometer (GC-MS) after prior extraction of hydrocarbon from the water samples by the Liquid-Liquid Extraction (LLE) method. The result revealed a total of fifty-three (53) VOCs across samples where nonanal, dodecane, methyl palmitate, heptanophenone, 13, hexyloxacyclotridec – 10 – en – 2 – one, cyclohexane, octyl, decahydro- 4, 4, 8, 9, 10 – pentamethyl naphthalene, (z) – 3 – heptene, were the most frequently occurring compounds, which could be traced to anthropogenic activities involving the use of paints, detergents, stain removers, leaking underground storage tanks, piped networks containing petroleum products as the possible sources of release into the environmental media. Related health impacts from exposure to these contaminants includes brain damage, cancer, tumours, anaemia, central and peripheral nervous system breakdown, liver, bones, autism, Skin, eye, and nose irritation, headache, dizziness, narcosis, and death at high levels of exposure. The study concluded that groundwater sources at close proximity to filling stations are susceptible to contamination through activities in the stations and such water resource should be treated before consumption and use to avoid negative health effects.

Keywords: Volatile Organic Compounds, Groundwater, Filling Stations, Ilorin Metropolis, Health Impact

1. Introduction

Ilorin Metropolis, the urban centre of the ancient Ilorin emirate (the present day capital town) of Kwara State, North-Central, Nigeria lies within coordinates of Latitude 8° 30'N and Longitude 4° 30'E respectively and it covers an approximated area of 180 sqkm within 765 sqkm of the three (3) local government areas in Ilorin town [1]. Ilorin is a fast growing town that is geographically divided into three Local government areas namely Ilorin East, Ilorin South and Ilorin West, with populations at 204,310, 208,691, 364,666 respectively as at the 2006 Nationwide census totally 777,667 [2], and geopolitically subdivided into 35 wards.

After the creation of Kwara State in 1967 and Ilorin made the state capital, with its North central geographical positioning in Nigeria aided various investors to come in and set up industries of different types and grades. The establishment of these industries led to relative increase in population and demand of fossil fuels and petroleum products for power generation, automobile and transport, household fuels amongst others which has indiscriminately promoted the siting of filling stations in all corners of the city.

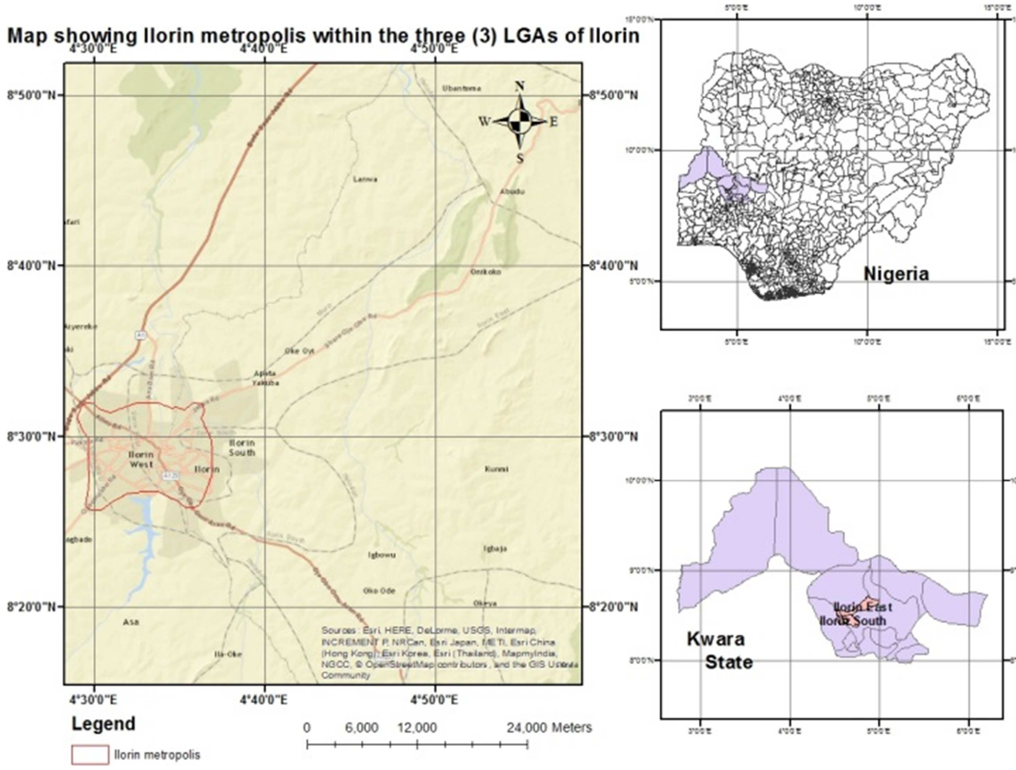

Figure 1. *Showing the map of Ilorin metropolis within the three (3) local government areas of Ilorin town [1].*

Many anthropogenic activities in our neighbourhood pollutes the environment where toxic and health threatening contaminants are released into soil, water and air. Activities in a filling station and possible leaking underground storage tanks can release numerous chemicals that also pollutes groundwater since the products available in these stations are complex blends of countless compounds majorly hydrocarbons. Examples of these contaminants are classified as volatile organic compounds (VOC), oxygenates, heavy metals, polycyclic aromatic hydrocarbon (PAH), phenols, chlorobenzenes, phthalates, and organochlorides etc. [3].

Hydrocarbons are organic compounds made up of carbon and hydrogen atoms only or with more elements like oxygen, sulphur, silicon, halogens etc., they are readily available substances around us for use such as in petroleum products, cosmetics, plastics, bleach, greases etc. [4].

The objective of this study therefore is to determine the concentration of volatile organic compounds present in groundwater obtained from within and around sampled filling stations in the metropolis and to evaluate the potential health risk from consumption and usage of these water resources.

2. Materials and Methods

2.1. Geology, Hydrogeology and Drainage Pattern of the Study Area

The occurrence of groundwater is greatly influenced by the local geological conditions which ultimately control yields. Groundwater resources are often, but not always renewable. Groundwater occurrence depends primarily on geology, geomorphology/weathering and rainfall (both current and historic). This interplay of these three factors gives rise to complex hydrogeological environments with countless variations in the quantity, quality, ease of access and renewability of groundwater resources [5].

The Ilorin Metropolis is underlain by the migmatite gneiss rock type of the Precambrian Basement Complex Rocks of Nigeria as shown in Figure 2 [6]. In basement complex area, groundwater is contained within the weathered and or fractured/jointed basement columns [7]. The availability of groundwater in areas underlain by crystalline basement rocks depends on the development of thick soil overburden (overburden aquifers), the presence of weathered layers or fractures that are capable of holding water (fractured crystalline aquifers). The storage of groundwater is confined to fractures and fissures in the weathered zone of crystalline rocks, the thickness of which range from <10 - 60 m in arid and humid environment. The groundwater resources here are usually limited.

The unconfined nature and the near-surface occurrence of the aquifer system makes it vulnerable to surface/near surface pollutants such as seepages from underground storage tanks of petroleum products.

Ilorin metropolis is mainly drained by River Asa, with many tributaries leading to a dendritic drainage pattern as shown in Figure 3 [8-10]. River Asa drains in a North-South direction before being dammed as Asa dam, its flow pattern divides the metropolis into eastern and western parts. Other rivers within the metropolis that drains into Asa river includes River Agba (also dammed), River Alalubosa, River Okun, River Osere, River Aluko, and River Odota.

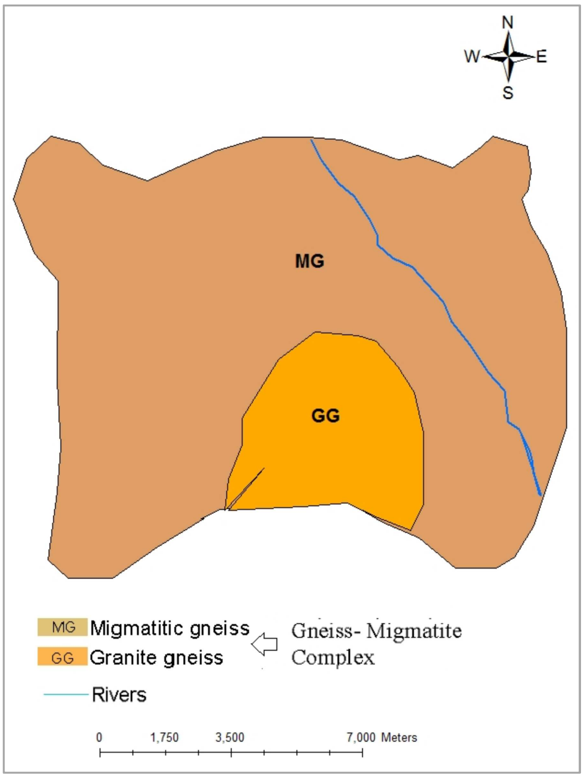

Figure 2. *Geological map of Ilorin metropolis.*

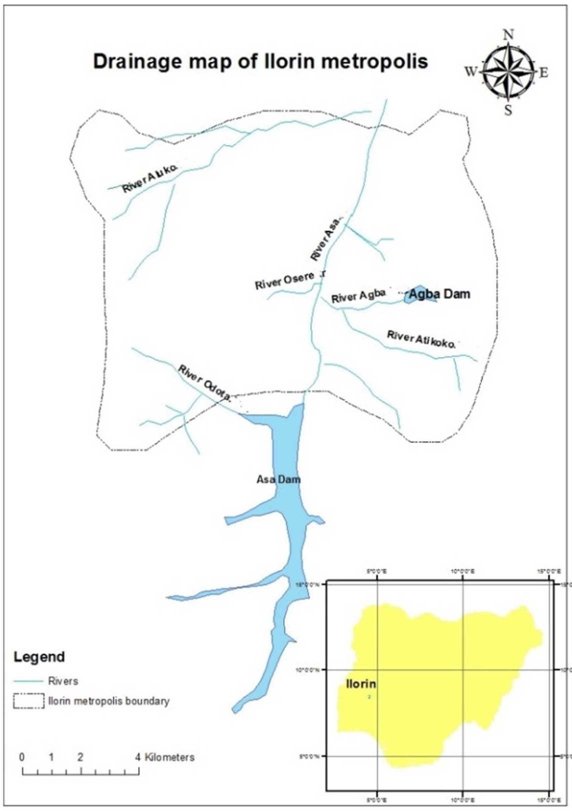

Figure 3. *The drainage pattern of Ilorin metropolis and major rivers.*

2.2. Methods

Laboratory analysis of groundwater samples collected from hand-dug wells within and around functioning filling stations of above 15 years of operation within the metropolis was collected to detect possible volatile organic compounds and their concentrations. Twenty-six (26) stations were sampled and a total of fifty-two (52) samples (including duplicates) were collected (Figure 4). Analyses carried out involved the extraction of hydrocarbon from the water samples and characterization using a gas chromatography from Agilent USA hypherated to a mass spectrophotometer (5975C) with triple axis detector equipped with an auto injector (10ul syringe) where Helium gas was used as a carrier gas.

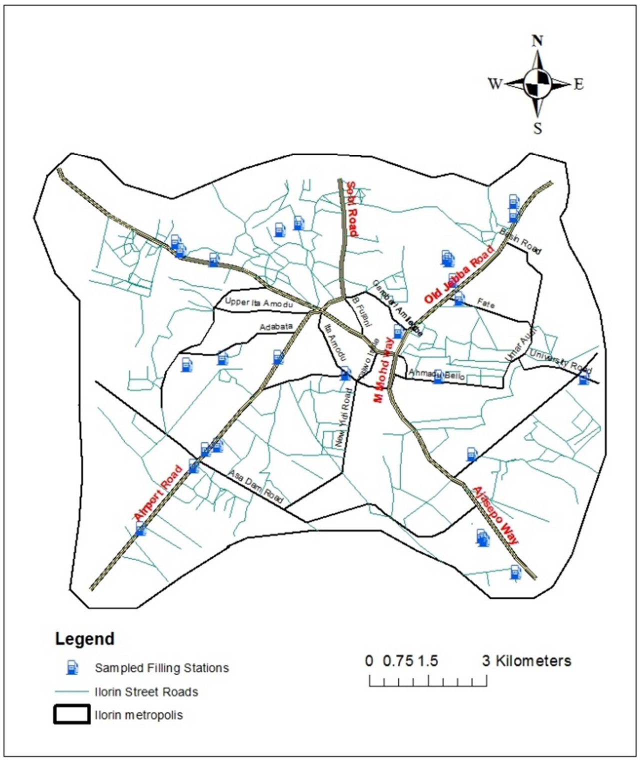

Figure 4. *The Spatial Distribution of the Selected Sample Stations.*

2.2.1. Procedure for Extraction of Hydrocarbon from Water Samples

For the extraction of hydrocarbon from the water sample, the Liquid-Liquid Extraction (LLE) method was used. The Liquid-Liquid extraction is a method used to separate compounds based on their relative solubilities in different immiscible liquids. In the LLE procedure, the sampled water was extracted by using organic solvents, the water sample was poured into a separatory funnel and the mixture of 100ml n-hexane and Dichloromethane (1:1 v/v) was added and well shaken for 2 minutes. The mixture in the separatory funnel was left to stand for 10minutes which allowed the separation of an aqueous phase from the organic phase. The aqueous phase was carefully drained away and then the organic phase was poured into a glass funnel containing 20g of anhydrous sodium sulfate and re-extracted with 50ml of the solvent mixture. The organic extract (free from water) was transferred into 2ml vial carefully for the next phase of organic characterization using the Gas Chromatography/ Mass Spectroscopy. All samples (including duplicates) were treated in the same manner as indicated above.

2.2.2. Procedure for Determining Petroleum Hydrocarbon Compounds Present and Their Concentrations

All experiments were performed with a high resolution GC-MS by Agilent Technologies of 7890A GC system and 5975C inert MSD with Triple-Axis Detector using the EPA Method 8021 for Volatile Organic Compounds at the Department of Chemical Engineering, University of Ilorin, Nigeria; a gas carrier of Helium at speed of 9 mL/min was measured at 35°C; the oven temperature was programmed as follows:

1. 35°C for 12 mins,
2. 35°C - 60°C at 5°C/min,
3. then 60°C for 1 min,
4. 60-200°C at 17°C/min and,
5. Final temperature at 200°C for 5min.

The analysis procedure started with a solvent blank followed by calibration verification standard, method blank and finally the extracts (oil extracts) analysis where 2 µL of samples were introduced into the injector.

The Chromatographic peaks were processed using the Ms Solution software provided by the supplier to control the system and acquire the data. Identification of the compounds was carried out by comparing the mass spectra obtained with those of the standard mass spectra from NIST library (NISTII).

3. Results

The result for volatile organic compounds and their concentrations across all samples is shown in the Table 1.

Table 1. *Occurrence frequency and area percent of VOCs identified across samples.*

Sample & No.		Compounds	Area	Frequency
A	1	1,2 benzisothiazol-3-amine	1.54	1
	2	Nonanal	1.42	7
B	1	Dodecane	2.11	4
	2	2 - undecanone,6,10 – dimethyl	2.38	1
	3	Phthalic acid, isobutyl octyl ester	2.08	1
	4	2-Nitro-4-(trifluoromethyl) phenol	1.49	1
C	1	Methyl palmitate	1.64	4
	2	1, 6 - octadien-3-ol,3,7,-dimethyl	4.92	1
	3	Estragole	40.70	1
D	1	m-Hydroxymandelic-acid, tris (trimethylsilyl)	4.49	1
E	1	Benzene, azido	1.21	4
	2	Butylated Hydroxytoluene	1.60	1
	3	3 – isoprophyphenol	2.94	1
F	1	1,2 - Bis (trimethylsilyl) benzene	1.64	1
	2	Heptanophenone	5.69	1
	3	13-Hexyloxacyclotridec-10-en-2-one	70.55	3
H	1	Benzoic acid, 2-6-bis [(trimethyl)oxy]-trimethyl silyl ester	5.44	3
I	1	trans-2-Decenoic acid	11.0	1
	2	Cycloctaneactic acid, 2-oxo	2.07	1
	3	1-[4-tert,-butyl] phenyl]-2(4-bluidino)-1-ethanone	2.52	1
J	1	2-p-Nitrophenyl-oxidiazol-1,3,4,-one-5	1.86	1
K	1	11-octadeconoic acid, methyl,(z)-	27.29	1
M	1	2-chloro-4,6-di-piperidin-1-yl-[1, 3, 5]	0.90	1
	2	m-fluoroanisol	0.81	1
	3	2-cyclohexen-1-ol	3.99	1
	4	3-Hexene,2,2,5,5-tetramethyl-(Z)	0.89	1
	5	2-octenal, (E)	4.74	1
	6	9-Octadecenoic acid, methyl ester (E)	15.15	1
N	1	Tridecane, 7-methyl -	0.67	1
	2	Napthalene, 2-methyl -	0.45	1
	3	Cyclohexane, octyl	0.56	2
	4	Pento barbital	1.69	1
	5	Decahydro-4,4,8,9,10-pentamethyl naphthalene	2.07	2
	6	2,10-Dodecadien-1-ol,3,7,11,-trimethyl, (2)-(+/-)-	0.63	1
	7	Napthalene,1,6,7-trimethyl	0.73	1
	8	(2H-[1,2,4] Tiazol-3yl) acetic acid	0.96	1
	9	Napthalene,1,4,6-trimethyl	1.46	1
	10	Pentadecane,2,6,10-trimethyl	2.52	1
O	1	(Z)-3-Heptene	22.83	2
	2	3,3, Diispropoxy-1,1,1,5,5,5-hexamethyl trisiloxane	1.61	1
R	1	Fa,9-(Iminoethano) phenothro [4,5-bcd] furam 4a.alpha, 5-dihydro-3-methyl-12-methyl	4.79	1
S	1	Cyclopentane,1,2-dipropyl	0.75	1
	2	n-Nonycyclohexane	1.90	1
	3	Magnesium bis (acetylacetonate)	0.92	1

Sample & No.		Compounds	Area	Frequency
	4	Cyclohexane decycl	0.84	1
T	1	Aziridine,1-hexyl	2.01	1
	2	1-phenizine carboxylic acid,6-1 (-1 hydroxy-ethyl) -methyl estr	1.68	1
V	1	Tetrasiloxane decamethyl	0.85	1
	2	Heneicosane	27.24	1
W	1	Cyclotetrasiloxane Octamethyl	2.51	1
	2	Methoxyacetic acid, 4-tetradecyl ester	0.92	1
	3	Diethyl 2,6-dimethyl-4-phenyl – 3, 5 – pyridine dicarboxylate	1.20	1
X	1	1-Hexanone, 5-methyl-1-phenyl	5.60	1
	2	Heptanophenone	3.90	1

4. Discussion

Of the 26 samples, a total 53 VOCs were found across all samples except in samples G, L, P, U, and V and Z. Nonanal; Dodecane; Methyl palmitate; Heptanophenone; 13, Hexyloxacyclotridec – 10 – en – 2 – one; Cyclohexane, octyl; Decahydro- 4, 4, 8, 9, 10 – pentamethyl naphthalene; (z) – 3 – Heptene, were the most frequently occurring compounds with frequencies of above one (Table 1).

Across these samples, volatile organic compounds were found at different concentration ranging from 0.45% - 70.55% area and possible contamination in this aquifers could be traced to conditions such as paints, detergents, stain removers, leaking underground storage tanks, piped networks containing petroleum products etc. (Table 2).

4.1. Possible Sources of Identified Volatile Organic Compounds

Table 2. *Volatile organic compounds with their possible sources.*

Compounds	Possible Sources
1,2 benzisothiazol-3-amine	emulsion paints, adhesives, inks, car care products, laundry detergents, gas and oil drilling in muds and packer fluids preservation [11].
Nonanal	Maintenance and repair of automobiles, Generic lubricants, lubricants for engines, brake fluids, oils, Personal care products, including cosmetics, shampoos, perfumes, soaps [12].
Dodecane	paraffin fraction of petroleum, breathing in gasoline fumes and automobile exhaust, inhaling some wood smoke, or skin contact with petroleum products containing dodecane, refined oil products [13, 14]
Phthalic acid, isobutyl octyl ester	plastic manufacturing, additive in paints, lubricants, adhesives and insecticides [15]
Methyl palmitate	detergents, emulsifiers, wetting agents, stabilizers, resins, lubricants, plasticizers [16]
1, 6 - octadien-3-ol,3,7,-dimethyl	perfumes, cosmetics and soaps, detergents and waxes [17]
Estragole	pesticide products, food flavoring and in perfumes, de-greasers, spot removers [18]
Benzene, azido	petroleum products, including motor fuels and solvents [19].
Butylated Hydroxytoluene	antioxidant, used to prevent oxidation in fluids (e.g. fuel, oil) [20].
3 – isoprophyphenol	Crude oil, crude petroleum, refined oil products, fuel oils, drilling oils, production of metals [21]
1,2 - Bis (trimethylsilyl) benzene	Crude oil, crude petroleum, refined oil products, fuel oils, drilling oils, production of metals [21]
13-Hexyloxacyclotridec-10-en-2-one	Fragrance [22]
1-[4-tert,-butyl] phenyl]-2(4-bluidino)-1-ethanone	cleaning_washing products [23]
9-Octadecenoic acid, methyl ester (E)	Personal care products, including cosmetics, shampoos, perfumes, soaps, lotions, toothpastes, detergents, emulsifiers, wetting agents, stabilizers, textiles treatment, plasticizers for duplicating inks, rubbers, waxes [16, 23]
Napthalene, 2-methyl -	Crude oil, crude petroleum, refined oil products, fuel oils, drilling oils, manufacturing of fertilizers, used for preventing, destroying or mitigating pests, home products (cleaners, laundry products, air fresheners) [24]
n-Nonycyclohexane	It is present in all crude oils, paint and varnish remover, nylon intermediates, solvent for lacquers, resins and synthetic rubber [25, 26]
Tetrasiloxane decamethyl	Functional fluids (closed systems), Intermediates, Lubricants and lubricant additives, Personal Care Additive [23]
Heneicosane	components in petroleum products [27]

4.2. Health Risk Associated with Identified Pollutants

The volatile organic compounds (VOCs) have also been reported to pose health risks, some of the compounds and reported health risks in Table 3:

Table 3. *Possible health impacts of some VOCs found in the samples.*

Compounds	Health impacts
1,2 benzisothiazol-3-amine	dermal exposure can cause skin sensitization and allergic contact dermatitis, also reported case of asthma when inhaled [28 – 30]
Nonanal	Autism, Crohn's disease, Uremia, Ulcerative colitis, Crohn's disease, Celiac disease [12, 31 – 33]
Dodecane	Cytotoxic effects, proinflammatory activities in human epidermal keratinocytes (HEK) [34]
Phthalic acid, isobutyl octyl ester	hormone disruption that affects development and fertility [35]
2-Nitro-4-(trifluoromethyl) phenol	Causes eye, skin and respiratory irritation [36]
Methyl palmitate	allergic skin reaction, skin irritation [37]

Compounds	Health impacts
1, 6 - octadien-3-ol,3,7,-dimethyl	Skin, eye, and nose irritation [17]
Estragole	suspected to be carcinogenic and genotoxic, nausea, vomiting, seizures and pulmonary edema [16, 18]
Benzene, azido	skin irritation, serious eye irritation, damage to organs through prolonged or repeated exposure [38]
Butylated Hydroxytoluene	possible link with cancer risk, asthma, and behavioural issues in children [39]
3 – isoprophyphenol	Causes severe skin burns and eye damage, Suspected of causing genetic defects, Causes damage to organs through prolonged or repeated exposure, Toxic to aquatic life with long lasting effects [37]
1,2 - Bis (trimethylsilyl) benzene	eye irritation [40]
Heptanophenone	Chemical poisoning, inhibitory effect on carbonyl reductase activity in pig heart has been examined [41, 42]
trans-2-Decenoic acid	skin burns and eye damage [43]
1-[4-tert,-butyl] phenyl]-2(4-bluidino)-1-ethanone	Flammable liquid and vapour [44]
11-octadeconoic acid, methyl,(z)-	Eye, skin irritation, and respiratory irritation [37]
2-chloro-4,6-di-piperidin-1-yl-[1, 3, 5]	Harmful if swallowed, eye damage, respiratory and skin irritation, Toxic to aquatic life with long lasting effects [37]
m-fluoroanisol	Flammable liquid and vapour [37]
2-cyclohexen-1-ol	Flammable liquid and vapour [37]
2-octenal, (E)	eye damage, respiratory and skin irritation [37]
9-Octadecenoic acid, methyl ester (E)	May cause mild irritation on contact with skin or mucous membranes [16, 45]
Napthalene, 2-methyl -	irritation of the skin, eyes, mucous membranes and upper respiratory tract. It may also cause headaches, nausea, vomiting, diarrhea, anemia, jaundice, euphoria, dermatitis, visual disturbances, convulsions and comatose [46]
Pento barbital	severe injury or death [47]
Napthalene,1,6,7-trimethyl	Harmful if swallowed, Very toxic to aquatic life [37]
(Z)-3-Heptene	May be fatal if swallowed and enters airways [37]
n-Nonycyclohexane	depress the central nervous system in humans, cause headache, dizziness, narcosis, and death at high levels of exposure [25, 48, 49]
Magnesium bis (acetylacetonate)	Acute toxicity – oral, dermal, eye irritation. Suspected of causing cancer [37]
Tetrasiloxane decamethyl	harmful effects to aquatic life [50]
Heneicosane	toxic effects in humans were not available. However, lesions in the liver, that did not cause liver dysfunction, have been associated the ingestion of mineral oils [27, 51]
Methoxyacetic acid, 4-tetradecyl ester	eye damage, respiratory and skin irritation [37]
Heptanophenone	eye damage, respiratory and skin irritation [37]

5. Conclusion

The sources of these contaminants may be geogenic and anthropogenic in origin, but some common sources are leaching of rusted USTs, emulsion paints, laundry detergents in car wash and lube bays within stations, lubricants, petroleum and engine fluids etc., and some reported health impacts are brain damage, cancer, tumours, neonatal defects, anaemia, central and peripheral nervous system breakdown, damage to the kidney, liver, bones, autism, Crohn's disease, uremia, ulcerative colitis, celiac disease, Skin, eye, and nose irritation, depress the central nervous system in humans, cause headache, dizziness, narcosis, and death at high levels of exposure.

Hence, the risk of contamination in groundwater resources at close proximities to filling stations is high and the impact of contaminants that can be released into the environment by the activities at these stations requires proper water treatment before use and consumption.

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