

Investigation of Heavy Metals in Zamzam Water

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ABSTRACT: Water is a basic need for humans and is made up of various heavy metals, which is essential for healthy biochemical function. The aim of this study therefore is to investigate or determine the different heavy metals and the level of concentration in Zamzam water sold in different locations in Nigeria. To achieve this, Zamzam water samples were obtained from three study points (Benin city, Warri city and Onitsha), and were analyzed using atomic absorption spectrophotometry. The results obtained indicated the presence of Zinc (Benin city (0.1mg/l), Warri city (<0.01mg/l) and Onitsha (0.02mg/l), Manganese (Benin city (0.01mg/l), Warri city (0.01mg/l) and Onitsha (0.01mg/l), Copper Benin city (<0.01mg/l), Warri (<0.01mg/l) and Onitsha (<0.01mg/l), Lead Benin (<0.01mg/l), Warri (<0.01mg/l) and Onitsha (<0.01mg/l) and Cadmium Benin (<0.01mg/l), Warri (<0.01mg/l) and Onitsha (0.01mg/l). Although the concentration levels were observed to be below the limits set by WHO (2011) guideline for drinking water. It can therefore be concluded that the Zamzam water samples from all three locations are safe for consumption and free from possible contamination.

Keywords: Heavy metals, Zamzam water

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INTRODUCTION

Water is the primary ingredient of earth's stream, lakes, and seas, as well as the fluids of most living species. It is clear, tasteless, odourless, and colourless (United State Geological Survey (USGS), 2019). It is needless to say that the drinking water quality is the most important issue to human health all over the world about 70% of an adult body weight is water.

Drinking water quality is defined as the water pure enough to be used with low immediate or long-term hazards. In many parts of the world especially in an environment, people have to use water either contaminated with disease, vectors, pathogens or unacceptable level of toxins and suspended solids (William, 2000). Zamzam water is a holy water that Muslims use for religious and medicinal purposes. According to Mahmond *et al.* (2020) Zamzam water is the most preferred potable water and is considered superior to other drinking water sources in all Arabic and Islamic countries. Zamzam water supplied by the well of Zamzam

is available through taps and containers that are distributed in the Masjid Al Haram in Mecca. This water is also available in bottled form to facilitate air transportation for pilgrims (Saudi Geological Survey, 2020). The Zamzam water is collected from a well located in Mecca which is about 30.5m deep with diameter ranges from 1.08 to 2.66m. The well is now located in ground floor surrounded by glass plates permitting a clear vision of the inside. The water is withdrawn by electrical pumps to become available in the taps distributed in specific areas in the mosque (Khalid, Ahmad, Ahmed and Irfan, 2014). Zamzam water contains some heavy metals they are (Lead (Pb), Arsenic (Ar), Zinc (Zn), Cadmium (Cd), Copper (Cu) and Iron (Fe)). Zamzam water is a colourless and odourless, but has a distinctive taste, and has a PH content 7-8 which is slightly alkaline. The aim of this study is to investigate or determine the different heavy metals in Zamzam water sold in different locations in Nigeria.

LITERATURE REVIEW

Water

Water is the primary ingredient of Earth's streams, lakes, and seas, as well as the fluids of most living species. It is clear, tasteless, odourless and nearly colorless (United State Geological Survey (USGS), 2019). Even though it contains no calories or organic nutrients, it is essential for all known forms of life. Its chemical formula is H_2O , which means that each of its molecules is made up of one oxygen and two hydrogen atoms that are joined together by covalent bonds. Water is necessary for all known forms of life and covers roughly 70.9% of the earth's surface (Foster, 2001). It can be sourced from various locations many of which are activated by anthropogenic activities.

Sources of water

Rain water

Rainwater is water that falls to the ground after evaporating from the surface. Rainwater storage is useful especially in locations with a prolonged dry season or where groundwater or surface water is scarce or polluted. The phrase Rainwater harvesting is sometimes used. It simply refers to collecting rainwater that runs off of hard surfaces and storing it in a tank or cistern. Rainwater has a number of benefits. Even if it only rains once or twice a year, it is free, relatively clean, and usually dependable (The Open University (TOU), 2016).

Surface water

Water on the planet's surface (such as in a river, lake, or marsh) is known as surface water. It evaporates, seeps into the earth, where it becomes groundwater, utilized by plants for transpiration, retrieved by people for agriculture, living, industry, and other purposes, or released into the sea, where it turns saline. A significant number of bacteria, viruses, and microorganisms can be found in surface water. Because of the varying quality of surface water, it must be treated before being used in the home. There are a variety of water treatment methods on a large and small scale (TOU, 2016).

Groundwater

Water that is found underground within rocks is known as groundwater. Its presence is mostly determined by the type of rock. Water and other fluids can travel through and be held inside the rock structure because permeable rocks have microscopic gaps between the solid rock particles (Akoteyon, 2011).

Physicochemical properties of groundwater

Temperature, pH, colour, turbidity, total dissolved solids, electrical conductivity, odour and taste are the most important physicochemical properties of groundwater in relation to its quality.

pH

pH is a measure of hydrogen ion (H^+) in water. The presence of organic acids in the soil, as well as those from the atmosphere into the water, causes the acidity of the water. Acid rain, which contains dissolved carbon dioxide (CO_2), nitrogen dioxide (NO_2), or sulfur dioxide (SO_2), frequently produces an enhanced hydrogen ion (H^+) ion concentration as well as carbonic acid (HCO_3), posing a major hazard to water pH. Chemical kinetics of key constituents is influenced by pH, which influences the solubility and toxicity of metals. Other acids, such as HNO_3 , HNO_2 , and humic acid, are made when organic matter decomposes, and sulphuric acid is produced when minerals like pyrite (FeS_2) decompose.

Total dissolved solids

The concentration of all dissolved minerals in water is known as total dissolved solids (TDS). The Total Dissolved Solids (TDS) in natural waters are made up of a variety of ionic and non-ionic species in varied amounts and proportions (Agbaire and Oyibo, 2009). TDS in water is caused by acids created as byproducts of the degradation process, which increase mineral weathering. As a result, TDS is a geochemical quantity that is strongly connected to microbial hydrocarbon breakdown (Atekwanna Estella and Rebecca, 2004). TDS levels more than 1000mg/L are generally found to be unpleasant or irritating to the tongue. Temperature and pH affect TDS levels. At higher temperatures and lower pH water dissolves more minerals.

Calcium carbonate

The capacity of water to generate suds with soap is referred to as hardness. Hard water leaves a ring in the bathtub, causes soap curds to form on clothing, and causes scale to build up in boilers and kettles (Wittmann Cote, Medici, Leech, and Turner, 1998). There are two types of hardness: carbonate hardness $Ca(HCO_3)_2$ and non-carbonated hardness $Mg(HCO_3)_2$. Salts such as Calcium Chloride ($CaCl_2$), Magnesium Sulphate ($MgSO_4$), and Magnesium Chloride ($MgCl_2$) cause non-hardness (Chris, 2012). Non-Carbonate hardness is quantified as Calcium Carbonate mg/L for any hardness larger than the alkalinity. Hardness is categorized as soft, moderately hard, hard and very hard. Regions with limestone formations have a higher hardness and alkalinity due to

the dissolution of Bicarbonates and Carbonates.

Iron

Although iron is not poisonous, it gives water an unpleasant taste and can leave brown stains on porcelain and clothing. Reduced form (Fe^{2+} and HS) has an unpleasant taste, and when exposed to air, water turns reddish brown due to Ferric Hydroxide, which can cause liver illness if consumed in large quantities (Ranjana, 2010). Largest donors of iron in groundwater are minerals located within the underlying bedrock, soil and sand, the most abundant is Ferrous Iron and borehole, limestone, shale and coal which often contain the Iron rich mineral. Iron is also released into groundwater by pyrite, an acidic rain (Lenntech, 2009). The amount of iron in the soil increases as it gets deeper.

Microbial parameters

According to Bodoczi (2010), the presence or absence of pathogenic microorganisms, as indicated by the presence of coliforms, determines the hygienic quality of water. There is virtually no geological situation at or near the earth's surface where the pH does not sustain some type of organic life, and water pressures are not high enough to prevent microbial activity at this depth. Pathogenic bacteria may persist for a long time underground, with a life span of up to four years. Coliform bacteria are a large group of disease-causing bacteria that dwell in the intestines of humans and animals (Singh, Khurana, Manish, Tadav, and Yadav, 2011). The World Health Organization stated that any source of potable drinking water should be free of faecal coliforms, with a maximum permissible number (MPN) of 0cfu/100ml.

Faecal coliforms

In different countries, the presence of faecal Coli is one of the most dependable indicators of faecal bacterial contamination of surface and groundwater sources (WHO, 1989). Faecal coliform bacteria are bacteria found in faeces. They are a subset of a broader group of organisms known as coliform bacteria, which are gram negative, non-spore forming, rod-shaped bacteria that digest lactose, creating gas and acid at temperatures about 35°C. Waterborne diseases such as diarrhea, typhoid, hepatitis, and flu-like symptoms such as nausea, vomiting, and fever are caused by human waste contaminants in water (Food and Agriculture Organization (FAO), 1995). Inadequate and unclean handling of solid wastes in rural and urban regions, according to Adekunle et al. (2007) leads to large concentrations of microbial organisms.

Groundwater quality

Groundwater quality comprises the physical, chemical, and biological qualities of groundwater. Groundwater is water that exists mainly in subsurface pore spaces but also in defined channels, which are created by dissolution of soluble rocks such as limestone (Edwin, Raj, Usha and Peter, 2016). Its quality depends primarily on the type of rock and can be extracted from boreholes and wells or collected from springs (Akoteyon, 2011). Groundwater is a worldwide significant and valuable renewable resource for human life and economic growth (Maiti *et al.*, 2016). In the world today, about half of the populations rely almost on groundwater for potable water supplies while in Africa, about 75% of the population rely on groundwater for water supply (UNEP, 2010). According to Kamble and Saxena (2017) the quality of groundwater varies with the location, geology, type, and quantity of dissolved ions present in it. This is because population growth, rapid urbanization, and industrialization have been observed to affect groundwater quantity and quality especially in the developing countries.

Zamzam water

Zamzam water is a holy water that Muslims use for religious and medicinal purposes. According to Mahmoud *at el.*, (2020) Zamzam water is the most preferred potable water and is considered superior to other drinking water sources in all Arabic and Islamic countries. Zamzam water supplied by the well of Zamzam is available through taps and containers that are distributed in the Masjid Al Haram in Mecca. This water is also available in bottled form to facilitate air transportation for pilgrims (Saudi Geological Survey, 2020). The Zamzam is collected from the water well located in Mecca which is about 30.5m deep with diameter ranges from 1.08 to 2.66m. The well is now located in ground floor surrounded by glass plates permitting a clear vision of the inside (Figure 1). The water is withdrawn by electrical pumps to become available in the taps distributed in specific areas in the mosque (Khalid et al., 2014).

Zamzam water quality

Zamzam water is colourless and odorless, but has a distinctive taste, due to its high pH content of 7 – 8 (Alfadul et al., 2011). Zamzam water has no indications of organic growth which makes its very reasonable for drinking purposes. According to Arab historians, the Zamzam well has been in use for around 4000 years (Khalid *et al.*, 2014). The major solute chemistry reveals that the water contains high concentration of calcium and its water type is calcium carbonate type. The distributions of major salts are magnesium bicarbonate, magnesium sulfate, sodium and potassium chloride (Shomar, 2012).

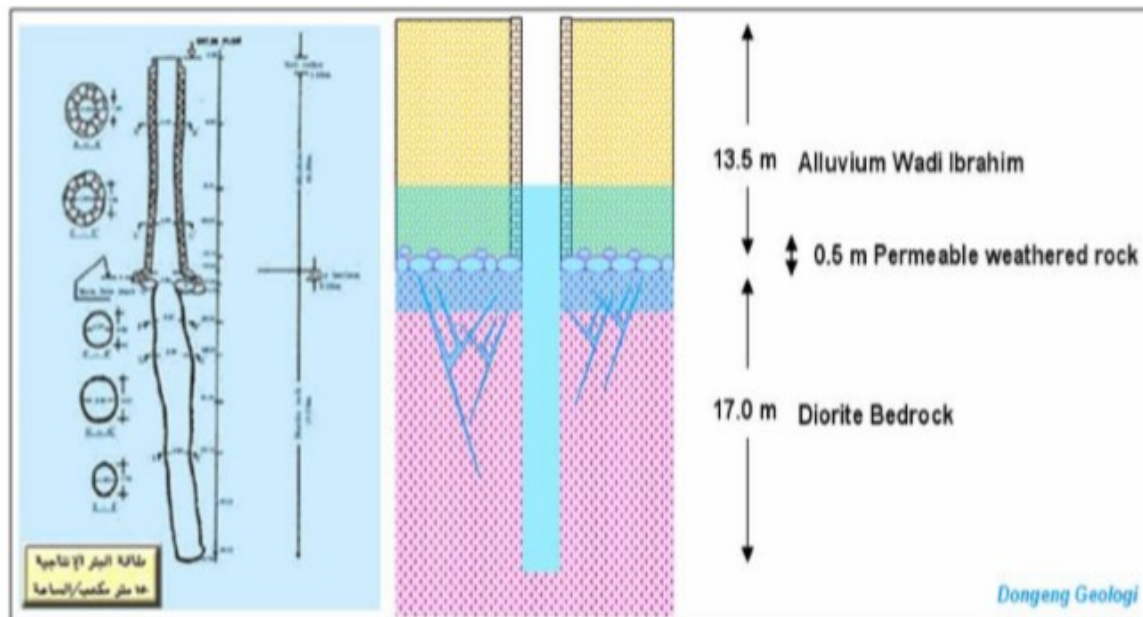


Figure 1: Zamzam Water Well (Husnah, 2020).

According to Shomar (2012) it has been reported that the Zamzam water contains high concentration of As, NO_3 and other heavy metals which raises concerns since these reports have been observed to exceed set permission limit of the World Health Organization. Microbial assessment of this water by Mashat (2010) reported that the Zamzam water has no sign of biological growth due to it is naturally pure and salt-sterilized contents. This water has been accounted to be soluble and furthermore plentiful in minerals which render it a potential cell reinforcement source (Kazmi and Aftab 2011).

Zamzam water contaminations

Zamzam water has been observed to comprise of radioactive materials. This is because natural radionuclides may be found in drinking water having gotten access to water wells through underground processes. Some of the identified radioactive materials found in Zamzam water are ^{238}U (uranium) series (^{226}Ra and ^{214}Bi), ^{232}Th (thorium) series (^{228}Ra (radium), ^{228}Ac (actinium), and (titanium) ^{208}Ti) (Al-Gamal, 2008). Aside these contaminants, reports have observed considerable concentrations of heavy metals in Zamzam water. According to study by Ahmed and Wael (2021) Zamzam water boost heavy metal presence in concentrations of iron (80.8mg/l), copper (1.8mg/l), lead (0.65mg/l), manganese (1.7mg/l) and zinc (13.7mg/l) and even more for bottled Zamzam water sold. Although these metals are present in small concentrations, they are concerns

regarding its accumulation especially for arsenic which has been detected in recent times (Food Standard Agency, 2021).

Heavy metals in Zamzam water

According to the Ahmed and Wael (2021) and Food Standard Agency (2021) on chemical composition of Zamzam Water, it was observed that the water comprises of various chemical constituents including heavy metals. Other studies also conducted on this subject matter shows that the water comprises of heavy metals such as lead (pb), Copper (Cu), Arsenic (Ar) amongst others. Heavy metals have been reported to be hazardous to human health and posing effect. These heavy metals include the following:

Lead (Pb)

Lead exposure can result in a wide range of biological effects depending on the level and duration of exposure. They can affect developing young and infants being more sensitive than adults. Lead poisoning is severe as it can cause evident illness. Lead performs no known essential function in the human body and can merely do harm after uptake from food, air, or water (Raymond and Felix, 2011).

Manganese

Manganese occurs naturally in many surface water and

groundwater sources. However, human activities are also responsible for much of the manganese contamination in water in some areas. According to World Health Organization (2011) manganese intake from drinking-water is normally substantially low. The central nervous system is the chief target of manganese toxicity with concentrations of between 1 to 150mg/kg producing neurological effect.

Zinc (Zn)

Zinc is added during industrial activities, such as mining of coal, waste combustion and steel processing. Many food stuffs contain certain concentrations of Zn. Drinking water also contains certain amounts of Zn, which may be higher than when it was stored in metal tanks (Raymond and Felix, 2011). Industrial sources or toxic waste sites may cause the concentrations of Zn in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health (Alysson and Fabio, 2014). Zinc shortages can cause birth defects (Wuana and Okieimen, 2011). A consequence is that Zn polluted sludge is continually being deposited by rivers on their banks.

Cadmium (Cd)

Cadmium with mercury (Hg) and Lead (Pb), Cd is one of the big three heavy metal poisons and is not known for any essential biological function (Raymond and Felix, 2011). In its compounds, Cd occurs as the divalent Cd (II) ion. Cadmium is directly below Zn on the Periodic Table and has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for Cd's toxicity; because Zn being an essential trace element, its substitution by Cd may cause the malfunctioning of metabolic processes (Cambell, 2006).

Copper (Cu)

Copper is an essential micronutrient required in the growth of both plants and animals while in humans, it helps in the production of blood hemoglobin (Raymond and Felix, 2011). In plants, copper is especially important in seed production, disease resistance, and regulation of water. Copper in high doses can cause anemia, liver and kidney damage, and stomach and intestinal irritation in human (Yruele, 2005). Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algae growth. While Cu's interaction with the environment is complex, research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment (Raymond and Felix, 2011).

MATERIALS AND METHODS

In assessing the presence of heavy metals in Zamzam water sold in different cities in Nigeria, Zamzam water samples were obtained from three study area as a means to determine the quality of water.

Sampling techniques

The grab method of water sampling technique was employed in the collection of water sample. Three samples of Zamzam water were obtained from local mosque within Warri, Onitsha and Benin City.

Determination of Lead, Copper, Total Iron, Cadmium and Chromium (ASTM D6785)

The machine was calibrated with various standard solutions of Lead, Copper, Zinc, Manganese and Cadmium. The specific wavelength for each heavy metal was selected. They include; Lead (283.3nm), cadmium (580nm), iron (248.3nm) and manganese (352nm). 10 – 30cm³ each of the samples was measured into a conical flask and a conveyor hose pipe will be dipped into the water sample. The conveyor hose pipe syphoned up the sample into the flame at a specific wavelength of the parameters to be measured given the concentration of parameters of interest.

Data analysis

Data obtained were cross tabulated after analysis of the water sample. This revealed the concentrations of the heavy metals as an average value in concentration (mg/l).

RESULTS AND DISCUSSION

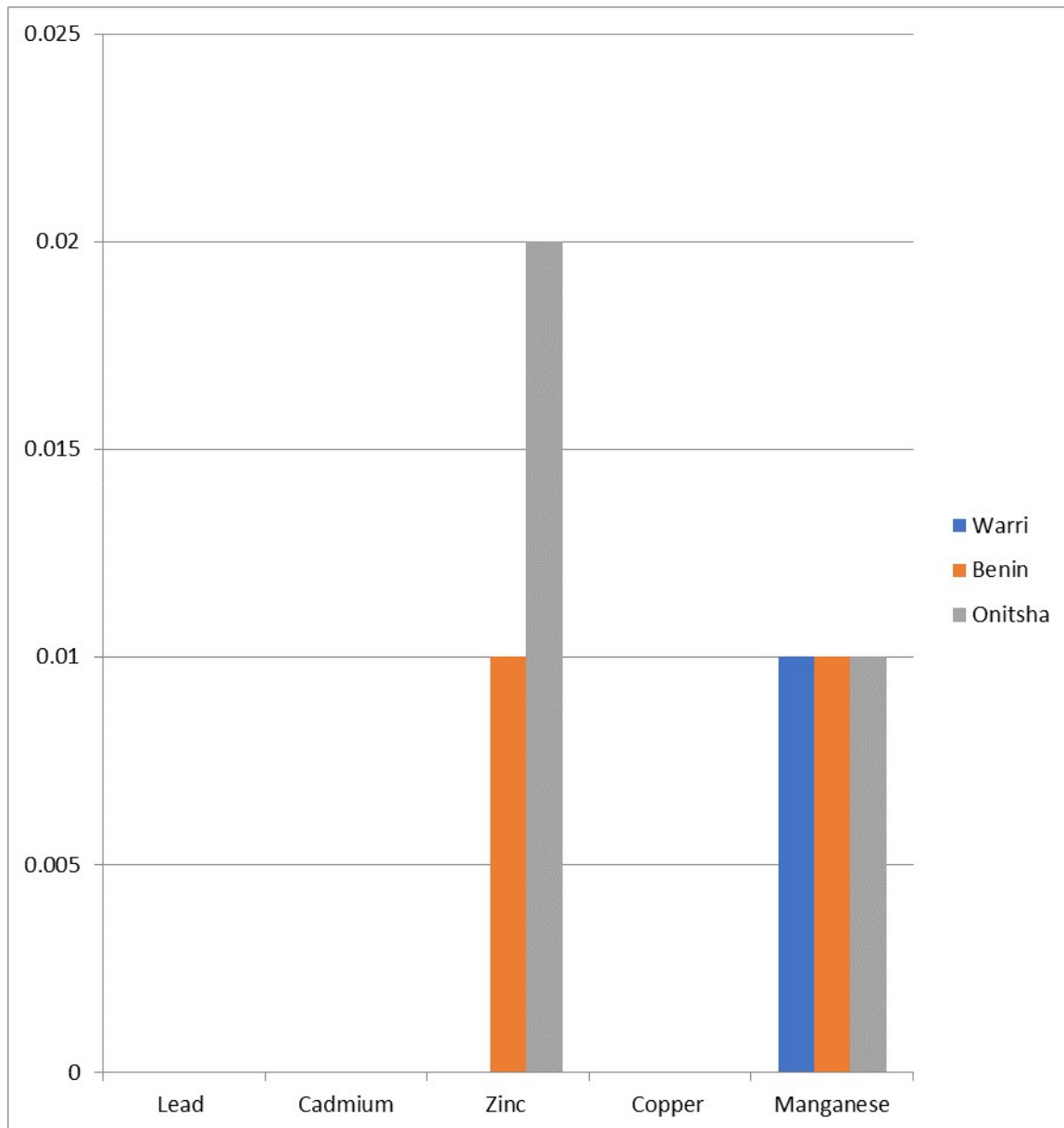
Heavy metals are metals with relatively high density and toxic even at low concentrations. They are found in minute amount in the earth and may also be released from industrial activities. These metals often find their way to human body through food and water consumption and poses relative health risk. One major effect is cause by the potential of these metals to bioaccumulate in the human body. Heavy metals concentration in water causes severe health effects which can be harmful when ingested. Zamzam water samples assessed from three different locations indicated the presence of certain heavy metals concentrations (Table 1 and Figure 2).

Lead (Pb)

Lead poisoning is severe as it can cause evident illness.

Table 3: Average Concentration of Heavy Metals in Zamzam Water Sample.

Locations	Lead (mg/l)	Cadmium (mg/l)	Zinc (mg/l)	Copper (mg/l)	Manganese (mg/l)
Warri	<0.01	<0.01	<0.01	<0.01	0.01
Benin	<0.01	<0.01	0.01	<0.01	0.01
Onitsha	<0.01	<0.01	0.02	<0.01	0.01
WHO Limit	0.05	0.003	3.0	2.0	0.1

**Figure 2:** Heavy Metals Concentrations in Zamzam Water Samples from Warri City, Onitsha and Benin City

This metal is often found to be released from industrial activities especially toxic waste release which may contaminant water wells. The results obtained did not

detect any presence of lead in Zamzam water from Benin city (<0.01mg/l), Onitsha (<0.01mg/l) and Warri (<0.01mg/l). The observed concentrations across all

three locations were below the permissible limit of 0.05mg/l. this reveals that the water samples did not contain any trace of lead and is hence from of contamination due to human activities. The observed values indicate that there are no likely possible contamination effects which may occur as a result of consumption of this water. This result is supported by study by Ahmed and Wael (2021) which reported a 0.54µg/l concentration of lead in Zamzam water.

Cadmium (Cd)

Cadmium occurs in water as the divalent Cd (II) ion. From table 4.1, it was observed that cadmium was not detected in water samples analyzed. This is similar to study by Fahad *et al.*, (2017) with observed concentration of 0.04µg/l as compared to observed values of <0.01mg/l across all locations. The observed concentrations were also observed to be lower than the permissible limit of 0.003mg/l set by WHO (2011) guideline for drinking water.

Zinc (Zn)

Zinc metal is often found in water from galvanized pipe in water collection/distribution. Its concentration levels may be elevated by the dissolution of zinc from pipes and other metal fittings. Result obtained indicates the presence of zinc in water samples from Benin city (0.01mg/l), Onitsha (0.02mg/l) and Warri (<0.01). which can be attributed to possible water treatment as reported by Al-ansi, Othman and Al-Tufail (2011) and Ahmed and Wael (2021) which revealed variation in collected and bottled Zamzam water attributing the variation to ozonation processes. However, the concentration level was observed to be lower than the permissible limit of 3.0mg/l set by WHO (2011) guideline for drinking water. This low concentration indicates that zinc concentration cannot be tied to toxic waste sites contamination of the water well.

Manganese (Mn)

The presence of manganese in water comes from the presence of available manganous salts which oxides in air and/or may be released from iron bacteria activities. This metal remains in water solutions for a long period of time and are also indicators of the presence of iron. Results obtained indicates the presence of manganese in Zamzam water samples from Benin (0.01), Onitsha (0.01) and Warri (0.01). It was observed that Zamzam water sold across all three locations contains manganese although in concentrations less than the permissible limit of its concentration in drinking water set by WHO (2011).

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Copper (Cu)

High dose of copper has been observed to cause anemia, liver and kidney damage, and stomach and intestinal irritation in human. Results obtained indicates the presence of manganese in Zamzam water samples from Benin, Onitsha and Warri was reported that concentration levels of copper were <0.01 and below acceptable limits.

Conclusion

The presence of heavy metals such as lead (pb), Copper (Cu), Zinc (Zn) amongst others have been reported to be hazardous to human health and posing effect. The result obtained indicated the presence of Zinc and Manganese which can be attributed to dissolution of pipes and the presence of iron in Zamzam water samples. Although the concentration levels were observed to be below the limits set by WHO (2011) guideline for drinking water. However, concentrations were observed to fluctuate for concentration of zinc which can be attributed to water treatment process. It can therefore be concluded that the water samples from all three locations are safe for consumption and free from possible contamination. However, the bioaccumulation potentials of these metals raise concerns as a result of long period of consumption.

Recommendations

It is recommended that;

- Water collection systems through assessed for possible dissolution of metals and changed.
- Zamzam water samples should be analyzed for heavy metals concentrations to evaluate possible presence of other metals.
- Water collection systems should be protected by either coating or use of cathode protection for galvanized pipes.

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