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Assessment of potential health impact of volatile organic compounds of underground water samples around fuel station in Okinni area Osogbo, Osun State, Nigeria

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Abstract

Levels and potential toxicity of volatile organic compounds (VOCs) were analyzed in underground water from six locations near a fuel station in Okinni, Osun State, Nigeria. Samples were collected and analyzed using standard procedures. A total number of seven VOCs were detected with varying concentrations, they were: benzene, toluene, chlorobenzene, ethylbenzene, m, p-xylene, o-xylene, and dichloromethane. One-way ANOVA results showed a significant difference ($p < 0.5$) in VOC concentrations across locations. Most VOCs exceeded USEPA and WHO threshold values, indicating contamination likely from fuel station leachates, as suggested by the low toluene to benzene ratio ($T/B < 2$). Odour Hazard Index (OHI) values were below 1 in all but location 3, where m,p-xylene, and o-xylene levels were 0.921 and 1.105, respectively, implying that the water from location 3 was not safe given the odour risk assessment. Carcinogenic risks were more significant through ingestion than dermal contact. Non-carcinogenic risk values were within safe limits except in location 3. Consequently, using the borehole water from location 3 for domestic activities could expose the people of these communities to serious health issues. Therefore, there is a need for urgent attention from the relevant authorities to safeguard the health of this populace.

Keywords Volatile Organic Compounds, Well water, Borehole, Petrol station, Okinni

Background

Volatile Organic Compounds (VOC) are organic compounds with high vapour pressure and low boiling point (usually below 250 °C). They are widely used in the production of daily needs and commercial products [1]. They are extremely reactive hydrocarbon compounds

and are regarded as highly toxic chemicals [2]. They are emitted from liquids, solids, and different parts of plants into both indoors and outdoors [3, 4]. They are ubiquitous Gaseous Organic Pollutants (GOP) which occur naturally and by anthropogenic activities. Natural VOCs are emitted into the environment by plants. These include monoterpenes, isoprene, limonene, and other reactive gaseous hydrocarbons [5]. Sources of anthropogenic VOCs include air fresheners, waxes, deodorants, fragrances, cleaning products, cooking practices, building and constructions, varnish office equipment, appliances, paint, furnishing, petroleum and its allied industries [6–8]. VOC is a well-known major contributor to the production and formation of secondary environmental pollutants such as photochemical smog, peroxyacetyl

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nitrate, and tropospheric ozone [1]. They usually have adverse effects on atmospheric ozone layers and may trigger the greenhouse effect through photochemical smog activities. It may also lead to the production of secondary organic aerosol [9]. Nine VOC were identified in the report by the European Commission Index strategy as priority pollutants that require adequate attention viz acetaldehyde, α -pinene, benzene, formaldehyde, limonene, naphthalene, toluene, styrene, and xylene [10]. However, a systematic review of forest VOC revealed that it has a positive health effect and enhances the general well-being of man [3]. Studies have shown that the pharmacological activities of forest VOC include; antioxidant, antinociceptive, antiproliferative, and anti-inflammatory [3]. It is noteworthy to include that forest bathing of VOC may enhance physiological relaxation and reduced hormonal stress level. This is because inhaling certain VOCs from forests can have beneficial antioxidant and anti-inflammatory effects on the airways. Additionally, the pharmacological properties of some terpenes absorbed through inhalation may also help enhance brain functions by reducing mental fatigue, inducing relaxation, and boosting cognitive performance and mood [3]. Studies have shown that exposure to VOC may lead to adverse health effects varying from allergic to chronic diseases. For instance, long-range exposure of the body to benzene may cause asthma, low birth weight, leukemia, and blood dyscrasias [11]. Exposure to trichloroethylene is associated with cancer of the liver and kidney [11]. Toluene, 1-propanol, 2-propanol, styrene, and ethylbenzene were associated with lung cancer [12]. Trichloroethylene, toluene. Tetrachlorocarbon, xylene and benzene were reported to be associated with cardiovascular effects [10]. Other health effects associated with VOC include dizziness, drowsiness, headache, and nausea, [13]. VOC may lead to acute respiratory problems, malfunctioning of lungs, gene mutation, endocrine disorders, chronic diseases of the nervous system, neurocognitive impairment, skin cancer, brain cancer, and other body tumors [9].

As the population increases in urban and rural areas so also the quest for high quality water increases. Therefore, it is imperative to examine water quality sources and their concomitant pollution load, especially when the water source is very close to conspicuous anthropogenic activities that may impair the water source. Despite the proximity of these wells to the fuel station and public outcry due to the physical state of the water from these wells, no report of the pollution load of these water sources exists according to the knowledge of the authors. However, this study aimed at determining the concentration of VOC in selected well water and borehole samples around the petrol station in Okinni area, Osogbo, compare the results with the approved standard, and explore

differences related to the pollution from the petrol station to sensitize the general public and the Government on the inherent danger associated with the use of these water for domestic purposes.

Methods

Study area

The studied sites were within the vicinity of a fuel station located in Okinni, a suburb town of Osogbo the capital of Osun State, Nigeria. Okinni is about 2 km from the central area of Osogbo. It is located along Osogbo-Ogbomoso road. It is one of the major towns in Egbedore Local Government area of Osun State. The population of the town increases almost on daily basis due to the effect of the regular expansion of the state capital. There are small-scale industries in the area. Underground water in form of wells and boreholes were the major sources of water in the area. These wells and boreholes provide water directly without any form of treatment for both domestic and industrial uses of the area. Unfortunately, there were insinuations of water contamination from the residents of this area. It was suspected that these waters were contaminated from the colour and odour thus the need to investigate the VOC contamination level of these water. There are six locations cited for this study of which five were wells water around the fuel station and the only one borehole sunk within the area. The locations were named, Well water 1 as L 1 with coordinates 7°49'23.0" N 4°31'15.4" E, Well water 2 as L 2 with coordinates 7°49'30.81" N 04°52'05.20" E, Borehole as L 3 with coordinates 7°49'23.6" N 4°31'14.4" E, well water 3 as L 4 with coordinates 7°49'33.45" N 04°52'06.08" E, well water 4 as L 5 with coordinates 7°49'33.40" N 04°52'04.95" E and well water 5 as L 6 with coordinates 7°49'37.55" N 04°52'11.96" E. The georeferencing map of the study area and locations is provided in Fig. 1.

Sample collection and preparation

Water samples were collected from each location with a cleaned amber glass bottle. The bottles were rinsed with the water to be collected before collection. The collected samples were labeled and stored at a temperature of 4 °C in a refrigerator to avoid contamination before further analysis.

Analysis of samples

The VOCs were extracted from the samples [14] and were analyzed using an Agilent 8860 Gas chromatograph coupled with a flame ionization detector (GC-FID) [15], fitted with an HP-5 capillary column coated with 5% Phenyl Methyl Siloxane (30 m length \times 0.32 mm diameter \times 0.25 μ m film thickness) (Agilent Technologies). The samples were injected in split-less mode at an injection

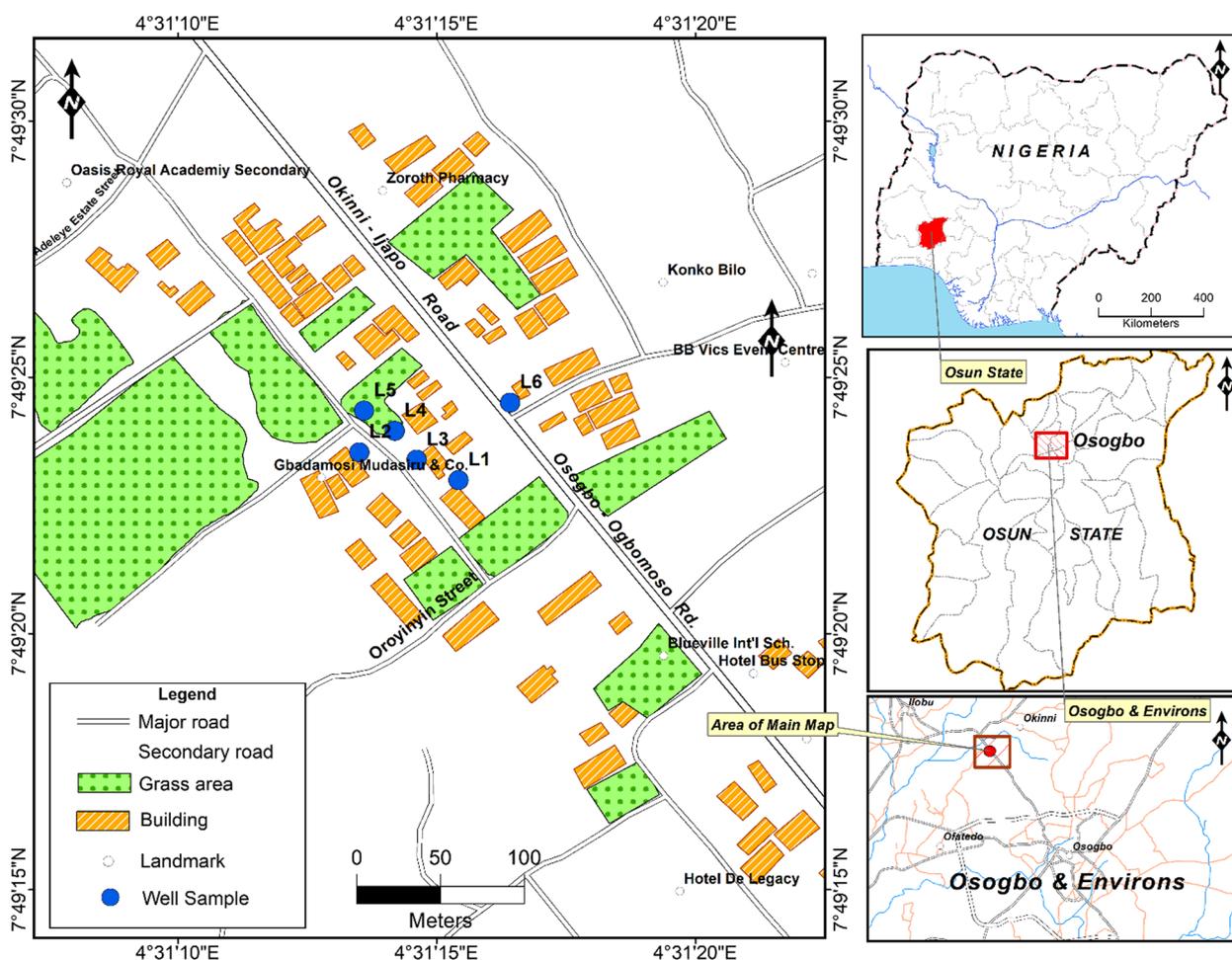


Fig. 1 Georeferencing map of the studied locations

temperature of 250 °C, at a pressure of 4.227 psi, and a total flow of 0.6 mL/min. The oven was initially programmed at 50 °C (2 min) and then ramped at 10 °C/min to 300 °C. FID temperature was 300 °C with Hydrogen: Air flow at 30 mL/min: 300 mL/min, nitrogen was used as makeup gas at a flow of 18 mL/min.

Calibration procedure

VOCs standard, 2000 ppm (Catalog Number: M-502A-R-10X) containing 54 VOCs components was purchased from AccuStandard,USA [16]. Four (4) point serial dilution calibration standards (0.1, 0.034, 0.019, 0.012 ppm) were prepared from the stock and used to calibrate the GC [14].

Quality control/ quality assurance

Sample collection, preparation, extraction procedures, and instrumental details, as well as quality control and quality assurance for the analyses of VOCs, have been described by USEPA [17], US EPA method 8260B [18,

19] were adopted in this study. The analysis recovery rate ranges from 81 to 100%. The limit of detection for benzene, toluene, chlorobenzene, ethylbenzene, m, p-xylene, o-xylene, and DCM were 0.0008, 0.0008, 0.0011, 0.0028, 0.0006, 0.0021 and 0.0007 respectively.

Statistical analysis

The data collected from the water samples were analyzed using the Statistical Package for Social Science (SPSS) Statistic 27 and Microsoft Excel. Mean values, standard deviation, and one-way ANOVA were determined.

Determination of health risk assessment

The determination of health risk assessment was proposed by USEPA [20]. The lifetime carcinogenic risk and the Hazard risk were determined to estimate the carcinogenic risks and non-carcinogenic risk respectively for each VOC through ingestion and dermal contact [21, 22].

Lifetime carcinogenic risk determination

The lifetime carcinogenic risk (LCR) for each VOC was determined by the summation of the carcinogenic risk via ingestion (CR_{in}) and carcinogenic risk via dermal contact (CR_{der}).

$$LCR = CR_{in} + CR_{der} \tag{1}$$

Carcinogenic risk determination for ingestion (CR_{in})

The carcinogenic risk via ingestion (CR_{in}) for each VOC was determined using Eq. (2) below.

$$CR_{in} = CDI_{in} \times SF_{in} \tag{2}$$

where CR_{in} is carcinogenic risk via ingestion; CDI_{in} is chronic daily intake ($\mu\text{g}/\text{kg}\text{day}$) via ingestion; SF_{in} is the slope factor ($\text{kg day}/\mu\text{g}$) via ingestion which was derived from the reference value of USEPA for each VOC.

The chronic daily intake for ingestion (CDI_{in}) was determined using Eq. (3) below.

$$CDI_{in} = \frac{CA \times IR \times EF \times ED}{BW \times AT} \tag{3}$$

where CA is the measured concentration of each VOC; IR is ingestion rate (L/day); EF is exposure frequency (day/year); ED is exposure duration (year); BW is average body weight (kg); and AT is average time (day).

Carcinogenic risk determination for dermal contact (CR_{der})

The carcinogenic risk via dermal contact (CR_{der}) for each VOC was determined using the Eq. (4) below.

$$CR_{der} = CDI_{der} \times SF_{der} \tag{4}$$

where CR_{der} is carcinogenic risk via dermal contact; CDI_{der} is chronic daily intake ($\mu\text{g}/\text{kg day}$) via dermal contact; SF_{der} is the slope factor ($\text{kg day}/\mu\text{g}$) via dermal contact which was derived from the reference value of USEPA. Table 1 lists the values of these parameters for each VOC.

The chronic daily intake for dermal contact (CDI_{der}) was determined using Eq. (5) below.

$$CDI_{der} = \frac{CA \times SA \times ET \times EF \times K_p \times ED}{BW \times AT} \tag{5}$$

where CA is the measured concentration of each VOC; IR is ingestion rate (L/day); EF is exposure frequency (day/year); ED is exposure duration (year); BW is average body weight (kg); AT is the average time (day); SA is exposed skin area (dm^2); K_p is dermal contact permeability coefficient (dm/h); ET is exposure time during bathing and showering (h/day).

Hazard Risk determination

The Hazard Risk is the non-carcinogenic risk assessment for each VOC. The Hazard Risk (HR) was determined through the summation of the Hazard quotient via ingestion (HQ_{in}) and Hazard quotient via dermal contact (HQ_{der}) as presented in Eq. (6) below.

$$HR = HQ_{in} + HQ_{der} \tag{6}$$

Determination of Hazard Quotient via Ingestion (HQ_{in})

The Hazard Quotient via Ingestion (HQ_{in}) for each VOC was determined using the Eq. (7) below.

$$HQ_{in} = \frac{CDI_{in}}{RfD_{in}} \tag{7}$$

where HQ_{in} is Hazard Quotient via Ingestion; CDI_{in} is chronic daily intake for ingestion (CDI_{in}); RfD_{in} is the reference dose ($\mu\text{g}/(\text{kg}\cdot\text{day})$) for ingestion for each VOC which is a standard value obtained from the reference value of USEPA.

Table 1 Slope factor (SF), Reference dose (RfD), Dermal Permeability coefficient (Kp), and odour threshold concentration (OTC) values of each VOC

	SF _{in} (mg/kg-day)	SF _{der} (mg/kg-day)	RfD _{in} (mg/m ³)	RfD _{der} (mg/kg-day)	K _p (dm/hour)	OTC
Benzene	0.0273	0.0550	0.0300	0.0040	0.0186	190
Toluene	NA	NA	5.0000	0.0800	0.0001	960
Chlorobenzene	NA	NA	NA	0.0200	0.0001	190
Ethylbenzene	NA	0.011	1.0000	0.1000	0.0001	150
m, p-Xylene	NA	NA	0.1000	0.2000	0.0001	20
o-Xylene	NA	NA	0.1000	0.2000	0.0001	20
Dichloromethane (DCM)	1 × 10 ⁻⁸	2 × 10 ⁻³	0.6000	0.0060	0.0001	250

NA Data not available

Determination of Hazard Quotient via Dermal contact (HQ_{der})

The Hazard Quotient via Dermal contact (HQ_{der}) for each VOC was determined using the Eq. (8) below.

$$HQ_{der} = \frac{CDI_{der}}{RfD_{der}} \tag{8}$$

where HQ_{der} is Hazard Quotient via Dermal contact; CDI_{der} is the chronic daily intake for Dermal contact (CDI_{der}); RfD_{der} is the reference dose (µg/(kg·day) for Dermal contact for each VOC which is a standard value obtained from the reference value of USEPA.

According to the literature [21, 23], the values of the above formula parameters are as follows: IR (1.85 L/day), EF (365 days/year), ED (70 years for carcinogenic and 30 years for Non-carcinogenic), SA 187.87 dm², ET (1 h/day for during bathing and showering), BW (65 kg male and 55 kg for female), and AT(ED×365 days) [20].

Determination of odour risk assessment

Individual’s reactions to fragrances can change over time in both individual cases and across groups of people, so evaluating olfactory perception is challenging. The Odour Hazard Index (OHI) was used to characterize the risk of odour exposure [24]. The OHI is the ratio of odour level and odour reference concentration. The OHI was determined using the Eq. (9) below.

$$OHI = \frac{CA}{OTC} \tag{9}$$

where OHI is the Odour Hazard Index; CA is the measured concentration of each VOC; OTC is the odour threshold concentration of each VOC which is a reference value obtained from Young et al. [25], and USEPA [26].

Results

The results of this study are summarized in Tables 2, 3, 4, 5, 6, 7 and Figs. 2, 3, 4.

Discussion

Levels of VOC in the studied locations

In this research work, water samples from five domestic wells and a borehole around a petrol station were collected and analyzed. A total number of seven VOCs were detected with varying concentrations, as listed in Table 2. They were: benzene, toluene, chlorobenzene, ethylbenzene, m, p-xylene, o-xylene, and DCM. The result of one-way ANOVA showed a *p*-value less than 0.5 (*P*<0.5) which indicates that there was a significant difference between the mean of each of the VOCs. The VOCs could be classified into aromatic and halogenated VOC, Aromatic VOC includes benzene, toluene, ethylbenzene, m, p-xylene and o-xylene. While halogenated VOC detected include: chlorobenzene and DCM. Most of these detected VOCs belong to the gasoline hydrocarbon VOC group. This suggested that they were mostly leachate from the petrol station due to the closeness (between 10 – 50 m) of the petrol station to the sample locations. The concentration of benzene in this study was 0.241 mg/l which was higher than benzene concentration of 22.000 µg/l and 0.735 µg/l reported for soil and underground water respectively in Oyigbo, River State Nigeria [27]. However, a lower than the mean value of 4.5 mg/l was reported for groundwater near the petrol filling station in two Local Government areas of metropolitan city of Ibadan, Oyo State Nigeria [28]. It was higher than the Maximum Contaminant Level (MCL) of 0.005 mg/l benzene value recommended by the United States Environmental Protection Agency USEPA [29]. Also higher than the 0.010 mg/l permissible limit in drinking water by WHO and United Kingdom [30]. Drinking water contaminated with high content of benzene may cause stomach upset, dizziness, vomiting, convulsion, increase in heart beat, coma and may lead to death [29]. Toluene ranges from 0.113

Table 2 List of VOC detected and their concentrations at different locations

Sample	Benzene (mg/l)	Toluene (mg/l)	Chlorobenzene (mg/l)	Ethylbenzene (mg/l)	M, P-Xylene (mg/l)	o-Xylene (mg/l)	DCM (mg/l)	Mean ± Standard Deviation
L1	ND	14.623	11.859	4.212	7.720	8.777	3.294	8.414 ± 3.977
L2	ND	3.891	17.976	2.200	0.688	5.150	2.487	5.399 ± 5.794
L3	ND	67.194	17.544	0.632	18.426	22.105	6.253	22.026 ± 21.524
L4	ND	ND	7.212	0.705	0.124	1.000	0.675	1.943 ± 2.650
L5	ND	0.113	10.232	0.889	0.127	1.737	0.644	2.290 ± 3.593
L6	0.241	0.339	3.323	ND	ND	0.735	ND	1.160 ± 1.263
MCL (mg/L)	0.005	1.000	0.100	0.700	10.000	10.000	0.005	

ND Not Detected, MCL Maximum contaminant level

mg/l to 67.194 mg/l which is greater than 10.070 µg/l and 23.060 µg/l reported for sediment and water respectively [31]. This was also higher than the 4.500 mg/l reported by Olukoya et al. [28]. The value of toluene observed in this study was higher than the threshold value of 1.000 mg/l in drinking water by USEPA in all locations except for locations L4, (where it was not detected) L5 and L6, and were higher than 0.700 mg/l permissible concentration limit in drinking water recommended by WHO [32]. Prolonged exposure to toluene may have adverse effect on the nervous system leading to general weakness of the body, loss of appetite, nausea, hearing impairment, and loss of vision and memory [33]. The observed values of chlorobenzene were higher than 2.090 µg/l reported for water in Epe Lagoon, Lagos, Nigeria [31]. They were far higher than 0.429–1.685 ng/ml reported for the Groot-draai dam in Mpumalanga Province, South Africa [34]. Also, the values in all the studied locations were in multiple fold higher than the permissible value of 0.100 mg/l (MCL) by USEPA [35]. They were higher than the maximum value of 5.000 µg/l reported for Canadian water [36]. Long exposure to chlorobenzene may have adverse effect on kidney, liver brain and nervous system [35]. The observed values for chlorobenzene were higher than the average of 20.573 µg/l and 483.315 µg/l reported for groundwater and soil in Oyigbo, River State, Nigeria [27]. It was in the range of 0.100 -3.000 mg/l reported for groundwater sources around Nigeria National Petroleum Cooperation (NNPC) oil depot Aba, South-Eastern Nigeria [37]. But chlorobenzene in this study was higher than 0.400 µg/l and 0.950 µg/l highest concentration observed for Minnesota surface and underground water respectively [38]. It should be noted that the concentration of ethylbenzene in the sampling sites was far higher than 0.700 mg/l (MCL) recommended by USEPA and 0.300 mg/l threshold value permissible by WHO [39] except for sites L3 which has values of 0.632 mg/l. Exposure to high dosages of ethylbenzene is carcinogenic, may affect the liver, kidney, eye, and throat and sometimes lead to

dizziness [38]. In this study, the concentration of isomers of xylene observed ranges from 0.124 mg/l to 18.426 mg/l. It was higher than the MCL of 5.000 mg/l and 10.000 mg/l permissible value in water by WHO and USEPA respectively in all the studied sites except for location L4-L6 [39]. O-xylene was higher than 23.050 µg/l observed as the highest concentration inside the classroom for the assessment of the BTEX concentrations and health risks in urban nursery schools in Gliwice, Poland [40]. Long-duration exposure of animals and man to xylene may have adverse effect on the kidney, nervous system, visual organs and cleft palate [41]. The concentration of DCM ranges from 0.644 mg/l to 6.253 mg/l. It was higher than the MCL value of 0.005 mg/l in all the studied sites. This may be due to the wide applications of DCM as solvent in industries and as a paint thinner. Long-time exposure to DCM may lead to hepatotoxicity, cancer and neurological effects [42].

Concentrations of VOCs in the studied locations

The concentration of VOC in the studied locations is presented in Fig. 2. One way ANOVA study revealed a statistically significant difference with a *p*-value of 0.023 which is less than 0.5 ($P < 0.5$). This indicated that there is a significant difference between the mean concentration of all VOCs in the five well water and the one borehole present in the study area. This may be due to the depth of the borehole which is much deeper than the well water.

Among VOC found at L1 were toluene, chlorobenzene, ethylbenzene, m,p-xylene, o-xylene and DCM with concentrations of 14.623, 11.859, 4.212, 7.730, 8.777 and 3.294 mg/l respectively. At L2 toluene, chlorobenzene, ethylbenzene, m,p-xylene, o-xylene and DCM were in abundance with concentrations: 3.891, 17.976, 2.200, 0.688, 5.150, 2.487 mg/l respectively. At L3, toluene, chlorobenzene, ethylbenzene, m,p-xylene, o-xylene and DCM were observed with concentrations of 67.194, 17.544, 0.632, 18.426, 22.105 and 6.253 respectively. At

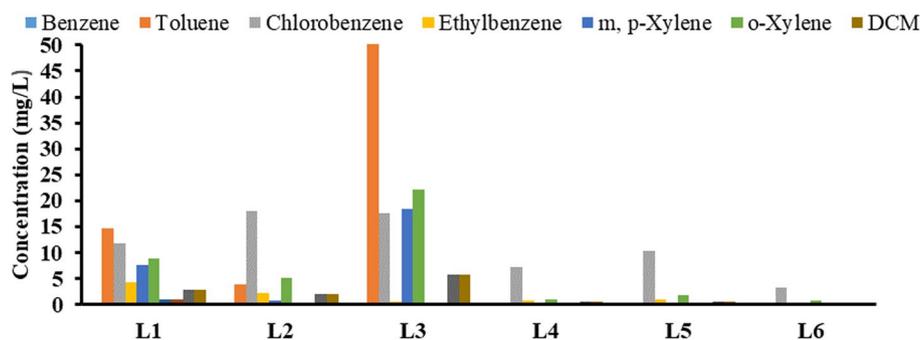


Fig. 2 Concentration of VOC in the studied locations

L4 chlorobenzene, ethylbenzene, m,p-xylene, o-xylene, and DCM were abundant with concentrations 7.212, 0.705, 0.124, 1.000 and 0.675 mg/l respectively. At L5, toluene, chlorobenzene, ethylbenzene, m,p-xylene, o-xylene and DCM were observed with concentrations of 0.113, 10.232, 0.889, 0.127, 1.737 and 0.644 mg/l respectively. While at L6, benzene, toluene, chlorobenzene and o-xylene were detected with concentrations 0.241, 0.339, 3.323 and 0.735 mg/l respectively. It was observed that benzene was only present at location 6. It was above the threshold concentration. This could be a culminating result of the direct petroleum leakage from the underground storage tank of the petrol station and leachate from nearby mechanic workshops. This raised a serious concern because the water from this particular site is used for domestic purposes by the people inhabiting this area, Toluene was observed in all the locations except location 4. It was found above MCL value in locations 1, 2, and 3. It was about three times higher (67.194 mg/l) than o-xylene (22.105 mg/l) which was the next in rank in location 3. Chlorobenzene was observed in all the locations at high concentrations (3.323 – 17.976 mg/l). It was highest in location 2 followed by location 3 and decreases in the order 1 > 5 > 6. It was the only pronounced VOC in locations 4 and 5. Ethylbenzene was found in all the locations except location 6. It was higher than the 0.700 mg/l recommended by USEPA and the 0.300 mg/l threshold value permissible by WHO in all the locations except location 3 where it was slightly below. m,p-xylene was found in all studied sites except location 6. It was slightly below the threshold level of 10 mg/l in location 1, but far below the threshold level in locations 2, 4 and 5. However, it was found to be far higher at location 3 (18.426 mg/l) than the regulatory value (10.000 mg/l). O-xylene was found in all the locations though at below MCL except at location 3 where it was far higher than the threshold value of 10 mg/l. DCM was found in all the studied sites except at location 6. It was found at a concentration far above the regulatory value of 0.005 mg/l.

Estimation of the sources of VOC

Benzene and toluene are found in greater quantities in gasoline but usually find their way into the environment through gasoline volatilization and emission from exhaust pipes from automobiles hence toluene to benzene ratio (T/B) is usually employed to estimate the source of VOC [22]. Also, the emission of toluene may arise from paint as a result of organic solvent volatilization. When the value of the T/B ratio is lower than 2.000, it implies that the main source of VOC is exhaust from vehicles or gasoline. Whereas a T/B value above 2.000 but less than 10.000 is an indication of the contribution from other sources while a T/B value above 10.000 indicates contributions from industrial areas with proximity to the studied sites [22, 43]. In this study, the T/B value for location 6 was 1.410 which is less than 2.000. Therefore, it could be deduced that the main source of VOC was from the gasoline leachate from the petrol station. Though benzene was not detected in other locations therefore, their T/B cannot be calculated.

Odour risk assessment

Emissions of unpleasant odour are regarded as air pollutant which may create annoyance to individuals as well as generating adverse health effects. Odour risk assessment of the seven VOCs detected in the study area was evaluated (See Table 3). Oduor hazard index (OHI) represents the degree of odour risk assessment of a given area. Zhang et al. [21] reported that when OHI is less than 1.000, the value is acceptable because it is an indication that the concentration will exert no detrimental health effect on an individual using the water for whatever purpose. However, if the OHI is greater than 1.000 it is an indication of possible adverse health effects such as headache, nausea, discomfort of nose and throat, conjunctival irritation, respiratory diseases, and other related health problems due to exposure to VOC. OHI of the seven VOCs based on their concentrations in water from different locations were presented in Fig. 3. It was observed that values of OHI in all locations were far less

Table 3 Odor hazard index (OHI) based on concentrations of VOCs in water from different locations

Sample	L1	L2	L3	L4	L5	L6
Benzene	0.000	0.000	0.000	0.000	0.000	0.001
Toluene	0.015	0.004	0.070	0.000	0.001	0.001
Chlorobenzene	0.062	0.095	0.092	0.038	0.054	0.017
Ethylbenzene	0.028	0.015	0.004	0.005	0.006	0.000
M, P-Xylene	0.386	0.034	0.921	0.006	0.006	0.000
o-Xylene	0.439	0.258	1.105	0.050	0.087	0.038
DCM	0.013	0.010	0.025	0.003	0.003	0.000

than 1.000 except for location 3 where the OHI for m, p-xylene, and o-xylene were 0.921 and 1.105 respectively. This could be attributed to the fact that location 3 was the closest location to the gasoline source. This implies that the water from location 3 was not safe. Therefore, it is recommended that the use of water from location 3 for household and industrial purposes be discontinued and that any violations be reported to the appropriate regulatory body.

Lifetime carcinogenic risk

Many VOCs are classified as potential carcinogens. These include benzene, ethylbenzene and DCM. For instance, both benzene and DCM were reported to cause human leukemia and cholangiocarcinoma respectively [21]. Ethylbenzene was considered as group D carcinogen. Its carcinogenic properties have been established

by International Agency for Research on Cancer. Long-time human exposure to ethylbenzene may lead to severe damage to the ear and kidney [44]. Male and female carcinogenic risk for ingestion and dermal contact (body contact) were estimated (see Tables 4 and 5) for some of the VOCs under investigation whose parameters were available and the result was as presented in Fig. 4A and B. The value of 1.0×10^{-6} was considered as a threshold safety value for carcinogenic risk in drinking water by USEPA. When the estimated value is less than 1.0×10^{-6} it is considered to be negligible and could be ignored. But when the value is in the range of 1.0×10^{-6} to 1.0×10^{-4} it represent a moderate risk for vulnerable people but still acceptable. While calculated value greater than 1.0×10^{-6} signifies potential carcinogenic danger for humans exposed to such drinking water [45]. In this study, it was observed as seen from Fig. 4A for ingestion

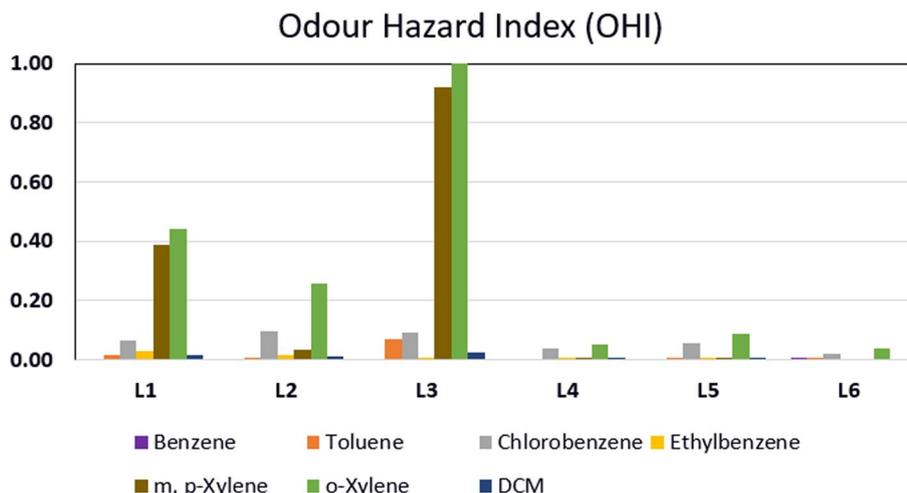


Fig. 3 Odour Hazard Index (OHI) of the VOCs in the studied locations

Table 4 Lifetime Carcinogenic Risk for Ingestion of VOCs in water from different locations

Sample	L1		L2		L3		L4		L5		L6	
	Male	Female										
Benzene	0.000E+00	3.210E-05	3.794E-05									
Ethylbenzene	2.261E-04	2.672E-04	1.181E-04	1.395E-04	3.392E-05	4.009E-05	3.784E-05	4.472E-05	4.771E-05	5.639E-05	0.000E+00	0.000E+00
DCM	1.607E-09	1.899E-09	1.213E-09	1.434E-09	3.051E-09	3.606E-09	3.293E-10	3.892E-10	3.142E-10	3.713E-10	0.000E+00	0.000E+00
Mean	1.130E-04	1.336E-04	5.904E-05	6.977E-05	1.696E-05	2.005E-05	1.892E-05	2.236E-05	2.386E-05	2.819E-05	3.210E-05	3.794E-05

Table 5 Lifetime Carcinogenic Risk for Dermal contact of VOCs in water from different locations

Sample	L1		L2		L3		L4		L5		L6	
	Male	Female										
Benzene	0.000E+00	1.222E-04	7.166E-05									
Ethylbenzene	4.591E-06	2.713E-06	2.398E-06	1.417E-06	6.889E-07	4.071E-07	7.685E-07	4.541E-07	9.691E-07	5.726E-07	0.000E+00	0.000E+00
DCM	3.264E-11	1.929E-11	2.465E-11	1.456E-11	6.196E-11	3.662E-11	6.689E-12	3.953E-12	6.382E-12	3.771E-12	0.000E+00	0.000E+00
Mean	2.296E-06	1.357E-06	1.199E-06	7.085E-07	3.445E-07	2.036E-07	3.842E-07	2.271E-07	4.845E-07	2.863E-07	1.222E-04	7.166E-05

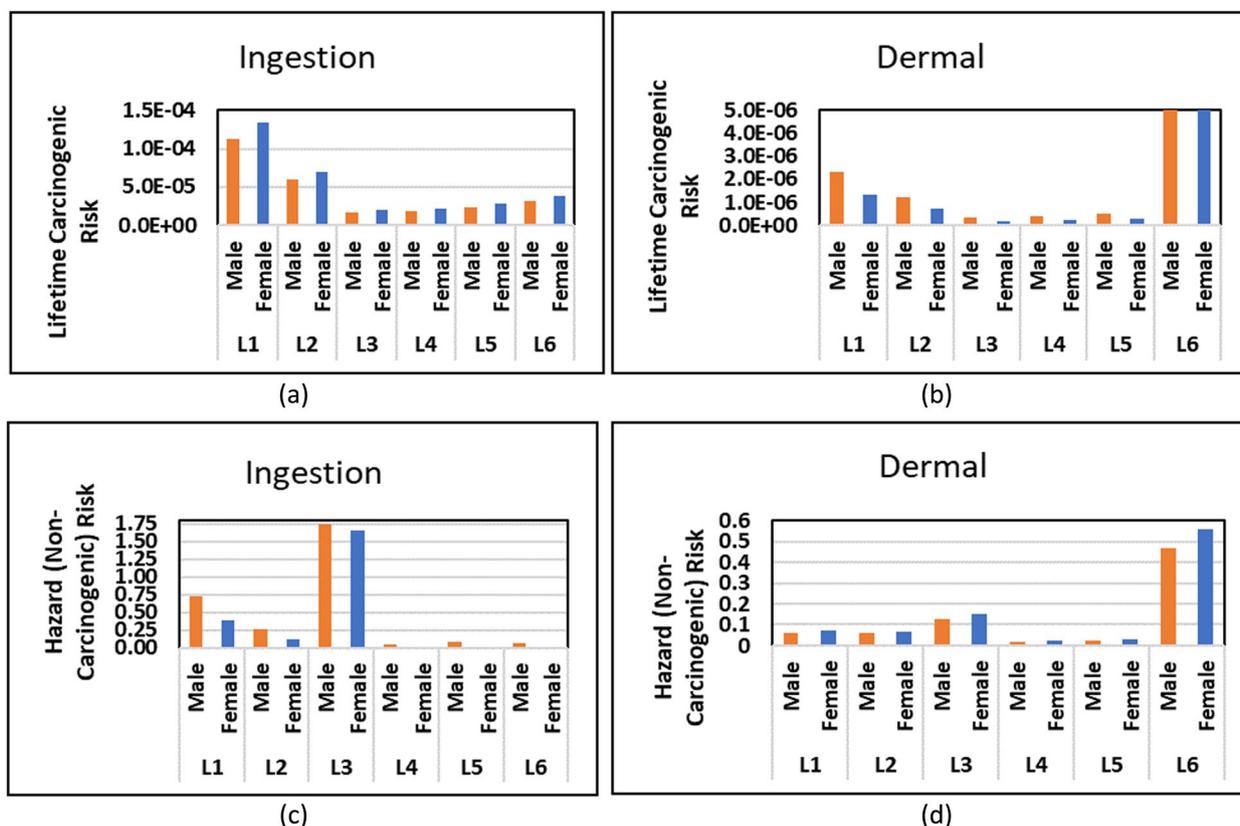


Fig. 4 **A** Lifetime carcinogenic risk for ingestion of the VOCs for males and females in the studied locations **B** Lifetime carcinogenic risk for dermal contact of the VOCs for males and females in the studied locations **C** Hazard (non-carcinogenic) risk for ingestion of the VOCs for male and female in the studied locations **D** Hazard (non-carcinogenic) risk for dermal contact of the VOCs for male and female in the studied locations

that the carcinogenic risks for female were higher than those of male in all studied locations. This result was in consistent with the report obtained for VOC in multiple drinking water sources in the Yangtze River Delta region, China [21]. It should be noted that the carcinogenic value for ingestion in location 1 was higher than 10^{-4} for both males and females. This value indicated that drinking water from the well water in location 1 may pose a significant carcinogenic risk to human health. However, from Fig. 4B, it was observed that carcinogenic risk for dermal contact in all locations was insignificant except for the well water in location 6 where the estimated value for males was above the threshold value of 10^{-4} . This result implied that males are vulnerable to carcinogenic risk through dermal contact by using water from location 6. However, this research work revealed that lifetime carcinogenic risk was more pronounced through ingestion than dermal contact. In addition, it was observed that there was moderate to no cancer risk in all locations through ingestion and dermal contact except for locations 1 and 6 where the use of water should be discouraged.

Non-carcinogenic or Hazard Risk

In this study, the non-carcinogenic risk of the seven VOCs under investigation was evaluated (Tables 6 and 7) for males and female and the results for ingestion and dermal contact were presented in Fig. 4C and D respectively. According to the relevant authority, USEPA, opined that when the estimated value of hazard risk exceeds the value of 1, the contaminant is presumed to pose a danger to human health. The estimated values for both ingestion and dermal contact was presented in Fig. 4C and D. It was observed that the calculated values were less than 1 in all locations for both ingestion and dermal contact except for location 3 for ingestion where estimated values for male and female were 1.748 and 1.655 respectively. This implies that drinking of water from location 3 may pose a significant danger to both male and female. It was observed that the value for males was higher than the females for ingestion while it was the other way round in dermal contact.

Table 6 Non-carcinogenic or Hazard Risk for Ingestion of VOCs in water from different locations

Sample	L1		L2		L3		L4		L5		L6	
	Male	Female										
Benzene	0.000E+00	2.286E-01	2.432E-04									
Toluene	8.324E-02	2.459E+00	2.215E-02	6.544E-01	3.825E-01	1.130E+01	0.000E+00	0.000E+00	6.432E-04	1.900E-02	1.930E-03	5.701E-02
Chlorobenzene	0.000E+00											
Ethylbenzene	1.199E-01	1.417E-01	6.262E-02	7.400E-02	1.799E-02	2.126E-02	2.007E-02	2.371E-02	2.530E-02	2.990E-02	0.000E+00	0.000E+00
M, P-Xylene	2.197E+00	2.597E-02	1.958E-01	2.314E-03	5.244E+00	6.198E-02	3.529E-02	4.171E-04	3.615E-02	4.272E-04	0.000E+00	0.000E+00
o-Xylene	2.498E+00	2.952E-02	1.466E+00	1.732E-02	6.291E+00	7.435E-02	2.846E-01	3.364E-03	4.944E-01	5.843E-03	2.092E-01	2.472E-03
DCM	1.563E-01	6.648E-02	1.180E-01	5.019E-02	2.966E-01	1.262E-01	3.202E-02	1.362E-02	3.055E-02	1.300E-02	0.000E+00	0.000E+00
Mean	7.221E-01	3.890E-01	2.663E-01	1.140E-01	1.748E+00	1.655E+00	5.314E-02	5.874E-03	8.386E-02	9.739E-03	6.282E-02	8.533E-03

Table 7 Non-carcinogenic or Hazard Risk for Dermal contact of VOCs in water from different locations

Sample	L1		L2		L3		L4		L5		L6	
	Male	Female										
Benzene	0.000E+00	3.2390E+00	3.8279E+00									
Toluene	5.8114E-02	6.8681E-02	1.5464E-02	1.8275E-02	2.6704E-01	3.1559E-01	0.0000E+00	0.0000E+00	4.4908E-04	5.3073E-04	1.3472E-03	1.5922E-03
Chlorobenzene	1.7138E-01	2.0254E-01	2.5978E-01	3.0701E-01	2.5354E-01	2.9964E-01	1.0422E-01	1.2317E-01	1.4787E-01	1.7475E-01	4.8022E-02	5.6754E-02
Ethylbenzene	1.2174E-02	1.4387E-02	6.3587E-03	7.5148E-03	1.8267E-03	2.1588E-03	2.0377E-03	2.4082E-03	2.5695E-03	3.0367E-03	0.000E+00	0.000E+00
M, P-Xylene	1.1157E-02	1.3185E-02	9.9427E-04	1.1750E-03	2.6628E-02	3.1470E-02	1.7920E-04	2.1178E-04	1.8353E-04	2.1690E-04	0.000E+00	0.000E+00
o-Xylene	1.2684E-02	1.4990E-02	7.4425E-03	8.7957E-03	3.1945E-02	3.7753E-02	1.4452E-03	1.7079E-03	2.5102E-03	2.9666E-03	1.0622E-03	1.2553E-03
DCM	1.5868E-01	1.8753E-01	1.1980E-01	1.4159E-01	3.0122E-01	3.5599E-01	3.2516E-02	3.8428E-02	3.1023E-02	3.6663E-02	0.000E+00	0.000E+00
Mean	6.0598E-02	7.1616E-02	5.8549E-02	6.9194E-02	1.2603E-01	1.4894E-01	2.0057E-02	2.3704E-02	2.6372E-02	3.1167E-02	4.6992E-01	5.5536E-01

Conclusion

Levels and possible toxicity of VOC were investigated from underground water in six locations around a fuel station within the Okinni locality, Osun State, Nigeria. Samples were collected and analyzed following the standard procedure. A total number of seven VOCs were detected with varying concentrations, they were: benzene, toluene, chlorobenzene, ethylbenzene, m, p-xylene, o-xylene, and DCM. The concentration of benzene in this study was 0.241 mg/l which was higher than the Maximum Contaminant Level of 0.005 mg/l recommended by the United States Environmental Protection Agency (USEPA) and also higher than 0.010 mg/l permissible limit in drinking water by WHO. Toluene ranges from 0.113 mg/l to 67.194 mg/l which was greater than the threshold value of 1.000 mg/l in drinking water by USEPA in all locations except for locations L4, (where it was not detected) L5 and L6, and was higher than 0.700 mg/l permissible concentration limit in drinking water recommended by WHO. The observed values of chlorobenzene range from 3.323 to 17.976 mg/l and were multiplefold higher than the permissible value of 0.100 mg/l by USEPA. It was observed that the concentration of ethylbenzene in the sampling sites was far higher than 0.7 mg/l recommended by USEPA and the 0.300 mg/l threshold value permissible by WHO except for sites L3 which

has values of 0.632 mg/l in this study, the concentration of isomers of xylene observed ranges from 0.124 mg/l to 18.426 mg/l. for m, p-xylene and 0.735 -22.105 mg/l for o-xylene. It was higher than 5.0 mg/l and 10.0 mg/l permissible value in water by WHO and USEPA respectively in all the studied sites except for location L4-L6. The concentration of DCM ranges from 0.644 mg/l to 6.253 mg/l. It was higher than the threshold value of 0.005 mg/l recommended by USEPA in all the studied sites. Most of the detected VOCs belong to the gasoline hydrocarbon VOC group and the T/B ratio was lower than 2. This suggested that they were mostly leachate from the fuel station. However, it was observed that values of OHI in all locations were far less than 1 except for location 3 where the OHI for m, p-xylene, and o-xylene were 0.921 and 1.105 respectively. This implies that the water from location 3 was not safe because of the odour risk assessment. However, this research work revealed that lifetime carcinogenic risk was more pronounced through ingestion than dermal contact.

In addition, it was noted that, except for locations 1 and 6, there was a moderate to non-existent cancer risk in all locations through ingestion and dermal contact. Furthermore, it was observed that the estimated value for non-carcinogenic risk for all locations was within the threshold value except for the borehole water in location

3. Thus, using the water from this location for domestic activities could expose the people of these communities to serious health issues. Therefore, there is a need for urgent attention from the relevant authorities to safeguard the health of this populace. Alternatively, the borehole water could be treated using *Moringa oleifera* seed powder and activated carbon as adsorbent [46–48].

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Authors' contributions

Each author made a contribution to the conception, and design of the study. GCA took part in the preparation, review, and data analysis of the manuscript. JTA assisted with sample collection, preparation, and analysis in addition to manuscript preparation. FA took part in the sample analysis, manuscript preparation, and first draft review. All authors have reviewed the submitted version of the manuscript and given their approval.

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Data availability

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Declarations

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