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Non-carcinogenic and carcinogenic health risks associated with heavy metals and polycyclic aromatic hydrocarbons in well-water samples from an automobile junk market in Ibadan, SW-Nigeria



Adeola Anike Oni^{a,*}, Stephen Olufemi Babalola^b, Adeyeri David Adeleye^a, Temidayo Ebenezer Olagunju^b, Ijeoma Anthonia Amama^a, Esther Onaopemipo Omole^a, Ezra Ajibola Adegboye^a, Obokparo Godspower Ohore^c

^a Department of Zoology, University of Ibadan, Ibadan 200284, Nigeria

^b Department of Biology, Alex Ekwueme Federal University, Ndufu-Alike Ikwo, Nigeria

^c Department of Veterinary Pathology, University of Ibadan, Ibadan 200284, Nigeria

HIGHLIGHTS

- Imported used cars dismantled in automobile junk markets in developing countries.
- Pollutant input into domestic water supply may result in adverse health effects.
- Used Health Risk Assessment model to quantify human-health risks.
- Pb, Cd, As, BaA, BaP > reg. limits; Pb, Cd, As, HQ>1; HI(1.12-10.07); PAHs HQ/HI<1.
- High Carcinogenic Risk, Children most vulnerable: Cd (1 in 100) – BaP (1 in 4329).

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G R A P H I C A L A B S T R A C T



ABSTRACT

Unserviceable vehicles imported from developed countries are often dismantled in automobile junk markets and the useable parts sold. This generates hazardous waste oils which contain contaminants detrimental to the environment and human health. In this study, we quantified the potential human health risks associated with oral and dermal exposure to heavy metals and PAHs in well-water samples from a major automobile junk market in Ibadan, SW-Nigeria. Twenty-four to thirty-one water samples from seven wells within the market were analyzed for seven metals and eight PAHs using standard methods. Hazard-Quotient (HQ), Hazard-Index (HI), and Carcinogenic-Risk (CR) were computed for children and adults based on the USEPA Human-Health Risk Assessment model.

Iron, Lead, Arsenic, Cadmium, Benzo(a)Anthracene, and Benzo(a)Pyrene exceeded regulatory limits. In children and adults, lead (1.14–3.71), cadmium (1.26–2.60) and arsenic (1.03–4.33) had HQ_{ingestion} values exceeding 1. In addition, cadmium also posed risks via the dermal route in children in two of the seven sampled wells with an HQ of 1.76. Hazard Index was >1 via both routes in children (HI_{ingestion}:- 5.04–10.07; HI_{dermal}:- 1.12–2.12) but only via ingestion in adults (HI _{ingestion}:- 2.36–4.85). Well-3 samples posed the greatest non-carcinogenic risks via ingestion with HI values of 10.07 (children) and 4.85 (adults) respectively. Cadmium, arsenic, lead, and

* Corresponding author. E-mail addresses: adeyoni2006@yahoo.co.uk, adeola.oni@mail.ui.edu.ng (A.A. Oni).

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chromium could also elicit carcinogenic risk, with CR values of 1.00E - 02, 1.95E - 03, 1.11E - 04, and 3.30E - 04 which exceeded the 10^{-4} limit indicating high risk, particularly in children.

However, HQ and HI values for PAHs were <1 via both pathways suggesting no non-carcinogenic risk from PAH exposure. Carcinogenic risk estimates for Benzo(a)Anthracene (9.66E - 04) and Benzo(a)Pyrene (2.31E - 04) suggest moderate risks in exposed children via the dermal route. Adverse health effects including cancer may occur in the exposed population on prolonged usage of these polluted water sources. Urgent remediation measures are therefore necessary to protect the exposed population.

1. Introduction

The transfer of used vehicles from industrialized countries in Europe, the United States, Japan, and China has led to a booming global trade valued at 17.6 billion USD as of 2014 (UNEP, 2020). Some of these vehicles are dismantled into their components in automobile junk markets in developing countries and sold after any necessary repairs are made. Waste oils are generated in the course of dismantling, repair, and/or servicing of these automobile engines, which when improperly disposed, contaminate the environment, causing serious damage to human and environmental health (Anoliefo and Vwioko 2001; Pelitli et al., 2017). Waste oils from gasoline engine crankcase, as well as other lubricants have been found to contain measured concentration of metals including arsenic (As), lead (Pb), and cadmium (Cd) from engine wear, additive breakdown products such as zinc (Zn), as well as other metals such as copper (Cu), iron (Fe), aluminium, silicon and tin. Other contaminants include chlorinated solvents and Polycyclic Aromatic Hydrocarbons (PAHs) which accumulate in the oil during its service life (Brinkman and Dickson, 1995; Vermont Agency, 1996; Denton 2007).

Although heavy metals are natural components of the earth's crust and hence can be released by natural resources, generally most heavy metal pollution is caused by human activities. Heavy metals such as Pb, As, Cd, and Cr are considered toxic even at low concentrations; while others such as Cu and Zn although beneficial for biological systems and normal body functions may also cause extensive damage to human health when inadvertently ingested at levels above acceptable internationally recommended limits (Mohammadi et al., 2019). High Pb concentrations can bring about health problems such as arterial pressure and behavioural complications, while cadmium is exceptionally toxic and its exposure can cause cancer (Jafarzadeh et al., 2022). Arsenic is also a carcinogenic element in groundwater (Shams et al., 2020). Heavy metals often bio-accumulate in target tissues such as the liver, kidney, brain, and bones in the human body following prolonged exposure leading to serious health hazards (Kamunda et al., 2016). The high bio-accumulative, abundance, and long retention potentials of heavy metals in living organisms including humans, further aggravate toxicity and the associated health risk following exposure (Mohammadi et al., 2019).

Polycyclic aromatic hydrocarbons (PAHs), on the other hand, are a class of persistent organic pollutants (POPs) primarily formed through biomass and fossil fuel combustion including the release of crude oil, petroleum, and coal tar products. Motor oils become enriched with PAHs during the operation of an engine and are transported to the crankcase and concentrated in the lubricating oil, increasing rapidly with increased vehicle mileage (Denton 2007). Due to their persistence, bio-accumulation, and bio-toxicity in the environment, PAHs have received widespread attention and are considered priority pollutants because they are carcinogenic and mutagenic.

When waste oils are consistently spilled on the soil, they are carried as part of runoffs during precipitation into adjoining water bodies, while other portions become leached through the soil resulting in groundwater contamination. Exposure to the toxic components of waste oil can be either through inhalation, ingestion, or dermal exposure. The ingestion and dermal absorption pathways are however of utmost health significance when it comes to liquid-based toxicants (Yuan et al., 2016; Edokpayi et al., 2018). Most workers in automobile repair garages and automobile junk markets do not use protective wear such as gloves. As a result, the waste oil is in frequent contact with their skin. They may also become exposed to the water-soluble forms of the spent oil via the ingestion of contaminated groundwater. These may pose major risks to their health over time.

Health risk assessment involves the identification and quantification of potential hazards to humans through exposure to exogenous agents from anthropogenic activities, and it is a useful tool in hazard prevention and management. The Araromi automobile spare - parts market in Ibadan is a major hub for the sales and repair of automobile parts in SW-Nigeria. It has been in existence for over 40 years and has an estimated population of about 5,000-10,000 (Pers. Comm.). The soils of the market are dark-colored, with a canvas-like feel on treading due to decades of spent oil discharge from the dismantled automobile parts displayed for sale within the market. Traders and residents at the market rely on groundwater mainly from shallow wells located within the market for their domestic needs (See Plates 1-4, Supplementary Material I). Groundwater contamination may elicit adverse health effects in the exposed population. Studies have shown that well-water samples from the site altered reproductive indices in exposed Swiss albino mice, suggesting that adverse health effects may occur in the exposed human population (Oni et al., 2019).

Our objectives were:

- (1) To obtain information on demographics and water usage from a randomly selected sample of the human population at the site.
- (2) Assess the water quality from seven selected wells at the market to quantify the concentrations of heavy metals and PAHs in the wellwater samples and;
- (3) Examine the consequent potential health risks associated with oral and dermal exposure to these heavy metals and PAHs.

2. Materials and methods

2.1. Study area

The study area is the Araromi Automobile spare parts market located in Ibadan North East Local Government Area of Oyo State, SW-Nigeria. Geographically, it lies between latitudes, 7° 23.35 North and 7° 23.49 North; longitudes 3° 55.80 East and 3° 55.23 East. At the site, dismantled automobile parts such as engine crankshafts are placed directly on the soil surface and during precipitation, contaminants may leach out into the groundwater. The climate of the area is a tropical wet and dry climate (Aw) according to the Koppen-Geiger system of climate classification, with two seasons (the wet season-April to October) and a dry season--November to March). Average annual temperature for Ibadan is 25.9 $^\circ\text{C}$ and about 1467 mm or 57.8 inches of precipitations falls annually. The drinking water in the study area is supplied mainly by shallow wells. Seven sample wells that serve as domestic water supply within the market were selected with the aid of a Garmin Etrex 10 GPS device and designated as Wells 1-7, as shown in Figure 1 [Supplementary material II].

2.2. Questionnaire administration

Following informed consent obtained from all willing participants, a structured questionnaire was administered to one hundred and forty randomly selected individuals in the study area, to obtain demographics and general information on the usage of the well-water. The questionnaires were administered to twenty randomly selected respondents domiciled around each of the seven selected wells making a total of 140 respondents in all. A sample of the questionnaire is included as supplementary data (See Supplementary Material III).

2.3. Water sampling and analysis

A maximum of thirty-one water samples were obtained fortnightly between April and May 2017 and analyzed for selected heavy metals (Pb, Cr, Cd, Zn, and As). Five samples were to be obtained from each of the seven sampled wells making a total of thirty-five samples. However, four wells were inaccessible (they were locked) on the second of the five sampling occasions, thus making thirty-one samples in all for heavy metals, instead of thirty-five. In addition, iron and copper were not determined in samples collected on the first sampling day. All other metals were however analyzed. For polycyclic aromatic hydrocarbons (PAHs), a total of twenty-four samples were analyzed. This was comprised of samples from the only three accessible wells on the second sampling occasion and twenty-one samples, (i.e. three from each of the seven wells) on sampling days three to five. PAHs could not be determined in samples collected on the first of the five sampling occasions due to logistics reasons. Three samples of distilled water were also analyzed for similar parameters and served as a comparative control. Water samples for heavy metal analysis were collected in clean plastic bottles pre washed with double distilled water and 20% nitric acid, preserved with 3ml of nitric acid, and stored in a refrigerator at 4 °C until analysis (Alidadi et al., 2019). The well-water samples and distilled water control were digested with nitric and perchloric acid in the ratio of 2:1 as stipulated by Franson et al. (1998) and analyzed for Fe, Cu, Pb, Cr, Cd, Zn, and As using Atomic Absorption Spectrophotometry. Blanks and standards were used to check measurement precision and analysis was conducted in triplicate.

Water samples for PAHs were collected in prE – washed glass bottles and stored at 4 °C until analysis. The spectrophotometric method was used to determine the PAH content of the water samples and analysis was done using a Cecil 2843 Spectrophotometer at wavelengths of 380, 415, 435, and 450 nm according to the protocol described by Lee et al. (1997). The PAHs determined were anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo (a) anthracene (BaA), Chrysene (CHR), Benzo (b) fluoranthene (BbF), Benzo (a) pyrene (BaP) and Benzo, 1, 2-anthracene (B-1,2-A).

2.4. Health risk assessment

The Average Daily Dose (ADD), Hazard Quotient (HQ), Hazard Index (HI), and Carcinogenic Risk (CR) indices were used to assess the noncarcinogenic and carcinogenic health risks for both heavy metals and PAHs in the well-water samples with exposure via the ingestion and dermal absorption pathways respectively.

2.4.1. Determination of average daily dose (ADD) via ingestion and dermal pathways

The Average Daily Dose (ADD) for the determination of human health risk through the two pathways has been described in the literature (Adamu et al., 2015; Adeniji et al., 2019a; b) and can be calculated using eqs. (1) and (2):

$$ADD_{ingestion} = \frac{CW \times IR \times EF \times ED}{BW \times AT}$$
(1)

$$ADD_{dermal} = \frac{CW \times SA \times Kp \times ET \times EF \times ED \times CF}{BW \times AT}$$
(2)

where ADD_{ingestion} and ADD_{dermal} are the Average Daily Dose associated with exposure to the well water via the oral (ingestion) and dermal routes respectively. The parameters and input assumptions for the exposure assessment were Cw = Concentrations of heavy metals and PAHs in mg/ L, IR = Ingestion Rate in L/day, which was given as 2.2 L/day for adults and 1 L/day for children (Koki et al., 2015). The Exposure Frequency (EF) in this study was taken as 310 days/year which represents the active working days for majority of the Araromi population (traders work all week except Sundays). Similarly, Exposure Duration (ED) was taken as 35 years for adults and 6 years for children. Body Weight (BW) for adults was taken as 70 kg, while 15 kg was taken as the body weight for children (Edokpayi et al., 2018; Onyele and Anyanwu 2018). The choice of 15 kg as body weight for children was also informed by the fact that some mothers brought their infants to the site, although due to their young age, they were not included in the questionnaire survey.

The average time (AT) in days was given as ED \times EF i.e. 10850 for adults and 1860 for children. Other input parameters included the exposed skin Surface Area (SA) given as 18000 cm² for adults, and 6600 cm² for children (Adeniji et al., 2019a; b), Kp = permeability coefficient in cm/hour given as 0.001 for Fe, Cu, Pb, Cd and As, 0.002 for Cr and 0.0006 for Zn (Caylak 2012; Edokpayi et al., 2018), while Kp for fluoranthene was given as 3.6E-1, benzo(a)anthracene and chrysene, 8.1E-1 and 1.2 for benzo(b)fluoranthene and benzo(a)pyrene. Exposure time (ET) in h/day was given as 0.58 for adults and 1 for children Adeniji et al. (2019a, 2019b), while the Conversion Factor (CF) was given as 0.001 (Adeniji et al., 2019a); 2019b).

2.4.2. Non-carcinogenic risk

The Hazard Quotient (HQ) and Hazard Index (HI) were used to estimating the potential non-carcinogenic health risks associated with exposure to heavy metals and PAHs in the contaminated water via the ingestion and dermal pathways using eqs. (3) and (4):

$$HQ_{ingestion/dermal} = \frac{ADD}{RFD}$$
(3)

$$HI_{ingestion/dermal} = \Sigma HQ$$
(4)

where HQ, HI, ADD and RfD are the Hazard Quotient, Hazard Index, Average Daily Dose, and Reference Doses for heavy metals and PAHs via the ingestion and dermal pathways. The Dermal Reference doses (RfD_{dermal}) of PAHs were derived from available oral or ingestion reference doses (RfD_{ingestion}) using the gastrointestinal tract absorption values (ABS_{GI}) of each compound according to the following eq. (5);

$$RfD_{dermal} = RfD_{ingestion} \times ABS_{GI}$$
(5)

The ABS_{GI} for each of the PAHs examined was estimated to be 1 (USEPA 2004). The Reference doses (RfD) for ingestion were 7.0E1 for Fe, 4.0E-2 for Cu, 3.5E-3 for Pb, 3.0E -3 for Cr, 5.0E-4 for Cd, 3.0E-1 for Zn and 3.0E-4for As. Reference doses via the dermal pathway for these metals were 1.4E-1, 1.2E -2, 5.3E-4, 6.0E-5, 5.0E-6, 6.0E-2, and 1.23E-4 for Fe, Cu, Pb, Cr, Cd, Zn and As respectively. For the PAHs, reference doses were only found in the literature for anthracene, fluoranthene, pyrene, and benzo(a)pyrene and these were 3.0E-1, 4.0E-2, 3.0E-2, and 3.0E-4 for both ingestion and dermal pathways respectively (Zhang et al., 2015; Wan et al., 2016; Onyele and Anyanwu 2018; Du 2019; USEPA 2020). The hazard quotient (HQ) is a numeric estimate of the toxicity potential posed by an element through a single route of exposure. An HQ under 1 is assumed to be safe, but HQ values above 1 may be a major potential health concern in association with overexposure of humans to the contaminants. To assess the overall potential non-carcinogenic effects posed by more than one metal or PAH, the sum of the computed HQs across all metals (and separately for PAHs) was expressed as the hazard index (HI) using eq. 4. A value of HI > 1 indicates that exposure to the well water could have a potentially adverse effect on human health

2.4.3. Carcinogenic risk

The carcinogenic risk, which is the probability of an individual developing cancer through exposure to a potential environmental carcinogen was assessed using eq. (6).

Cancer risk(CR)_{ingestion/dermal} = ADD_{ingestion/dermal}

$$\times$$
 SF_{ingestion/dermal}(mg / kg / day) (62)

where ADD is the Average Daily Dose and SF is the Cancer Slope Factor. The dermal Slope Factors (SF_{dermal}) of PAHs were derived from available oral or ingestion Slope Factors (SF_{ingestion}) using the gastrointestinal tract absorption values (ABS_{GI}) of each compound according to the following eq. (7);

$$SF_{dermal} = SF_{ingestion} / ABS_{GI}$$
 (7)

The ABS_{GI} for each of the PAHs examined was estimated to be 1 (USEPA, 2004). A metal or PAH poses an acceptable cancer risk if CR values lie between 1E-6 \leq CR \leq 1E-4. The cancer risks were evaluated via both the oral and dermal routes using the cancer slope factors (SF). Cancer slope factors (SF_{ingestion}) for the heavy metals were 8.5E-3 for Pb, 0.5 for Cr, 15 for Cd, and 1.5 for As, while SF_{dermal} for Pb was given as 1.5, 20 for Cr, and 3.66 for As. Slope factors for the other metals were not found in the literature. Similarly, the cancer slope factors used for the computation of the cancer risk were only available for benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene, and these were given as 7.3E-1, 7.3E-3, 7.3E-1 and 7.3 for both the ingestion and dermal pathways respectively (USEPA 2007; Zhang et al., 2015; Adeniji et al. 2019; USEPA 2020).

2.5. Statistical analysis

Analysis of Variance (ANOVA) and Duncan post hoc test were used to compare the mean values of heavy metals and PAHs obtained for each of the well-water samples and control at the 95% confidence limit.

3. Results and discussion

3.1. Questionnaire analysis

3.1.1. Demographics of the Araromi population

The mean percentage distribution of the Araromi population by sex, age, residential status, and the number of years living or working at the market are shown in Figure 2(a, b, c, d) (Supplementary material II). Most respondents within the market were males (81.74%), while the females constituted 18.26% of the population (Figure 2a). The majority of respondents were between the ages of 31-40 years, with a mean percentage contribution of 28.4%. This was closely followed by the 10-20 age range (23.8%) to which children and adolescents belong. The age bracket with the least number of respondents was 60 years and older with a mean percentage contribution of 2.2%. The other age brackets were 21-30 (21%), 41-50 (13%) and 51-60 (11.6%). Considering the generally recognized age of an adult at 21 years, it implies that 76.2% of the population sampled were adults, while 23.8% were children and/or adolescents (Figure 2b). A limitation of the study was that infants could not be included in the questionnaire survey due to their young age. However, their age group was taken into account in the health risk assessment, considering their vulnerability. Figure 2c shows that most of the respondents sampled (89.5%) do not reside at the site, while only 10.5% are residents. Figure 2d shows the number of years respondents have worked or lived at the market (A few residential houses are present within the market). Approximately 5% of the respondents have never



Figure 1. Map of Ibadan North-East LGA, Oyo state, Nigeria showing the Araromi spare-parts market with the study wells 1-7 highlighted.



Figure 2. (a-d) Mean percentage distribution of Araromi population by (a) sex (b) age (c) number of years living or working at the market (d) residential status.

worked or resided within the market suggesting they are likely buyers of spare parts or visitors to the residents. Apart from 15.8% who had worked or lived within the market for between 1-5 years, the greater majority (78.9%) have lived or worked at the market for between 6 to 30 years (Figure 2d; SM II). The mean percentage distribution of the Araromi population by occupation is presented in Figure 3 [Supplementary Material II]. Automobile spare parts dealers were the largest group at 31.5%, while apprentices represented 20.2%. This was closely followed by food vendors at 16.1%, some of whom use water sourced from the wells within the market for food preparation. Other related occupations include automobile upholstery dealers (11.7%), panel beaters (5%), welders (4.5%), iron benders (3.6%), and automobile mechanics' who

3.6 ^{4.5 1.4}

16.1

20.2

constituted the least occupational group at 1.4%. Other occupations represented 6% (Figure 3; SM II).

3.1.2. Well-water usage pattern of the Araromi population

The water usage pattern by respondents in the Araromi automobile spare parts market is shown in Figure 4a and b [Supplementary material II]. Most of the respondents (85.19%) used the well-water every day (daily), compared to 11.65% and 3.16% that used the water occasionally every week but not every day (weekly), and those who used it occasionally every month but not every week (monthly) respectively (Figure 4a). In addition, five major purposes of water usage were identified which were cooking and drinking which constitutes the ingestion

- Spare parts dealers
 - Upholstery dealers
 - Panel beaters
 - Food vendors
 - Apprentices
 - Iron benders
 - Welders
 - Automobile mechanics
 - Others

Figure 3. Mean percentage distribution of Araromi population by occupation.

31.5

5.0

11.7

a

b



Figure 4. Water usage pattern of Araromi population (a) frequency of usage (b) purpose of water use.

exposure pathway; and washing, bathing, and ablution for religious purposes by Islamic faith adherents, which constitutes the dermal exposure pathway. Washing, bathing, and ablution constituted the greater proportion of water usage with 89%, 73.6%, and 54% of the respondents utilizing the water for these purposes respectively; when compared to 27.2% and 29.3% of respondents who use the water for cooking and drinking respectively (Figure 4b; SM II). Here, we considered each purpose separately, but multi-purpose usage and consequently multiplE – exposure pathways cannot be ruled out.

3.2. Contaminant levels in well water samples

3.2.1. Heavy metals

The range and mean concentrations of the heavy metals assessed in the well-water samples and distilled water control are presented in Table 1a and b . The raw data used to generate the above data both for heavy metals and PAHs are available for download [dataset–Oni et al., 2022; Supplementary material IV]. The levels of all heavy metals in the distilled water control were 0.00 mg/l. A comparison of the mean concentrations for all metals in the seven wells showed that they decreased in the order Fe >Zn > Pb > Cu >Cd > As > Cr (Table 1a and b). Mean iron levels ranged from 0.76 ± 0.49 mg/L in Well 7 to 2.87 ± 0.55 mg/L in Well 1 and they differed significantly from mean iron levels in Wells 3, 5, 6, and 7 (Table 1). Iron levels in all well-water samples exceeded regulatory limits given by the Standards Organization of Nigeria (SON 2015), and the European Union (EU 1998). No limits were given for iron by WHO and USEPA. The WHO states that values of iron up to 2 mg/L do not present a hazard to health and concentrations between 1-3 mg/L can be acceptable for people drinking anaerobic well-water (WHO 1996).

Table.	1	Damage	(:	has alreta)	and measure	o o m o o m two ti o m	of hoors	- mantala im	a a m t m a 1		usell susation.	~~~~l~~	(- /T)
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Samples	Fe (mg/L)	Cu (mg/L)	Pb (mg/L)	Cr (mg/L)
Control	0.00 ± 0.00^a	$0.00\pm0.00^{\rm a}$	$0.00\pm0.00^{\rm a}$	0.00 ± 0.00^a
Well 1	(2.40–3.48); 2.87 \pm 0.55 d	(0.058–0.09); 0.07 \pm 0.02^{ab}	(0.08–0.48); 0.19 \pm 0.21 b	(0.00–0.03); 0.01 $\pm~0.02^{a}$
Well 2	(1.69–2.99); 2.26 \pm 0.67 ^{cd}	(0.03–0.07); 0.05 $\pm~0.20^{\rm b}$	(0.12–0.39); 0.20 \pm 0.17 b	(0.00–0.03); 0.01 \pm 0.01 $^{\rm a}$
Well 3	(0.89–2.26); 1.54 \pm 0.69 ^{bc}	(0.03–0.05); 0.04 \pm 0.11 ^{ab}	(0.001–0.31); 0.14 \pm 0.13 ab	(0.00–0.02); 0.01 \pm 0.01 $^{\rm a}$
Well 4	(0.79–2.82); 2.09 \pm 0.90 cd	(0.04–0.12); 0.09 \pm 0.04 ^{ab}	(0.003–0.21); 0.09 \pm 0.09 ab	(0.00–0.02); 0.01 \pm 0.01 $^{\rm a}$
Well 5	(0.23–1.99); 0.92 \pm 0.76 ab	(0.00–0.11); 0.06 \pm 0.05 ab	(0.0007–0.27); 0.10 \pm 0.12 ab	(0.00–0.02); 0.01 \pm 0.01 $^{\rm a}$
Well 6	(0.84–1.89); 1.32 \pm 0.53 bc	(0.00–0.11); 0.04 \pm 0.06 ab	(0.00–0.20); 0.10 \pm 0.08 ab	(0.00–0.01); 0.01 \pm 0.01 $^{\rm a}$
Well 7	(0.37–1.47); 0.76 \pm 0.49 ab	(0.00–0.11); 0.04 \pm 0.05 ab	(0.00-0.14);0.06 \pm 0.06 ab	(0.00–0.02); 0.01 \pm 0.01 $^{\rm a}$
SON (2015)	0.3	1.0	0.010	0.05
WHO (2017)	-	2.0	0.010	0.05
EU (1998)	0.2	2.0	0.010	0.05
USEPA (2009)	<u>-</u>	1.3	0.015	0.1

*: Statistically significant = $P \le 0.05$. Values are mean \pm S.D, Superscripts differ significantly (P < 0.05) from Duncan post hoc test analysis and means with the same letter across the groups are not significantly different from each other. Italicized values exceeded one or more drinking water regulatory standards.

Table 1b. Range (in brackets), and mean concentration of heavy metals in control and well-water samples (mg/L).

Samples	Cd (mg/L)	Zn (mg/L)	As (mg/L)
Control	$0.00\pm0.00^{\rm a}$	$0.00\pm0.00^{\rm a}$	$(0.000.03);0.00\pm0.00^{\mathrm{a}}$
Well 1	(0.00–0.05); 0.01 ± 0.03 ^a	(0.00–0.12); 0.04 \pm 0.06 $^{\rm a}$	(0.00–0.02); 0.01 \pm 0.01 ^a
Well 2	(0.00–0.06); 0.02 ± 0.03 ^a	(0.00–0.1); 0.07 \pm 0.06 ^a	(0.00–0.04); 0.01 \pm 0.01 ^a
Well 3	(0.00–0.08); 0.02 \pm 0.04 a	(0.12–0.29); 0.22 \pm 0.12 ^{ab}	(0.00–0.04); 0.02 \pm 0.02 a
Well 4	(0.00–0.05); 0.01 ± 0.02 ^a	(0.16–0.34); 0.27 \pm 0.07 ^{bc}	(0.00–0.04); 0.02 \pm 0.02 ^a
Well 5	(0.00–0.05); 0.01 ± 0.02 ^a	(0.00–0.29); 0.09 \pm 0.12 ^c	$(0.000.04); 0.02\pm0.02^a$
Well 6	(0.00–0.04); 0.01 \pm 0.02 a	(0.06–0.13); 0.10 \pm 0.03 ^{ab}	(0.00–0.02); 0.01 \pm 0.01 ^a
Well 7	(0.00–0.03); 0.01 ± 0.01 ^a	(0.009–0.17); 0.07 \pm 0.06 $^{\rm ab}$	(0.00–0.02); 0.01 \pm 0.01 ^a
SON (2015)	0.003	3.0	0.01
WHO (2017)	0.003	-	0.01
EU (1998)	0.005	-	0.01
USEPA (2009)	0.005	-	0.01

*: Statistically significant = $P \le 0.05$. Values are mean \pm S.D, Superscripts differ significantly (P < 0.05) from Duncan post hoc test analysis and means with the same letter across the groups are not significantly different from each other. Italicized values exceeded one or more drinking water regulatory standards. Cd=Cadmium; Zn = Zinc; As=Arsenic.

Mean lead levels ranged from 0.06 \pm 0.06 mg/L in Well 7, to 0.20 \pm 0.17 mg/L in Well 2. Lead levels in all samples except the control were statistically similar at the 5% level of significance (Table 1a and b). Lead levels in all the wells exceeded SON, WHO, EU, and USEPA regulatory limits. Though its widespread use has been discontinued in many countries of the world, lead is still used in many industries such as automobile repair, battery manufacturing, recycling, smelting, and refining amongst others. It is a highly toxic metal that affects multiple organs in the body. The nervous system is however the most affected target in lead toxicity, both in children and adults. Long-term exposure to lead has been linked to decreased cognitive performance, anemia and blood disorders, increased blood pressure, severe brain and kidney damage, miscarriages in pregnant women, and reduced fertility in males (Wani et al., 2015). Previous studies on the effects of groundwater within the Araromi automobile spare-parts market on some reproductive indices in male Swiss albino mice indicated the adverse effects of the well-water samples in reducing male fertility, possibly due to the elevated lead levels. A significant reduction in sperm count and motility was observed in mice exposed to higher concentrations (50-100% groundwater samples from wells 1 and 7) compared to those exposed to the control and lower concentration group (25% groundwater).

In addition, various morphological abnormalities were observed in the spermatozoa of mice exposed to the two highest concentrations (75% and 100%) of the groundwater from both wells on day 84, while significantly elevated follicle – stimulating and luteinizing hormones were also observed in mice exposed to the highest concentration (100% groundwater) on day 84 (Oni et al., 2019); indicating alterations in levels of reproductive hormones following ingestion of the contaminated water. Cadmium levels ranged from 0.01 mg/L in Wells 1, 4, 5, 6 and 7 to 0.02 \pm 0.03 mg/L in Wells 2 and 3. No significant differences existed in cadmium levels between all samples (p < 0.05). However, similar to lead, cadmium levels in all well-water samples exceeded all four regulatory limits (Table 1a and b).

The kidney is the critical organ of intoxication following long-term exposure to cadmium, and some studies suggest that at moderate exposure, cadmium may exacerbate the agE – related decline in renal function ((Hutton 1987)). In humans and other mammals, cadmium exposure can also result in a variety of adverse effects including testicular damage, pulmonary edema, hepatic dysfunction, and osteomalacia (Arroyo et al., 2012). Thus, the high levels of cadmium observed in the well water can be injurious to the health of the exposed population over time.

Arsenic levels ranged between 0.01 mg/L in Wells 1, 2, 6, and 7 to 0.02 mg/L in Wells 3–5 with no significant differences at the 5% level. Mean arsenic levels in wells 3–5 also exceeded all four regulatory limits of 0.01 mg/L. Effects of acute exposure to arsenic compounds include nausea, vomiting, abdominal pain, muscle cramps, and diarrhea

Samples	ANT	FLT	PYR	BaA
Control	(0.001–0.002) 0.001 $\pm~0.00^{a}$	(0.00–0.00) 0.00 \pm 0.00 ^a	$(0.000.00)\ 0.00\ \pm\ 0.00^a$	(0.011–0.014) 0.01 ± 0.00^{a}
Well 1	$(0.044 0.062) \ 0.05 \pm 0.01^{c}$	(0.013–0.023) 0.02 \pm 0.006 ^{ab}	(0.019–0.425) 0.27 \pm 0.22 ^{bc}	(0.541–0.698) 0.64 \pm 0.08 ^b
Well 2	(0.0255–0.026) 0.03 \pm 0.00 $^{ m abc}$	(0.009–0.012) 0.01 \pm 0.002 ^{ab}	(0.150–0.240) 0.20 \pm 0.05 abc	(0.466–0.521) 0.49 \pm 0.03 ^b
Well 3	(0.028–0.045) 0.03 \pm 0.01 $^{\rm bc}$	(0.01–0.014) 0.01 \pm 0.002 ^b	$(0.1640.415)\ 0.31\ \pm\ 0.13^c$	(0.511–0.590) 0.56 \pm 0.04 ^b
Well 4	(0.0015–0.039) 0.02 ± 0.02^{abc}	(0.00–0.008) 0.004 $\pm~0.003^a$	(0.011–0.215) 0.14 \pm 0.09 ^{abc}	(0.529–0.565) 0.42 \pm 0.26 ^b
Well 5	(0.0005–0.021) 0.01 \pm 0.01 $^{\rm ab}$	(0.00–0.006) 0.003 $\pm~0.002^{ab}$	(0.009–0.120) 0.06 \pm 0.05 ^{ab}	(0.007–0.461) 0.31 ± 0.21 ^{ab}
Well 6	(0.0085–0.025) 0.01 \pm 0.01 $^{\mathrm{ab}}$	$(0.0040.012)\ 0.007 \pm 0.004^{ab}$	(0.095–0.140) 0.12 ± 0.02^{abc}	(0.003–0.540) 0.45 \pm 0.09 ^b
Well 7	$(0.000.091) \ 0.05 \pm 0.04^c$	(0.00–0.031) 0.02 \pm 0.01 ab	$(0.0050.535)\ 0.30 \pm 0.22^c$	(0.725–0.881) 0.62 \pm 0.42 ^b
SON (2015); WHO (2017)	-	-	-	-
EU (1998)	-	-	-	
USEPA (2009)	-	-	-	-
INS (2011)				0.18

Table 2a. Range and mean concentrations of Polycyclic Aromatic Hydrocarbon (PAHs) in Control and Well-water samples (µg/L).

*: Statistically significant = $P \le 0.05$ Values are mean \pm S.D, Superscripts differ significantly (P < 0.05) from Duncan post hoc test analysis and means with the same letter across the groups are not significantly different from each other. Except for the International and National Environmental Quality Standards for Substances in the Netherlands (INS, 2011), which stated a regulatory limit for benzo (a) anthracene, all other regulatory limits given were for benzo (a) pyrene while SON limits were not specific with respect to a particular PAH. Italicized figures exceeded one or more drinking water regulatory standards. Ant = Anthracene; Flt = Fluoranthene; Pyr =Pyrene; BaA =Benzo(a)Anthracene.

Table 2b. Range and mean	concentrations of Polycyclic	Aromatic Hydrocarbon (PA	AHs) in Control and Well-	water samples (μ g/L).
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Samples	CHR	BbF	BaP	B-1,2A
Control	(0.00–0.00) 0.00 \pm 0.00 ^a	(0.001–0.002) 0.001 $\pm~0.00^a$	(0.00–0.00) 0.00 \pm 0.00 ^a	$(0.0020.005)\ 0.003\pm 0.002^a$
Well 1	(0.004–0.019) 0.01 \pm 0.008 ^c	(0.022–0.046) 0.03 ± 0.01^{ab}	(0.044–0.093) 0.06 \pm 0.03 $^{\circ}$	$(0.330.465)\ 0.38\pm0.08^{c}$
Well 2	(0.003–0.009) 0.006 \pm 0.003 ^{abc}	$(0.0120.057)~0.04\pm0.03^{b}$	(0.031–0.043) 0.04 \pm 0.006 abc	(0.233–0.310) 0.28 \pm 0.04 bc
Well 3	(0.006–0.017) 0.01 \pm 0.006 ^{bc}	(0.01–0.025) 0.02 \pm 0.009 ^{ab}	(0.034–0.073) 0.05 \pm 0.02 ^{bc}	$(0.260.394)~0.32\pm0.07^{bc}$
Well 4	(0.004–0.01) 0.006 \pm 0.003 ^{abc}	(0.00–0.017) 0.01 \pm 0.007 ^{ab}	(0.00–0.055) 0.03 \pm 0.02 abc	(0.016–0.317) 0.17 \pm 0.13 ^{ab}
Well 5	(0.0015–0.006) 0.004 $\pm~0.002^{ab}$	(0.00–0.004) 0.003 \pm 0.002 ^a	(0.00–0.016) 0.01 \pm 0.007 ^a	$(0.0010.11)~0.08\pm0.05^{ab}$
Well 6	(0.003–0.004) 0.004 \pm 0.001 ab	(0.002–0.009) 0.004 \pm 0.004 $^{\rm a}$	(0.016–0.023) 0.02 \pm 0.004 ab	$(0.1260.170)\ 0.15\pm0.02^{ab}$
Well 7	(0.001–0.01) 0.01 \pm 0.01 $^{ m abc}$	(0.00–0.082) 0.05 \pm 0.04 ab	(0.00–0.093) 0.05 \pm 0.04 bc	$(0.0020.638)\ 0.42\pm0.29^{c}$
SON (2015); WHO (2017)	-	-	0.7; 0.7	
EU (1998)	-	-	0.01	
USEPA (2009)	-	-	0.2	
INS (2011)				

*: Statistically significant = $P \le 0.05$ Values are mean \pm S.D, Superscripts differ significantly (P < 0.05) from Duncan post hoc test analysis and means with the same letter across the groups are not significantly different from each other. Except for the International and National Environmental Quality Standards for Substances in the Netherlands (INS, 2011), which stated a regulatory limit for benzo (a) anthracene, all other regulatory limits given were for benzo (a) pyrene while SON limits were not specific with respect to a particular PAH. Italicized figures exceeded one or more drinking water regulatory standards.

Chr = Chrysene; BbF = Benzo(b)Fluoranthene; BaP = Benzo(a)Pyrene; B-1,2A = Benzo 1, 2-Anthracene.

(Kamunda et al., 2016). Mean copper, chromium, and zinc levels did not differ significantly between the wells except for zinc in wells 4-5 (p <0.05), and these three metals were within limits of local and international standards (Table 1a and b). These results show obvious infiltration of heavy metals either by percolation or surface run-off into these well-water samples, and iron, lead, cadmium, and arsenic levels call for concern as they exceed the permissible limits in the well water samples. Abdul Zali et al. (2015) determined the concentration of 23 elements in virgin, used, recovered, and waste oil, and they observed an increase in wear elements such as iron and chromium in spent lubricating oil when compared to the respective virgin oil, including considerable amounts of lead in the waste oil samples. Lead can also be generated from main and rod bearings. Other wear and contaminant metals identified in the oil samples included copper, cadmium, and arsenic amongst others (Abdul Zali et al., 2015). Except for copper and chromium which were within regulatory limits, the presence of iron, lead, cadmium, and arsenic in well-water samples at levels above regulatory limits suggests that lubricating oils from the automobile parts may be a continuous source of heavy metal input to the groundwater, and potential sources of toxicity to human and perhaps animal populations that are continuously exposed to these water sources.

3.2.2. PAHs concentration in well water samples

The range and mean concentrations of the eight PAHs assayed in the control and well-water samples are presented in Table 2a and b. Except for anthracene, benzo(a)anthracene, benzo(b)fluoranthene, and benzo, 1, 2, anthracene with mean values of 0.001, 0.01, 0.001, and 0.003 ug/L respectively, all other PAHs were undetected in the distilled water control sample. The values for PAHs in the control sample were all within regulatory limits. Mean concentrations of PAHs in the test water samples were in the order: Benzo(a)Anthracene (BaA)>Benzo, 1, 2-Anthracene > Pyrene (Pyr)>Benzo(a)Pyrene (BaP)>Anthracene (Ant) = Benzo(b)Fluoranthene (BbF)>Fluoranthene (Flt)>Chrysene (Chy). Concentrations of benzo(a)anthracene concentrations in test well-water samples ranged from 0.31 \pm 0.21 ug/L in Well 5, to 0.64 \pm 0.08 ug/L in Well 1 and the values were significantly higher than the control and exceeded the regulatory limits of 0.18 ug/L for BaA in drinking water (INS 2011). The levels of benzo (a) pyrene observed ranged from 0.01 \pm 0.01 ug/L in well 5 to 0.06 \pm 0.02 ug/L in Well 1, with the observed differences significant at p < 0.05 (Table 2a and b). However, these values were within the regulatory limits given by USEPA (2009); SON (2015), and WHO (2017), but exceeded limits given by the EU (EU 1998). Levels of BaP in samples

Table 3. Average Daily Dose (ADD) for both oral and dermal exposure to heavy me	tals in the seven wells.
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	0						2							
METALS	Well 1		Well 2		Well 3		Well 4		Well 5		Well 6		Well 7	
	Oral	Dermal												
Children														
Fe	1.9E - 1	1.26E - 3	1.5E - 1	9.94E – 4	1.0E - 1	6.78E - 4	1.4E - 1	9.20E - 4	6.1E - 2	4.05E - 4	8.8E-2	5.81E - 4	5.1E - 2	3.34E – 4
Cu	4.6E – 3	3.08E - 5	3.3E – 3	2.20E - 5	2.6E - 3	1.76E – 5	6.0E - 3	3.96E – 5	4.0E - 3	2.64E - 5	2.6E - 3	1.76E – 5	2.7E - 3	1.76E – 5
РЬ	1.3E - 2	8.36E – 5	1.3E - 2	8.80E - 5	9.3E – 3	6.16E – 5	6.0E - 3	3.96E – 5	6.6E-3	4.40E – 5	6.7E-3	4.40E – 5	4.0E – 3	2.64E – 5
Cr	6.6E - 4	8.80E - 6	6.6E-4	8.80E - 6	6.6E - 4	8.80E – 6								
Cđ	6.7E - 4	4.40E - 6	1.3E - 3	8.80E - 6	1.3E - 3	8.80E - 6	6.6E-4	4.40E – 6	6.7E – 4	4.40E - 6	6.6E-4	4.40E - 6	6.6E - 4	4.40E – 6
Zn	2.6E - 3	1.06E - 5	4.7E – 3	1.85E - 5	1.5E - 2	5.81E – 5	1.8E - 2	7.13E – 5	6.0E - 3	2.38E - 5	6.6E-3	2.64E - 5	4.7E – 3	1.85E – 5
As	6.6E - 4	4.40E - 6	6.6E - 4	4.40E - 6	1.3E - 3	8.80E - 6	1.3E - 3	8.80E - 6	1.3E - 3	8.80E - 6	6.6E - 4	4.40E - 6	6.6E - 4	4.40E – 6
Adults														
Fe	9.0E - 2	4.28E – 4	7.1E - 2	3.37E – 4	4.8E - 2	2.30E - 4	6.6E - 2	3.12E - 4	2.9E - 2	1.37E - 4	4.1E - 2	1.97E - 4	2.4E - 2	1.13E – 4
Cu	2.2E - 3	1.04E - 5	1.6E - 3	7.46E – 6	1.3E - 3	5.97E – 6	2.8E - 3	1.34E - 5	1.9E - 3	8.95E – 6	1.3E - 3	5.97E – 6	1.3E - 3	5.97E – 6
Pb	6.0E - 3	2.83E - 5	6.3E-3	2.98E - 5	4.4E - 3	2.09E - 5	2.8E - 3	1.34E - 5	3.1E - 3	1.49E – 5	3.1E - 3	1.49E - 5	1.9E - 3	8.95E – 6
Cr	3.1E - 4	2.98E - 6	3.1E - 4	2.98E – 6										
Cd	3.1E - 4	1.49E - 6	6.3E - 4	2.98E - 6	6.3E - 4	2.98E - 6	3.1E - 4	1.49E – 6	3.1E - 4	1.49E - 6	3.1E - 4	1.49E - 6	3.1E - 4	1.49E – 6
Zn	1.3E - 3	3.58E - 6	2.2E - 3	6.26E - 6	6.9E-3	1.97E – 5	8.5E - 3	2.42E - 5	2.8E - 3	8.05E - 6	3.1E - 3	8.94E - 6	2.2E - 3	6.26E – 6
As	3.1E-4	1.49E - 6	3.1E-4	1.49E - 6	6.3E-4	2.98E - 6	6.3E - 4	2.98E - 6	6.3E - 4	2.98E - 6	3.1E - 4	1.49E – 6	3.1E-4	1.49E – 6

from wells 1, 3, and 7 also exceeded the limits for Canadian Drinking Water Quality (Health Canada, 2016) of 0.04 ug/L.

Benzo(a)Pyrene is a skin sensitizer that can also cause an allergic reaction in the skin of animals and humans. Laboratory studies conducted on mice showed that the ingestion of high levels of BaP resulted in neonatal defects and decreased body weight, although it is not known whether these effects can occur in humans (Abdel-Shafy et al. 2016). There are three recognized sources of PAHs in the environment which are: pyrogenic, petrogenic, and biological. Petrogenic PAHs are common due to widespread transportation, storage, and use of crude oil and crude oil products. The accumulation of vast numbers of small releases of gasoline, motor oil, and related substances associated with transportation are major sources of petrogenic PAHs (Abdel-Shafy et al. 2016). Gasoline, motor oil, and other lubricants associated with the automobile spare parts sold at the market suggest that the observed PAHs may have originated from petrogenic sources.

3.3. Health risk assessment

3.3.1. Average daily dose (ADD)

3.3.1.1. Heavy metals. The Average Daily Dose (ADD) in children and adults through oral and dermal exposure to heavy metals in water from the seven wells are presented in Table 3 . The ADD by ingestion for heavy metals measured in the seven wells were observed to exceed the values through dermal exposure, with ADD_{ingestion} accounting for up to 99% of ADD_{total} (ADD_{total} = ADD_{ingestion} + ADD_{dermal}) for metals such as iron and lead in both children and adults. This implies that daily exposure to these heavy metals through drinking or food prepared with the well water (ingestion) is the most important contribution to the average daily exposure. Oral ingestion is therefore more likely the course of impact to the health of exposed populations when compared to dermal exposure. Previous reports showed that the most important exposure route for heavy metals in water is via the ingestion pathway Hutton (1987) and (Alidadi et al., 2019).

3.3.1.2. PAHS. The Average Daily Dose (ADD) for both oral and dermal exposure to PAHs in the seven wells is presented in Table 5. Unlike for heavy metals, the average daily dose for dermal exposure for all PAHs in all the seven wells in both groups was found to exceed the ADD for oral exposure. For instance, in contrast to the heavy metals where ADD_{ingestion} contributed up to 99% of the total ADD, ADD_{dermal} for BaP in children and adults contributed up to a maximum of 89% of the total ADD. Therefore, daily exposure to the PAHs in the well water through dermal pathways is the major contributor to the average daily dose. Exposed populations are thus likely to experience adverse health effects from PAHs in the water sample through dermal exposure to PAHs in drinking water also observed that dermal exposure to PAHs in water sources poses more risks to human health than oral water ingestion.

3.4. Hazard quotient (HQ)

3.4.1. Hazard quotient (HQ) for heavy metals

3.4.1.1. Children. The Hazard Quotients (HQ) for both oral and dermal exposure of children and adults to heavy metals in water samples from the seven wells are presented in Table 4. The HQ values of water ingestion for lead exceeded 1 in samples from all wells and ranged from 1.14 in well 7, to 3.71 in wells 1 and 2. The HQ for cadmium ranged from 1.32 in wells 1, 4, 6, and 7 to 2.60 in wells 2–3; while HQ for As ranged from 2.20 in wells 1, 2, 6, and 7 to 4.33 in wells 3–5. HQ via dermal exposure to Cd also exceeded 1 in wells 2 and 3 (Table 4).

4. Hazard Onotient (HO) for both oral and dermal exposing to beavy metal

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AETALS	Well 1		Well 2		Well 3		Well 4		Well 5		Well 6		Well 7	
	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal
Children														
e	2.71E - 1	9.00E - 3	2.14E - 1	7.10E - 3	1.43E - 1	4.84E - 3	2.00E - 1	6.57 E - 3	8.71E-2	2.89E – 3	1.26E - 1	4.15E – 3	7.29E - 2	2.39E – 3
Ju L	1.15E – 1	2.57E – 3	8.25E – 1	1.83E – 3	$6.50 \mathrm{E} - 2$	1.47E - 3	1.50E - 1	3.30E - 3	1.00E - 1	2.20E - 3	$6.50 \mathrm{E} - 2$	1.47E - 3	6.75E - 2	1.47E - 3
b b	<u>3.71E0</u>	1.66E - 1	<u>3.71E0</u>	1.66E - 1	<u>2.66E0</u>	1.16E - 1	<u>1.71E0</u>	7.47E - 2	<u>1.89E0</u>	8.30E - 2	<u>1.91E0</u>	8.30E - 2	<u>1.14E0</u>	4.98E – 2
1	2.20E - 1	1.47E - 1	2.20E - 1	1.47E - 1	2.20E - 1	1.47E - 1	2.20E - 1	1.47E - 1	2.20E - 1	1.47E - 1	2.20E - 1	1.47E - 1	2.20E - 1	1.47E - 1
p	<u>1.32E0</u>	8.80 E - 1	2.60E0	<u>1.76E0</u>	2.60E0	<u>1.76E0</u>	<u>1.32E0</u>	$8.80 \mathrm{E} - 1$	<u>1.33E0</u>	8.80E - 1	1.32E0	8.80E - 1	<u>1.32E0</u>	8.80 E - 1
ľ	8.67E – 3	1.77E - 4	1.53E - 2	3.08E - 4	4.90 E - 2	9.68E - 4	6.00E - 2	1.19E - 3	2.00E-2	3.97E - 4	2.20E-2	4.40E - 4	1.53E - 2	3.08E – 4
IS	<u>2.20E0</u>	3.58E - 2	2.20E0	3.58E – 2	4.33E0	7.15E - 2	4.33E0	7.15E - 2	4.33E0	7.15E - 2	2.20E0	3.58E - 2	2.20E0	3.58E – 2
fazard Index (HI)	7.85E0	<u>1.24E0</u>	<u>9.78E0</u>	<u>2.12E0</u>	<u>10.07E0</u>	<u>2.10E0</u>	8.00E0	<u>1.18E0</u>	7.97E0	<u>1.19E0</u>	5.86E0	<u>1.13E0</u>	5.04E0	<u>1.12E0</u>
Adults														
ē	1.3E - 1	3.06E - 3	1.0E - 1	2.41E - 3	7.0E - 2	1.64E - 3	9.0E-2	2.23E - 3	4.1E - 2	9.79E – 4	5.9E - 2	1.41E - 3	3.4E - 2	8.07E – 4
E	5.5E - 2	8.67E – 4	3.9E - 2	6.21E - 4	3.3E - 2	4.98E - 4	7.0E-2	1.12E - 3	4.8E-2	7.46E – 4	3.3E - 2	4.98E - 4	3.3E-2	4.98E – 4
b b	<u>1.80E0</u>	5.69 E - 2	1.80E0	5.69E – 2	<u>1.26E0</u>	3.99 E - 2	8.0E - 1	2.56E - 2	8.9E - 1	2.84E - 2	9.0E - 1	2.80E - 2	5.4E - 1	1.71E - 2
5	1.0E - 1	4.97E - 2	1.0E - 1	4.97E – 2	1.0E - 1	4.97E - 2	1.0E - 1	4.97 E - 2	1.0E - 1	4.97E - 2	1.0E - 1	4.97E - 2	1.0E - 1	4.97E - 2
p	6.2E – 1	2.98E - 1	<u>1.26E0</u>	5.96E - 1	<u>1.26E0</u>	5.96E - 1	$6.2 \mathrm{E} - 1$	2.98E - 1	6.3E - 1	2.98E - 1	6.2E - 1	2.98E - 1	$6.2 \mathrm{E} - 1$	2.98E – 1
ų	4.33E – 3	5.97E – 5	7.33E – 3	1.04E - 4	2.30E - 2	3.28E – 4	2.83E – 2	4.03 E - 4	9.3E – 3	1.34E - 4	1.03E - 2	1.49E - 4	7.33E – 3	1.04 E - 4
ls	<u>1.03E0</u>	1.21E - 2	1.03E0	1.21E - 2	<u>2.1E0</u>	2.42E – 2	<u>2.1E0</u>	2.42E – 2	<u>2.1E0</u>	2.42E – 2	<u>1.03E0</u>	1.21E - 2	<u>1.03E0</u>	1.21E - 2
Hazard Index (HI)	<u>3.74E</u>	$4.20 \mathrm{E} - 1$	<u>4.34E0</u>	7.18E - 1	<u>4.85E0</u>	7.12E - 1	<u>3.81E0</u>	4.01E - 1	<u>3.82E0</u>	4.02E – 1	<u>2.75E0</u>	3.84E – 1	<u>2.36E0</u>	3.78E - 1
Values in bold and	underlined ex	ceed unity. Ex	posure to thes	se would elicit	non-carcinogei	nic health risks	S.							

3.4.1.2. Adults. Lead, cadmium, and arsenic were also metals of concern in adults, with HQ values via ingestion exceeding 1 in water samples from wells 1–3 for Pb; 2, and 3 for Cd, and all seven wells for As. Lead, cadmium, and arsenic were thus the main contributors to the non-carcinogenic health risk via the ingestion route among all the heavy metals examined. This result also indicates that populations orally exposed to toxic metals in the well water samples may be at greater risk of adverse non-carcinogenic health effects, as all HQ values for ingestion for all metals in all the studied wells exceeded the HQ values for dermal exposure. No non-carcinogenic risk is indicated via the dermal route in this group as all HQ values were below 1 (Table 4).

3.4.2. Hazard index (HI) for heavy metals

Hazard index values via the ingestion route in children ranged from 5.04 in samples from well 7 to 10.07 in samples from well 3 (Table 4). In adults, HI values via ingestion ranged from 2.36 in well 7 to 4.85 in samples from well 3 via the same route. On the other hand, hazard index values via the dermal route in children ranged from 1.12 in well 7, to 2.12 in well 2. In adults, HI levels for heavy metals were of no remarkable concern via the dermal route as all HI values were below 1. Arsenic, lead, and cadmium were the greatest contributors to the observed risks via the ingestion pathway. In children, twenty-two to fifty-four percent, and in adults, twenty-four to fifty-five percent of the HI in wells 2, and 4-5 respectively was due to As, while Pb contributed 21-47%, and 21-48% of the HI in children and adults via ingestion respectively. Cadmium accounted for between 16% (Wells 4–5; adults), 16.5% (Well 4; children) of the HI via the ingestion pathway to 29% and 27% for adults and children respectively in well 2. On the other hand, cadmium was the major contributor to dermal exposure as it accounted for between 79% (well 7) and 84% (well 3) of the HI in children. The high HI value in the sampled wells (>1) would be indicative of remarkable potential noncarcinogenic health risks in both children and adults attributable to the elevated heavy metal levels, particularly arsenic, lead, and cadmium in the well-water samples. Children in particular will be the most vulnerable to the adverse health effects via both routes, while for adults the wellwater samples portend non-carcinogenic risks only through ingestion (Table 4).

The implications of heavy metals concerning children's health have been observed to be more severe compared to adults (Al-Osman et al., 2019). The greater vulnerability of children has been partly attributed to the blood-brain barrier which is less developed in children and results in higher permeability to heavy metals such as lead (Jarup 2003). Gastrointestinal uptake is also higher in children making them absorb 4–5 times as much lead as adults. These higher uptake factors coupled with the long biological half-life of metals such as lead makes children more vulnerable to the effects of these contaminants than adults (Aendo et al., 2019). This may perhaps explain the observed higher HQ and HI values in children when compared to adults. Nonetheless, the levels of these contaminants constitute health hazards even for adults as compounds such as lead can still cross the blood-brain barrier in adults to result in lead encephalopathy (Jarup 2003).

3.4.3. Hazard quotient (HQ) for PAHs

The Hazard Quotients (HQ) for both oral and dermal exposures to PAHs in the seven studied wells are presented in Table 6. The oral HQ of four of the eight PAHs assayed and dermal HQ of two PAHs were estimated. The HQs of the other PAHs could not be estimated due to the lack of reference doses for them in the literature. The results show that the HQ values for both oral and dermal exposure to the four PAHs were below 1, indicating that exposure to these PAHs through ingestion or dermal absorption is unlikely to exert adverse non-carcinogenic risks in the exposed population.

3.4.4. Hazard index for PAHs

The Hazard Index of both direct ingestion and dermal absorption for PAHs is presented in Table 6. The HI for the PAHs was also found to be

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Table 3. Average Day	TV) DOOL (III)			uiai exposure		רווב אבעבוו אנ										
PAHs	Control		Well 1		Well 2		Well 3		Well 4		Well 5		Well 6		Well 7	
	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal
Children																
Anthracene	6.67E – 8	NA	3.33E – 6	NA	2.00E – 6	NA	2.00E – 6	NA	1.33E – 6	NA	6.67E – 7	NA	6.67E – 7	NA	3.33E – 6	NA
Fluoranthene	0.00E00	0.00E00	1.33E - 6	3.17E – 6	6.67E – 7	1.58E – 6	6.67E – 7	1.58E – 6	2.67E – 7	6.34E – 7	2.0E - 7	4.75E – 7	4.67E – 7	1.11E – 6	1.33E – 6	3.17E – 6
Pyrene	0.00E00	NA	1.80E - 5	NA	1.33E – 5	NA	2.07E – 5	NA	9.33E – 6	NA	4.00E - 6	NA	8.00E - 6	NA	2.00E - 5	NA
Benzo(a)anthracene	6.67E – 7	3.56E – 6	4.27E – 5	2.28E – 4	3.27E – 5	1.75E – 4	3.73E – 5	2.00E - 4	2.80E - 5	1.50E - 4	2.07E – 5	1.11E – 4	3.00E – 5	1.60E - 4	4.13E – 5	2.21E - 4
Chrysene	0.00E00	0.00E00	1.33E - 6	7.13E – 6	4.00E – 7	2.14E – 6	1.33E – 6	7.13E - 6	4.00E - 7	2.14E – 6	2.67E – 7	1.43E – 6	2.67E – 7	1.43E – 6	6.67E – 7	3.56E – 6
Benzo(b)fluoranthene	6.67E – 8	5.28E – 7	2.00E - 6	1.58E – 5	2.67E – 6	7.16E – 6	1.33E – 6	1.06E - 5	6.67E – 7	5.28E – 6	2.00E – 7	1.58E – 6	2.67E – 7	2.11E – 6	3.33E – 6	2.64E – 5
Benzo(a)pyrene	0.00E00	0.00E00	4.00E – 6	3.17E – 5	2.67E – 6	2.11E – 5	3.33E – 6	2.64E – 5	2.00E – 6	1.58E – 5	6.67E – 7	5.28E – 6	1.33E – 6	1.06E - 5	3.33E – 6	2.64E – 5
Benzo-1,2-anthracene	2.00E – 7	NA	2.53E – 5	NA	1.87E – 5	NA	2.13E – 5	NA	1.13E – 5	NA	5.33E – 6	NA	1.00E - 5	NA	2.80E – 5	NA
Adults																
Anthracene	3.14E – 8	NA	1.57E - 6	NA	9.43E – 7	NA	9.43E – 7	NA	6.29E – 7	NA	3.14E – 7	NA	3.14E – 7	NA	1.57E – 6	NA
Fluoranthene	0.00E00	0.00E00	6.29E – 7	1.07E - 6	3.14E – 7	5.37E – 7	3.14E – 7	5.37E – 7	1.26E - 7	2.15E – 7	9.43E – 8	1.61E – 7	2.20E - 7	3.76E – 7	6.29E – 7	1.07E - 6
Pyrene	0.00E00	NA	8.49E – 6	NA	6.29E – 6	NA	9.74E – 6	NA	4.40E – 6	NA	1.89E – 6	NA	3.77E – 6	NA	9.43E – 6	NA
Benzo(a)anthracene	3.14E – 7	1.21E - 6	2.01E - 5	7.73E – 5	1.54E – 5	5.92E – 5	1.76E – 5	6.77E – 5	1.32E – 5	5.07E – 5	9.74E – 6	3.74E – 5	1.41E - 5	5.44E – 5	1.95E – 5	7.49E – 5
Chrysene	0.00E00	0.00E00	6.29E – 7	2.42E – 6	1.89E – 7	7.25E – 7	6.29E – 7	2.42E - 6	1.89E – 7	7.25E – 7	1.26E - 7	4.83E – 7	1.26E - 7	4.83E – 7	3.14E – 7	1.21E - 6
Benzo(b)fluoranthene	3.14E – 8	1.79E - 7	9.43E – 7	5.37E – 6	1.26E – 6	7.16E – 6	6.29E – 7	3.58E – 6	3.14E – 7	1.79E – 6	9.43E – 8	5.37E – 7	1.26E - 7	7.16E – 7	1.57E – 6	8.95E – 6
Benzo(a)pyrene	0.00E00	0.00E00	1.89 E - 6	1.07E - 5	1.26E – 6	7.16E – 6	1.57E – 6	8.95E – 6	9.43E – 7	5.37E – 6	3.14E – 7	1.79E – 6	6.29E – 7	3.58E – 6	1.57E – 6	8.95E – 6
Benzo-1,2-anthracene	9.43E – 7	NA	1.19E - 5	NA	8.80E – 6	NA	1.01E - 5	NA	5.34E – 6	NA	2.51E – 6	NA	4.71E – 6	NA	1.32E – 5	NA

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PAHs	Control		Well 1		Well 2		Well 3		Well 4		Well 5		Well 6		Well 7	
	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal
Children																
Anthracene	2.22E – 7	NA	1.11E – 5	NA	6.66E – 6	NA	6.66E – 6	NA	4.43E – 6	NA	2.22E – 6	NA	2.22E – 6	NA	1.11E – 5	NA
Fluoranthene	0.00E00	0.0E00	3.33E – 5	7.93E – 5	1.67E - 5	3.95E – 5	1.67E – 5	3.95E – 5	6.68E – 6	1.59E – 5	5.00 E - 6	1.19E – 5	1.17E - 5	2.78E – 5	3.33E – 5	7.93E - 5
Pyrene	0.00E00	NA	6.00E – 4	NA	4.43E – 4	NA	6.90E - 4	NA	3.11E – 4	NA	1.33E – 4	NA	2.66E – 4	NA	6.66E – 4	NA
Benzo(a)pyrene	0.00E00	0.0E00	1.33E – 2	1.06E - 1	8.90E – 3	7.03E – 2	1.11E - 2	8.80E – 2	6.66E – 3	5.26E – 2	2.22E – 3	1.76E – 2	4.43E – 3	3.53E – 2	1.11E – 2	8.80E - 2
HAZARD INDEX	2.22E – 7	0.0E00	1.39E – 2	1.06E – 1	9.36E – 3	7.03E – 2	1.18E – 2	8.80E – 2	6.98E – 3	5.26E – 2	2.36E – 3	1.76E – 2	4.71E – 3	3.53E – 2	1.18E – 2	8.81E – 2
Adults																
Anthracene	1.05E – 7	NA	5.23E – 6	NA	3.14E – 6	NA	3.14E – 6	NA	2.10E - 6	NA	1.05E - 6	NA	1.05E - 6	NA	5.23E – 6	NA
Fluoranthene	0.00E00	0.0E00	1.57E – 5	2.68E – 5	7.85E – 6	1.34E – 5	7.85E – 6	1.34E – 5	3.15E – 6	5.38E – 6	2.36E – 6	4.03E – 6	5.50E – 6	9.40E – 6	1.57E – 5	2.68E - 5
Pyrene	0.00E00	NA	2.83E – 4	NA	2.10E - 4	NA	3.25E - 4	NA	1.47E - 4	NA	6.3E – 5	NA	1.26E - 4	NA	3.14E – 4	NA
Benzo(a)pyrene	0.00E00	0.0E00	6.3E – 3	3.57E – 2	4.2E – 3	2.39E – 2	5.23E - 4	2.98E – 2	3.14E - 3	1.79E - 2	1.05E - 3	5.97E – 3	2.10E – 3	1.19E - 2	5.23E – 3	2.98E - 2
HAZARD INDEX	1.05E – 7	0.0E00	6.65E – 3	3.57E – 2	4.42E – 3	2.39E – 2	8.97E – 4	2.98E – 2	3.29E – 3	1.79E – 2	1.12E – 3	5.97E – 3	2.23E – 3	1.19E – 2	5.56E – 3	2.98E – 2

less than 1. This suggests that exposure to PAHs via ingestion and dermal routes may not pose non-carcinogenic health risks in the exposed population. In general, the health risk assessment indices using the overall non-carcinogenic risk assessment via ingestion and dermal absorption routes would be significant mainly for heavy metals and with this study, particularly public health attention needs to be paid to well 3 as the risk index for heavy metals is extremely high, especially through both exposure pathways.

3.5. Carcinogenic risk (CR)

Carcinogenic risk is the probability that an individual will develop cancer during their lifetime due to exposure to an environmental toxin or carcinogen. The carcinogenic risks for selected metals and PAHs were calculated in this study. Most regulatory authorities provide that CR values between 10^{-6} and 10^{-4} indicate acceptable cancer risk. This translates to a cancer risk of between 1 in 1,000,000 to 1 in 10,000 persons. The United States EPA, for example, considers a risk level negligible when CR is below 10^{-6} , while it becomes a serious or high priority when the value exceeds 10^{-4} (USEPA 2004; Zhang et al., 2015).

3.5.1. Heavy metals

The estimated carcinogenic risk (CR) values through oral and dermal exposure to heavy metals from the contaminated water are presented in Table 7. The CR for Pb, Cr, Cd, and As were calculated for the oral route, while for the dermal route, only the carcinogenic risks for Pb, Cr, and As could be estimated, because reference carcinogenic slope factors for the other metals: Fe, Cu, and Zn via the ingestion route and Fe, Cu, Cd, and Zn via the dermal pathway could not be found in the literature. Values for CR for Cd and As via ingestion in children and adults, Pb via both routes (in wells 1 and 2) in children, as well as Cr via both routes in all wells in children, as well as via the oral route in adults, were all observed to exceed the 10^{-4} limit for carcinogenic risks (Table 7), implying a cancer risk of greater than 1 in 10,000 persons.

Carcinogenic risk values for cadmium in children, in particular, ranged from 9.90E-3 in wells 1, 4, 6, and 7 to 1.00E-2 in well 5, implying a cancer risk of about 1 in a hundred children. Arsenic in children also ranged from 9.90E-4 in wells 1, 2, 6, and 7 to 1.95E-3 in wells 3-5 (Table 7) implying a cancer risk of between 1 in 512, to 1 in 1010 children. These values suggest a high carcinogenic risk in individuals exposed to these metals through oral usage of the contaminated water as observed in this study. The carcinogenic risk values for Pb in the wellwater samples via ingestion ranged from low to moderate with values of 3.40E-5 in well 7 (i.e. 1 in approximately 29,000 children), to 1.11E-4 in wells 1 and 2 for children (i.e. 1 in about 9000 children); and 1.62E-5 also in well 7 (i.e.1 in almost 62,000 adults) to 5.36E-5 in wells 1 and 2 for adults (i.e. 1 in approximately 19,000 adults). Interestingly, while CR values for the oral route were consistently higher than those via the dermal route for all other metals in both groups, dermal route CR values for lead in children were higher than oral route CR in all samples (Table 7), suggesting that cutaneous exposure to Pb could likely pose an additional carcinogenic risk in children. Chromium could also pose a carcinogenic risk via ingestion in both children and adults, as well as via the dermal routes in children with risks ranging from 1 in about 6000 adults (1.55E-4) to 1 in about 3000 children (3.3E-4)-Table 7.

The International Agency for Research on Cancer (IARC) classifies cadmium as a human carcinogen (group I) based on sufficient evidence in both humans and experimental animals (Jarup 2003). Cadmium has been associated with prostate cancer, although some other studies have not found any association between the two. The previous report has also indicated an association between cadmium exposure and kidney cancer, and a few studies have shown its association with lung cancer in occupationally exposed populations (Jarup 2003). Other metals such as arsenic, chromium, and lead also posed varying degrees of risk. Arsenic exposure via drinking water has been reported by WHO, (2001) and Jarup (2003) to be causally associated with cancer of the lungs, kidney, bladder, and skin. Briffa et al.

(2020) also reported arsenic as carcinogenic to humans and long-term oral intake has been associated with cancers of the skin, bladder, liver, and kidney. Evidence has shown that drinking up to a liter per day of water containing an As dose of 50 ug/l and a Cr dose of 8.3-5 ug/l over one's lifetime may lead to cancers of the lung, liver, bladder, and kidney (Alidadi et al., 2019). In children and adults, the observed Cr and Pb levels may also pose an additional cancer risk, although the CR values were lower. The results of the study also showed that exposure to the well-water via the dermal pathway could also pose a carcinogenic health risk through Pb and Cr in children. This highlights the need for urgent action to protect the health of the exposed population at the site.

3.5.2. PAHs

The estimated carcinogenic risk values for both oral and dermal exposure to PAHs are presented in Table 8. Of the eight PAHs evaluated in this study, only the carcinogenic risks of four PAHs, Benzo(a)anthracene, Chrvsene, Benzo(b)fluoranthene, and Benzo(a)pyrene, were estimated for both oral and dermal exposure routes. The carcinogenic slope factors for Anthracene, Fluoranthene, Pyrene, and Benzo, 1,2-anthracene via oral and dermal routes could not be found in the literature. Cancer risk values for the PAHs were generally higher via the dermal route. The results showed that except for benzo(a)anthracene and benzo(a)pyrene which could pose a moderate risk in children, exposure to PAHs generally poses a very low to low carcinogenic risk to children and adults in the study area. Carcinogenic risks for control samples were extremely low. Samples from well 1 and 7 showed the highest CR values. Benzo(a)pyrene and benzo(a)anthracene posed the greatest cancer risks (moderate risk) in well 1 with values of 2.31E-4 and 1.66E-4 via the dermal route in children. This was followed by well 7 with a CR value of 1.61E-4 and 1.93E-4 also via the dermal route for benzo(a)anthracene and benzo(a)pyrene respectively (Table 8).

Some PAHs are classified as potential carcinogens to humans (Group 1, 2A, or 2B) (Abdel-Shafy et al. 2016). Benzo(a)pyrene is listed as a group 1 carcinogen, while benzo(a)anthracene is listed as a group 2B carcinogen (IARC 2010). The carcinogenic effects are compounded by the fact that some exposures may involve more than one route simultaneously, affecting the total absorbed dose, and exposure to PAHs is never to single PAHs. Evidence has shown that exposure to multiple PAHs poses a carcinogenic risk to humans with long-term studies indicating an increased risk to predominantly skin, lung, bladder, and gastrointestinal cancers (Abdel-Shafy et al. 2016). Overall estimation of the carcinogenic risk of exposure to heavy metals and PAHs through oral and dermal exposure in this study, therefore, suggests that water samples from all the wells studied may elicit carcinogenesis in the exposed population in the study area, with children being the most vulnerable group. Information on the demographics and water usage supported the existence of a complete exposure pathway. According to the Public Health Assessment guidance manual of the Agency for Toxic Substances and Diseases Registry of the United States Department of Health and Human Services Public Health (ATSDR 2005), there are five elements in a complete exposure pathway: (1) a source of contamination; (2) a release mechanism into the water, soil, air, and biota; (3) exposure points such as a drinking water well or residential yard; (4) exposure route(s) (ingestion, inhalation, and dermal contact) and (5) a potentially exposed population. The five elements in a complete exposure pathway are present at the site.

At the study site, the lubricated automobile spare parts serve as a source of environmental contamination—(element 1), the presence of heavy metals and PAHs above regulatory standards in the sampled wells within the spare – parts market confirms contaminant release into the underlying groundwater from the automobile spare – parts and related activities—(elements 2 and 3). We also established from the questionnaire survey that the exposed population at the site is dominated by adults (106; \approx 76%), and males (115; \approx 82%) who are non-residents (126; \approx 90%) at the site. The predominant occupation of the people is trading in automobile spare parts (45; \approx 32%), while the others consist of closely related activities, indicating that hazard exposure at the site is mainly occupationally related-(element 5). The water usage pattern confirms both exposure to

METALS	Well 1		Well 2		Well 3		Well 4		Well 5		Well 6		Well 7	
	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal
Children														
Pb	1.11E - 4	1.32E - 4	1.11E - 4	1.32E - 4	7.91E - 5	9.24E - 5	5.10E - 5	5.94E – 5	5.61E - 5	6.60E – 5	4.51E – 5	5.28E – 5	3.40E - 5	3.96E – 5
Cr	3.30E - 4	1.76E - 4	3.30E - 4	1.76E - 4	3.30E - 4	1.76E - 4	3.30E - 4	1.76E - 4	3.30E - 4	1.76E - 4	3.30E - 4	1.76E – 4	3.30E - 4	1.76E - 4
Cd	<u>9.90E – 3</u>	T	<u>1.95E – 2</u>	I	<u>1.95E – 2</u>	,	<u>9.90E – 3</u>	1	<u>1.00E – 2</u>	1	<u>9.90E – 3</u>	I	<u>9.90E – 3</u>	
As	9.90E – 4	1.61E - 5	9.90E – 4	1.61E - 5	<u>1.95E – 3</u>	3.22E - 5	<u>1.95E – 3</u>	3.22E – 5	<u>1.95E – 3</u>	3.22E - 5	9.90E – 4	1.61E - 5	9.90E - 4	1.61E – 5
Adults														
Pb	5.36E - 5	4.47E – 5	5.36E – 5	4.47E - 5	3.74E - 5	3.13E - 5	2.38E - 5	2.01E - 5	2.64E - 5	2.24E - 5	2.13E – 5	1.79E - 5	1.62E – 5	1.34E - 5
Ŀ	1.55E - 4	5.96E – 5	1.55E - 4	5.96E - 5	1.55E - 4	5.96E – 5	1.55E - 4	5.96E – 5	1.55E - 4	5.96E – 5	1.55E - 4	5.96E – 5	1.55E - 4	5.96E – 5
cd	<u>4.65E - 3</u>	,	<u>9.45E – 3</u>		<u>9.45E – 3</u>	1	<u>4.65-3</u>	1	<u>4.71E – 3</u>		<u>4.65E – 3</u>	1	<u>4.65E - 3</u>	,
As	4.65E – 4	5.45E – 6	4.65E – 4	5.45E – 6	9.45E – 4	1.09E - 5	9.45E – 4	1.09E - 5	9.45E – 4	1.09E - 5	4.65E – 4	5.45E – 6	4.65E – 4	5.45E – 6
^a Italicize	l values are indi	cative of mode	rrate cancer risk	. Italicized, em	boldened and u	mderlined valu	les indicate higl	ı cancer risk. V	'alues in norma	ll font are indic	cative of low ca	ncer risk.		

AHs	Control		Well 1		Well 2		Well 3		Well 4		Well 5		Well 6		Well 7	
	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal
Children																
3enzo(a)anthracene	4.87E – 7	2.60E – 6	3.12E – 5	1.66E – 4	2.39E – 5	1.28E – 4	2.72E – 5	1.10E – 4	2.04E – 5	1.10E - 4	1.51E - 5	8.10E - 5	2.19E – 5	1.17E – 4	3.01E – 5	1.61E – 4
Chrysene	0.00E0	0.00E0	9.71E – 9	5.20E – 8	2.92E – 9	1.56E – 8	9.71E – 9	5.20E - 8	2.92E – 9	1.56E – 8	1.95E – 9	1.04E - 8	1.95E – 9	1.04E - 8	4.87E – 9	2.60E – 8
senzo(b)fluoranthene	4.87E – 8	3.85E – 7	1.46E – 6	1.15E - 5	1.95E - 6	5.23E – 6	9.71E – 7	7.74E – 6	4.87E – 7	3.85E – 6	1.46E – 7	1.15E – 6	1.95E – 7	1.54E - 6	2.43E – 6	1.93E – 5
senzo(a)pyrene	0.00E0	0.00E0	4.38E – 5	2.31E – 4	1.95E - 5	1.54E – 4	2.43E – 5	1.93E – 4	1.46E – 5	1.15E – 4	4.87E – 6	3.85E – 5	9.71E – 6	7.74E – 5	2.43E – 5	1. <i>93E –</i> 4
Vdults																
3enzo(a)anthracene	2.29E – 7	8.83E – 7	1.47E – 5	5.64E – 5	1.12E - 5	4.32E – 5	1.28E – 5	4.94E – 5	9.64E – 6	3.70E – 5	7.11E – 6	2.74E – 5	1.03E - 5	3.97E – 5	1.42E – 5	5.47E – 5
Chrysene	0.00E0	0.00E0	4.59E – 9	1.77E – 8	1.38E – 9	5.29E – 9	4.59E – 9	1.77E – 8	1.38E – 9	5.29E – 9	9.20 E - 10	3.92E – 9	9.2E - 10	5.23E – 9	2.29E – 9	6.53E – 8
3enzo(b)fluoranthene	2.29E – 8	1.30E - 7	6.88E – 7	3.92E – 6	9.20E – 7	5.23E – 6	4.59E – 7	2.61E – 6	2.29E – 7	1.31E – 6	6.88E – 8	3.92E – 7	9.19E – 8	5.23E – 7	1.15E – 6	6.53E – 6
3enzo(a)pyrene	0.00E0	0.00E0	1.38E – 5	7.81E – 5	9.20E – 6	5.23E – 5	1.15E – 6	6.53E – 5	6.88E – 6	3.92E – 5	2.29E – 6	1.31E – 5	4.59E – 6	2.61E – 5	1.15E – 5	6.53E – 5
Italicized values are	indicative of	f moderate ca	ancer risk, wi	hile those in	normal font	are indicati	ve of very lo	w to low ca	ncer risk.							

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hazardous substances in the water of the human population and the frequency of the exposure, with daily usage of the water by 119 of the 140 sampled respondents being the highest at approximately 85%. Most respondents were observed to use the water for washing (125; \approx 89%) and bathing (104; \approx 74%) compared to use for cooking (38; \approx 27%) or direct drinking (41; \approx 29%). These confirm contact/exposure of workers and residents of the site, mainly through the dermal rather than ingestion routes—(element 4), both of which present public health hazards from exposure to PAHs as observed by Jarup (2003)

4. Conclusion

This study indicates that well water from the Araromi automobile spare - parts market in Ibadan, Nigeria is not safe for domestic use due to the high concentration of some toxic compounds such as lead, cadmium, arsenic, benzo(a)anthracene, and benzo(a)pyrene that exceeded recommended regulatory limits. Results from a questionnaire survey also confirmed the existence of a complete exposure pathway and showed that exposure in the majority of the population occurs mainly via the dermal route and is occupationally related. The average daily exposure doses for the heavy metals however show that exposure through direct ingestion contributes more to the total daily exposure than dermal exposure. Dermal exposure, on the contrary, contributes more to exposure to PAHs. Hazard quotient values for lead, cadmium, and arsenic were >1 in all sampled wells via the ingestion route in children, indicative of adverse risks in children that are orally exposed to these metals in the well-water. Hazard quotient values for cadmium were also of concern in children via the dermal route in samples from wells 2 and 3. In adults, lead had HQ values >1 in wells 1-3, cadmium in wells 2 and 3, while arsenic had HQ values >1 in all samples, all via the ingestion route.

Consequently, HI values were also >1 in all well-water samples via the ingestion and dermal routes for children, and the ingestion route alone for adults. Wells 2 and 3 had the highest HI values of up to 9.78 and 10.07 in children, as well as 4.34 and 4.85 in adults respectively. Arsenic, lead, and cadmium was of particular concern in well water samples via the ingestion pathway for both children and adults. The dermal route was also of particular concern in children, with cadmium as the major contributor to the observed risk via this route. This implies non-carcinogenic risks in children exposed to water from all wells via both ingestion and dermal pathways, as well as in orally exposed adults. All HQ and HI values for PAHs were less than 1 in all wells via both pathways suggesting that there might be no non-carcinogenic health risk due to PAH exposure. Lead, chromium, arsenic, and cadmium had carcinogenic risk values indicative of varving degrees of risk via both pathways. The greatest carcinogenic risk was observed with cadmium via the ingestion pathway in both children and adults, with samples from well 5 suggestive of cancer risk of 1 in 100 for children, and samples from wells 1, 4, 6, and 7 suggestive of cancer risk of 1 in 215 for adults. Lead in wells 1 and 2, and chromium in all sampled wells could also pose a carcinogenic risk in children via the dermal route.

Benzo(a)anthracene and benzo(a) pyrene also showed a moderate potential for cancer risk in children. These results are indicative of serious public health hazards at the study site and call for urgent action by the regulatory authorities. It also highlights the need for awareness of the dangers of prolonged usage of the well-water. Urgent remedial action is necessary to clean up groundwater of the site and adequate measures should be put in place to protect all environmental compartments and safeguard the health of the exposed population. This study also highlights the need for proper management of hazardous wastes such as waste oils at the study site.

Declarations

Author contribution statement

Adeola Anike Oni: Conceived and designed the experiments; Wrote the paper.

Temidayo Ebenezer Olagunju; Ijeoma Anthonia Amama; Esther Onaopemipo Omole; Adeyeri David Adeleye; Ezra Ajibola Adegboye: Performed the experiments.

Stephen Olufemi Babalola: Analyzed and interpreted the data.

Obokparo Godspower Ohore: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data associated with this study has been deposited at 4TU.Research Data, v2. https://doi.org/10.4121/19918654.v2.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

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