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Comparative Analysis of Selected Heavy Metals in Surface and Groundwater Sources near the General Hospital Water Tank, Agbarho, Delta State

***[1]Erienu, O.K., [2]Akpeji, B.H., [3]Akakabota, A.O., [2]Obruche, A.S., [4]Awodi, G.O., [5]Otite-Douglas, M.I., & [6]Ovili, V.U.**

[1]Department of Chemistry, Delta State College of Education, Mosogar, Delta State, Nigeria
[2]Department of Chemistry, Federal University of Petroleum Resources, Effurun, Nigeria
[3]Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Nigeria
[4]Department of Industrial Chemistry, Mewar International University, Nasarawa State, Nigeria
[5]Department of SLT, Petroleum Training Institutes, Effurun, Delta State, Nigeria
[6]Department of Chemistry, Nigeria Maritime University, Okerenkoko, Delta State, Nigeria

***Corresponding author email:** erienuobruche@gmail.com

Abstract
In the area around the main hospital in Agbarho, Delta State, an evaluation of the ground and surface water sources was carried out. Eight (8) water samples were taken from eight (8) different locations within the study region (S1, S2, S3, S4, U1, U2, U3, and U4). We used an Atomic Absorption Spectrophotometer (AAS) to check for heavy metal contamination in these samples. The APHA, 1998 method was used to analyze the amounts of seven (7) heavy metals in the water samples: manganese, cadmium, chromium, cobalt, lead, iron and nickel. Cr levels in sites S1–S4 ranged from 0.16 to 0.58 mg/L, Pb levels from 1.10 to 2.60 mg/L, Cd levels from 0.04 to 0.10 mg/L, Fe levels from 4.10 to 9.70 mg/L, Mn levels from 0.04 to 0.64 mg/L, and Ni levels from 0.05 to 0.63 mg/L, Cr ranged from 0.50 to 0.90 mg/L, Pb from 1.71 to 3.20 mg/L, Cd from 0.02 to 0.10 mg/L, Fe from 2.19 to 11.40 mg/L, Mn from 0.05 to 0.50 mg/L, Ni from 0.04 to 0.14 mg/L, and Co from 0.22 to 0.40 mg/L compared to sites U1-U4. For the majority of the sites, the levels were found to be higher than the WHO recommended limit. This study demonstrates that human activities, including hospital effluent, negatively impact water quality. Therefore, it is advised that general hospitals in Agbarho, Delta State, strictly adhere to government regulations regarding waste management and disposal.

Keywords: Heavy Metals, Agbarho, AAS, General Hospital, Surface

Introduction

Harvested water containing heavy metals has been shown to have a variety of chemical pollutants. According to Obruche et al. (2021), water is highly sought for since it is a distinctive characteristic of every community. Life depends on water (Lu & Hegeann, 1998). Every human being on the planet needs an adequate supply of clean, fresh drinking water. Surface and ground water are the primary sources of fresh water. Pollution, inadequate management, and overuse are threatening these freshwater resource sources. Hospital wastewater, also known as hospital waste, is a unique type of trash that includes all waste, whether it be biological or non-biological, heavy metals, or chemicals that is not meant for future use and is thrown away from hospitals and healthcare facilities (Oyeleke et al., 2008). There are differences in the quantity of waste water that hospitals release. Hospital waste water production per capita was estimated by Tsakona et al. (2006) to be 1000 litres per person per day. In the United States, approximately 85% of hospital waste is considered non-hazardous (non-infectious), 10% is hazardous or infectious, and 5% is not (Oyeleke & Istifanus, 2009). Ineffective waste material sorting, the buildup of hazardous, non-

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biodegradable (non-infectious) hospital waste products, the accumulation of heavy metals, and contamination of surface and ground water are the main health risks that hospital wastewater poses to the residents of the terrestrial and aquatic ecosystem (Jha et al., 2008). Metallic elements with a high atomic weight and density are known as heavy metals (Obruche et al., 2022). These consist of actinides, lanthanides, transition metals, and certain metalloids.

Because they are metal ions and cannot be broken down or eliminated, heavy metals are persistently harmful chemicals in the environment. The air, soil, and water all contain heavy metals, which are environmental pollutants that are harmful to people's health. There have been numerous reports on the environmental impact. According to Obruche et al. (2021), eutrophication and a mixture of heavy metals and nutrients created water pollution in the Gulf of Thailand, which led to the degradation of their habitat, especially the coral reef and mangrove forest. Particulate matter has been found to have an attraction for both organic and inorganic pollutants, including metals. As a result, a number of potentially hazardous materials have been stored in sediments. Toxic metals can be held down for extended periods of time by a mixture of chemical and physical processes that govern the stability of these contaminants, lowering the risk of toxicity. It is probable that the poisonous materials released into water bodies would build up via the food chain (Odiete, 1999). However, methods for comprehensive hospital effluent control are being installed in several nations. For instance, all healthcare facilities in Greece are required to create and carry out a thorough management plan in order to protect the environment and the general population (Tsakona et al., 2006). However, several nations—particularly developing nations—have not yet passed legislation to lessen the negative environmental effects of hospital effluents (Ibeh & Omoruyi, 2011). Many hospitals and healthcare facilities in Nigeria lack effluent treatment facilities; as a result, untreated waste is either dumped on the ground or dumped into adjacent bodies of water, which could seriously harm the host communities' health (Odiete, 1999; Obruche et al, 2021). Even at low amounts, this type of hospital waste can have consequences. For example, formaldehyde, a common contaminant in hospital effluents, has a negative effect on aquatic organisms (Murphy et al., 1989). Because they are frequently (mostly) at the top of the aquatic food chain, fish can absorb large (huge) amounts of heavy metals from contaminated water ion-exchange of dissolved metals (IEDM) across lipophilic membranes and absorption on tissue and membrane surfaces (Mendil et al., 2005; Agbozu et al., 2007). Human health depends on certain metals. Because of the metals' toxicity, heavy metal contamination is a severe and pervasive environmental issue (Kalay & Canli, 2000). Numerous diseases, including cancer, neurological disorders, asthma, and chronic bronchitis, are caused by pollutants. Accordingly, pollutants have been divided into two categories: primary pollutants, which have negative effects in the form that they enter the environment, and secondary contaminants, which are created by chemical reactions from less hazardous environmental precursors (Kalay & Canli, 2000). The majority of contaminants reach the environment through emissions (or discharges) to water bodies from either diffuse sources like runoff from agricultural lands or discrete points like factories and hospitals.

The impact of a pollutant released into the environment is influenced by several factors, including its level of toxicity, how long it persists, how easily it spreads, its chemical interactions—such as how it breaks down—its potential to accumulate (assemble) in the food chain, and how manageable it is. Each form of pollution follows a specific pathway involving the pollutant itself, its origin, the medium through which it travels (such as air, water, or soil), and the final target, often the ecosystem (Obruche et al., 2023). The capacity of a water body to sustain aquatic organisms and its usability for other purposes is influenced by the presence of trace elements. Certain metals like manganese (Mn), zinc (Zn), and copper (Cu) play essential roles in biological systems at low concentrations, supporting vital physiological and biochemical processes. However, these same metals can become highly toxic when introduced into natural waters in elevated amounts through sources such as sewage, hospital waste, industrial discharges, or mining activities. Heavy metal contamination from human actions has become a serious ecological concern in many global regions, worsened by the fact that natural water systems lack mechanisms to effectively eliminate these metals (Ekhaise & Omavwoya, 2008). Metals tend to migrate between different components of aquatic environments, including organisms, often resulting in harmful consequences. When these metals accumulate through the food chain, they pose increasing health risks to humans. Due to processes like adsorption, sediments at the bottom of water bodies often contain metal concentrations far higher than the overlying water, which can lead to secondary pollution(contamination). The toxicity of metals in water varies depending on their oxidation state and the chemical form they take (Ekpo et al., 2023). Generally, metals in ionic form are more toxic, although this can be mitigated when they bind to organic substances like humic and fulvic acids. In some cases, metal-organic compounds formed naturally in water—such as methylmercury, produced by microbes from elemental mercury—

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can be even more toxic than their unbound counterparts. Metals in water can appear in suspended, colloidal, or dissolved forms, and the proportions of these forms differ across metals and water sources, affecting both their toxic potential and how they settle in sediments. For this reason, evaluating metal contamination is a crucial component of water quality monitoring (Chapman & Kimstach, 1996; Gartiser, 1996; Ogwuche & Obruche, 2020).

This study aims to determine the concentrations of heavy metals—specifically lead, cadmium, iron, nickel, manganese, cobalt, and chromium in surface and groundwater sources near the General Hospital in Agbarho.

Materials and Methods

Study area

General Hospital in Agbarho is the research area. Additionally, Agbarho General Hospital is situated in Nigeria's Delta State. The area is located in the oil-rich Niger Delta region, which is located between latitudes 4° 30'N and 5° 21'N and longitudes 3°E and 9°E (Obruche et al., 2023). With yearly rainfall ranging from 2500 to 4500 mm, the delta area is recognised as a region with frequent precipitation (Obruche et al., 2021). The excessive rainfalls, humidity and rivers discharge during the rainy(wet) season combined with the low, flat topography and poorly drained soils result in severe floods (Obruche et al.,2022). The climate of warri follows a tropical pattern with the rainy season lasting for about eight to ten months between early March to late November with an interruption in August (commonly known as August break) and the dry season running through late November till mid-February. Warri being a great and one of the most social and economic city in the Delta area has drawn the attention of many researchers and scholars in recent decades for several reasons known to them.

Pre-treatment of Sampling Container

Appropriate sample pre-treatment techniques were used to remove any possible contamination from the collected rainwater samples in order to produce accurate results (WHO, 2011; Obruche et al., 2023). Sample containers were cleansed and rinsed with weak nitric acid, HNO_3, then dried in the sun for 24 hours. Four (4) sampling stations separated from one another (or each other) by a distance of roughly 10 m apart were selected on the surface waters. These were assigned the respective designations S1, S2, S3, and S4. Additionally, the subterranean water surrounding the water tank was examined. The subsurface water supply came from four hand-dug wells. The farmers in the area utilise these for drinking and irrigation. The wells were given the respective designations U1, U2, U3, and U4.

Sample Collection

A random sampling method was employed as outlined by APHA (1998), WHO (2011), and Obruche et al. (2023). A total of eight samples were gathered for analysis over a four-month period, from August to December 2024, across eight distinct locations within the study area. The surface water samples were collected from 4 designated points (S1, S2, S3, and S4). Prior to sampling, the water body was agitated in aerated vessels, and 500 cm^3 of surface water was then obtained from each point using a water sampler (Wyasu, 2011). Groundwater samples were collected from four hand-dug wells (U1, U2, U3, and U4) located within a small farming community in the study area. A 500 cm^3 groundwater sample was taken from each well and transported (moved) to the laboratory within 2 hours of collection. These samples were collected to provide a representative overview of the entire study area.

Digestion of Ground and surface Water Samples

Surface water and groundwater samples intended for Atomic Absorption Spectroscopy (AAS) analysis were each collected from a depth of 500 cm below the water surface. The water samples were filtered using laboratory filtered paper called Whatman 0.45µm filter paper into clean plastic containers and acidified with 3 cm^3 of concentrated HNO_3 per liter of water (WHO, 1999; Obruche et al., 2023). They were then frozen to prevent metal loss due to surface adsorption before analysis.

Additionally, 25 cm^3 of concentrated HNO_3 and 20 cm^3 of concentrated perchloric acid ($HClO_4$) were added to 50 cm^3 of each sample in a 250 cm^3 beaker. The mixture was gently heated on a hot plate until it became clear, with white or colourless fumes of $HClO_4$ appearing. After cooling, 20 cm^3 of distilled water was added. The solution was then filtered, made up to 50 cm^3 in a volumetric flask, and transferred into a labeled plastic bottle with a cap for immediate analysis. The ratio of acids and other reagents used for digestion is (HNO_3:$HClO_4$) was 5:1 (Obruche et al., 2022). A blank sample was also prepared in the laboratory by digesting the same proportion (amount) of reagents used in the sample digestion under identical experimental conditions, but without the sample.

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Preparation of Standard Solutions

A series of standard solutions for cobalt, chromium, cadmium, lead, manganese, nickel, and iron were prepared using salts such as lead nitrate ($Pb(NO_3)_2$), potassium dichromate ($K_2Cr_2O_7$), anhydrous cadmium sulfate ($CdSO_4.8H_2O$), ammonium iron(II) sulfate ($Fe(NH_4)_2SO_4.6H_2O$), dry nickel sulfate ($NiSO_4.6H_2O$), cobalt sulfate ($CoSO_4.7H_2O$) and potassium permanganate ($KMnO_s$) to calibrate the instruments. Standard stock solutions of the individual metals were prepared by weighing the appropriate metal salt according to its formula weight, dissolving it in a 1000 cm³ volumetric flask, and filling it up to the brim mark with distilled water (WHO, 2011; Obruche et al., 2023). Nickel working standard solutions of 1.0, 2.0, 3.0, 4.0, and 5.0 mg/L were made by diluting 1.0, 2.0, 3.0, 4.0, and 5.0 cm³ of the stock solution with distilled water, then adjusting the volume to 100 cm³ in a volumetric flask for calibration of the AAS equipment. Similarly, working standard solutions for the other heavy metals were prepared by diluting the appropriate volumes of the stock solutions with distilled water and making up to 100 cm³ in a volumetric flask for use in calibrating the AAS equipment.

Characterization of the Samples

The filtrates (or filtered) obtained from the digestion process were subsequently characterized for heavy metals (chromium, cadmium, lead, manganese, nickel, and iron) using Atomic Absorption Spectrophotometer. The whole laboratory analysis were carried out at Tudaka Environmental Consultants' facility, in Warri, Delta State, Nigeria.

Results

The mean levels of the heavy metal concentration in the surface water samples are presented in Table 1.

Table 1: Analyzed Heavy Metal results of Surface Water (mg/L)

Metal	Site S1	Site S2	Site S3	Site S4
Cr	0.58±0.11	0.51±0.06	0.29±0.12	0.16±0.14
Pb	1.14±0.73	1.10±0.87	1.25±0.93	2.60±0.80
Cd	0.04±0.01	0.10±0.01	0.10±0.01	0.10±0.00
Fe	9.60±0.60	9.70±1.33	4.30±0.45	4.10±0.10
Mn	0.04±0.04	0.43±0.04	0.31±0.16	0.64±0.10
Ni	0.05±0.06	0.60±0.03	0.63±0.05	0.20±0.03
Co	0.90±0.50	0.60±0.07	0.50±0.30	0.80±0.40

Values are mean± SD of the heavy metal concentration of the surface water samples

Table 2. Analysed Heavy Metal results of Ground Water (mg/L)

Metal	Site U1	Site U2	Site U3	Site U4
Cr	0.20±0.10	0.80±0.11	0.22±0.14	0.44±0.04
Pb	1.71±1.20	3.01±0.83	3.20±1.51	1.90±0.71
Cd	0.03±0.00	0.06±0.01	0.02±0.11	0.10±0.01
Fe	2.19±1.32	11.40±0.30	2.50±0.65	5.20±0.44
Mn	0.10±0.01	0.20±0.05	0.50±0.10	0.05±0.10
Ni	0.04±0.10	0.11±0.05	0.14±0.10	0.06±0.05

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Co	0.40±0.33	0.22±0.14	0.35±0.04	0.40±0.20

Values are mean± SD of the heavy metal concentration of the underground water samples.

Discussion

The amount or concentration of chromium in the surface water sites varied from 0.16 to 0.58 mg/L, as shown in Table 1. The highest observed value (0.58 mg/L) was lower than the highest reported value of 0.6093 mg/L. In the groundwater sites, Cr concentrations ranged from 0.20 to 0.80 mg/L, as shown in Table 2. The highest value of 0.80 mg/L exceeded the 0.40 mg/L value reported by Adefemi and Awokunmi (2010) for water analysis from River Ona and hand-dug wells in the Itaogbolu community area of Ondo State, Nigeria. All the Cr values in this study exceeded the WHO (2011) permissible limit of 0.05 mg/L. High Cr levels in groundwater pose risks to rural residents, as chromium and its compounds are linked to lung, nasal cavity, and sinus cancers, and may also contribute to stomach and laryngeal cancer (ATSDR, 2008). Lead concentrations in surface water in the study area ranged from 1.10 to 2.60 mg/L, as shown in Table 1, while in groundwater, Pb levels ranged from 1.71 to 3.20 mg/L, as shown in Table 2. These values were significantly higher than the maximum value of 0.55 mg/L found by Owuna (2012) for groundwater analysis in Otukpo, Benue State, Nigeria. Pb is a cumulative poison associated with a serious or severe health risks such as anemia and reproductive issues (Moore, 1988; Wildt et al., 1983). Based on the results, all Pb values in both ground and surface water exceeded the WHO (2011) permissible or recommended limit of 0.01 mg/L. Cadmium (Cd) concentrations in surface water ranged from 0.04 - 0.10 mg/L, as shown/presented in Table 1. With the exception of site S1, all values exceeded the WHO (2011) permissible level of 0.05 mg/L. Also, the mean Cd concentration in the groundwater sites ranged from 0.02 to 0.06 mg/L, as shown/indicated in Table 2. This range was lower than the 0.07 to 0.108 mg/L reported by Fagbote and Olanipekun (2013) for surface and groundwater in the Agbabu Bitumen Deposit Area. All groundwater sites except for U2 and U4, had Cd concentrations below the WHO limit of 0.05 mg/L. The mean value of iron (Fe) in surface water ranged from 4.10 to 9.70 mg/L, as shown or presented in Table 1, which was higher than the 5.30 mg/L value reported by Adefemi and Awokunmi (2010) for their water analysis from River Onia and hand-dug wells in Ondo State, Nigeria. In the groundwater sites, Fe concentrations ranged from 2.19 to 11.40 mg/L, as shown or indicated in Table 2. The elevated Fe levels could be linked to the use of iron coagulants or the rust/corrosion of pipes releasing effluent. While excessive iron in drinking water is not typically harmful, very high amounts can lead to hemochromatosis, a condition that damages organs (Ekhaise & Omavwoya, 2008; Sinclair, 2011).

Manganese (Mn) concentrations in surface water ranged from 0.04 to 0.64 mg/L, as shown or indicated in Table 1. The highest value of 0.64 mg/L of Mn was lower than the 1.373 mg/L reported by Fagbote and Olanipekun (2013) for the Agbabu Bitumen Deposit Area. With the exception of site S1, all values exceeded or above the WHO (2011) permissible level of 0.05 mg/L. In groundwater, Mn concentrations ranged from 0.05 to 0.50 mg/L, as shown or indicated in Table 2. All values exceeded the WHO limit of 0.05 mg/L, except for site U4. While Mn is an essential nutrient, high exposure to it in drinkable water can damage the respiratory system and brain, leading to symptoms such as hallucinations, memory loss, and nerve damage. Mn poisoning can also contribute to Parkinson's disease and other lung issues (Fagbote & Olanipekun, 2013). Nickel (Ni) concentrations in all the surface water sites ranges from 0.05 to 0.63 mg/L, as shown or indicated in Table 1, with the highest value of 0.63 mg/L surpassing the 0.1 mg/L value reported by Adefemi and Awokunmi (2010) for water samples analysis from River Onia and hand-dug wells in Ondo State, Nigeria. All surface water values, except for site S1, exceeded the WHO (2011) permissible level of 0.07 mg/L. In groundwater, Ni concentrations or amounts ranged from 0.03 to 0.14 mg/L, as shown in Table 2. Except for sites U1 and U4, all values exceeded or above the WHO limit of 0.07 mg/L. Cobalt (Co) concentrations in surface water ranged from 0.50 to 0.90 mg/L, with the highest value of 0.90 mg/L exceeding the 0.2093 mg/L value reported by Wyasu (2011) for the ansalysis of liquid waste treatment plant at Ahmadu Bello University (ABU) Teaching Hospital in Zaria, Nigeria. However, this increase may be attributed to the accumulation of Cobalt in the water over time. Co concentrations in groundwater ranged from 0.06 to 0.40 mg/L, as shown in Table 2. Long-term exposure to high Co levels can cause severe lung issues, including asthma, pneumonia, and wheezing (ATSDR, 2004; ATSDR, 2008).

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Conclusion

The current study examined the levels of Ni, Pb, Co, Cd, Fe, Mn, and Cr. In some of the surface and underground water sources, the concentrations of certain metals were below the WHO permissible limits, except for Pb and Cr, which exceeded or above the acceptable limits at all the sites examined. This poses a potential risk to rural populations who rely fully on these water sources for drinking and other purposes. Iron (Fe) levels were found to be high across all sites, which may be due to its natural presence in the environment and its crucial role in haemoglobin. It is highly recommended that government policies regarding waste disposal and management be developed and strictly enforced. Additionally, further research should focus on methods to degrade, reduce, or remove heavy metals from the soil near the general hospital in Agbarho.

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