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Evaluating Groundwater Quality in the Asante Akyem Central District of Ghana

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ABSTRACT: Groundwater is the primary water supply source for many people living on the surface of the earth. They depend on this valuable resource for their daily needs. But this natural resource is continuously being threatened by both natural and anthropogenic activities. Therefore, continuous monitoring and assessment of the water quality of this resource is important to keep check of the effects of water contaminants especially on human health. This study assessed the levels of Fe, Cd, Mn, and Hg in hand-dug wells at 4 communities (Ahyiayem, Odumasi Zongo, Apeboaso, and Kwaakyewaso) in the Asante Akyem Central District of Ghana and evaluated its sources and potential health risk associated with their exposure. These communities are known for illegal small-scale mining. The analysis also included other water quality parameters such as pH, nitrate, potassium, sodium, total hardness, calcium hardness, Phosphate, chloride, and total dissolved solids. From the research, there was no carcinogenic health risk to the communities concerning Fe, Mn, and Hg through ingestion and dermal contact because the hazard quotients and health hazard indices recorded in both adults and children were below one (<1). However, from the research, Cd exhibited carcinogenic health risk because its Cancer risk (CR) index exceeded 10-6 for both adults and children. This implies that there is a risk of cancer infection from ingesting water from the hand-dug wells in the study areas. According to the analysis of the Water Quality Index (WQI), the wells at Ahyiayem, Apeboaso, and Kwaakyewaso recorded indexes that were between 15 and 50, signifying that the hand-dug wells in these communities are safe for human consumption. However, about 90% of the wells at Odumasi Zongo recorded WQI values that were between 80 and 320. This means the hand-dug wells at Odumasi Zongo are highly polluted and not safe for human consumption.

KEYWORDS: Environmental science, water quality, small scale mining, groundwater

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Introduction

Groundwater is an essential resource for sustaining life and can be used in many other aspects such as agriculture and energy production. It is a natural resource that is generally free of impurities. However, human population growth and urbanization have led to the contamination of this resource. These contaminants come from both natural and anthropogenic sources, such as rock weathering and industrial activities. According to Antony Ravindran and Selvam¹, groundwater can also be contaminated by disease-causing microorganisms, hazardous household items, agricultural pollutants, and underground sewage systems. According to Van Ryneveld and Fourie², each year millions of lives are lost in developing countries because lack of access to safe drinking water. According to Vanloon and Duffy³, the concentrations of these contaminants especially the heavy metals can be very lethal even in low doses. Research conducted by Fatoki et al⁴, revealed that there is a potential danger to human health because of the high accumulation of heavy metals because they are extremely toxic. This is because, according to Carter and Fernando⁵, there is no homeostatic mechanism that can operate to regulate the levels

of toxic heavy metals such as Lead, mercury, and cadmium, and these metals are known to have harmful effects on humans even in small doses.

Water quality assessment can be described by a variety of methods. The traditional water quality assessment is most often carried out where individual water quality parameters are compared to their guideline or standard values. This method of evaluation is straightforward and detailed, but it fails to provide a thorough and interpreted picture of water quality, which is particularly important for managers and decision-makers who need quick access to information regarding water bodies. As a result, other water quality indices have been developed to convert water quality parameter values to an integrated indicator value to tackle this decision-making dilemma. An example is the water quality index (WQI). This tool is a mathematical strategy for converting a large amount of water characterization data into a single value that is easily understandable by policymakers and concerned individuals.^{6,7} However, WQI has some limitations. According to Ukah et al8, WQI may not provide sufficient information regarding the true state of water quality. Also, the index may not meet the needs of many users

of water quality data. Nevertheless, it seems that WQI has some benefits as well. According to Ravikumar et al⁹, it is a simple and valuable tool for conveying water quality information to the public and decision-makers. Other studies also integrate GIS into water quality assessment to describe spatial and temporal variations. The spatial analysis can give pictorial evidence of how an area is polluted and recommends areas for remediation. It is also good for easier analysis and interpretation of results. High-quality statistical analysis in research is also vital to making it clear what the importance of the research is and helping future researchers build on your work. It can also make it easier for laypersons to understand the significance of complex academic research and helps to make informed and correct decisions. According to Kelly et al¹⁰, It also allows the researcher to determine trends and correlations among 2 or more variables.

In this study, we combined the water quality Index (WQI), statistical analysis, and spatial methods to describe groundwater quality trends. The results presented here will contribute to a more comprehensive method for groundwater quality monitoring data analysis. The results, which are easily visualized, can then be helpful for groundwater supply and management.

Globally, research on groundwater quality has become very important. Although groundwater plays a critical role in human life by being a source of drinking water, especially in developing countries, it also has the potential of transmitting a wide variety of diseases and illnesses.

In Ghana, one main activity that has contributed to the pollution of the environment is illegal small-scale mining. ¹¹ The impact of this activity is enormous. It does not only cause land degradation, deforestation, and deaths but it also affects surface and groundwater resources as well. Mining activities can generate a significant amount of runoff that can flow into surface water bodies or seep down into the water table, contaminating the groundwater. ¹² According to Minnaar ¹², this runoff can contain a variety of pollutants, such as heavy metals, acid mine drainage, and other chemicals used in the mining process. Anim-Gyampo ¹³, researched the effects of illegal artisanal gold mining operations on groundwater quality in Ghana at the Ahafo Ano South District of Ghana and found significant effects of mining activities on groundwater resources.

The increasing occurrence of environmentally harmful mining operations in Ghana has become a significant cause for national concern. The Asante Akyem Central District in the Ashanti Region of Ghana is predominantly a peri-urban district with few rural dwellings where illegal small-scale gold mining activities occur. Consequently, there has been a significant increase in the number of individuals, predominantly youth, coming from various regions of Ghana to take part in this activity. According to Anim-Gyampo et al¹⁵, per the national water policy of Ghana, groundwater is the major source of potable water in rural Ghana. The noticeable and swift arrival of individuals in the region to engage in unauthorized small-scale gold mining necessitates the extensive extraction of

groundwater to fulfill the continually growing need for drinking water. As a result, according to World Health Organization (WHO)¹⁶, an assessment of the groundwater quality in the area has become essential. According to Asare-Donkor et al¹⁷, poor drinking water quality can expose humans to potential health risks. In terms of drinkability, groundwater is typically of superior quality compared to surface water. Nonetheless, its quality may deteriorate gradually due to natural processes and human activities. Hydrogeochemical processes such as water-rock interaction, soil-water interaction, cationic exchange reactions, and mixing of waters; and certain biological processes affect groundwater quality according to Appelo and Postma¹⁸. Human activities that can lead to the seepage of harmful substances into the groundwater include the use of agrochemicals and organic fertilizers for agricultural purposes, urban and municipal wastewater sites, mining operations, and the improper disposal of mining waste.

This study used the human health risk assessment methods, Water Quality Index (WQI), and spatial distribution to assess the groundwater quality of the Asante Akyem Central District of Ghana which has one of the largest gold reserves in the country and is noted for small-scale illegal mining activities.

The objective of this study is to assess the water quality of hand-dug wells in 4 communities in the Asante Akyem Central district of Ghana and to evaluate its potential risk to human health in the district which is a small-scale gold mining area. This research will provide a framework for any future groundwater quality monitoring and evaluation exercise to ensure sustainable utilization of the resource.

Methodology

Description of the study area

The Asante Akyem Central District covers an area of 1462 km² forming 1.6% of the total land area of the Ashanti Region of Ghana. The district is located within longitude 6°37′15" to 6°37′15″ and latitude 1°13′25″ to 1°13′46″. The district can be found in the semi-equatorial regions with bimodal rainy seasons with the major season running from April-July and the minor season August-October. The total population in the district is 91,673 with farming as the predominant occupation.¹⁹ The landscape of the district is typically undulating with elevation between a range of 97 and 642 m.20 The district is drained by several rivers which include Anum, Owerri, Bomire, and Abosomtwe which are sources of water supply to some of the communities. The volume, flow, color, and aquatic habitat of the rivers in the study area is mostly affected by the activities of these illegal miners. Apart from the Tarkwain formation, the Asante Akyem Central District is dominated by northeast trending rocks of the Birimian Supergroup which is made up of metavolcanic and metasedimentary units. The metasediment consists of meta-greywacke, meta-sandstone, phyllite, and tuffaceous. The metavolcanic unit on the other hand consists mainly of metabasalt, metadolerite, Meta-rhyolites,

quartz-feldspar porphyry, felsites, and quartz chlorite-schists as well as Meta-tuffaceous greywacke. The Tarkwaian is made up of Quartzites, sandstones, grits, phyllites, and conglomerates. The rock formations are twisted, metamorphosed, and intruded by syn- and post-granitoid during the Eburnean Orogeny about 2130 to 1980 Ma. According to Kesse²⁰, the gold mineralization in the district is being hosted by a series of northeastsouthwest trending shear zones and other deformational structures. According to Boadi et al²¹, fractured schist, fractured phyllite, and fractured meta-volcanic rocks are the most common aquifer systems in the study area. The best aquifers in the district are found on the slopes of synclinal troughs where significant amounts of degraded materials have been collected. According to Oberthür et al²², several major companies as well as illegal mining (locally refers to as galamsey) have been attracted to the district due to its large gold deposits.

Sampling and analytic procedure

Sampling. The study was conducted in 4 towns within the district namely, Ahyiayem, Odumasi Zongo, Apeboaso, and Kwaakyewaso. These communities are known for illegal small-scale mining activities. The communities are characterized by excavation activities mostly using excavators, picks, and shovels. There are mine pits that are scattered throughout the mining areas and are generally 10 m deep. The mining areas are also characterized by heaps of sand from the mine pits and crushed rocks. This sand is washed to remove the gold nuggets and this process normally takes place near a water supply source such as rivers or hand-dug wells. These communities are also characterized by a lot of dust, smoke, and noise usually from mining activities.

Forty (40) water samples (Figure 1) were collected into 750 mL plastic bottles which have been washed with distilled water, sterilized with alcohol, and dried. To prevent bias during the sample collection, 10 (10) wells were chosen from each of the communities for the sampling. A random sampling technique was used for the sample collection. Duplicate samples were taken from each well using alcohol-sterilized buckets. The samples were collected in the morning before sunrise and then kept at a temperature of 4°C and transported to the laboratory for analysis. $0.45\,\mu m$ cellulose acetate filter membrane and Sartorius polycarbonate filtering apparatus were used to remove particulate matter from the samples.

Analytical procedures. The concentrations of the heavy metals (Lead, Iron, Arsenic, Manganese, Cadmium, and Mercury) were determined using the Atomic Absorption spectrometer. Samples were initially acidified with a known volume of concentrated nitric acid. The samples were then digested using HClO₄ and HNO₃ in a ratio of 4:9 respectively. Analytical blanks were prepared and a series of calibration solutions containing known amounts of analyte elements (standard solutions) were also prepared. These standards and their blanks

were atomized sequentially, and their responses were measured. A calibration curve indicating the response obtained for each solution was plotted. The sample solution was also atomized, and the response was also measured. The concentration of the heavy metals in the sample solution was determined from the calibration curve based on the absorbance obtained. The Chloride concentrations in the samples were determined by titrating the samples with Silver Nitrate (AgNO₃) solution and potassium chromate as the indicator. The endpoint of the titration was determined when all the chloride ions precipitated to form a red-brown coloration. Alkaline concentrations of the samples were determined by titration of the samples with 0.01 M H₂SO₄ with Phenolphthalein and methyl orange indicators. The final endpoint occurred when there was a color change from pink to light orange. Ethylenediaminetetraacetic acid (EDTA) and Eriochrome Black T indicators were also used to determine total hardness concentrations in the samples through a titration process. The final endpoint occurred when there was a color change from wine red to sky blue. Concentrations of potassium and sodium in the samples were obtained using a flame photometer. The photometer detected the concentrations of potassium and sodium in the form of an emitted light. Potassium concentrations were determined at a wavelength of 766.5 nm whilst the concentrations of Sodium were determined at a wavelength of 589 nm. The concentrations of nitrates and phosphates samples were obtained using a spectrophotometer. The concentration of Nitrate was measured in mg/L as NO₃-N whilst the concentration of phosphates was also measured in mg/L as PO₄3-. The pH was determined using a pH meter whilst the electrical conductivity and total dissolved solids were analyzed using the conductivity meter.

Quality control. To guarantee the accuracy of the water quality analysis, quality control measures were adhered to during the analytical procedures. Established protocols for sampling, preserving samples, and calibrating instruments, were duly followed. In addition, all glassware used during the analysis was soaked in 5% HNO $_3$ and then rinsed with distilled water thoroughly.

Analysis of pollution levels

Water quality index. Water Quality Index (WQI) is a convenient tool for determining the quality of ground and surface water resources and representing it in a simple and understandable form.²³ According to Brown et al²⁴, this index gives a thorough summary of the state of groundwater quality for residential and domestic use. However, WQI has some limitations. According to Ukah et al⁸, WQI may not provide sufficient information regarding the true state of water quality. Also, the index may not meet the needs of many users of water quality data.⁸ Nevertheless, it seems that WQI has more benefits than drawbacks. According to Ravikumar et al⁹, it is a simple and valuable tool for conveying water quality information

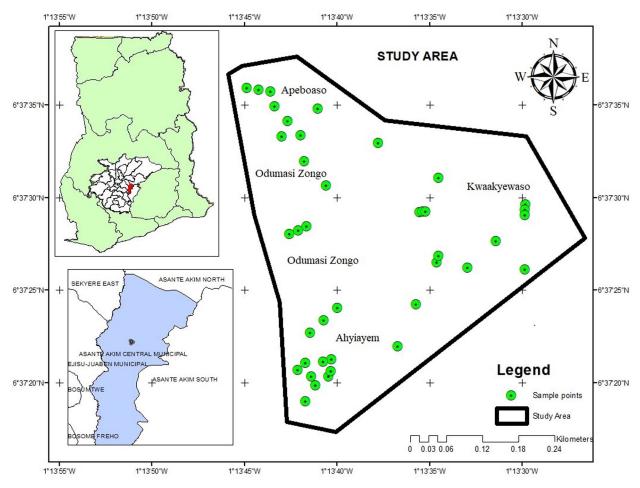


Figure 1. Sampling points at Asante Akyem Central District of Ghana.

to the public and decision makers. WQI represent water quality by a simple value that can be easily interpreted.²⁵ According to Yisa and Oladejo²⁶ and Tyagi et al²⁷, WQI has the advantage of representing complex and bulky data in a simple and understandable way. Mathematically, it is calculated using the expression as stated in equation (1)

$$WQI = \sum W_n Q_i \tag{1}$$

Where Wn represents the relative weight, equation (2) is represented as

$$W_{n} = K/Si$$
 (2)

Equation (3) is also represented as

$$K = 1/\sum \frac{1}{Si} \tag{3}$$

Qi represents the sub-index of the parameter as can be seen in equation (4)

$$Q_i = 100 \frac{V_i}{S^i} \tag{4}$$

where V_i is the monitored value of the parameter and \mathbf{S}_i is the regulatory standard.

Table 1. Classification of WQI values (WQI table developed by Brown et al. 24).

| WQI | WATER QUALITY |
|--------|-----------------------|
| 0-25 | Excellent |
| 26-50 | Good |
| 51-75 | Poor |
| 76-100 | Very Poor |
| >100 | Unfit for consumption |

For the classification of the pollution in water, the calculated WQI values are classified into 5 types as shown in Table 1.

Multivariate techniques

In this study, the data were analyzed using 2 multivariate techniques namely, Principal component analysis (PCA) and Pearson correlation. Data verification was conducted by conducting the analysis in replicates. Skewed datasets were log-transformed. So as not to severely affect the data analysis outputs obtained; the data was standardized prior to the analysis. This was done to make the different-scaled multiple

Table 2. Pearson correlation matrix table of the metals and physicochemical parameters.

| | PH | NITRATE | K | NA | FE | CD | MN | T.H | C.H | PHOSP | HHG | CHLORIDE | TDS | E.C | ALKALINITY |
|------------|-------|---------|------|------|------|------|------|------|------|-------|------|----------|------|------|------------|
| рН | 1.00 | | | | | | | | | | | | | | |
| Nitrate | -0.60 | 1.00 | | | | | | | | | | | | | |
| K | -0.44 | 0.80 | 1.00 | | | | | | | | | | | | |
| Na | -0.54 | 0.90 | 0.93 | 1.00 | | | | | | | | | | | |
| Fe | -0.54 | 0.91 | 0.84 | 0.92 | 1.00 | | | | | | | | | | |
| Cd | -0.46 | 0.78 | 0.91 | 0.94 | 0.85 | 1.00 | | | | | | | | | |
| Mn | -0.63 | 0.87 | 0.92 | 0.94 | 0.93 | 0.92 | 1.00 | | | | | | | | |
| T.H | -0.56 | 0.86 | 0.81 | 0.86 | 0.91 | 0.83 | 0.91 | 1.00 | | | | | | | |
| C.H | -0.61 | 0.92 | 0.63 | 0.78 | 0.77 | 0.62 | 0.72 | 0.77 | 1.00 | | | | | | |
| Phosphate | -0.59 | 0.97 | 0.76 | 0.87 | 0.92 | 0.73 | 0.86 | 0.88 | 0.88 | 1.00 | | | | | |
| Hg | -0.54 | 0.77 | 0.63 | 0.69 | 0.81 | 0.58 | 0.72 | 0.84 | 0.68 | 0.84 | 1.00 | | | | |
| Chloride | -0.63 | 0.89 | 0.83 | 0.90 | 0.91 | 0.81 | 0.91 | 0.90 | 0.79 | 0.89 | 0.76 | 1.00 | | | |
| T.D.S | -0.72 | 0.85 | 0.64 | 0.76 | 0.82 | 0.65 | 0.80 | 0.87 | 0.85 | 0.87 | 0.82 | 0.90 | 1.00 | | |
| E.C | -0.72 | 0.85 | 0.64 | 0.76 | 0.82 | 0.65 | 0.80 | 0.87 | 0.85 | 0.87 | 0.82 | 0.90 | 1.00 | 1.00 | |
| Alkalinity | -0.56 | 0.92 | 0.88 | 0.96 | 0.92 | 0.90 | 0.93 | 0.91 | 0.81 | 0.90 | 0.74 | 0.94 | 0.84 | 0.84 | 1.00 |

K, Potassium; Na, Sodium; Fe, Iron; Cd, Cadmium; Mn, Manganese; T.H, total hardness; C.H, calcium hardness; Hg, Mercury; T.D.S, total dissolved solids; E.C, electrical conductivity.

variables comparable. Z-score normalization or standardization was done using the formula as seen in equation (5).

$$\frac{x_i - mean(x)}{sd(x)} \tag{5}$$

Where mean(x) is the mean of x values, and sd(x) is the standard deviation (SD).

PCA analysis. According to Helena et al²⁸, Principal component analysis (PCA) can be used to reduce the dimensions of multivariate data to understand the problems and their controlling factors. To explore the relationships that exist among metals, principal component analysis can be used. According to Ackah²⁹, PCA was conducted using principal component extraction with a Eugen value >1 after varimax rotation.²⁹ PCA discloses a pattern of correlation between the metals concentration and properties related to emission sources. It was used in this research to discover latent patterns in the datasets.

By using principal component analysis, it is possible to identify a complicated linear relationship among heavy metal concentrations. This, in turn, allows for the interpretation of how different elements are correlated in the study area. After performing varimax rotation, the factor matrix was used to identify the elements belonging to a specific component. Those that exhibited strong correlations were grouped together within the same component. The principal component technique is

used to determine the way of distribution of the individual association of components in both surface and groundwater. PCA, or principal component analysis, simplifies the complexities of a dataset by creating new latent variables that are uncorrelated and orthogonal to each other. These variables are formed by a linear combination of the original data. Varimax rotations with Kaiser normalization is used to reduce the dimensionality of the data, identify the most important variables, and infer the mechanisms that regulate water chemistry when the principal components (PCs) generated from PCA are not always easily interpreted. Varimax factor loading coefficients with a correlation of >.75 is explained as a strong significant factor loading (FL); .75 to .50 are considered moderate FL; and .50 to .30 are considered as weak FL.

Pearson correlation. An essential statistical technique for assessing the strength of links and interrelationships among variables are Pearson's correlation analysis (Table 2). A correlation coefficient of +1 signifies a direct relationship between variables, while a value of -1 indicates a perfect relationship but with an inverse variation. On the other hand, a correlation coefficient of zero denotes the absence of any relationships between the variables. A strong correlation according to Pearson's correlation coefficient (r) is one where the value is greater than .7, while a moderate correlation is one where the value is between .5 and .7.17

Spatial distribution

Geospatial maps of water quality indices and Nemerow pollution index showing the spatial distributions of the metals and metalloids were produced using Geosoft Version 7.2 software packages. The lowest curvature technique was used to grid the data at a quarter of the profile spacing. This approach, which is based on splines in tension, significantly improves the output grids' lateral consistency and smoothness. This tool creates a map of the spatial distribution of different heavy metals and their indices to pinpoint any potential risk-prone areas in the vicinity. Using IBM-SPSS V. (20) software, the raw data were processed into easily comprehensible data for statistical analysis. PCA (Principal Component Analysis) calculations were made using the Microsoft Excel-2013 and XLSTAT-2016 software, respectively. The Varimax rotation approach was used in PCA analysis to incorporate the most variables possible.

Health risk assessment methodologies

According to Dippong et al³¹, human health risk assessment is an important tool used in the management of polluted areas. It also helps with risk management and hazardous area remediation by identifying risks related to exposure to chemical pollutants according to Cabral Pinto et al³². The present study employed the human health risk model, which was developed by the US Environmental Protection Agency as an innovative approach to assessing health risks. The Human health risk analysis model is known for its ability to provide quick and accurate risk analysis. According to Tenebe et al³³, the human health risk analysis code allows for conducting concurrent risk assessments without any restrictions on the number of water quality parameters, its spatial and temporal distributions. To aid in the evaluation and management of water quality, it is crucial to determine the likelihood that heavy metals will have harmful impacts on human health.³⁴ In this research, the USEPA model was used to evaluate the non-carcinogenic and carcinogenic health risks of heavy metals such as Fe, Cd, Mn, and Hg in 2 different age groups (adults and children).35 Literature has outlined the approaches for assessing the risks to human health posed by aquatic ecosystems.³⁴⁻³⁷ When humans are exposed to water, ingestion, and cutaneous absorption are frequent.35-37 According to the USEPA's Risk Assessment Guidance for Superfund (RAGS) approach,35 the following numerical expressions for risk assessment are provided below in both equations (6) and (7) respectively.

$$D_{ing} = \frac{C_{water} \times IR \times EF \times ED}{BW \times AT} \tag{6}$$

$$D_{derm} = \frac{C_{water} \times SA \times KP \times ET \times EF \times ED \times CF}{BW \times AT} \tag{7}$$

where $D_{\rm ing}$ refers to the exposure dose through ingestion of water (µg/kg/day); $D_{\rm derm}$ refers to the exposure dose through dermal absorption (µg/kg/day); $C_{\rm water}$ refers to the exposure

concentration of the estimated metals in water (µg/L); IR refers to the ingestion rate (2.21/day for adults; 1.81/day for children); EF refers to the exposure frequency (350 days/year); ED refers to the exposure duration (70 years for adults; and 6 years for children); BW refers to the average body weight (70 kg for adults; 15 kg for children); AT refers to the averaging time (25 550 days for adults; 2190 days for children); SA refers to the exposed skin area (18 000 cm² for adults; 6600 cm² for children); ET refers to the exposure time (0.58 hour/day for adults; 1 hour/day for children); CF refers to the unit conversion factor (0.0011/cm³); and K_p refers to the dermal permeability coefficient (cm/h). The dermal permeability coefficient for Fe, Pb, Zn, Cr and Ni are given as 1.0×10^{-3} , 4.0×10^{-3} , 6.0×10^{-3} , 2.0×10^{-3} and 4.0×10^{-3} cm/h respectively. 35-38

By contrasting the predicted contaminant exposures from each exposure route with the reference dosage (RfD), potential non-carcinogenic risks for exposure to contaminants were identified.³⁵ The relationship between the hazard quotient (HQ), a numerical measure of the systemic toxicity potential posed by a single element within a single route of exposure is given below as stated in equation (8) below.

$$HQ_{ing}/_{derm} = \frac{D_{ing}/_{derm}}{RfD_{ing}/_{derm}}$$
(8)

where $HQ_{ing/derm}$ refers to the hazard quotient via ingestion or dermal contact and $RfD_{ing/derm}$ refers to the oral/dermal reference dose ($\mu g/kg/day$). The RfD_{ing} and RfD_{derm} values were obtained from the literature (39,35,37,38 ;). The overall potential for non-carcinogenic effects posed by more than one element was evaluated by integrating the computed HQs for each element and expressed as a hazard index (HI) 35 : This formula can be seen in equation (9) below.

$$HI = \sum_{i=1}^{n} HQ_{ing/derm}$$
 (9)

where $HI_{ing/derm}$ refers to the hazard index via ingestion or dermal contact.

The Cancer risk (CR) was calculated using the formula as stated in equation (10) below;

$$CR_{ing} = \frac{D_{ing}}{SF_{ing}} \tag{10}$$

where SF_{ing} refers to the cancer slope factor. The SF_{ing} for Pb is 8.5 and Cr is 5.0 \times 10² mg/kg/day.^{35,36,40,41} The acceptable threshold for CR is 10⁻⁶, and if it exceeds 10⁻⁴, the risk is unacceptable^{42,43}

Result and Discussion

Statistical analysis of parameters

Analytical statistics of the water quality data such as that is, the minimum, maximum, mean, and standard deviation of the

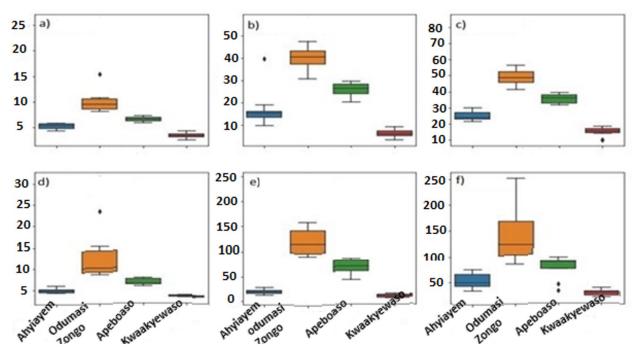


Figure 2. Box plots of concentrations: (a) nitrates, (b) potassium, (c) sodium, (d) phosphate, (e) alkalinity, and (f) chlorides in the study area.

water quality parameters (pH, nitrate, potassium, sodium, iron, cadmium, manganese, total hardness, calcium hardness, phosphate, mercury, chloride, total dissolved solids, electrical conductivity, and alkalinity) concentrations of 40 samples were calculated. A geospatial map below illustrates the regional and temporal fluctuations in individual heavy metal concentrations along the sampling locations. From the analyses, nitrate concentrations (Figure 2a) ranged from 2.6 to 25.9 mg/l with an average of $6.70 \pm 4.02 \,\mathrm{mg/l}$. All the wells in the study area had their nitrate concentrations below the WHO limit of Fifty mg/l. Similarly, Potassium concentrations (Figure 2b) ranged from 3.5 to 56.8 mg/L with an average of 22.52 ± 14.07 mg/l. Also, the chloride concentrations (Figure 2f) ranged from 20.1 to 252.2 mg/l with a mean of 76.45 ± 53.71 mg/l. The wells at Odumasi Zongo recorded the highest chloride concentrations whilst the wells at Kwaakyewaso recorded the lowest concentrations. Except for some of the wells at Odumasi Zongo, all the remaining wells in the other communities had their chloride concentrations below WHO⁴⁴ standards for drinking water of 250 mg/l. High chloride concentrations in water samples are indicators of permanent hardness. Chloride is distributed in nature and is commonly found in mining communities due to geology. It occurs as sodium chloride, very soluble in water and it is mostly related to the geology of the study area (45). Alkalinity concentrations ranged between 5.5 and 246.7 mg/l with an average of 56.58 ± 53.45 mg/l. Wells at Odumasi Zongo on average recorded the highest levels of alkalinity whilst the wells at Kwaakyewaso recorded the lowest alkalinity levels on average. Comparing the concentrations of Alkalinity in the hand-dug wells to the (WHO) guideline value of 100 mg/l, it can be inferred that the wells at Odumasi

Zongo were above the guideline value and unwholesome for drinking. Similarly, the water in mining areas (Odumasi Zongo) has higher alkaline concentrations (Figure 2e) compared to the other communities due to the presence of high bicarbonate ions in mining areas. Comparatively, untreated water in mining areas has high chloride concentrations compared to other communities due to the nature of rocks in mining communities (45).

The pH values ranged from 5.6 to 7.4 with a mean of 6.48 ± 0.31 . From the study, most of the wells in the study area had their pH concentrations within the WHO⁴⁴ limit of 6.5 to 8.0. The lowest pH was recorded at Odumasi Zongo (5.59) whilst the highest pH was recorded at Apeboaso (7.42). The ore formations that are mostly associated with mining communities are made up of sulfides and carbonaceous matter and these minerals affects the pH of groundwater, hence the disparities in pH. Also, according to Bartley et al⁴⁶, the pH fluctuations in the hand dug wells could be because of the natural geochemical and biochemical degradation (oxidation) which occurs in the ore formations of the geology at the study area. These processes normally cause pH fluctuations. Even though, the hand-dug wells at Odumasi Zongo recorded the lowest pH values, their alkalinity concentrations were the highest compared to the other communities in the study area. Alkalinity refers to the buffering capacity of a water sample or the ability of a water sample to resist a change in pH whilst pH describes the acidity, basicity, or neutrality of water. According to Fernandez⁴⁷, a water sample can have a low pH and a high alkalinity concurrently. A high alkalinity concentration means that the water sample has a high buffering capacity, and the pH does not change easily or quickly. This means it will take a long

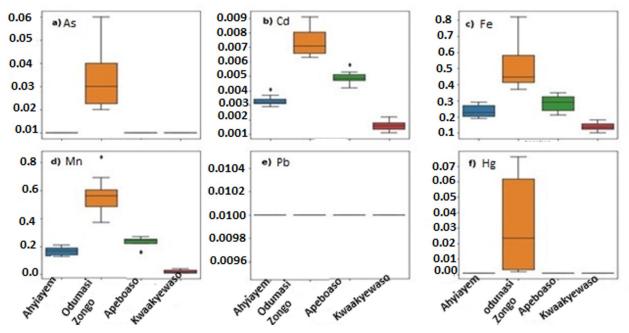


Figure 3. Boxplots of concentrations of: (a) arsenic, (b) cadmium, (c) iron, (d) manganese, (e) lead, and (f) mercury.

time for the low pH of the hand-dug wells at Odumasi Zongo to change quickly.

Total hardness concentrations in the communities ranged between 41.0 and 950.0 mg/l with a mean of 255.78 \pm 234.04 mg/l. From the study, wells at Odumasi Zongo recorded the highest concentration of hardness (571.5 mg/l) compared to the rest of the communities. About 80% of their wells recorded average hardness above the threshold guideline value by WHO (200 mg/l). This disparity in hardness is also due to the geology of the study area. The study area is characterized by calcium and magnesium-containing minerals such as limestone, chalk, and dolomite, the water becomes hard. 21

Total dissolved solids (TDS) in the communities ranged from 39.0 to 1785.5 mg/L with a mean value of 258.79 ± 396.82 mg/l. The highest concentrations were recorded at Odumasi Zongo with some of the individual wells having concentrations as high as 1785 mg/L which was far above the standard by WHO. Wells at Kwaakyewaso recorded the lowest concentrations of TDS. The findings indicated that the changes in total dissolved solids might be linked to the aquifer's natural geochemical and biochemical degradation processes, which result in the dissolution of dissolved ions. This is because most of the wells at Odumasi Zongo are poorly designed, which makes it easier for the internal walls of the wells to carve in thereby increasing the dissolved substances. In addition, the wells were not covered and were exposed to the changes in weather and climatic conditions.

Heavy metal analysis was undertaken to determine the concentrations of Iron (Fe), Manganese (Mn), and Cadmium (Cd), in the hand-dug wells. According to Dzigbordi-Adjimah⁴⁸ due to the geology of the study area, it is imperative to analyze the presence of these heavy metals in the groundwater to serve as a baseline for this study. Arsenopyrite (FeAsS), magnetite, pyrite

(FeS₂), chalcopyrite (CuFeS₂), marcasite (FeS₂), sphalerite (ZnS), bornite (CuFeS₄), Galena (PbS) and iron-rich carbonates are examples of rock mineral types found in the study area. Fe concentrations ranged from 0.1 to 0.82 mg/L with a mean value of $0.29 \pm 0.16 \,\text{mg/l}$ (Figure 4c). Amongst the communities, Odumasi Zongo recorded the highest iron concentrations. About 80% of its wells recorded Iron concentrations above the WHO threshold value of 0.3 mg/l for drinking water. This phenomenon is due to the geology of the study area. According to Applin and Zhao⁴⁹, the study area is also characterized by ironcontaining minerals such as siderite and marcasite. As a result, if these Fe-rich minerals interact with organic substances, Fe₂CO₃ is released through an oxidation process leading to increased levels of Iron in some of the aquifers in the study area.⁵⁰ When water is retrieved from these hand-dug wells, it is initially clear but soon it will turn hazy and eventually brown because of Fe (OH)₃ precipitation. Similarly, manganese concentrations ranged from 0.01 to 0.84 mg/L with a mean value of 0.24 ± 0.21 mg/l. From this, Odumasi Zongo recorded the highest mean Mn concentration of 0.56 ± 0.13 mg/l (Figure 3d). At Odumasi Zongo about 70% of the samples recorded Mn values above the guideline value of (0.5 mg/l) which can be attributed to the leaching of the Mn from geological materials from the processing of gold ore in the community.⁵⁰ According to Dzigbordi-Adjimah⁴⁸, the source of Mn in groundwater can also be attributed to the dissolution of geologic minerals and materials. There were concentrations of Cadmium in all the hand-dug wells in the communities. Cd concentrations ranged between 0.00 and 0.009 mg/L with a mean value of 0.004 ± 0.002 mg/l. Cd concentrations recorded at Odumasi Zongo were the highest whilst concentrations at Kwaakyewaso were the lowest. At Odumasi Zongo, about 70% of the wells had Cd concentrations above the WHO standard of 0.005 mg/l.

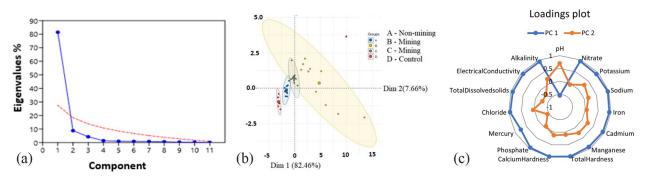


Figure 4. Principal component analysis of the metals and physicochemical parameters consisting of: (a) Scree plot, (b) 2D plot, and (c) Loadings plot.

From the analysis, mercury concentrations (Figure 3f) ranged from 0.001 to 0.076 mg/l. Apart from the wells at Odumasi Zongo where small-scale mining activity is rampant, all the communities recorded Hg concentrations below the World Health Organization threshold value (0.006 mg/l) for drinking water. Mercury concentrations were low in the wells at Kwaakyewaso because there were no mining activities. At Odumasi Zongo, 50% of the wells had mercury concentrations above the WHO guideline value. Statistically, Hg concentrations at Odumasi Zongo where mining activities are very rampant were compared to the other communities. At a 95% confidence interval, the error bars of Odumasi Zongo did not overlap with the other communities, hence there is statistical evidence to suggest that there is a significant difference between the mean of Hg concentrations at Odumasi Zongo and that of Kwaakyewaso. Therefore, it can be concluded that the major sources of mercury in the wells at Odumasi Zongo can be attributed to illegal small-scale mining. According to Akabzaal⁵¹, Gold recovery by mercury amalgamation by smallscale miners is a significant source of mercury contamination in mining towns. It was also observed that the miners use water from the wells for the washing of the gold and as such, they can cross-contaminate the ropes and buckets for the abstraction of the water.

Odumasi Zongo which is a major illegal small-scale gold mining processing town is observed to have high values in all the parameters. It is also worth noting that the large error bar, as well as the number of outliers on the boxplots, were observed on all the measured parameters at the processing town. The high accumulation of these heavy metals at Odumasi Zongo is a result of the pollution from the mining activities since all these towns are in the same geological regime Griffis et al⁵² and hence were expected to have a similar geogenic concentration of these elements. The large error margin and high outliers at the main processing town show a general localization of the processing activities in the town.

PCA analysis

According to Wang et al⁵³, principal component analysis (PCA) is used to reduce multivariate data's dimension to understand the problems and its controlling factors.

The heavy metal concentration and physicochemical parameter dataset were subjected to a principal component analysis to identify hidden patterns. The scree plot (Figure 4a) shows that the first 2 principal components with values >1 accounted for 89% of the total variance. The first dimension accounted for 81.9% of the total variance and the second accounted for 7.1% of the total variance. Strong positive loadings (>0.2) were observed for all the parameters in the sample except the pH according to Loading Plot (Figure 4c). In effect EC, TDS, Total Hardness, Calcium Hardness, Nitrates, Phosphates, Chlorides, Sodium, Potassium, Manganese, and other heavy metal contaminants such as Iron and Mercury all contribute almost equally to the formation of the axis. pH trends were all in the opposite direction, indicating an opposite relationship with the other physicochemical parameters. The trend of these parameters indicates that the pollution originated from the same source, that is, an anthropogenic activity in the catchment area of the wells. Strong positive loadings (>2) were also observed in pH, K, Na, Mn, Cd, and Fe in the second component. The trend of these parameters also supports the fact that there were some contributions from natural geochemical reactions within the geology of the study area. Figure 4b demonstrates how significantly different the mining areas are from non-mining and control areas. The 95% ellipses drawn around each category show that the mean of the generated dataset would lie anywhere within the ellipses if new points were added to each category. Thus, without the need for additional sampling campaigns, this can be utilized to forecast the results of various scenarios. One can infer that there was greater pollution from the mining sites because the data from mining sites B and C load more positively and strongly to the first component.

Pearson's correlation matrix of the heavy metals described Mn–Fe (.93), Cd–Mn (.92), Fe–Cd (.84), and Fe–Hg (.80) as having strong correlation values. This correlation means that in areas where Iron concentrations are high, there is a strong possibility that the Mn concentrations will also be high. In areas where Cd concentrations are high there is a strong indication that Mn concentrations will also be high. In areas where we have high Fe concentrations, there is the possibility that Cd concentrations will also be high. There was also a strong correlation between Nitrate–Phosphate (.96), Nitrate–TDS (.85), Chloride–TDS (.90), Chloride–E.C (.90), Alkalinity–Total

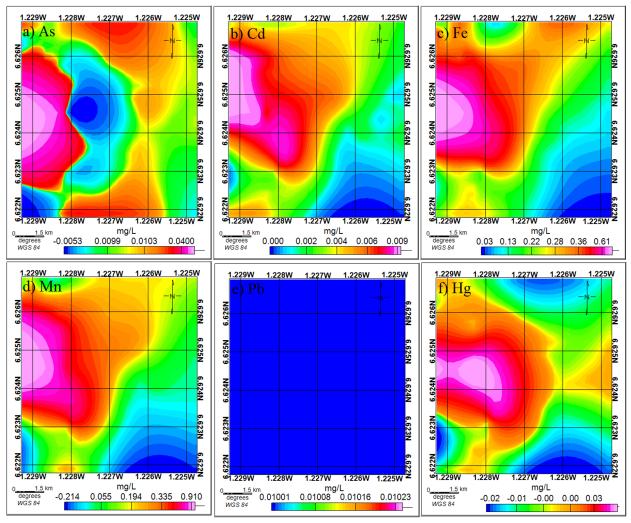


Figure 5. Distribution of: (a) arsenic, (b) cadmium, (c) iron, (d) manganese, (e) lead, and (f) mercury.

hardness (.90). This means, if the nitrates concentration is high, the total dissolved solids concentration in that same water sample will also be high. Similarly, if the chloride concentrations in the water sample are high, its electrical conductivity will also be high. There was also a strong relationship between Total Hardness–Alkalinity (0.92), Total Hardness–Chloride (0.90), and Electrical Conductivity–Total Hardness (0.86). This signifies that they affect each other. This means the higher the chloride concentrations, the harder the water will be.

Distribution of heavy metals spatially

Figure 5 is the gridded map showing the spatial distribution of the various heavy metals in the study areas. From these images, the western side of the area (light pink to pink) corresponds to Odumasi Zongo. It recorded the highest concentration of heavy metals (metalloids) and other water quality parameters. The south and the eastern sides of the area (light blue to blue) corresponding to Kwaakyewaso recorded the lowest concentrations of all the parameters. The northern side of the image (green to yellow) corresponding to Apeboaso recorded a medium value of all the measured parameters. The area with

high values of these metalloids and other water quality parameters (Odumasi Zongo) is noted with high mining activities whilst the area with low concentration of heavy metals (Kwaakyewaso) represents no mining activity. The Pb concentrations in the study area were below detection limits that is why it is shown blue (Figure 5e).

Spatial distribution of physicochemical parameters

The distribution of the physicochemical parameters was like the heavy metals as shown in Figure 6. The areas shown light pink to pink represent Odumasi Zongo (highly polluted), light blue to deep blue represents Kwaakyewaso (not polluted) green to yellow represents Apeboaso (slightly polluted) whilst light red to red represents Ahyiayem (slightly polluted).

Water quality index

Water Quality Index (WQI) is a special formula for assessing the quality of water. In principle, this aggregation technique is employed to reduce large quantities of water quality data to a single value or index. Generally, WQI between 0 and 50 is

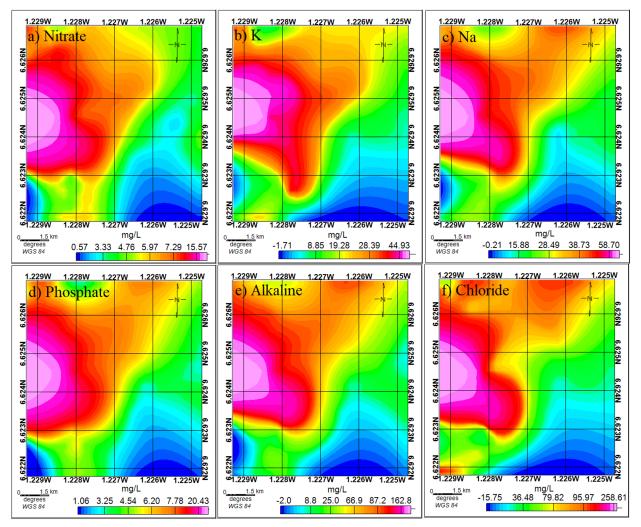


Figure 6. Spatial distribution of Nitrate, Potassium, Sodium, Phosphate, Alkalinity, and Chloride concentrations in the study area.

classified as "Good" for drinking water purposes. According to Brown et al²⁴, an index between 51 and 75 is classified as poor, 76 to 100 is classified as very poor and those that are more than 100 are not good for human consumption. The water quality index (WQI) at Ahyiayem was in the range of 39.04 to 52.63 with an average of 43.63. The samples from Odumasi Zongo recorded values in the range of 87.82 to 318.16 with an average of 318.16. The samples from Apeboaso and Kwaakyewaso recorded values in the range of 53.69 to 71.05 and 19.78 to 31.67 with averages of 61.26 and 25.24 respectively. Based on this classification, f all the wells at Kwaakyewaso and about 80% of the wells at Ahyiayem are good and safe for human consumption whilst the wells at Apeboaso and Odumasi Zongo are poor and not good for human consumption.

Heavy metals and its health risk assessment

Tables 3 to 5 provide information on the health risks assessment of the heavy metals for children and adults in the study area. This information pertains to both ingestion and dermal exposure routes and focuses specifically on carcinogenic and

non-carcinogenic health risks. Humans can be exposed to trace metals in different ways. Some of these exposure pathways are consumption through food and water, inhalation through the nose or the mouth, and skin absorption. The weight of an individual and the amount of water consumed plays a critical role in influencing the effect of heavy metal on the health of an individual. The health risks of Fe, Cd, Mn, and Hg were assessed in adults and children through ingestion and dermal exposure route. According to the findings of the study, the hazard quotient for all the metals through ingestion was below one. This means that the potential health risk posed by these metals to both children and adults through ingestion is minimal.³⁷ The hazard quotient for dermal absorption HQ_{derm} was also below one. This also means that there is little to no health risk through dermal contact with these metals. Also, according to the study, the health hazard index (HI) for ingestion and dermal contact for both adults and children was also below one and as such there is no significant health risk from consuming the water in the hand-dug wells in the study area.

The Carcinogenic health risk (CR) of Fe, Cd, Mn, and Hg was assessed in adults and children as seen in Table 5. According

Table 3. Health risk assessment of the hand dug wells at Ahyiayem and Odumasi Zongo.

| HEAVY RFD _{ING} METALS (μG/KG/ DAY) | | RFD _{DERM} | AHYIAYEM | | | | ODUMASI ZONGO | | | |
|--|-----------------|---------------------|-------------------|--------------------------------------|----------|--------------------|-------------------|--------------------|-------------------|--------------------|
| | (μG/KG/ DAY) | ADULTS | | CHILDREN | | ADULTS | | CHILDREN | | |
| | | | HQ _{ING} | HQ _{ING} HQ _{DERM} | | HQ _{DERM} | HQ _{ING} | HQ _{DERM} | HQ _{ING} | HQ _{DERM} |
| Fe | 700 | 700 | 1.01E-05 | 4.12E-09 | 3.86E-05 | 1.42E-07 | 2.2E-05 | 8.95E-09 | 8.4E-05 | 3.08E-07 |
| Cd | 0.5 | 0.0125 | 1.98E-04 | 3.22E-06 | 7.55E-04 | 1.11E-04 | 4.42E-04 | 7.12E-06 | 1.69E-03 | 2.47E-04 |
| Mn | 1.4 | 0.96 | 3.51E-03 | 2.08E-06 | 1.34E-02 | 7.1E-05 | 1.21E-02 | 7.18E-06 | 4.62E-02 | 2.47E-04 |
| Hg | 0.3 | 0.3 | 1.0E-04 | 4.09E-05 | 3.84E-04 | 1.41E-03 | 3.19E-03 | 1.29E-03 | 1.22E-02 | 4.46E-02 |
| HI | | | 3.81E-03 | 4.62E-05 | 1.46E-02 | 1.58E-03 | 1.58E-02 | 1.31E-03 | 6.01E-02 | 4.52E-02 |

Table 4. Health risk assessment of the hand dug wells at Apeboaso and Kwaakywaso.

| "" | RFD _{ING} | RFD _{DERM} (μG/KG/ DAY) | APEBOASO | | | | KWAAKYEWASO | | | |
|----|--------------------|--|-------------------|--------------------|--------------------------------------|----------|-------------------|--------------------|-------------------|--------------------|
| | (μG/KG/ DAY) | | ADULTS | | CHILDREN | | ADULTS | | CHILDREN | |
| | | | HQ _{ING} | HQ _{DERM} | HQ _{ING} HQ _{DERM} | | HQ _{ING} | HQ _{DERM} | HQ _{ING} | HQ _{DERM} |
| Fe | 700 | 700 | 1.22E-05 | 5.78E-08 | 4.65E-05 | 1.71E-07 | 6.05E-06 | 1.15E-08 | 2.32E-05 | 8.5E-08- |
| Cd | 0.5 | 0.0125 | 2.95E-04 | 5.61E-05 | 1.13E-03 | 1.65E-04 | 9.70E-05 | 7.37E-06 | 3.71E-04 | 5.43E-05 |
| Mn | 1.4 | 0.96 | 4.89E-03 | 3.38E-05 | 1.7E-02 | 9.98E-05 | 4.52E-04 | 1.25E-06 | 1.73E-03 | 9.23E-06 |
| Hg | 0.3 | 0.3 | 1E-04 | 4.77E-04 | 3.84E-04 | 1.41E-03 | 1.0E-04 | 1.91E-04 | 3.84E-04 | 1.41E-03 |
| Н | | | 5.29E-03 | 5.67E-04 | 2.02E-02 | 1.67E-03 | 6.55E-04 | 1.99E-04 | 2.50E-02 | 1.47E-03 |

Table 5. Carcinogenic risk assessment (CR) of Cd in the groundwater of the wells at the study area.

| TOWNS | D _{ING} | | CR | CR | | | | |
|---------------|------------------|----------|----------|-------|----------|----------|--|--|
| | CW | ADULTS | CHILDREN | SFING | ADULTS | CHILDREN | | |
| Ahyiayem | 3.28E-03 | 9.88E-05 | 3.77E-04 | 6.1 | 1.62E-05 | 6.19E-05 | | |
| Odumasi Zongo | 7.33E-03 | 2.21E-04 | 8.43E-04 | 6.1 | 3.62E-05 | 1.38E-04 | | |
| Apeboaso | 4.9E-03 | 1.48E-04 | 5.64E-04 | 6.1 | 2.42E-05 | 9.24E-05 | | |
| Kwaakyewaso | 1.61E-03 | 4.85E-05 | 1.85E-04 | 6.1 | 7.95E-06 | 3.04E-05 | | |

to the USEPA database, a CR value exceeding 1 in a million (10⁻⁶) is considered significant. From the study, the CR of all the metals were below 10⁻⁶ with the exception of Cd which recorded its CR value above the threshold limit. This suggests that consuming water from the hand-dug wells in the study areas could pose a carcinogenic risk related to the concentration of Cd.

Conclusion

The study evaluated the water quality of hand-dug wells in the Asante Akyem Central District of Ghana. The objective of this study is to assess the water quality of hand-dug wells in 4 communities in the Asante Akyem Central district of Ghana and to evaluate its potential risk to human health in the district which is a small-scale gold mining area. The communities were

Apeboaso, Ahyiayem, Odumasi Zongo, and Kwaakyewaso. According to the PCA analysis, the sources of heavy metals in the hand-dug wells in the communities were from both natural and anthropogenic activities such as small-scale mining. There was no carcinogenic health risk to the communities with respect to Fe, Mn, and Hg through ingestion and dermal contact because the hazard quotients and health hazard indices recorded in both adults and children were below one (<1). However, Cd exhibited carcinogenic health risk because its Cancer risk (CR) index exceeded 10-6 for both adults and children. This implies that there is a risk of cancer infection from ingesting water from the hand-dug wells in the study areas. According to the analysis of the Water Quality Index (WQI), the wells at Ahyiayem, Apeboaso, and Kwaakyewaso recorded indexes that were between 15 and 50, signifying that the hand

dug wells in these communities are safe for human consumption. However, about 90% of the wells at Odumasi Zongo recorded WQI values that were between 80 and 320. This means the hand dug wells at Odumasi Zongo are highly polluted and not safe for human consumption. This study will be helpful for effective groundwater management programs in the Asante Akyem Central District of Ghana and for other mining communities in the country. This study will also trigger further research on heavy metal speciation, bioaccumulation, and their mode of transport in groundwater.

Merits of the study, limitations, and perspectives for future research

The overall findings of this research unequivocally demonstrate that both natural and human activities can impact the physical and chemical properties of groundwater. This study has significant benefits as it equips decision-makers with a useful tool to promptly identify the communities in the Asante Akyem Central District that are exposed to high levels of heavy metal contamination based on the current study's results and findings. Since there is a scarcity of literature examining the health risks associated with heavy metal contamination in the Asante Akyem Central District, this study is noteworthy for being the first to address this topic and makes a substantial contribution to the global body of knowledge. The study employed an integrated approach to investigate the sources of groundwater contamination, which yielded robust results. However, it is important to acknowledge some limitations of the study that can be addressed in future research. For instance, the study did not account for the influence of long-term seasonal variations, so future studies should consider this aspect. Furthermore, the study was also constrained by the limited number of water samples analyzed, suggesting that future research should encompass a greater number of hand-dug wells and other groundwater sources to allow for more comprehensive and comparative analyses. Also, for improved monitoring of the groundwater contamination, machine learning and other artificial intelligence techniques are recommended for future studies. Lastly, it is crucial for water management authorities in the region to enhance their strategies and awareness efforts to safeguard groundwater from human-related activities, such as illegal small-scale mining, especially considering the anticipated population growth in the area.

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About the Author

Augustine Owusu Sekyere is a Ph.D. candidate whose research interest is in water quality analysis. He conducts research on water quality, waste management, and environmental sanitation in Ghana. This work is one of his outputs targeting the effect of small-scale mining on the water quality in some mining communities in Ghana.

Public Interest Statement

Identifying the consequence of illegal small-scale mining on water supply is important in informing mitigation strategies and policies. Residents in these mining areas are viewed to be at a considerable risk of exposure to toxic heavy metals. It is therefore important to assess the pollution risks and the spatial distribution of heavy metals and other water quality parameters in these illegal small-scale mining towns. In this research paper, we interrogate the quality of water in handdug wells in communities such as Odumasi Zongo, Apeboaso, Ahyiayem, and Kwaakyewaso which are all in the Asante Akyem municipality. Our research reveals a high concentration of heavy metals(metalloids) and other water quality in the communities that have high small-scale mining activities compared to the rest. Nonetheless, our findings also suggest that natural geogenic processes can also contribute to the dense accumulation of heavy metals in the localities.

Data Availability Statement

The authors confirm that the data supporting the findings of this research are available within this research article.

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