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Assessment of Physicochemical Properties and Heavy Metal Concentration in Hand-dug Wells within the Vicinity of Lead Smelting Area in Ibadan, Oyo State, Nigeria

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ABSTRACT: Public and environmental health agencies are particularly tasked with monitoring of different water sources; Hence, the objective of this study was to assess physicochemical properties and heavy metal concentration in hand dug well around lead smelting areas in Ibadan, Oyo State, Nigeria Using appropriate standard methods. The results showed that none of the water samples' electrical conductivity (EC) values were within the WHO range (1000 µS/cm). Only 10% of the water samples' TDS are within the WHO's recommended range (600 mg/l). 30% of the water samples have water hardness levels that are within the WHO's recommended range (100 mg/l). All of the water samples' chloride ion (Cl^-) concentrations did not meet the WHO standard of 250 mg/l. Sample H has unusually high levels of Zn and Pb, and 40% of the samples also included Mn and Fe. The samples' high concentrations of physiochemical and heavy metals in some of the well water can have significant health repercussions, and can also give water a disagreeable taste and render it unsafe for home use.

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One of the most menacing challenges facing developing countries such as Nigeria is the quantity of waste disposal, without commensurate facilities and resources to face this challenge. Inability of waste management authorities to cope with waste generated and consequent indiscriminate disposal of waste has turned many beautiful Nigerian cities into mega ghettos. This leads to unmitigated pollution of land, air and water which exposes the population to health hazards (Ajah *et al.,* 2015). Water contamination usually results from industrial effluent discharges, agricultural runoff and sewage disposal and other anthropogenic activities. One of the two major concerns regarding waste disposal on land include surface and ground water contamination by leachate. According to W.H.O., (2011) supply of safe drinking and domestic water is crucial to human life, and safe drinking and domestic water should not impose a significant risk to humans. Although few heavy metals are essential for human health, an excess amount of these metals can have negative effects (USEPA, 2015). Groundwater such as hand dug well contamination has been a subject of concern to the environmental health specialists. Even though some elements are crucial for the normal growth of humans and animals, excessive consumption and deficiency of important elements could result in toxicological and nutritional deficiency, respectively (Chen *et al.,* 2007). Micro-elements and other parameters in the drinking water could pose adverse health effects to their consumers. Generally, physical, chemical and micro-elements in well water could be derived from either crustal or man-made

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sources (Mondal *et al.,* 2010; Muhammad *et al.,* 2011). Groundwater such as well water is widely known as one of the major sources of freshwater. Decades ago, there has been gradual deterioration in the water quality is largely due to various man-made activities which has exposed groundwater resource to the risk of contamination (Tirkey *et al.,* 2017). The constant increase in general population has results in the increase in the demand for water supply resulting in acute water shortage for sustaining the daily water demand needed by the populace (Boskabady *et al.,* 2018). Previous studies have reported heavy metals in drinking water, including their types and quantities, factors affecting metal concentrations, sources, human exposure, risk, and removal. Despite significant progress, research is needed to ensure safe drinking water. Of particular concern, many low- and medium-income countries are faced with the challenge of reducing few heavy metals below the proposed limits, possibly due to their limited economic capacities (World Bank, 2016). Communities and individuals in developing countries such as Nigeria often consume water with a higher level of heavy metals than the guideline values (WHO, 2011). Further, populations are exposed to drinking water from wells. This research hereby focuses on the occurrences, pollution compared to the W.H.O permissible limit and human risks of potentially toxic metals in well within the vicinity of lead smelting activities in Ibadan, Oyo state, South-West Nigeria. The water pollution threatens food production and is raising both environmental and human health concerns (Musa *et al.,* 2014). Water pollution causes the reduction of water quality which in turns leads to a human health hazard (Varol and Sen, 2018). According to Junaidu *et al.* (2011), Nigeria has been challenged with various water supply inadequacy, more so some of this are of great significance to public health. Although the effects of chemical contamination of water are not noticed immediately, their accumulation in the body over time has major health consequences (Musa *et al.,* 2014). Heavy metals contaminate surface and ground water, resulting in deterioration of drinking, domestic water and irrigation water quality and can enter into the human food chain, posing a risk to human health (Naveedullah *et al.,* 2013; Varol and Sen, 2018) Some metals, including chromium, lead, cadmium, arsenic and mercury are known to be highly toxic to humans and aquatic life, causing liver and kidney problems in addition to genotoxic carcinogens (Nguyen *et al.,* 2018). Others, such as copper, iron, zinc, manganese and cobalt, are essential elements which play important roles in biological metabolism at very low concentrations (Galadima, *et al*., 2012). Heavy metal such as lead is considered the number one health threat to children, whose effects can last a lifetime. Some of such effects include child's growth, damage the nervous system, and cause learning disabilities, but also it is now linked to crime and anti-social behavior in children (Salem *et al*., 2000). It is indicated that the majority of ingested lead is removed from an individual's body through urine; there is still the risk of buildup especially in children. Also, toxicity due to lead accumulation may lead to a decrease in hemoglobin production, kidney, joint, reproductive and cardiovascular systems disorders and long-term injury to the central and peripheral nervous systems (Nolan, 2003; Galadima, *et al*., 2012).

Long term exposure to cadmium in humans may lead to renal dysfunction; while high exposure levels could cause obstructive lung disease, cadmium pneumonitis, bone defects, osteomalacia, osteoporosis and spontaneous fractures, increased blood pressure and myocardic dysfunctions (Duruibe *et al*., 2007). The discharge of lead and other pollutants into the air, water, and soil during lead smelting can have a number of negative impacts on the environment and human health. Lead and other metals can contaminate neighboring soil as a result of particulate emissions from lead smelters. This pollution can linger for a very long time, endangering ecosystems and decreasing agricultural yield. The possibility of human exposure across the food chain is increased as a result of the transmission of lead to agricultural products (Ankush *et al.,* 2023) Hence, the objective of this paper was to assess the physicochemical properties and heavy metal concentrations in hand-dug wells around lead smelting areas in Ibadan, Oyo State, Nigeria.

MATERIALS AND METHODS

Study Area: The study took place in Ibadan, a significant metropolis in southwest Nigeria. It is the seat of the Oyo State government and, after Lagos and Kano, is the third most populous city in Nigeria. Ibadan is a diversified and prosperous city known for its rich cultural legacy, historical sites, and bustling markets. Ibadan is a busy metropolis today that successfully combines its ancient traditions with contemporary infrastructure. The city is home to a number of famous landmarks that show its historical importance. The Mapo Hall, a colonial-style structure that served as the colonial administrative center, is one of the most well-known locations. The University of Ibadan, the oldest university in Nigeria, is another notable monument. It is known for its academic prowess and lovely campus. A historic tower called The Cocoa House serves as a reminder of Ibadan's past as a significant hub for cocoa manufacturing in Nigeria. Ibadan is renowned for its bustling markets, which sell a variety of commodities and showcase the active trade in the area. The Oje Market, in the center of the city, is well known for its wide selection of goods, which includes clothing, food, and traditional crafts. Another well-liked market is the Bodija Market, which is renowned for its vibrant ambiance and fresh products. Ibadanites, the locals of Ibadan, are renowned for their kind hospitality and deep feeling of belonging. People from various ethnic backgrounds and cultural traditions cohabit peacefully in the city, which has a diversified population (Encyclopedia Britannica, 2023).

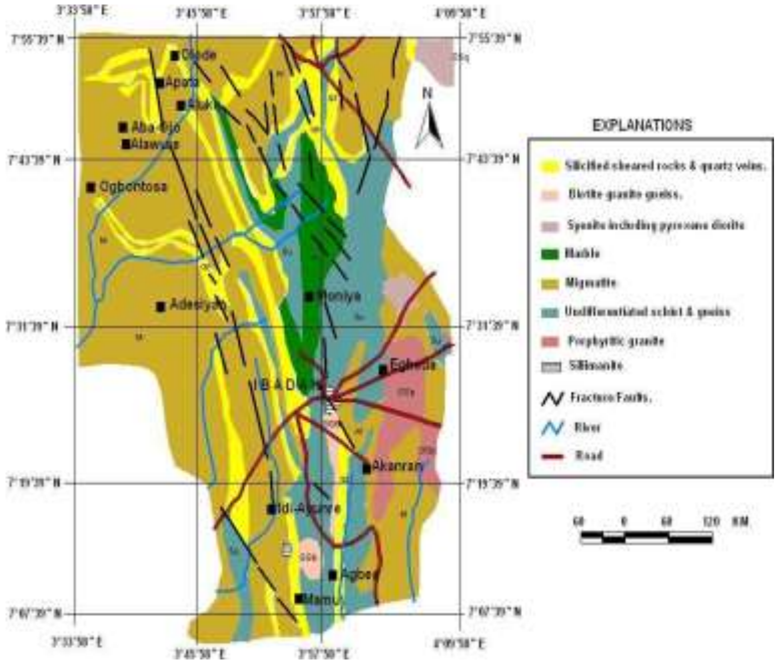

Fig.1: Generalized geological map of Ibadan showing the study area Ganiyu *et al.*, 2017)

Sampling Procedure: Ten (10) water samples were taken from hand-dug wells near a lead smelting location in Ibadan, Oyo state of Oyo, Nigeria using a pre-treated (5% Nitric acid overnight) 1L plastic container. Samples were properly labeled and were transferred to the Central Laboratory unit and Environmental Management and Toxicology Laboratory, both of Federal University of Agriculture, Abeokuta (FUNAAB) for physico-chemical parameters and heavy metal.

Table 1: Coordinates of sampled Hand Dug Wells

Samples	Longitude	Latitude
A	7.379820	3.884125
B	7.379740	3.884001
C	7.380003	3.883655
D	7.379456	3.883590
E	7.380440	3.884185
F	7.380410	3.883307
G	7.380670	3.883244
H	7.380544	3.883398
I	7.381088	3.883224
J	7.380673	3.880514

Physicochemical Analysis: The physicochemical quality of the water samples was carried out using standard methods (AOAC, 2019). The pH of the samples was determined using a pH meter (electrometric method). Temperature and pH were measured in situ. Total dissolved solids and Electrical conductivity were determined using a digital water quality meter, Turbidity was determined using a Turbid meter. The total Hardness of water was carried out using an EDTA titrimetric method with Eriochrome Black T as an indicator. Chloride (mercuric nitrate colorimetric method). The water sample (100 cm^3) was measured in the conical flask using Potassium Chromate as the indicator. The solution was then titrated against a dilute silver nitrate. A brick red coloration indicates the endpoint.

Determination of Sulphate: Sulphate was carried out gravimetrically using barium chloride as a precipitator. A sample volume of 50 cm^3 was measured into a 250 cm^3 beaker and diluted with distilled water to a volume of 150 cm^3. Four drops of the methyl orange indicator and 1 cm^3 of concentrated HCl were added. Barium chloride (10 cm^3 of a 10% solution) was then added to it, and the mixture was heated for five minutes. The solution was kept overnight and then filtered with Whatman filter paper. Distilled water was used to rinse the filter paper to remove the chloride ions. The filter paper was heated to 800°C in a muffle furnace for 60 minutes, ignited at 80°C in an oven using a silica crucible, cooled in a desiccator, and then weighed. After repeating the steps of ignition, cooling, and weighing to produce a constant figure, the sulphate content was measured.

Heavy metal Analysis: The water sample (10 cm^3) was measured using a measuring cylinder. The sample was poured into a 250cm^3 of sterilized conical flask and treated with 20cm^3 of concentrated Nitric acid (NHO_3). The mixture was placed on a hot plate at 90 ^oC in a fume cupboard until a clear solution was achieved. The flask was allowed to cool to ambient temperature, then the digest was then filtered with Whatman No. 42 filter paper and diluted up to mark with deionized water in a 250 cm^3 standard volumetric flask (AOAC, 2019; Famuyiwa *et al.*, 2023), then

Heavy metals were estimated using Atomic Absorption Spectroscopy.

Analysis of data: Data were analyses using the Statistical Package for Social Sciences (SPSS) Version 21.0 while Microsoft Excel 2016 version were used for graphical presentation.

RESULTS AND DISCUSSION

Physiochemical properties: The results of the physicochemical characteristics and heavy metal concentration in the well water samples are given in the tables 2 – 5. Tables 2 and 3, presents the physicochemical properties. The water has a pH ranged between 1.28 – 7.99, water sample with the highest pH recorded in Sample A while the lowest was in Sample H. 80% of the samples are in compliance with the WHO Standard (6.5-8.5). The temperature of the water sample ranged between 27.0– 29.7°C. The underground water with the highest temperature was that of sample A while the lowest was recorded in sample B. 90% of the samples are in compliance with the WHO standard (25.0 - 29.0 °C). The Electrical conductivity (EC) of the water sample ranged between 1120 – 13700 µS/cm. The highest EC was recorded in sample H while the lowest was in sample I. All water samples are not in compliance with the WHO value (1000 µS/cm). The turbidity of the water sample ranged from 0.051 - 38.8 NTU. The highest turbidity was recorded in sample H while the lowest was in sample J. 90% of the water samples are in compliance with the WHO value (5.0NTU). Total dissolved solids (TDS) in the underground water sample ranged between 554 – 7759 mg/l. The highest TDS was recorded from Sample E while the lowest in Sample I. Only 10% of the water samples are in compliance with the WHO value (<600 mg/l). Total alkalinity of the underground water sample ranged between 17.25 – 519.68 mg/l. The highest alkalinity was recorded from sample H while the lowest in sample E. 80% of the water samples are in compliance with the WHO value (200 mg/l). Total hardness in the underground water sample ranged between 31.36 – 153.52 mg/l. The highest hardness was recorded from Sample C while the lowest in Sample H. 30% of the water samples are in compliance with the WHO value (100 mg/l). Chloride ion (Cl^-) in the underground water sample ranged between 259.63– 988.46 mg/l. The highest Cl^- was recorded from Sample H while the lowest in Sample I. All the water samples were not in compliance with the WHO value (250 mg/l). Sulphate ion (SO_4^{2-}) in the underground water sample ranged between 40.56 – 724.98 mg/l. The highest SO_4^2 was recorded from sample H while the lowest in sample E. 90% of the water samples were not in compliance with the WHO value (250 mg/l). Nitrate (NO_3) in the underground water sample ranged between 24.38 – 618.16 mg/l. The highest NO_3 was recorded from sample H while the lowest in sample E. 80% of the water samples were not in compliance with the WHO value (50 mg/l). Bicarbonate (HCO_3) in the underground water sample ranged between 30.67 – 486.14 mg/l. The highest HCO_3 was recorded from sample H while the lowest in sample E. All the water samples are in compliance with the WHO value (550 mg/l).

Table 2: Physicochemical Quality of well samples

	Sample										
Parameters	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**WHO**
pH	7.99	7.90	7.52	7.63	7.57	7.5	6.5	1.28	5.55	7.65	6.5-8.5
Temp (°C)	29.7	27.0	29.0	28.8	28.8	28.5	27.5	28.8	28.9	28.5	25.0-29.0
EC(µS/cm)	1940	1950	1980	1920	1530	1520	1760	13700	1120	1780	1000
Turbidity (NTU)	0.204	0.155	0.179	0.664	0.256	0.35	0.32	38.8	0.894	0.051	5.00
TDS (mg/L)	997	960	981	955	7759	1045	895	6840	554	886	<600
Alkalinity (mg/L)	28.2	25.3	29.1	19.67	17.25	23.5	30.3	519.68	267.15	28.87	200
Hardness (mg/L)	131.65	120.4	153.52	133.45	117.23	120.2	60.2	31.36	56.35	119.93	100
Cl^- (mg/L)	427.35	420.4	398.87	456.22	321.75	341.2	320.3	988.46	259.63	312.55	250
SO_4^{2-} (mg/L)	50.14	50.5	59.08	45.35	40.56	42.3	51.2	724.98	69.3	58.45	250
NO_3 (mg/L)	31.86	34.7	36.41	27.15	24.38	25.5	37.2	618.16	57.34	35.11	50
HCO_3 (mg/L)	45.67	43.5	48.88	33.15	30.67	47.5	38.6	486.14	166.37	41.69	550
Na^+ (mg/L)	252.81	105.20	71.14	57.67	58.46	64.30	68.50	316.0	67.15	221.20	200
Ca^{2+} (mg/L)	105.23	112.80	133.08	102.22	86.45	35.40	22.30	1.81	37.60	100.21	100
Mg^{2+} (mg/L)	25.36	20.30	17.42	22.32	20.21	21.50	22.50	26.74	16.58	19.42	60
K^+ (mg/L)	56.98	55.80	44.66	50.05	33.11	22.80	23.70	19.25	49.28	56.21	-

Sodium (Na^+) in the underground water sample ranged between 57.67 – 316.0 mg/l. The highest Na^+ was recorded from sample H while the lowest in sample D. 60% of the water samples are in compliance with the WHO value (200 mg/l). Calcium (Ca^{2+}) in the underground water sample ranged between 1.81 – 133.08 mg/l. The highest Ca^{2+} was recorded from sample H while the lowest in sample H. 50% of the water samples are in compliance with the WHO value (100 mg/l). Magnesium (Mg^{2+}) in the underground water sample ranged between 16.58 – 26.74 mg/l. The highest Mg^{2+} was recorded from sample C while the lowest in sample I. All the water samples were in compliance with the WHO value (60 mg/l). Potassium (K^+) in the underground water sample ranged between 19.25 – 56.98 mg/l. The highest Mg^{2+} was recorded from sample J while the lowest in sample H.

Heavy metal concentration: Tables 4 and 5, presents the concentration of some heavy metal in well water sample. Zinc (Zn) concentration in the water sample ranged between 0 – 39.2 mg/l, the highest Zn concentration was recorded in sample H while the lowest was in sample J. 90% of the samples are in compliance with the WHO standard (3.00 mg/l). Lead (Pb) concentration in the water sample ranged between 0 – 1.12 mg/l, Pb was only recorded in sample H while none was detected in other samples. 90% of the samples are in compliance with the WHO standard (0.01 mg/l). Cadmium (Cd) concentration in the water sample ranged between 0 – 0.41 mg/l, Cd was recorded in 50% of the sample with highest was recorded in sample H. 50% of the samples are in compliance with the WHO standard (0.003 mg/l). Manganese (Mn) concentration in the water sample ranged between 0 – 10.4 mg/l, Mn was recorded in 40% of the sample with highest was recorded in sample H. 70% of the samples are in compliance with the WHO standard (0.05 mg/l). Iron (Fe) concentration in the water sample ranged between 0 – 455 mg/l, Fe was recorded in 40% of the sample with highest was recorded in sample H. 80% of the samples are in compliance with the WHO standard (01- 03 mg/l). Copper (Cu) concentration in the water sample ranged between 0 – 21.8 mg/l, Cu was only recorded in sample H. 90% of the samples are in compliance with the WHO standard (2.0 mg/l).

Table 4: Heavy metals concentration ((mg/L)) in of well samples

	Sample										
Parameters	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**WHO**
Zn	0.036	0.040	0.31	0.069	0.038	0.042	0.06	39.2	0.065	nd	3.00
	nd	Nd	Nd	Nd	nd	nd	nd	1.12	nd	nd	0.01
Cd	0.01	0.01	0.01	0.01	nd	nd	nd	0.41	nd	nd	0.003
Mn	nd	Nd	Nd	Nd	0.09	nd	0.05	10.4	0.14	nd	0.05
Fe	nd	Nd	Nd	1.17	nd	nd	nd	455	0.05	0.03	0.1-0.3
Cu	nd	nd	Nd	Nd	nd	nd	nd	21.8	nd	nd	2.00

**nd =not detected*

Physicochemical Properties: The pH of water is the hydrogen ion concentration of a solution (well water sample). The pH for 70% of the water samples are alkaline while 30% are acidic. High acidic sample in some of the wells are associated with their very close proximity with the smelting workshops. This is contrary to the previous result reported from the same areas (Ganiyu *et al.,* 2017), showing that all water is generally alkaline. According to Isa *et al.* (2013), a harm as a result of extreme pH in water was not recorded but an alteration in the normal human body physiology can emerge. The temperature of the water sample from the study are normal and within standards. The electrical conductivity of water are physical properties of water utilizes in estimating the potential of a water sample to conduct electric charge due to an occurrence of certain dissolved inorganic solids. Although it has not been attributed to harmful effect (WHO, 2011). The EC of water samples from the study was high, this is largely due to an elevated amount of inorganic dissolved solid in the water, which could emanate from different substances finding their ways into this well water due to ignorance of improper care of the well. The water turbidity state is used to determine the transparency of the water, and occurrence of turbidity can be as a result of increase in microbial population in the water as described by Isa *et al.* (2013). The turbidity detected in the water samples were in compliance except for the sample H. TDS are water property used for evaluating the number of solid substances in a water sample (W.H.O., 2011). The high TDS detected from the study might have emanated from geogenic sources and sewage, High TD in water does no cause harmful effect but may affect the taste of the well water (W.H.O., 2011). The TDS from the study is exponentially higher to the report from KNUST campus, Ghana (51.96 mg/l) (Hayford and Appiah-Adjei, 2022). The Total Alkalinity reported from this study are higher than the report from well in Kano (16.3 mg/l) by Abubakar and Sa'id (2022). Water hardness occurs as a result of alkaline earth metallic cations (Ca^{2+} and Mg^{2+}) in water (W.H.0., 2011). The total alkalinity in the water sample from the study was high in sample H and I. The water hardness report from this study is higher than the report from KNUST campus, Ghana (58.8 mg/l) (Hayford and Appiah-Adjei, 2022) and so of the samples are not compliance with guideline value. The chloride ion detected from the samples was higher than the guideline value. Azizullah *et al.* (2011) documented that an extreme concentration of chlorine in water leads to a salty taste of the water and making it unpalatable on ingestion. Additionally, increase in chloride level is injurious to people suffering from diseases of heart or kidney (Ganiyu *et al.,* 2017). The concentration of sulphate ion in the water samples except for sample H are in compliance with guideline values. The high sulphate concentration in sample H could be due to septic tank around the area. The concentration of Nitrate in 20% of water sample from the study are higher than the guideline value, high nitrate value in water may cause "blue baby" syndrome (Cyanosis)in infant who drink water or formula made from water containing nitrate levels higher than recommended. Presence of nitrate is attributed to discharge of household, municipal sewage and other effluents containing nitrogen (Ganiyu *et al.,* 2017). High nitrates have also been associated to an elevated risk of bladder and ovarian cancer, insulin-dependent diabetes, and gene mutation (Azizullah *et al.,* 2011). The concentration of bicarbonate in the water sample from the study were in compliance with the guideline value. The concentration of Na and Ca from the study were high in 30% and 40% of the samples respectively. The concentration of Mg and K in water samples from the study was in compliance with the guideline value.

Heavy Metal concentration: The concentration of Zn in majority of the water samples was low except for sample H. High Zn concentration in water causes an unpalatable taste at a level >4 mg/l, more so, causing opalescent and developing scums when boiled at a level > 3-5 mg/l (W.H.O., 2011). No health implication however has been attributed to Zinc in water. Lead was absent in the water sample except for sample H which was exponentially higher the guideline value. This is of great concern as lead can cause death or permanent damage to the central nervous system, the brain and kidney. Lead has been recognized for centuries as a cumulative general metabolic poison (Ganiyu *et al.*, 2017). Cadmium toxicity from this sampling station can result in health issues such as respiratory and kidney dysfunctions on prolonged exposure (WHO 2011). Cd level in 50% of the samples are higher than the guideline value. The concentration of Mn in 40% of the samples are high, a prolonged ingestion of Mn has been reported to result in a decline in brain cells of the Nervous system (Tenge *et al.*, 2015). The concentration of Fe in 20% of the samples are high, Although, Fe does not pose a health hazard but result in the unpalatable taste of the water. However, Fe in water promotes the development of iron-reducing bacteria that help with the oxidation process that transforms iron II into iron III (WHO 2011).

Conclusion: Physicochemical and heavy metal concentration of 10 hand dug well water samples collected and evaluated around lead smelting areas in Ibadan, Oyo State, Nigeria show that results were not compliance with WHO guidelines for almost all the parameters. It is therefore concluded that the high levels of physiochemical and heavy metals in the samples have substantial health implications, and make the water unfit for domestic use. Based on the study, it is advisable that hand dug wells in this vicinity should be avoided completely due to their metal toxicity. Improved hygiene methods, continuous environmental intervention by Government agencies as well as routine monitoring and assessment of water quality index of the visited hand-dug wells are recommended.

Conflict of interest: The authors declare no conflict

Data Availability Statement Data are available upon request from the first author

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