Human Exposure Risks Assessment of Heavy Metals in Groundwater within the Amansie and Adansi Districts in Ghana using Pollution Evaluation Indices

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Abstract

Non-carcinogenic risk assessment was done using Hazard Quotient ($HQ_{ing/derm}$) and Hazard Index ($HI_{ing/derm}$) following USEPA methodology for a total of 59 boreholes and 12 hand dug wells sampled between July and October 2012. The objective was to assess the potential human health risks caused by exposure to non-carcinogenic heavy metals and estimate the potential environmental risk exposure in order to ensure the health safety of consumers within the Amansie and Adansi Districts. The results shows that, the heavy metal abundance in groundwater within the districts is in the order: Fe > Mn > As > Zn > Cu = Pb > Cd > Hg, for borehole water and Fe > As > Mn > Zn > Cu > Cd > Pb > Hg, for well water. The percentage contributions are: Fe (60%), Mn (20%), As (7%), Zn (5%), Cu (4%), Pb (4%), Cd (0%) and Hg (0%). The results also show that, the potential non-carcinogenic risks of exposure ($HQ_{ing/derm}$) posed by Fe, Mn, Cd, Cu, Zn, Pb, As and Hg within a single route of exposure via ingestion or dermal contact is 3.30 x 10^{-2}, 1.40 x 10^{-1}, 5.00 x 10^{-4}, 3.70 x 10^{-2}, 3.00 x 10^{-1}, 3.60 x 10^{-2}, 3.00 x 10^{-4} and 3.00 x 10^{-4} respectively for both adults and children, suggesting a decreasing order of Zn > Mn > Cu > Pb > Fe > Cd > As = Hg, for borehole water, and Zn > Mn > Cu > Fe > Cd > As = Hg, for well water. The concerns for potential human health risks caused by exposure to non-carcinogenic heavy metals for Fe, Mn, Cd, Cu,Zn, Pb, As, and Hg are: 6.0 x10^{-2}, 2.56 x 10^{-1}, 9.15 x 10^{-4}, 6.77 x 10^{-2}, 5.49 x 10^{-1}, 6.59 x 10^{-2}, 5.49 x 10^{-4}, 5.49 x 10^{-4} for boreholes, and 6.46 x 10^{-2}, 2.74 x 10^{-1}, 9.79 x10^{-4}, 7.25 x 10^{-2}, 5.88 x 10^{-1}, 5.88 x 10^{-4}, 5.88 x 10^{-4} for well water, suggesting that there is no concern for potential human health risks caused by exposure to non-carcinogenic toxic heavy metals in groundwater within the Districts (i.e HQ/HI <1). The study further show that, the risk index factor (Ri) for heavy metals was in the order: Hg > As > Cd > Pb > Cu > Zn, for borehole water, and As > Cd > Cu > Zn for well water, suggesting that, groundwater within the Districts is potentially threatened by anthropogenic activities primarily, mining activities where, chemicals such as arsenic (As) and mercury (Hg) are used to recover gold from its amalgam. Based on the classification of environmental risk using comprehensive risk factor (CRI), borehole water within the districts could be classified as very high risk, while, well water could be classified as high risk. Generally, the main environmental heavy metals that poses pollution risk in groundwater within the Districts were Hg, As and Cd and contributed mostly to the Risk index factor (Ri).

Introduction

Heavy metals are a group of contaminants which have been identified as posing serious threat to aquatic environments and humans, even at trace concentrations (Vergas et al., 2001), and are known for their toxicity and persistence in the environment (Duruibe et al., 2007; Ahmad et al., 2010). Due to their refractory characteristics and bioaccumulation, heavy metal contamination of surface and groundwater resources is increasingly becoming a major global environmental problem as evidenced by the numerous previous studies such as; Vodela et al., 1997; Pawar et al., (1999); Koukal et al., (2004); Marcovecchio et al., 2007; Akhilesh et al., (2009); Öztürk et al., 2009; Ahmad et al., (2010); Aktar et al., (2010); Mushtaq et al., (2014). The anthropogenic activities responsible for heavy metal contamination are varied. Notable among them are; landfill, mining, tanning, textile and various cottage industries (Bhuiyan et al., 2011). The problem of heavy metal contamination of surface and groundwater is more severe in developing countries due to the inadequate and non-continuous monitoring of these water resources. In Ghana, the problem is even more heightened as a result of the scattered large-scale mining and illegal small-scale miming

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activities popularly known as *"Galamsey"* along the Ashanti gold belt. *"Galamsey"* is the amalgamation of gold ore with Hg to extract the fine gold. This has necessitated numerous studies previously to determine the presence of different heavy metals, their sources and levels of contamination in surface and groundwater as well as other environmental matrices in Ghana. These studies include but not limited to; Carboo et al., (1997); Kumar et al., (2004); Manu et al., (2004); Obiri (2007); Kuma (2007); Armah et al., (2010). These studies have shown that the occurrence of toxic heavy metals in groundwater in areas possessing mineral deposits and associated mining activities are common.

Even though mineral extraction especially gold mining has contributed substantially to the socio- economic development of Ghana, its associated environmental degradation through ore transportation, refining, smelting and disposal of tailings and wastewaters is a cause of concern to the state.

In recent times, heavy metal contamination studies in water resources and in other matrices is not only focused on presence, sources and levels but also includes the possible risks to human health. This is because; long-term exposure of humans to toxic heavy metals may cause severe disruptions in the normal functioning of the organs. For instance, Pb has been reported to be linked extensively to pregnancy disruption, cardiovascular diseases, early membrane rupture and erectile dysfunction (USEPA, 1986). Pb exposure in children and adults is capable of causing a wide range of health problems including convulsion, renal failure, coma, and death (USATSDR, 1999). Pb toxicity in children have still not been well researched even though its toxicity poses risk to fetuses via mobilization of long-term skeletal Pb accumulation in pregnant women (Silbergeld, 1991). Cd has also been, linked to several cases of food poisoning. Even at low concentrations, Cd is capable of causing kidney damage through adverse changes in the arteries of human kidney (Rajappa, 2010). In the human blood stream, Cd is capable of biochemically replacing Zn resulting in high blood pressures (Rajappa, 2010). It is also worthy to note that, the World Health Organization (WHO) has listed As, Pb, Hg and Cd in its list of ten chemicals as a major public health concern.

In this regard, several studies on the human health effects of heavy metals in drinking water have been conducted previously (Yu et al., 2010; Badr et al., 2011; Zhang et al., 2013; Boateng et al., 2015; Demir et al., 2015; Tay et al., 2016; Elumalai et al., 2017).

Some heavy metals at minute concentrations are required for normal functioning of the human body, however, long-term direct or indirect exposure to excess levels of these heavy metals may lead to health risks. For instance, heavy metals such as Zn, Co and Cu are essential for the normal functioning of many organs including growth of the body, while, excessive quantity of metals such as Cd, Pb ard Mn are potential poisons to human health and aquatic organisms (Ouyang et al., 2002). According to Storelli et al. (2005), heavy metals when in excess either, essential or non-essential are harmful to biotic component of an ecosystem.

The Amansie and Adansi Districts in the Ashanti Region of Ghana is endowed with water resources, which serves as potable sources for drinking water. However, the districts are located within the Ashanti Gold Belt, where both "large-scale" and "small-scale" – *galamsey* activities using chemicals such as arsenic (As) and mercury (Hg) to recover gold takes place. It is therefore, hypothesized that, mining activities and natural geochemical processes could introduce toxic heavy metals of serious health concerns in ground and surface water resources within these districts.

It is against this background that, this study seeks to (I) identify and quantify the human exposure risks of selected heavy metals likely to be associated with the consumption of surface and groundwater resources; (2) assess the potential human health risks caused by exposure to non-carcinogenic heavy metals; (3) estimate the potential environmental risk exposure, in order to ensure the health safety of consumers within the Amansie and Adansi Districts.

Health Risk Assessment of heavy metals

Long-term exposure to toxic heavy metals and other chemicals in the environment through ingestion, inhalation and dermal contact may pose potential risk to human health. Health risk assessment of environmental contaminants such as toxic metals have been used previously to estimate the nature and probability of adverse health effects in humans exposed to contaminants in environmental media (USEPA (1989); USEPA (2005); Khan et al., (2008). Risk assessment procedures are based on source-pathway-receptor models and involves the examination of site characteristics, environmental behavior and toxicity of the contaminant, its potential route of entry into the receptor (humans), exposure of the receptors to the contaminants and their response to the dose (Lee et al., 2005). According to Paustenbach, 2002; Wongsasuluk et al., 2014, risk assessment is the process of estimating the probability of occurrence of an event and the probable magnitude of adverse health effects on human exposure to environmental hazards over a specified time period. Risk assessment consists of hazard identification, exposure assessment, dose response and risk characterization (Lee et al., 2005).

Materials and methods

Study area

The Amansie and Adansi Districts lie between 6^{o} 00" and 6^{o} 30"N and 1^{o} 15" and 1^{o} 60"W (Figure 1). The area falls within the Ashanti Gold Belt, the most famous of all gold belts in Ghana and extends over 200 km from Akanko, near the coast, through Prestea and Obuasi to Konongo within the central parts of the country.

Climate and Vegetation

According to Dickson and Benneh (1980), the climate is within the wet semi-equatorial climatic zone of Ghana. Two rainy seasons span the districts, with the major rainy season between May and July while, the minor rainy season is between September and October (Dickson and Benneh, 1980). The area is fairly, humid with an average monthly relative humidity of, 75 - 80 % during the two rainy seasons (Dickson and Benneh, 1980). According to Dickson and Benneh (1980), annual rainfall ranges between 1250 – 1750 mm with a mean annual temperature of about 25.7^{o}C. The vegetation is principally, a semi-deciduous and degraded forest consisting of limited species of hardwood, which are generally harvested as lumber (Dickson and Benneh, 2004). Large quantities of the original forest have been depleted resulting in secondary forest in most areas due to the rapid expansion of the cocoa industry in this vegetation belt, (Dickson and Benneh, 2004). The secondary vegetation is made up of shrubs, soft woody plants and climbers (Dickson and Benneh, 2004).

the Lower Birimian is pelitic in nature and consists of silts and muds with beds of coarser sediments (Kesse, 1985). According to Kesse (1985), the Upper Birimian is basically of

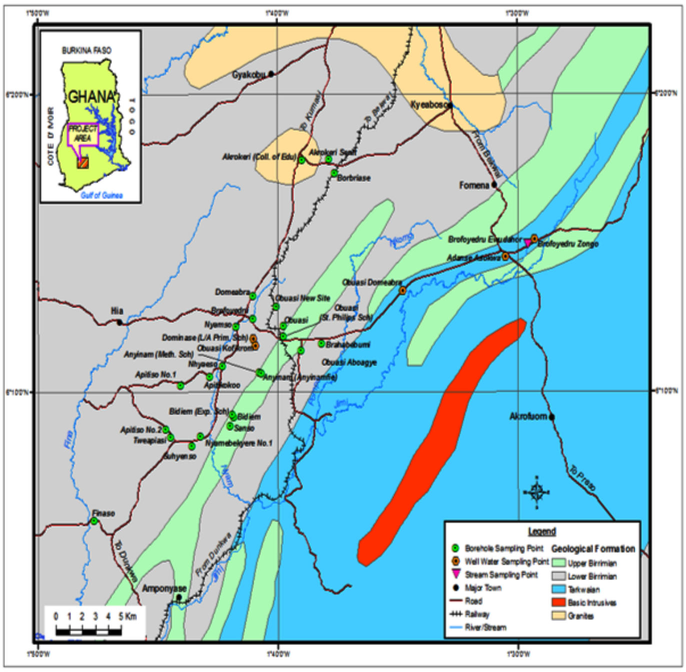


Figure 1 Map of the Amansie and Adansi Districts (insert map of Ghana) with the different geological settings showing sampling communities

Geology and soil

The ochrosol soils contain high quantities of nutrients and are generally alkaline (Dickson and Benneh, 2004). The soil supports numerous tree crops including cocoa. According to Dickson and Benneh (2004) nearly, all the cocoa in Ghana is grown in these soils. Dickson and Benneh (2004) reported that, the area is principally characterized by forest ochrosol soils which, develop over similar highly weathered parent materials. The Amansie and Adansi Districts are located within the Birimian Supergorup and Tarkwaian System.

Birimian Supergroup

The rocks of the Birimian comprises of the Lower and Upper Birimian Supergroup (Kesse, 1985). A major unconformity separates the Birimian Supergroup from the Tarkwaian system (Kesse, 1985). Essentially, pyroclastic and volcanic in nature. The rocks consist of bedded group of tuffs, sediments and mafic lavas (greenstones), jointly with minor bands of phyllite that include a zone of manganiferous phyllites containing manganese ore (Kesse, 1985). Kesse (1985) also reported that, batholithic masses of granite and gneiss intrude the sequence. The mostly argillaceous sediments have metamorphosed to schist, slate and phyllite jointly with some interbedded greywacke (Kesse, 1985).

The Tarkwaian

According to Junner et al., (1942), the Tarkwaian essentially consists largely of fining-upwards broad clastic series of argillaceous and arenaceous sediments. Within the lower members of the system, these sediments are together with two well-defined zones of pebbly beds and conglomerates (Junner et al., 1942). The Tarkwaian rocks consist fairly of metamorphosed, shallow-water and sedimentary strata (Junner et al., 1942). They are generally quartzite, sandstone, shale and conglomerate resting unconformably on and obtained from the Birimian supergroup rocks (Junner et al., 1942). Junner et al., (1942) reported that, thick laccoliths and sills of epidiorite infringe the rocks. Reminiscent of the Birimian rocks, they are folded along axes that trend northeast (Junner et al., 1942).

Sampling and analysis

Water samples were collected from boreholes and shallow wells during the dry and wet seasons in 2012. A total of 59 boreholes and 12 hand dug wells were sampled between July and October 2012. During sample collection, the design of sampling protocols reported by Claasen (1982) and Barcelona et al., (1985) were rigorously followed. The bottles were cleaned at the Environmental Chemistry and Sanitation Engineering Laboratories of the Council for Scientific and Industrial Research-Water Research Institute (CSIR-WRI) in Accra using detergent and allowing them to stand for at least 24 hours. The bottles were then, rinsed three times with distilled and de-ionized water. The water samples were acidified to a pH < 2 using Conc HNO_3. On-site measurements of pH were carried out using a Hach Sens ion 1 Meter. The water samples were then stored on ice in an ice-chest and transported to the CSIR -Water Research Institute laboratories in Accra, stored in a refrigerator at a temperature of < 4^{o}C and analyzed within one week. The concentrations of Cu, Fe, Mn, Cd, Zn, Pb were determined using Agilent 240FS Atomic Absorption Spectrometer by direct aspiration of water samples into an air acetylene flame. As was determined using a hydride generator attached to the Atomic Absorption Spectrometer, while, Hg was determined using AAS- Cold Vapour (VGA77) attached to the Atomic Absorption Spectrometer. The detection limits for the selected heavy metals were; Cu (0.02), Cd (0.002), Mn (0.005), Fe (0.01), Pb (0.005), Hg (0.0001), As (0.001), Cd (0.002).

Quality Control

To ensure the accuracy of the heavy metal data, Standard Reference material (NIVA 1042L) for all heavy metals (except, Hg and As) from the Norwegian Institute for Water Resources were analyzed alongside the water samples. In the case of Hg and As, Internal Control Standards were prepared using high purity commercially prepared reagents. All glass wares used during analysis were thoroughly washed by soaking them in 5% HNO_3 overnight followed by thorough rinsing in distilled water three times before use. To ensure reproducibility, readings were replicated after every ten samples.

Data Analysis

The study employed descriptive statistics as well as the human health risks assessment methods recommended by the USEPA (1989) as proposed in the Risk Assessment Guidance for Superfund (RAGS), which, provides guidance, tools and databases useful for preparing human health, and ecological risk assessment studies. A risk index factor due to the presence of toxic metal in water as proposed by Hakanson (1980) was also, employed.

Estimation of the Pollution Indices and Degree of Metal Contamination

According to the USEPA (1989) as proposed in the Risk Assessment Guidance for Superfund (RAGS) methodology, the numeric expressions for risk assessment may be presented as in Eqns 1 and 2:

$$D_{ing} = \frac{C_{water} \times IR \times EF \times ED}{BW \times AT} \qquad (1)$$

$$D_{derm} = \frac{C_{water} \times SA \times K_p \times ET \times EF \times ED}{BW \times AT} \qquad (2)$$

Where, D_{ing} is defined as the average daily dose (exposure dose) via ingestion of water (μg/kg-day); D_{derm} is defined as average daily dose (exposure dose) via dermal absorption (μg/kg-day); C_{water} is defined as the estimated concentration of metals in surface water (μg/L). The other input parameters are presented in Table 1, while, the dermal permeability coefficient (Kp) of heavy metals as proposed by USEPA (1989) are presented in Table 2. Table 3 presents the Oral reference dose of the various heavy metals used for the determination of toxicity responses.

TABLE 1
Input parameters to characterize the Average Daily Dose

Exposure parameters	Symbols	Units	Value	
			Adults	Children
Ingestion rate	IR	L/day	2.2	1.8
Exposure frequency	EF	Days/year	350	350
Exposure duration	ED	Years	70	6
Body weight	BW	Kg	70	15
Average time	AT	Years	25550	2190
Exposed skin area	SA	cm^2	18000	6600
Exposure time	ET	hrs/day	0.58	1.0
Unit conversion factor	CF	L/cm^3	0.001	0.001

(After Wongsasuluk et al., 2014)

TABLE 2
Dermal permeability coefficient of heavy metals

Heavy Metal	Dermal permeability coefficient (Kp) in cm/h
Cd	0.001
Fe	0.001
Cu	0.001
Mn	0.001
Zn	0.0006
Pb	0.004
As	0.001
Hg	1.00

TABLE 3
Oral reference dose of the various heavy metals used for the determination of toxicity responses

Heavy Metal	Oral RfD (mg/kg/day)
Cd	5.0×10^{-4}
Cu	4.0×10^{-2}
Pb	3.5×10^{-3}
Zn	3.0×10^{-1}
Fe	7.0×10^{-1}
Mn	1.4×10^{-2}
As	3.0×10^{-4}
Hg	3.0×10^{-4}

Potential non-carcinogenic risks for exposure to contaminants were assessed by comparison of the calculated contaminant exposures with respect to each exposure route and the reference dose (RfD) so as to produce the hazard quotient (HQ). The HQ may be defined as in Eqn 3 (USEPA 1989):

$$HQ_{ing/derm} = \frac{D_{ing/derm}}{RfD_{ing/derm}} \quad (3)$$

where, $HQ_{ing/derm}$ is defined as the hazard quotient via ingestion or dermal contact and is unitless, and $RfD_{ing/derm}$ is defined as the oral/dermal reference dose in μg/kg-day. The RfD_{ing} and RfD_{derm} values were obtained from the literature elsewhere (USEPA 2010; Li and Zang, 2010).

The hazard quotient (HQ) is a numeric estimate of the systemic toxicity potentially posed by a single element within a single route of exposure. According to Amirah et al., (2013); Naveedullah et al., (2014); Ayantobo et al., (2014), the toxic risk due to potentially hazardous substances in the same environmental media is presumed to be additive and the arithmetic sum of individual target hazard quotient and is equal to the hazard index (HI). To estimate the overall potential for non-carcinogenic effects posed by potentially hazardous substances, the computed HQs for each element are integrated and expressed as a hazard index (HI) as defined by Eqn 4:

$$HI = \sum_{i=1}^{n} HQ_{ing/derm} \quad (4)$$

where, $HI_{ing/derm}$ is defined as the hazard index via ingestion or dermal contact (unitless).

The metal pollution index is then, defined by HQ/HI (Prasad et al., 2001). According to the USEPA (1989) where, HQ/HI < 1, there is no concern for potential human health risks caused by exposure to non-carcinogenic elements and where, HQ/HI >1, there may be a concern for potential human health risks caused by exposure to non-carcinogenic elements. Other metal pollution evaluation method include the method known as the degree of contamination. The degree of contamination (C_d) method used as reference for the estimation of the extent of metal pollution (Rubio et al., 2000). In this method, the quality of water is, evaluated by computing the extent of contamination using the sum of the contamination factors of each metal component exceeding the upper permissible limit (Boateng et al., 2015). The C_d method thus, summarizes the combined effects of a number of quality parameters considered to be, unsafe in drinking water (Boateng et al., (2015). Backman et al., (1997) proposed that, the degree of toxic heavy metal contamination (C_d) may be presented as in Eqn 5:

$$Cd = \sum_{i=1}^{n} C_{fi} \quad (5)$$

where, C_{fi} is the contamination factor calculated using Eqn 6:

$$C_{fi} = \frac{CMi}{CSi} \quad (6)$$

where, CM_i, and CS_i, are the analytical value and upper permissible concentration for the i^{th} component respectively. The degree of toxic heavy metal contamination in any water resource have been categorized as, low (Cd < 1), medium (C_d =1-3), and high (C_d > 3) (Rubio et al., (2000).

In order to compute the overall potential for non-carcinogenic effects posed by potentially toxic heavy metals in groundwater from the study area, this study adopted the method proposed by USEPA (1989) in which the ratio of the hazard quotient (HQ) and the hazard index (HI) are evaluated (i.e HQ/HI) for each metal and its exposure effects calculated for adults and children and the concern for potential human health risks caused by exposure to non-carcinogenic toxic heavy metals (i.e HQ/HI <1 or HQ/HI>1) deduced from these ratios.

Estimation of potential environmental risks

A risk index factor due to the presence of toxic heavy metal in water was proposed by Hakanson (1980). According to Hakanson (1980), a risk index factor (R_i) for a toxic metal may be expressed as in Eqn 7:

$$\text{Risk index factor } (Ri) = Ti \times \text{OC}/\text{NOEC} \qquad (7)$$

where *Ti* is the toxicity coefficient of a given metal *i* (Hg = 40, Cd = 30, As = 10, Cu = Pb = 5, Zn = 1), OC is the mean concentration of metal and NOEC is the maximum allowable concentration (permissible limit).

The classification of the risk index factor (Ri) is as presented in Table 4 (Hakanson, 1980):

TABLE 4
Potential environmental risk of toxic trace metal in water using risk index factor

Range of Risk index factor (Ri)	Potential environmental risk
Ri < 1	No potential environmental risk
1 ≤ Ri < 40	Low potential environmental risk
40 ≤ Ri < 80	Moderate potential environmental risk
80 ≤ Ri < 160	Considerable potential environmental risk
160 ≤ Ri < 320	High potential environmental risk
Ri ≥ 320	Very high potential environmental risk

(After Hakanson, 1980)

The comprehensive risk index (CRI), which is the summation of risk index factor (Ri) is expressed as in Eqn 8:

$$\text{Comprehensive risk index (CRI)} = \Sigma^{n}{}_{i}\, Ri \qquad (8)$$

where, Ri is the risk factor for each metal.

The classification of the comprehensive risk index (CRI) is as presented in Table 5 (Hakanson, 1980):

TABLE 5
Classification of environmental risk using comprehensive risk factor

Range of comprehensive risk factor	Classification
CRI < 60	Low
60 ≤ CRI <120	Moderate
120 ≤ CRI < 240	High
CRI ≥ 240	Very high

(After Hakanson, 1980)

Results and Discussion

Table 6 presents the statistical summary of the heavy metal levels in groundwater within the Districts. Table 7 presents the summary of the non-carcinogenic heath risk assessment for the selected heavy metals in boreholes within the Amansie and Adansi Districts, while, Table 8 presents the summary of the non-carcinogenic health risk assessment for the selected heavy metals in well water within the Amansie and Adansi Districts. Table 9 presents the estimation of Risk index factor (Ri) and Comprehensive risk index (CRI) for borehole water in the Amansie and Adansi Districts and Table 10 presents the estimation of Risk index factor (Ri) and Comprehensive risk index (CRI) for well water in the Amansie and Adansi Districts , while, Table 11 presents the potential environmental risk in borehole and well water within the Districts.

The results show that the mean values of Fe, Cd, Pb, As and Hg for boreholes and Cd, and As for well water were above the WHO (2004) guideline values. Cd, Pb, As and Hg have been listed in its list of ten chemicals by the World Health Organization (WHO) as a major public health concern and therefore, should be of concern for the Institutions responsible for public health such as the Environmental Protection Agency (EPA) and the Health Authorities within the Districts. The heavy metal abundance in groundwater within the Districts is in the order: Fe > Mn > As > Zn > Cu = Pb > Cd > Hg for borehole water and Fe > As > Mn > Zn > Cu > Cd > Pb > Hg for well water. Fig 2, shows that the percentage heavy metal contributions in groundwater within the Districts are: Fe (60%), Mn (20%), As (7%), Zn (5%), Cu (4%), Pb (4%), Cd (0%) and Hg (0%). This trend suggests that, natural geochemical processes such as rock-water-soil interactions are, more pronounced in the water resources within the Amansie and Adansi Districts. Even though Fe and Mn are naturally occurring elements and are essential nutrients, they are toxic at very high levels. For instance, Manganese toxicity can result in permanent neurological disorders called manganism with symptoms such as impotence and loss of libido in men (Food and Nutrition Board/Institute of Medicine, 2001).Of the environmental heavy metals, As contribution to the water resources is relatively higher and suggests inputs from anthropogenic origin.

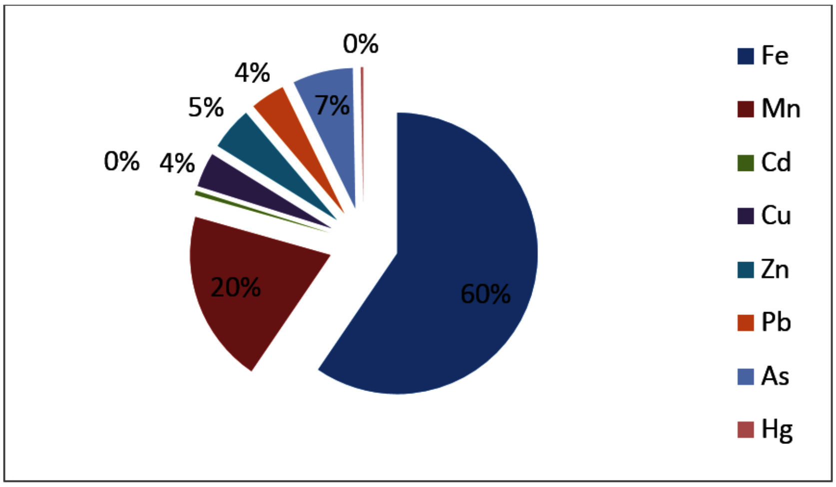


Figure 2 Percentage contribution of selected heavy metals in groundwater within the Amansie and Adansi Districts

TABLE 6

Statistical summary of heavy metal levels in groundwater within the Amansie and Adansi Districts

Element	Borehole water		Well water		WHO guideline (2004)
	Range	**Mean**	**Range**	**Mean**	
Fe	< 0.01- 5.1	0.60	< 0.01- 0.37	0.14	0.3
Mn	< 0.005 - 1.17	0.20	< 0.005 - 0.17	0.05	0.4
Cd	< 0.002 - 0.009	0.005	< 0.002 - 0.006	0.004	0.003
Cu	< 0.02 - 0.1	0.04	< 0.02 - 0.04	0.03	2.0
Zn	<0.005 -0.51	0.05	<0.005- 0.05	0.04	3.0
Pb	< 0.005 – 0.19	0.04	< 0.005 - 0.009	-	0.01
As	< 0.001 - 0.09	0.07	< 0.001 - 0.2	0.11	0.01 (p)
Hg	< 0.001 - 0.009	0.003	< 0.001	-	0.001(p)

TABLE 7

Summary of the non-carcinogenic heath risk assessment for selected heavy metals in boreholes within the Amansie and Adansi Districts

Heavy metal	Dderm		Ding		Ding/Dderm		RfD	RfDing/derm		HQing/derm		HQ/HI	
	Adults	Children	Adults	Children	Adults	Children	(µg/kg-day)	Adults	Children	Adults	Children	Adults	Children
Fe	5.60×10^{1}	1.21×10^{3}	1.18×10^{4}	3.31×10^{2}	2.11×10^{2}	2.73×10^{-1}	7.00×10^{-1}	6.39×10^{3}	8.26×10^{0}	3.30×10^{-2}	3.30×10^{-2}	6.0×10^{-2}	6.04×10^{-2}
Mn	1.87×10^{1}	4.05×10^{2}	3.93×10^{3}	1.10×10^{2}	2.11×10^{2}	2.73×10^{-1}	1.40×10^{-1}	1.51×10^{3}	1.95×10^{0}	1.40×10^{-1}	1.40×10^{-1}	2.56×10^{-1}	2.56×10^{-1}
Cd	9.34×10^{-1}	2.02×10^{1}	9.84×10^{1}	2.76×10^{0}	1.05×10^{2}	1.36×10^{-1}	5.00×10^{-4}	2.11×10^{5}	2.73×10^{2}	5.00×10^{-4}	5.00×10^{-4}	9.15×10^{-4}	9.15×10^{-4}
Cu	2.24×10^{0}	4.86×10^{1}	7.87×10^{2}	2.21×10^{1}	3.51×10^{2}	4.55×10^{-1}	3.70×10^{-2}	9.49×10^{3}	1.23×10^{1}	3.70×10^{-2}	3.70×10^{-2}	6.77×10^{-2}	6.77×10^{-2}
Zn	1.87×10^{1}	4.05×10^{2}	9.84×10^{2}	2.76×10^{1}	5.27×10^{1}	6.82×10^{-2}	3.00×10^{-1}	1.76×10^{2}	2.27×10^{-1}	3.00×10^{-1}	3.00×10^{-1}	5.49×10^{-1}	5.49×10^{-1}
Pb	1.49×10^{1}	3.24×10^{2}	7.87×10^{2}	2.21×10^{1}	5.27×10^{1}	6.82×10^{-2}	3.60×10^{-2}	1.46×10^{3}	1.89×10^{0}	3.60×10^{-2}	3.60×10^{-2}	6.59×10^{-2}	6.59×10^{-2}
As	6.54×10^{0}	1.42×10^{2}	1.38×10^{3}	3.86×10^{1}	2.11×10^{2}	2.73×10^{-1}	3.00×10^{-4}	7.02×10^{5}	9.09×10^{2}	3.00×10^{-4}	3.00×10^{-4}	5.49×10^{-4}	5.49×10^{-4}
Hg	2.80×10^{2}	6.07×10^{3}	5.90×10^{1}	1.66×10^{0}	2.11×10^{-1}	2.73×10^{-4}	3.00×10^{-4}	7.02×10^{2}	9.09×10^{-1}	3.00×10^{-4}	3.00×10^{-4}	5.49×10^{-4}	5.49×10^{-4}

TABLE 8

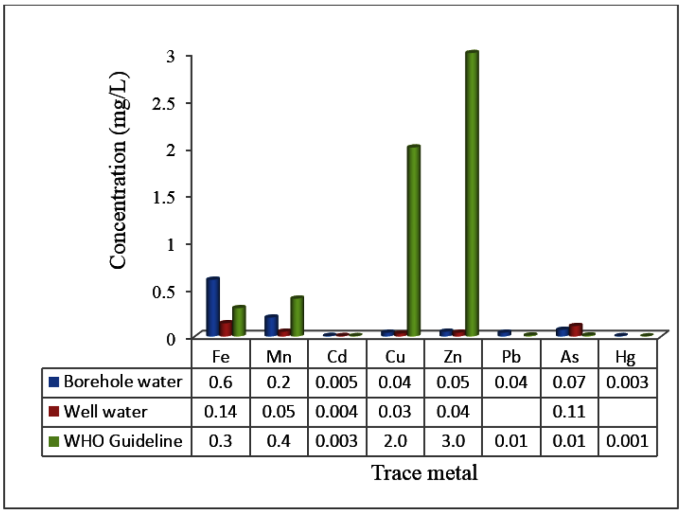
Summary of the non-carcinogenic heath risk assessment for selected heavy metals in well water within the Amansie and Adansi Districts

Heavy metal	Dderm		Ding		Ding/Dderm		RfD	RfDing/derm		HQing/derm		HQ/HI	
	Adults	Children	Adults	Children	Adults	Children	(µg/kg-day)	Adults	Children	Adults	Children	Adults	Children
Fe	1.31×10^{1}	2.83×10^{2}	2.75×10^{3}	7.73×10^{1}	2.11×10^{2}	2.73×10^{-1}	7.00×10^{-1}	6.39×10^{3}	8.26×10^{0}	3.30×10^{-2}	3.30×10^{-2}	6.46×10^{-2}	6.46×10^{-2}
Mn	4.67×10^{0}	1.01×10^{2}	9.84×10^{2}	2.76×10^{1}	2.11×10^{2}	2.73×10^{-1}	1.40×10^{-1}	1.51×10^{3}	1.95×10^{0}	1.40×10^{-1}	1.4×10^{-1}	2.74×10^{-1}	2.74×10^{-1}
Cd	7.47×10^{-1}	1.62×10^{1}	7.87×10^{1}	2.21×10^{0}	1.05×10^{2}	1.3×10^{-1}	5.00×10^{-1}	2.11×10^{5}	2.73×10^{2}	5.00×10^{-4}	5.00×10^{-4}	9.79×10^{-4}	9.7×10^{-4}
Cu	1.68×10^{0}	3.64×10^{1}	5.90×10^{2}	1.66×10^{1}	3.5×10^{2}	4.55×10^{-1}	3.70×10^{-2}	9.49×10^{3}	1.23×10^{1}	3.70×10^{-2}	3.70×10^{-2}	7.25×10^{-2}	7.25×10^{-2}
Zn	1.49×10^{1}	3.24×10^{2}	7.87×10^{2}	2.21×10^{1}	5.27×10^{1}	6.82×10^{-2}	3.00×10^{-1}	1.76×10^{2}	2.27×10^{-1}	3.00×10^{-1}	3.00×10^{-1}	5.88×10^{-1}	5.88×10^{-1}
Pb	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
As	6.54×10^{0}	1.42×10^{2}	1.38×10^{3}	3.86×10^{1}	2.11×10^{2}	2.73×10^{-1}	3.00×10^{-4}	7.02×10^{5}	9.09×10^{2}	3.00×10^{-4}	3.00×10^{-4}	5.88×10^{-4}	5.88×10^{-4}
Hg	2.80×10^{2}	6.07×10^{3}	5.90×10^{1}	1.66×10^{0}	2.11×10^{-1}	2.73×10^{-4}	3.00×10^{-4}	7.02×10^{2}	9.09×10^{-1}	3.00×10^{-4}	3.00×10^{-4}	5.88×10^{-4}	5.88×10^{-4}

NA-not available

From Fig 3, Mn, Cu and Zn do not seem to be of public concern in the water resources within the Districts. According to Duruibe et al., (2007) and Ahmad et al., (2010), some heavy metals are known for their toxicity and persistence in the environment. Literature also indicates that, the World Health Organization (WHO) has listed As, Pb, Hg and Cd in its list of ten chemicals as a major public health concern. Thus, the need to monitor the long-term health impact of these heavy metals on the consuming public within the Districts is paramount.

The hazard quotient (HQ) for each heavy metal was then integrated and expressed as a hazard index (HI) in order to assess the overall potential for non-carcinogenic risks posed by the total toxic effect of the heavy metals. The results show that, the potential non-carcinogenic risks of exposure ($HQ_{ing/derm}$) which is the estimate of the systemic toxicity potential posed separately by Fe, Mn, Cd, Cu, Zn, Pb, As and Hg within a single route of exposure via ingestion or dermal contact were: 3.30×10^{-2}, 1.40×10^{-1}, 5.00×10^{-4}, 3.70×10^{-2}, 3.00×10^{-1}, 3.60×10^{-2}, and 3.00×10^{-4}, for



	Fe	Mn	Cd	Cu	Zn	Pb	As	Hg
Borehole water	0.6	0.2	0.005	0.04	0.05	0.04	0.07	0.003
Well water	0.14	0.05	0.004	0.03	0.04		0.11	
WHO Guideline	0.3	0.4	0.003	2.0	3.0	0.01	0.01	0.001

Figure 3 Bar graph of the heavy metal concentrations compared to WHO

The exposure dose via ingestion (D_{ing}) of water and dermal (D_{derm}) absorption in μg/kg-day for adults and children were computed using the concentration of the estimated metals in groundwater (μg/L), the ingestion rate (L/day), the exposure frequency (days/year), average body weight (kg), the averaging time (days), the exposed skin area (cm^2), the exposure time (h/day), the unit conversion factor (L/cm^3), and the dermal permeability coefficient (cm/h) (Tables 1 and 2). Using the reference oral dose (RfD) as in Table 3, the hazard quotient ($HQ_{ing/derm}$) for each heavy metal was computed to assess the potential non-carcinogenic risks (Tables 7 and 8). both adults and children as well as for borehole well water (Tables 5 and 6). This suggests a decreasing order of Zn > Mn > Cu > Pb > Fe > Cd > As = Hg, for borehole water and Zn > Mn > Cu > Fe > Cd > As = Hg, for well water. Thus, the potential non-carcinogenic risks of exposure for both borehole and well water follows similar trend. The results show that the hazard quotient (HQ) values of all heavy metals were <1 for both borehole and well water and therefore, suggests that, there are no potential health risks from exposure to these heavy metals in groundwater within the Districts.

The concerns for potential human health

risks (HQ/HI) caused by exposure to non-carcinogenic heavy metals as calculated for adults and children for Fe, Mn, Cd, Cu,Zn, Pb, As, and Hg were: 6.0×10^{-2}, 2.56×10^{-1}, 9.15×10^{-4}, 6.77×10^{-2}, 5.49×10^{-1}, 6.59×10^{-2}, 5.49×10^{-4}, 5.49×10^{-4} for boreholes (Table 5), while, that for wells (with exception of Pb) were: 6.46×10^{-2}, 2.74×10^{-1}, 9.79×10^{-4}, 7.25×10^{-2}, 5.88×10^{-1}, 5.88×10^{-4}, 5.88×10^{-4} (Table 6). The trend of potential human health risk (HQ/HI) in boreholes within the Districts was in the order: Zn > Mn > Cu > Pb > Fe > Cd > As = Hg (Fig 4), while, the trend of potential human health risk (HQ/HI) in well water within the Districts was in the order: Zn > Mn > Cu > Fe > Cd > As = Hg (Fig 5). Thus, similar trends exist for the potential for human health risks in both boreholes and well water. Computed values for all the HQ/HI ratios are less than 1 (i.e HQ/HI<1) for both boreholes and wells. According to the USEPA (1989) where, HQ/HI < 1, there is no concern for potential human health risks caused by exposure to non-carcinogenic elements. This suggests that, there is no concern for potential human health risks caused by exposure to non-carcinogenic toxic heavy metals in groundwater within the Amansie and Adansi Districts. Consistent with this study, the trend of overall potential for non-carcinogenic risks posed by more than one element (HI) in drinking water resources with previous studies such as Nasrabadi (2015)-Tehran; Abdul et al., (2016) – Zanzibar Island; Tay et al., (2016)- Lower Pra Basin, Ghana; Muhammed et al., (2011)-Kohistan region, northern Pakistan; Çelebi et al., (2014)-Melen watershed, Turkey; Li (2010)-upper Han River, China; show that, the overall potential for non-carcinogenic risks posed by more than one element (HI) in most drinking waters is less than one (i.e HI <1).

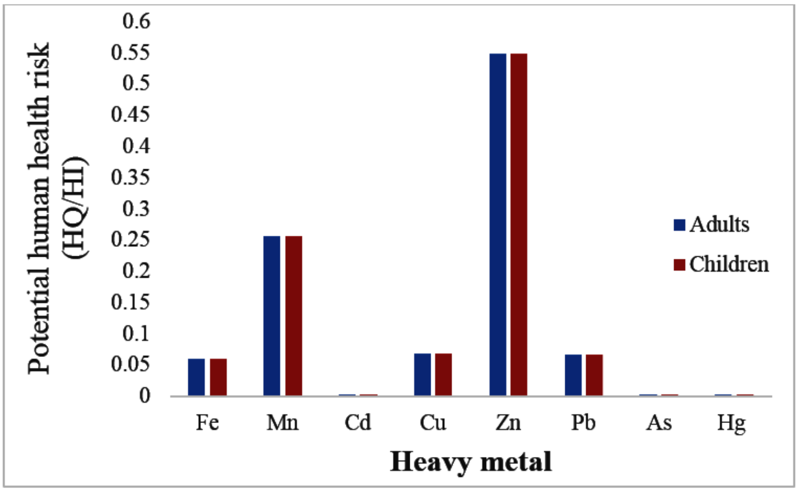


Figure 4 Potential human health risk posed by heavy metals in boreholes within the Amansie and Adansi Districts

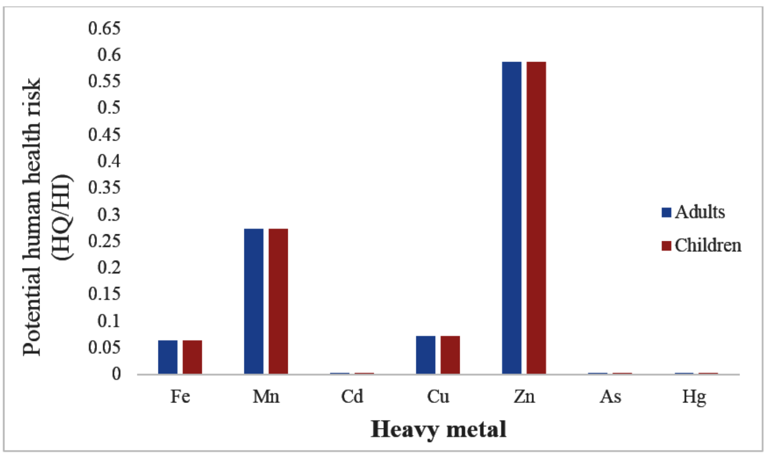


Figure 5 Potential human health risk posed by heavy metals in well water within the Amansie and Adansi Districts

Generally, the trend of the average daily dose for Zn, Cu, Fe, and Cd in water sources is: Zn > Cu >Fe > Cd (Abdul et al., 2016). With respect to severity of toxicity, Cd is highly toxic, and therefore, this trend does not show alarming situation in the context of Cd risk in drinking water sources due to the factors that governs severity of toxicity such as dose, nutrition, age and lifestyle. However, this trend might not guarantee the absence of human health risk. This study however, recorded a trend of average daily dose of: Fe < Zn > Cu > Cd though consistent with severity of toxicity in relation to Cd. This suggests low degree for potential human health risks caused by exposure to non-carcinogenic heavy metals in groundwater within the districts, and therefore, consumption of groundwater within the Amansie and Adansi Districts pose little or no adverse concerns for potential human health risks caused by exposure to non-carcinogenic elements

With respect to the World Health Organization (WHO) list of ten chemicals considered as a major public health concern which lists As, Pb, Hg and Cd as major public health concern, groundwater resources which serve as drinking water sources to the communities within the Amansie and Adansi Districts have As, Pb, Hg and Cd levels which do not pose public health concerns based on available data on heavy metals from this study.

Assessment of potential environmental risks

The potential environmental risk of groundwater within the Districts was estimated using Risk index factor (Ri) and the Comprehensive risk index (CRI). The standardized response coefficient for the toxicity of heavy metals, as proposed by Hakanson (1980), was adopted as the evaluation criteria. The corresponding coefficients based heavy metal toxicity are: Hg = 40, Cd = 30, As = 10, Cu = Pb = 5, Zn = 1. Tables 9 and 10 presents the degree of environmental risk associated with boreholes and wells within the Amansie and Adansi Districts respectively. From Table 9, the Risk index factor (Ri) for the heavy metals in borehole water was in the order: Hg > As > Cd > Pb > Cu > Zn. Table 10 also shows that, the Risk index factor for well water was in the order: As > Cd > Cu > Zn. Thus, the trend for potential environmental risk for groundwater (both borehole and well water) show that, the groundwater within the Districts is potentially threatened by anthropogenic activities primarily, mining activities, where, chemicals such as As and Hg are used to recover gold from its amalgam. Nevertheless, other anthropogenic activities also takes place, where, Cd, Cu and Zn could also find their way into groundwater within the Districts. The Ri for the individual heavy metals in borehole water show that, Cu (Ri = 0.1) and Zn (Ri = 0.017) have no potential environmental risks, Pb (Ri = 20) have low potential environmental risk, Cd (Ri= 50) have moderate potential environmental risk, As (Ri = 70) have moderate potential environmental risk and, Hg (Ri = 120) have considerable potential environmental risk (Table 11), while, the Ri for the individual heavy metals in well water show that, Cu (Ri = 0.075) and Zn (Ri = 0.013) have no potential environmental risks, Cd (Ri= 40) have low potential environmental risk and, As (Ri = 110) have considerable potential environmental risk (Table 11). Generally, the main environmental heavy metal that poses pollution risk in groundwater within the Districts were Hg, As and Cd and contributed mostly to the Risk index factor (Ri).

TABLE 9
Estimation of Risk index factor (Ri) and comprehensive risk index (CRI) for borehole water in the Amansie and Adansi Districts

Heavy metal	OC	Ti	NOEC	OC/NOEC	Ri
Cd	0.005	30	0.003	1.67	50
Cu	0.04	5	2	0.02	0.1
Zn	0.05	1	3	0.02	0.017
Pb	0.04	5	0.01	4	20
As	0.07	10	0.01	7	70
Hg	0.003	40	0.001	3	120
					CRI=260.1

(After Hakanson, 1980)

TABLE 10
Estimation of Risk index factor (Ri) and comprehensive risk index (CRI) for well water in the Amansie and Adansi Districts

Heavy metal	OC	Ti	NOEC	OC/NOEC	Ri
Cd	0.004	30	0.003	1.33	40
Cu	0.03	5	2	0.02	0.075
Zn	0.04	1	3	0.01	0.013
As	0.11	10	0.01	11.00	110
					CRI=150.1

(After Hakanson, 1980)

TABLE 11
Potential Environmental Risk (Ri) of toxic trace metal in groundwater within the Amansie and Adansi Districts

Heavy metal	Potential Environmental Risk (Ri)	
	Borehole water	Well water
Cd	Moderate	Low
Cu	No	No
Zn	No	No
Pb	Low	-
As	Moderate	Considerable
Hg	Considerable	-

(After Hakanson, 1980)

Similarly, based on the classification of environmental risk using Comprehensive risk factor (CRI) (Table 5) borehole water within the districts could be classified as very high risk (CRI = 260.1) (Table 9), while, well water could be classified as high risk (CRI= 150.1) (Table 10).

Conclusion

Results from this study show that, the mean values of Fe, Cd, Pb, As and Hg for boreholes and Cd, and As for well water were above the WHO (2004) guideline values. The heavy metal abundance in groundwater within the districts was in the order: Fe > Mn > As > Zn > Cu = Pb > Cd > Hg for borehole water, and

Fe > As > Mn > Zn > Cu > Cd > Pb > Hg, for well water. The percentage contributions were: Fe (60%), Mn (20%), As (7%), Zn (5%), Cu (4%), Pb (4%), Cd (0%) and Hg (0%), suggesting that, natural geochemical processes such as rock-water-soil interactions are more pronounced in the water resources within the Amansie and Adansi Districts. The results also show that, the potential non-carcinogenic risks of exposure ($HQ_{ing/derm}$) posed by Fe, Mn, Cd, Cu, Zn, Pb, As and Hg within a single route of exposure via ingestion or dermal contact was: 3.30×10^{-2}, 1.40×10^{-1}, 5.00×10^{-4}, 3.70×10^{-2}, 3.00×10^{-1}, 3.60×10^{-2}, 3.00×10^{-4} and 3.00×10^{-4} respectively for both adults and children, suggesting a decreasing order of Zn > Mn > Cu > Pb > Fe > Cd > As = Hg, for borehole water, and Zn > Mn > Cu > Fe > Cd > As = Hg, for well water. The concerns for potential human health risks (HQ/HI) caused by exposure to non-carcinogenic heavy metals for Fe, Mn, Cd, Cu,Zn, Pb, As, and Hg were: 6.0×10^{-2}, 2.56×10^{-1}, 9.15×10^{-4}, 6.77×10^{-2}, 5.49×10^{-1}, 6.59×10^{-2}, 5.49×10^{-4}, 5.49×10^{-4} for boreholes, and 6.46×10^{-2}, 2.74×10^{-1}, 9.79×10^{-4}, 7.25×10^{-2}, 5.88×10^{-1}, 5.88×10^{-4}, 5.88×10^{-4} for well water, suggesting that there is no concern for potential human health risks caused by exposure to non-carcinogenic toxic heavy metals in groundwater within the Districts (i.e HQ/HI <1). The study further show that, the Risk index factor (Ri) for heavy metals was in the order: Hg > As > Cd > Pb > Cu > Zn, for borehole water, and As > Cd > Cu > Zn for well water, suggesting that, groundwater within the Districts is potentially threatened by anthropogenic activities primarily, mining activities where, chemicals such as arsenic (As) and Hg are used to recover gold from its amalgam. Based on the classification of environmental risk using Comprehensive risk factor (CRI), borehole water within the districts could be classified as very high risk, while, well water could be classified as high risk. Generally, the main environmental heavy metals that poses pollution risk in groundwater within the Districts were Hg, As and Cd and contributed mostly to the Risk index factor (Ri).

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