Water Quality Assessment of the Southwestern and Coastal River Systems of Ghana

Authors: Humphrey F. Darko and Osmund D. Ansa-Asare.
CSIR Water Research Institute, P.O. Box AH38, Achimota, Accra, Ghana
Corresponding author's email: humdarko@hotmail.com

Abstract
Investigation into physico-chemical water quality and dissolved heavy metal contents of major rivers from the Southwestern and Coastal River Systems of Ghana from 19 stations was undertaken from 2007 to 2010**.** The waters are used in their raw states for domestic purposes including drinking in most communities in the study area. The concentrations of the various parameters were assessed in relation to the Ghana Raw Water Quality Criteria and Guidelines for raw water, and in few instances, are compared with the WHO guidelines where the waters are known to be sources of drinking water. Turbidity, Total Suspended Solids (TSS) and Total Hardness were the physical parameters selected for the quality assessment of the waters in relation to domestic use. An Adapted Water Quality Index (WQI) was used to characterize the overall water quality status of the waters. Turbidity and TSS were found to be above their respective Target Water Quality Range (TWQR) values for raw water, while Total Hardness concentration were within guideline values. The levels of the trace metals investigated in the waters, Fe, Mn, Zn, Pb, Cr, Ni, Cu, As, Cd, and Hg, were found to be generally low, and do not yet pose health risks in the dissolved form. However, Fe and Mn levels were moderately high, exceeding their respective TWQR values stipulated for Ghanaian freshwaters. An assessment of non-cancerous health risk from exposure to Fe, Mn, and Zn was performed with the Risk Integrated Software for cleanup (RISC 4.02) developed by the USEPA. Results of the risk assessment, however, revealed a hazard quotient greater than 1 in some locations, indicating that the risk of adverse health effects associated with exposure to zinc, manganese and iron is high in those locations. Efforts should therefore be made to prevent metal pollutants, mainly from mining activities, from entering our water bodies to keep them suitable for their intended uses.
Keywords: Risk assessment, Southwestern Rivers Systems, Coastal Rivers Systems, Water Quality, Water Quality Index.

1.0 INTRODUCTION

A study to investigate the physico-chemical water quality and dissolved heavy metal contents of major rivers from the Southwestern and Coastal River Systems of Ghana from 19 stations was carried out from 2007-2010. The concentration of the various water quality parameters were assessed in relation to the Ghana Raw Water Quality Criteria and Guidelines for raw water (WRC, 2003a).

A number of physico-chemical and bacteriological parameters, as well as trace metals were determined. Most of the river basins studied were affected by illegal mining activities where the wastewaters drain into nearby water bodies. The objective of the study was to evaluate levels of specific water quality variables in these major rivers and reservoirs in the Southwestern and Coastal River Systems that serve as drinking water sources, and to determine whether the levels found pose any potential risks to human health. An Adapted Water Quality Index (WQI) was used to aggregate selected physical, chemical and microbiological water quality parameters to describe the overall water quality status of the waters.

An assessment of non-cancerous health risk from exposure to Fe, Mn, and Zn was performed using the Risk Integrated Software for cleanup (RISC 4.02) developed by the USEPA. Results of the risk assessment, however, revealed a hazard quotient greater than 1 in some locations, indicating that the risk of adverse health effects associated with exposure to zinc, manganese and iron is high in those locations.

In this paper, aspects of the physicochemical water quality parameters and trace metal concentrations are evaluated and their possible health impacts on the communities. The assessment of the overall water quality status by the Adapted Water Quality Index (WQI) is also provided. The effect of long term exposure to Fe, Mn and Zn in drinking water to consumers in the study area is also discussed.

2.0 MATERIALS AND METHODS

2.1 Study areas

The Southwestern Rivers System: The Southwestern Rivers Systems is made up of the Bia, Tano, Ankobra , Pra Birim and Offin River Basins in Ghana, and is located approximately between latitudes 5 ° N and 7.7 ° N and longitudes 0.3 ° W and 3.2 ° W (Fig. 1). Their drainage areas cover about 22 % of the country. Major water uses of all the basins are for domestic, industrial, irrigation and fishing purposes. The mean annual rainfall of the entire Southwestern Rivers System ranges from 1137 mm to 2156 mm with two rainfall seasons peaking in May/June and September/October. The Southwestern System falls within the Rain Forest Zone of Ghana with extensive cocoa farms, with a small percentage of forest remaining. The farming practice in the basin is mainly land rotation. There are also forest reserves and large established commercial tree plantations like rubber. Coconut plantations were also abundant in the southern portions towards the coastal areas until the onset of the Cape Saint Paul's Wilt disease that has rapidly destroyed vast areas of plantations and virtually collapsed the coconut industry (Darko *et al., 2*013).

The Coastal Rivers System: The Coastal Rivers System comprises the Densu, Ayensu, Ochi-Amisa, Ochi-Nakwa, Kakum and Odaw River Basins. The Coastal Rivers System covers an estimated area of 21,146 km^2, with a total annual flow volume of 1491.2×10^6 m^3. It covers a large portion of the Central, Eastern and the Greater Accra Regions of Ghana.

Land uses include cultivation of cocoa and fruit crops like oranges, and oil palm in the forested upper areas. Oil palm and rubber plantations can also be found in some other areas. Food crops including plantains, cocoyam, maize, cassava, vegetables, and fruit crops like pineapples are also under cultivation in the Coastal Rivers System. Coconut plantations occur on the sandy soils on the beachheads along the coast. Large numbers of cattle are known to be kept on the coastal plains (Darko *et al., 2*013).

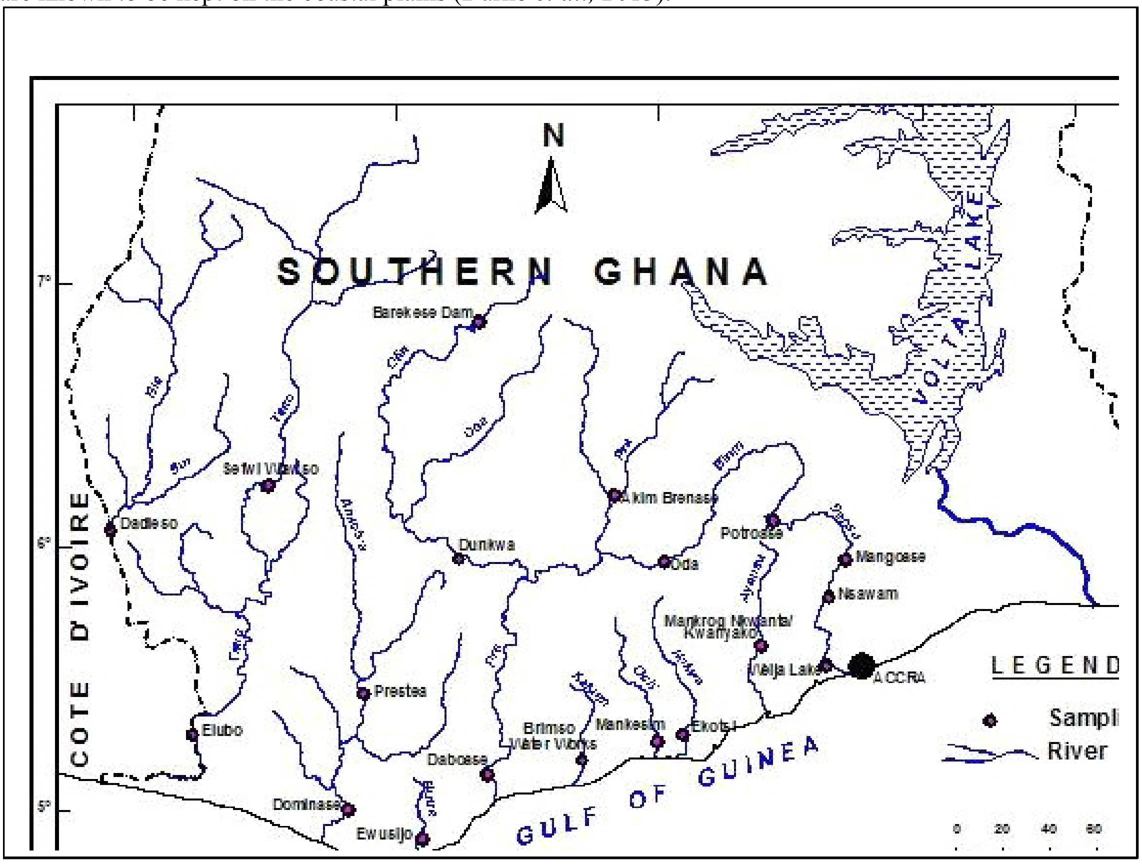

Fig.1: Map of Ghana showing the locations of sampling sites in Southwestern and Coastal Rivers Systems.

2.2 Sampling

Surface water samples were collected from 19 selected locations in the basins for 4 years (February 2007 to October 2010) on bi-monthly intervals. Various water quality parameters including physico-chemical water quality parameters, and bacteriological water quality parameters, as well as trace metals were determined in all the waters. Samples for physico-chemical parameters were collected into 1 L clean plastic bottles. Samples for dissolved heavy metal analysis were collected and filtered through 0.45 μm membrane filter papers into clean 50 ml plastic bottles which have been washed with 1+1 HNO_3 (APHA, 1998) and thoroughly rinsed with distilled water. The metal samples were immediately acidified with concentrated nitric acid after filtration. The samples for physico-chemical parameters and the bacteriological samples were preserved in ice-chest containing ice before transporting them to the Laboratory for analysis. Temperature, pH and transparency were measured *in situ* in the field using a calibrated digital thermometer and a calibrated pH meter for temperature and pH respectively, while transparency was measured with a Secchi disc. The metal concentrations were determined by the Atomic Absorption Spectrophotometric (AAS) Method by direct aspiration of the filtered acidified samples using the UNICAM 969 Atomic Absorption Spectrophotometer. The physico-chemical and bacteriological parameters were determined according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998).

The Southwestern stations sampled were Dadieso, Sefwi-Wiawso, Prestea, Dominase, Ewusijo, Daboase, Brenase, Akim Oda, Dunkwa , Brimso, and Barekese; while the the Coastal stations sampled were Mankesim, Ekumfi Ekotsi, Mankrong Junction, Potroase, Mangoase, Nsawam and Weija.

2.3 Health risk assessment from exposure to trace metals (Fe, Mn, and Zn).

A non-cancerous health risk assessment was performed using the Risk Integrated Software for cleanup (RISC 4.02) to estimate the adverse health effects that might occur from ingestion of Mn, Zn and Fe from drinking of stream water in the study areas.

3. RESULTS AND DISCUSSION

The concentration of the various parameters in the waters from the Southwestern and the Coastal Rivers Systems of Ghana were assessed in relation to Ghana Raw Water Quality Criteria and Guidelines for raw water. Datasets obtained from the monitoring programme were used to assess levels of pollution in the waters. The concentrations of the parameters were compared with their respective Target Water Quality Range (TWQR) values for assessment. In the Ghana Raw Water Quality Criteria and Guidelines, the range of concentrations at which the presence of a particular water quality constituent would have no known or anticipated adverse effects on the fitness of water for a particular use, or on the protection and maintenance of the health of aquatic ecosystems is referred to as the Target Water Quality Range (TWQR) value (WRC, 2003a). The selected physical parameters were Total Suspended Solids (TSS), Turbidity and Total Hardness. The Water Quality Index (WQI) was used to assess the overall water quality status of the basins.

A total of ten trace metals were determined: Iron (Fe), Lead (Pb), Manganese (Mn) Zinc (Zn), Chromium (Cr) Nickel (Ni), Copper (Cu) Arsenic (As) Cadmium (Cd) and Mercury (Hg). A non-cancerous health risk assessment was performed using the Risk Integrated Software for cleanup (RISC 4.02) to estimate the adverse health effects that might occur from ingestion of Mn, Zn and Fe from drinking of stream water in the study areas.

3.1 Physical parameters

3.1.1 Turbidity

Turbidity is an important water quality parameter because of pathogenic properties it has on drinking water. Turbidity can provide food and shelter for pathogens and if not removed, can promote regrowth of pathogens in water distribution system, leading to waterborne disease outbreaks (EPA, 1999). The higher the turbidity level, the more likely taste and odour problems may arise. Turbidities above 5.0 NTU may be visible and may be objectionable to consumers. Transmission of disease by micro-organisms associated with particulate matter may also occur at Turbidity values above 5.0 NTU (WRC, 2003a).

The turbidity of the waters was relatively high compared to the guideline target range of 0 – 1 NTU stipulated for raw water in Ghana. The mean turbidity of the waters over the study period is shown in Table 1. These values indicate that the waters could be sources of water-borne diseases to the consumers who drink these raw waters without treatment. The maximum and minimum values of Turbidity in the 4-year dataset of 380 were 309 NTU and 1.31 NTU respectively, while the median value was 20.9 NTU, and the mode was 10.0 NTU. Typical sources of turbidity include wastewater discharges, runoff from watersheds, algae or aquatic weeds and products of their breakdown in water reservoirs, rivers, or lakes, humic acids and other organic compounds resulting from decay of plants, leaves, etc. in water sources, and high iron concentrations which give waters a rust-red coloration (EPA 1999).

3.1.2 Total Suspended Solids (TSS)

Suspended solids give rise to turbidity in water. Soil particles constitute the major part of the suspended matter contributing to the turbidity in most natural waters (WRC, 2003a). The mean values of TSS at the stations are shown in Table 1. The maximum and minimum values of TSS in the dataset of 380 were 260 mg/l and 1.00 mg/l respectively, while the median value was 16.0 mg/l and the mode was 8.00 mg/l. The mean values were all above the Target Water Quality Range value of 0 – 5 mg/l, the guideline requirement for raw water in Ghana stipulated by the WRC. The high values indicate the presence of high loads of suspended particles in the water. These high occurrences of TSS in the waters may be as a result of run-offs washing soil particles into the rivers, and also due to anthropogenic activities such as wastewater from illegal mining activities draining into the rivers.

Table 1: Mean values of selected physical parameters during the period (n = 20)

Station	**TSS (mg/l)**	**Turbidity (NTU)**	**Total Hardness (mg/lCaCO$_3$)**
Weija Reservoir (R. Densu)	17.4 ±35.7	9.04 ±4.06	81.6±17.9
Potroase-R. Densu	14.0 ± 21.3	8.94 ±8.83	67.1±10.7
Mangoase-R.Densu	32.9 ±34.2	23.2 ±16.5	94.3±27.3
Nsawam- R. Densu	28.4 ±29.2	20.9 ±17.8	99.6±33.8
Mankrong J-R.Ayensu	34.0 ±28.3	48.9 ±48.8	52.3±15.2
Akim Oda-R Birim	48.3 ±38.2	66.6 ±65.1	30.7±11.8
A Brenase-R.Pra	16.2 ±15.1	20.4 ±15.2	49.6±15.7
Daboase - R. Pra	42.6 ±34.8	51.5 ±35.9	39.0±15.3
Dunkwa- R.Offin	31.6 ±22.3	45.3 ±28.2	46.1±16.9
Barekese Reservoir-R. Offin	10.3 ±12.8	6.66 ±3.18	30.1±14.6
Ekotsi-R.Ochi-Nakwa	36.5 ±37.0	43.3 ±47.4	30.2±10.0
Mankesim-R.Ochi-Amisa	46.7±56.6	52.5 ±49.5	28.4±10.5
Brimso Reservoir-R. Kakum	15.6±19.9	18.1 ±30.0	29.7±11.1
Ewusijo-R. Butre	18.9 ±13.7	23.7 ±18.2	26.7±8.90
Dominase-R.Ankobra	41.5 ±37.5	45.5 ±30.4	23.7±11.8
Prestea-R.Ankobra	37.1±25.0	53.7 ±25.6	25.5±10.8
Elubo - R. Tano	19.6 ±14.0	24.6 ±15.2	30.3±9.89
Sefwi-Wiawso - R. Tano	18.0 ±21.7	19.0 ±13.4	55.9±12.1
Dadieso-R. Bia	20.1±19.9	19.8 ±12.3	34.9±7.50
TWQR	**0 – 5**	**0 - 1**	**0 – 250**

3.1.3 Total Hardness

Magnesium and calcium salts are the major contributors to water hardness. Hard water does not lather properly with soap when used for laundry and forms scums with soap. Excessive hardness of water can give rise to scaling in hot water systems and heat exchangers and hence has adverse economic implications. Excessive softness, on the other hand, may lead to aggressive and corrosive water characteristics. The classification of water hardness according to the Ghana Raw Water Quality Criteria and Guidelines (WRC, 2003a) is presented in Table 2.

The mean values of Total Hardness in the waters were mainly below 50.0 mg/lCaCO$_3$(62.9 %), and just a few between 50.0 – 100 mg/lCaCO$_3$ range(31.8 %), implying that the waters were generally soft (Table 1). The maximum and minimum values of Total Hardness in the dataset of 380 were 206 mg/lCaCO$_3$ and 8.00 mg/lCaCO$_3$ respectively, while the median value was 38.0 mg/lCaCO$_3$ and the mode was 24.0 mg/lCaCO$_3$. The modal value of 24.0 mg/lCaCO$_3$ for Total Hardness in the waters again indicates that the waters can generally be described as soft waters and would lather well with soap when used for laundry purposes. The Target Water Quality Range limit value of Total Hardness for raw water intended for domestic use (drinking) is 250 mg/lCaCO$_3$. The maximum value of Hardness encountered in the waters was 206 mg/lCaCO$_3$, an indication that Hardness will not pose a problem for the suitability of the water for potable purposes when the waters undergo appropriate treatment processes.

Table 2: Classification of Hardness of Water

Hardness Range (mg CaCO$_3$/l)	Description of Hardness	Percentage of dataset (from this study)
0 – 50	Soft	62.9
50 – 100	Moderately soft	31.8
100 – 150	Slightly hard	4.5
150 – 200	Moderately hard	0.8
200 – 300	Hard	0
> 300	Very Hard	0

Source: WRC, 2003a.

3.2 The overall water quality status of the waters from the Water Quality Index (WQI).

Water Quality Index (WQI) is a systematic way of interpreting water quality data in a consistent manner to management and the public in a way that describes the overall quality of water bodies, and can indicate whether the overall quality poses a potential threat to various uses of the water, such as drinking, irrigation, etc. The WQI provides a general means for comparing water quality of different water bodies, and evaluating trends in quality in a water body over time (Darko *et al.,* 2013). Different types of Water Quality Indices exist. The water Quality Index that was used in classifying the overall status of the water quality in the basins is the Adapted Water Quality Index based on the Solway River Purification Board (RPB) Weighted Water Quality Index. This is the general water quality indices type in which various physical, chemical and microbiological variables are aggregated to produce an overall index of water quality. The Adapted Water Quality Index (WQI) is a classification system that uses an index calculated from selected water quality parameters. The index classifies water quality into one of four categories: good, fairly good, poor, and grossly polluted (Table 3). Each category describes the state of water quality compared to objectives that usually represent the natural state. The index thus indicates the degree to which the natural water quality is affected by human activity (WRC, 2003a).

Table 3: WQI criteria for classification of surface waters*

WQI Range	Class	Description
>80	I	Good – Unpolluted and/or recovering from pollution
50 – 80	II	Fairly good
25 – 50	III	Poor quality
<25	IV	Grossly polluted

** Source: WRC, 2003a.*

A total of ten parameters were used to determine the Water Quality Index (WQI) for the river basins: Dissolved Oxygen (DO % Saturation), Biochemical Oxygen Demand (BOD), Ammonium Nitrogen (NH_4-N), Faecal Coliform (FC), pH, Nitrate as Nitrogen (NO_3-N), Phosphate as Phosphorus (PO_4-P), Total Suspended Solids (TSS), Conductivity and Temperature.

The Adapted Water Quality Index (WQI) is calculated from the following equation:

$$\text{Water Quality Index} = \mathbf{1/100 \times} \left(\sum_{i=1}^{n} q_i w_i\right)^2$$

Where, q_i = water quality score of parameter i; w_i = weighting factor of parameter i and n = number of parameters.

The aggregation equation generates a single number between 0 and 100, with 0 indicating worst water quality and 100 indicating best water quality.

3.2.1 Classification of Water Quality for the River Basins

The annual mean WQI was calculated from the arithmetic mean of the separate WQIs of each of the 5 sampling months of each year, and used to evaluate the water quality of the River Basins. Figure 2 shows the annual WQIs of the waters and their quality designations.

A general overview of the Water Quality Indices show that the quality status of all the waters fell into the Class II state, or the “fairly good water quality” state throughout the study period, except Nsawam and Dunkwa-On-Offin which fell into Class III each, at two different years respectively. However, there was variation in water quality within the same class interval at the different stations each year, and from year to year. These variations in the class interval of water can be due to different anthropogenic activities going on in the basins that have different degrees of impact on the waters, as well as other environmental factors. Rainfall variations within basins accounted for the differences observed in WQI at the different stations as a result of high surface runoffs occurring in some basins than others (Darko *et. al*, 2013). Three stations, Potroase, Barekese and Ewusijo, though in Class II, had outstanding Water Quality Indices indicating relatively higher water quality in those stations than others. These are the three maxima observed in Figure 2. In most of the stations, the WQI (water quality) decreased from 2007 to 2008, then increased in 2009 and decreased again in 2010. This phenomenon can be attributed to the yearly patterns in rainfall, resulting in different amounts of yearly surface runoffs, and ultimately, variable yearly pollution loads into the waters.

The current quality status of the waters is suitable for domestic water supply when the waters are treated. In the raw state the waters can be put to uses such as irrigation, industrial uses, livestock watering, aquaculture, etc.

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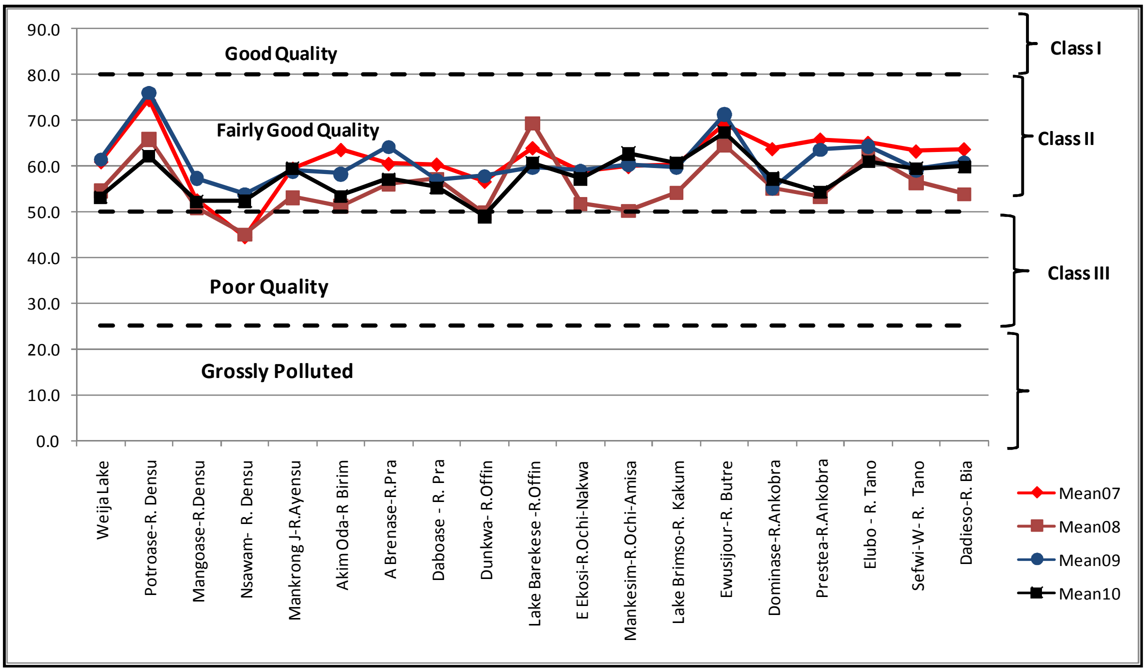

Fig. 2: Water Quality Indices (WQIs) of the basins showing water quality levels.

3.3 Health risk assessment from exposure to Fe, Mn, and Zn in the basins.

The trace metal concentration of the waters from the Southwestern and the Coastal Rivers Systems of Ghana were assessed in relation to Ghana Raw Water Quality Criteria and Guidelines for raw water to determine whether their concentrations were within guideline values. A total of ten trace metals were determined: Iron (Fe), Lead (Pb), Manganese (Mn) Zinc (Zn), Chromium (Cr) Nickel (Ni), Copper (Cu) Arsenic (As) Cadmium (Cd) and Mercury (Hg). The concentrations of these metals were compared with their respective Target Water Quality Range (TWQR) values for assessment. Among the 10 metals, the concentrations of Pb, Cr, Ni, Cu, As, Cd and Hg in the waters were very sporadic, with most of the values measuring less than their respective detection limits. In this study Fe, Mn and Zn were the only metals with environmentally significant concentrations in the waters, and therefore are the only metals discussed in detail and used for the risk assessment. A non-cancerous health risk assessment was performed using the Risk Integrated Software for cleanup (RISC 4.02) to estimate the adverse health effects that might occur from ingestion of Mn, Zn and Fe from drinking of stream water in the study areas.

3.3.1 Fe Concentration in the waters

Figure 3 shows the maximum, minimum and median Fe concentrations in the waters. Iron concentrations in the waters ranged from <0.010 mg/l to 5.62 mg/l during the study period. The highest concentrations were observed at Brimso Reservoir (5.62 mg/l), Ekumfi Ekotsi (4.96 mg/l), Mangoase (4.47 mg/l), Mankrong Junction (4.47 mg/l), Prestea (4.53 mg/l), and Dunkwa-On-Offin (4.14 mg/l). The highest levels observed in the Weija Reservoir and the Barekese Reservoir which are municipal sources of water supply were 0.257 mg/l and 0.876 mg/l respectively (Fig. 3).

Annual mean Fe concentrations exceeded the TWQR value of 0.1 mg/ in all the waters except Weija Reservoir, where the lowest annual mean value was 0.032 mg/l and the highest annual mean value was 0.113 mg/l during the study period. The Weija Reservoir recorded the least annual mean Fe concentrations for all the years, and was followed after by the Barekese Reservoir for all the years. Weija Reservoir is the source of water supply for Western Accra, the capital city of Ghana, therefore its low Fe content makes it suitable for water supply. The Weija Reservoir was formed from damming of the Densu River in 1977 (Ansa-Asare *et al.*, 1999). The upper reaches of the Densu River at Nsawam and Mangoase had higher concentrations of Fe. However, Fe concentration is attenuated considerably in the Reservoir itself which may be due to effects of dilution. The lowest annual mean Fe concentration in the rest of the waters was 0.280 mg/l at Barekese and the highest annual mean concentration was 2.84 mg/l in the Brimso Reservoir. The Barekese Reservoir is the source of water supply for the city of Kumasi, thus its low Fe content makes the Reservoir waters suitable for water supply. The Highest annual mean Fe concentration of 2.84 mg/l was observed in Brimso Reservoir in 2007, followed by similarly high values in the subsequent years. The Brimso Reservoir is the source of water supply for the city of Cape Coast in Ghana and therefore, its high Fe content may cause problems in water supply. The lowest annual mean values of Fe were observed in Weija Reservoir, Barekese Reservoir, Potroase (situated on the headwaters

of R. Densu) and Ewusijo (situated on R. Butre). The Southwestern River basin waters seem to abound in Fe more than the Coastal River basin waters. This is not unexpected since more illegal mining is carried out in the Southwestern River basins than the Coastal River basins which gives rise to more metal pollution in the waters.
Compared to the WHO (2006) guideline value of 0.30 mg/l for Fe in drinking water, annual mean concentration of Fe in the waters exceeded this guideline except in Weija Reservoir. Thus it is important that Fe be effectively removed during water treatment from the waters that serve as sources of domestic water supply. The mode of Fe in all the waters during the study period was 1.71 mg/l, and a median of 1.43 mg/l. Among the 3 Reservoirs, the concentration of Fe followed the order Brimso > Barekese > Weija. The source of Fe pollution in the waters was generally coming from non-point sources.

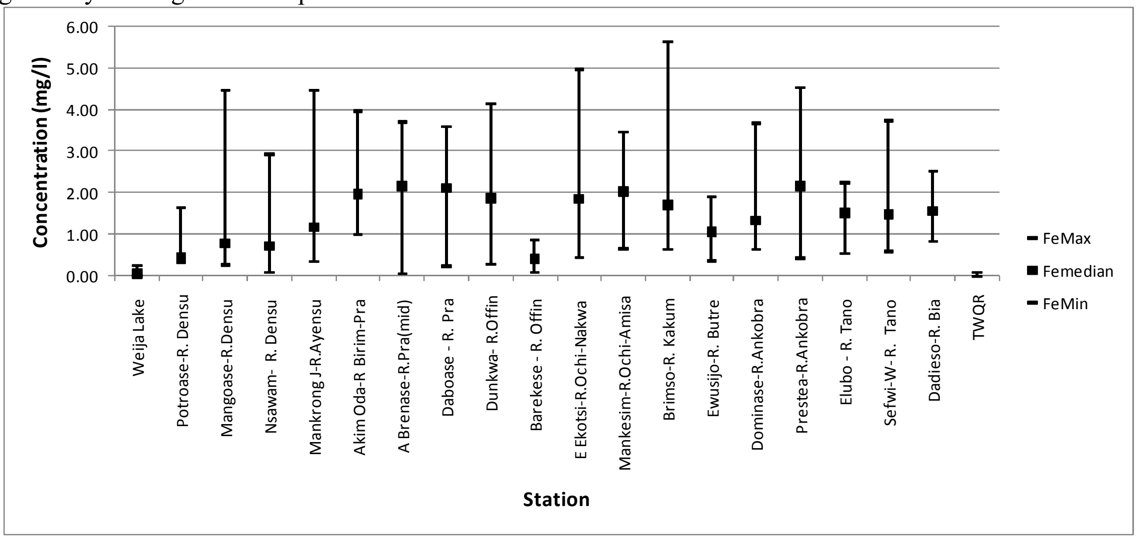

Fig. 3: Maximum (Fe_{Max}), minimum (Fe_{Min}), and median (Fe_{median}), Fe concentrations in the waters. TWQR is the Target Water Quality Range guideline value (0.10 mg/l) for comparison.

3.3.2 Mn Concentration in the waters

Manganese supports the growth of certain nuisance organisms in water distribution systems, giving rise to taste, odour and turbidity problems (WRC, 2003a). High concentrations of Mn in waters abstracted for water supply, eg the Weija and the Barekese Reservoirs in Ghana, are therefore undesirable for water supply. Adverse aesthetic effects such as unpleasant taste and staining of laundry limit the acceptability of manganese-containing water for domestic use at concentrations exceeding 0.15 mg/l (WRC 2003a).
The concentration of Mn in the waters ranged from < 0.005 mg/l at Nsawam to 2.41 mg/l at Akim Brenase. The lowest annual mean value was 0.046 mg/l at Ewusijo, and the highest annual mean value was 0.913 mg/l at Akim-Oda on River Birim, where illegal mining activities are rampant. In this study, the annual mean concentration at all the stations was in excess of 0.05 mg/l, the TWQR value for raw waters in Ghana. The concentrations of Mn at the stations indicate that there is a gradual increase of Mn pollution in the waters as was iron. Manganese concentrations in the Weija Reservoir were greater than Fe concentrations, and ranged from 0.025 mg/l to 1.54 mg/l, while Fe concentrations ranged from <0.010 mg/l to 0.257 mg/l in the Weija Reservoir. However, in the Brimso and Barekese Reservoirs, average iron concentrations were higher than average Mn concentrations.
The mode of Mn in all the waters during the 4 year period was 0.032 mg/l, and a median of 0.120 mg/l. Typically, the median concentration of manganese in freshwater is 0.008 mg/l (WRC, 2003a). However, in comparison to the WHO (2006) guideline value of 0.5 mg/l for Mn in drinking water, the Mn levels measured in this study were relatively lower.
Relatively high values of Fe and Mn were observed in the dry season at Nsawam which indicates point sources of pollution for these metals. Since Nsawam is an urbanized town, the stretch of the River Densu through the town receives high inputs of solid wastes, domestic and industrial wastes, which accounts for this point-source of pollution. In urban dominated catchments, trace metal concentrations are generally several times higher than background levels and may result in significant damage to ecosystems (Pierre-Yves *et al*., 2013). The rest of the stations indicated diffuse sources of pollution for Fe and Mn. However, Prestea (R. Ankobra) and Sefwi-Wiawso (R. Tano) also indicated point sources of pollution for Mn but not Fe.

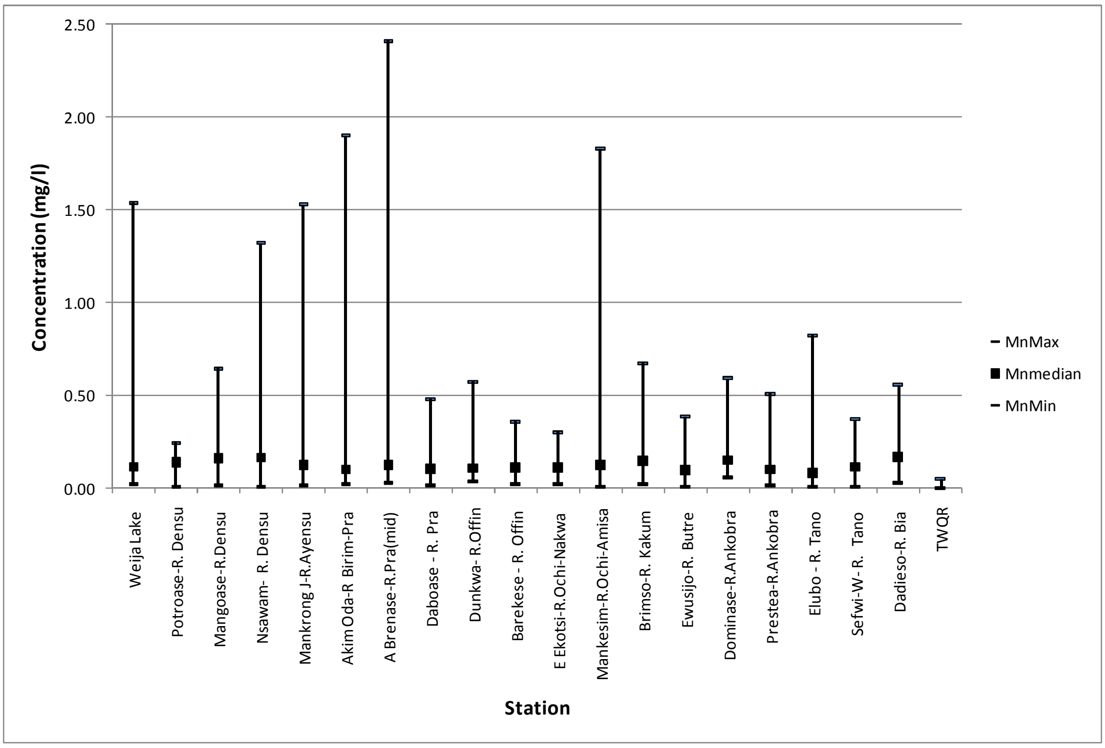

Fig. 4: Maximum (Mn_{Max}), minimum (Mn_{Min}), and median (Mn_{median}), Mn concentrations in the waters. TWQR is the Target Water Quality Range guideline value (0.05 mg/l) for comparison.

3.3.3 Zn Concentration in the waters

Zn is known to be very toxic to fish, whereas humans have a high tolerance to zinc (Jesper, 2010, WRC, 2003b). Concentration of Zn was low in the waters, ranging from <0.005 mg/l to 2.02 mg/l during the 4-year period. Zinc values were below the guideline value (TWQR) of 3.0 mg/l stipulated for fresh waters by the Water resources Commission (WRC) of Ghana. Concentration of Zn is therefore not currently a treat in surface waters in Ghana, since its concentration was far below the guideline value.

The lowest annual mean Zn concentrations was 0.007 mg/l at Weija Reservoir in 2008, while the highest annual mean Zn concentration was 1.02 mg/l, observed in River Bia in 2007. The highest Zn concentrations were generally observed during the rainy seasons, indicating that Zn in the waters were coming from non-point sources Generally, the Southwestern Rivers Systems exhibited higher Zn concentrations than the Coastal Rivers Systems. The mode of Zn in all the waters during the 4 years was 0.005 mg/l, with a median of 0.020 mg/l.

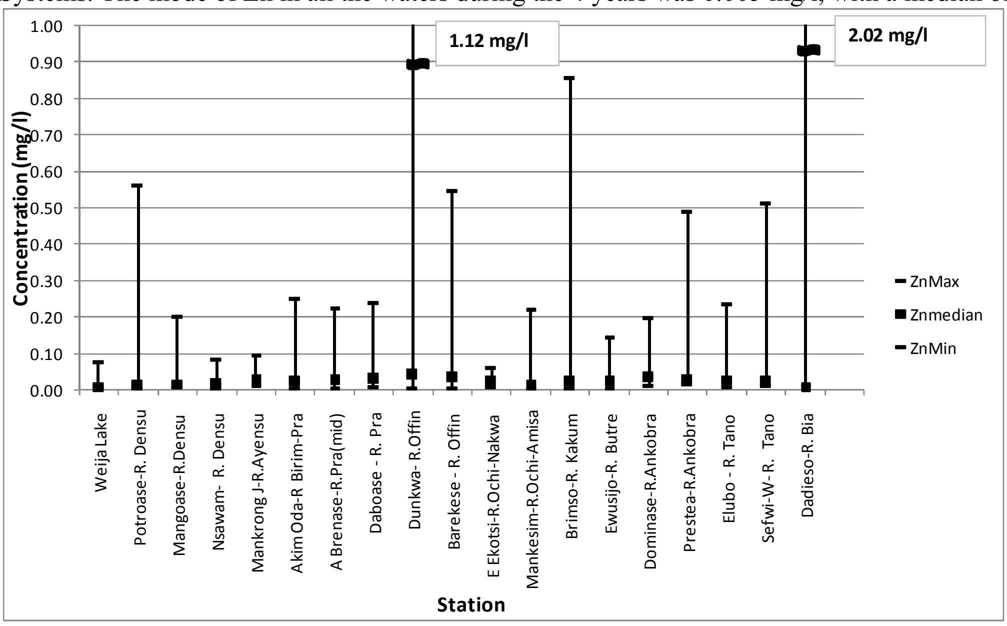

Fig. 5: Maximum (Zn_{Max}), minimum (Zn_{Min}), and median (Zn_{median}), Zn concentrations in the waters.

3.3.4 Concentrations of Pb, Cr, Ni, Cu, As, Cd, and Hg in the waters

The concentrations of the other 7 metals Pb, Cr, Ni, Cu, As, Cd, Hg in the waters were very sporadic with most of the values measuring less than their respective detection limits. Comparing the concentrations of these 7 metals to their TWQRs, the concentrations of Pb, Cr, Ni, Cu, As, Cd, and Hg are not currently a treat in Ghanaian surface waters.

3.4 Risk assessment process

Risk assessment is a process of estimating the probability of the occurrence of an event and the probable magnitude of adverse health effects on human exposures to environmental hazards (Kollunu *et al*., 1996; Paustenbach, 2002). It consists of four steps which are iterative, namely: the hazard identification, exposure assessment, toxicity assessment and risk characterization. This study assessed cancer and non - cancer health risk to resident adults in the affected area who are exposed to Fe, Mn and Zn present in contaminated rivers.

This is the process of estimating the health effects that might result from exposure to carcinogenic and non-carcinogenic chemicals (Obiri *et al*., 2010; Artiola *et al*., 2004; USEPA, 2001). In this study, non-carcinogenic health risk refers to harm done to the central nervous and other adverse health effects (except cancer) due to exposure to neurotoxic chemicals such as Mn. The risk assessment process is made up of four iterative steps namely, hazard identification, exposure assessment, dose-response assessment and risk characterization (Obiri *et al*., 2006; USEPA, 2001; Asante-Duah, 1996).

Hazard Identification

Hazard identification basically defines the hazard and nature of the harm. This is the first step of the risk assessment process that was used to establish a link between the toxic chemicals identified and their health effects on residents in the study area (Obiri *et al.*, 2010). In this study, Fe, Mn and Zn were identified as possible hazards that the community are confronted with as a result of the activities of small-scale miners.

Exposure assessment

Exposure assessment is the process of measuring or estimating the intensity, frequency, and duration of human exposures to an environmental agent. It also helps in estimating the rate of intake of a contaminant by the target organism. In the exposure assessment, the average daily dose (ADD) of Mn, Zn and Fe ingested from drinking of stream water in the study area was calculated using:

$$ADD = \frac{EPC \times IR \times ED \times EF \times 10^{-6}}{BW \times AT \times 365} \qquad (1)$$

Where, EPC is exposure point concentration of toxicant in the drinking water (mg/L), IR is the ingestion rate per unit time (L/day), ED is the exposure duration (years), EF is the exposure frequency (days/year), BW is the body weight of receptor (kg) and AT is the averaging time (years) which is equal to the life expectancy of a resident Ghanaian, 365 is the conversion factor from year to days. The ADD is the quantity of Mn, Fe and Zn ingested per kilogram of body weight per day (Obiri *et al*., 2010; Asante-Duah, 2002; Kollunu *et al*., 1996). With the exception of EPC and BW, the rest were default values in the Risk Integrated Software for cleanup (RISC 4.02) developed by the USEPA. Body weights of 13.5 kg and 58.6 kg were used for resident children and resident adults, respectively in line with Ghana Statistical Service (GSS, 2008). The exposure scenario evaluated in this study was residential. Resident adults aged 18 years and above who are exposed to Fe, Mn and Zn in water samples from the Southwestern River Systems in Ghana via oral ingestion. The average daily dose for each of the toxic contaminant (i.e., Mn, Fe, and Zn) ingested in surface water from the Southwestern River Systems by resident adults was calculated using the analytical concentrations of Pb, Mn and Zn in the water samples from the study area as an input parameter (EPC) in equation (1) above.

Dose-response assessment

The term dose-response assessment is basically defined as the quantitative relationship that indicates a contaminants degree of toxicity to exposed species. In this study, oral reference dose and cancer slope factor values for Mn, Zn and Fe from RISC 4.02 software were used in characterizing cancer and non-cancer health risk from exposure to the aforementioned toxic chemicals in the study area (USEPA, 2008).

Risk characterization

Risk characterization is the final phase of the risk assessment process. In this phase, exposure and dose-response assessments are integrated to yield probabilities of effects occurring in human beings under specific exposure conditions. In line with USEPA risk assessment guideline, the risk characterization process incorporated all the information gathered from hazard identification, exposure assessment and dose-response assessment to evaluate the potential cancerous and non-cancerous health risk of resident adults in the study area from exposure to the toxicants in drinking water (USEPA, 2004). In this study, the extent of non - cancerous harm incurred by the resident adults was expressed in terms of hazard quotient:

$$HQ = \frac{ADD}{RfD} \ldots (2)$$

Where, ADD is the average daily dose a resident adult is exposed to via drinking water containing Mn, Fe and Zn. RfD is the reference dose which is the daily dosage that enables the exposed individual to sustain level of exposure over a prolonged time period without experiencing any harmful effect. In this study, oral reference doses (RfDoral) for the respective toxicants were used.

A hazard quotient greater than 1 means that risk of adverse health effects associated with exposure to zinc, manganese and iron is very high. For example, in Dunkwa, a resident child exposed to manganese via CTE and RME is 4.6 and 4.5 respectively (Table 4). This means that approximately 5 children are likely to suffer from manganese related diseases such as low IQ (manganese is neurotoxic), and other diseases. In other places like Akim-Brenase, Daboase and Dunkwa-On-Offin, very high hazard quotients were found for Fe, where resident adults exposed to Fe via CTE were 230, 370, 370, and via RME were 480, 740, 730, respectively. This means that these number of adults will suffer iron related diseases like haemochromatosis, wherein tissue damage occurs as a consequence of iron accumulation, etc.

The risk assessment of Fe, Mn, and Zn indicate that, long term exposure by residents through drinking of the raw water are at risk of suffering negative health effects associated with these metals.

Table 4: Hazard quotients for Non – cancer risk assessment

Sample location	Exposure route	Children						Adults					
		Fe		Zn		Mn		Fe		Zn		Mn	
		CTE	RME	CTE	RME	CTE	RME	CTE	RME	CTE	RME	CTE	RME
Weija Reservoir - R. Densu	Oral	0.098	0.780	3.20	4.30	4.30	5.70	0.220	2.20	4.60	4.50	0.480	0.910
Potroase – R. Densu	Oral	1.200	34.0	0.028	0.010	5.1	10	7.10	2.30	0.230	0.150	3.10	7.00
Mangoase – R. Densu	Oral	0.097	1.90	0.002	0.006	0.39	0.89	0.050	0.350	0.230	0.190	2.70	1.40
Nsawam – R. Densu	Oral	0.040	0.140	0.004	0.140	5.1	10	5.10	10.0	0.230	0.150	0.270	0.620
Akim-Oda – R. Pra	Oral	0.020	0.710	0.044	1.60	0.2	0.071	2.70	5.30	0.130	0.100	4.30	9.70
Akim-Brenase – R. Pra	Oral	0.170	6.30	0.053	1.90	0.71	6.3	230	480	0.120	0.910	3.00	6.60
Daboase – R. Pra	Oral	2.70	99.0	0.015	0.560	2.7	99	370	740	1.90	14.0	0.860	0.190
Dunkwa – R. Offin	Oral	1.90	67.0	0.014	0.500	4.6	4.5	370	730	4.10	7.30	0.430	0.970
Barakese Reservoir – R. Offin	Oral	0.056	0.065	0.003	0.110	0.23	0.015	7.40	1.50	0.120	0.210	0.360	0.820
Brimso – R. Kakum	Oral	0.980	11.0	0.003	0.036	0.13	0.010	3.70	7.40	0.600	0.620	0.540	1.20
Dominase – R. Ankobra	Oral	0.063	0.780	0.540	1.90	0.12	0.91	1.70	3.20	0.510	0.900	0.030	0.230
Elubo – R. Tano	Oral	0.027	0.210	0.036	0.081	1.9	14	4.60	9.20	0.750	1.30	0.360	0.280
Sefwi-Wiawso – R. Tano	Oral	0.013	0.010	0.011	0.073	0.023	0.19	2.00	4.00	0.100	0.580	1.10	0.081
Dadieso – R. Bia	Oral	0.120	0.910	0.370	2.80	3.9	4.2	0.310	0.970	0.120	0.950	0.940	0.073

4.0 CONCLUSIONS

The water quality studies of the Southwestern and the Coastal Rivers Systems of Ghana indicated that Total Suspended Solids (TSS) and Turbidity levels were moderately high in the waters, and were above their respective recommended values for raw water. Total Hardness levels were within the TWQR values, and the waters can generally be described as soft waters. The Water Quality Index classification of the waters revealed that all the waters were of the Class II state, or the “fairly good water quality” state. This means that the waters can be put to domestic use, as well as other uses like irrigation, livestock watering, etc.

The analysis of dissolved concentrations of heavy metals in the river basins found the concentrations of Fe, Mn, Zn, Pb, Cr, Ni, Cu, As, Cd, and Hg to be low in the waters. However, the concentrations of Fe and Mn were relatively higher, exceeding their TWQR values (guideline values) stipulated for Ghanaian freshwaters. Concentrations of Pb, Cr, Ni, Cu, As, Cd, and Hg in the waters were very low and sporadic, with most of the values measuring less than their respective detection limits.

A non-cancer risk assessment performed on Fe, Mn and Zn with the Risk Integrated Software for cleanup (RISC 4.02), however, revealed a hazard quotient greater than 1 in some locations in the study area. This indicates that the risk of adverse health effects associated with exposure to Fe, Mn and Zn in the long term (spanning over about 70 years of life time) is high in those locations.

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REFERENCES
1. Ansa-Asare, O.D., Marra I.L., Cresser, M.S., 1999. Evaluation of cycling patterns of dissolved oxygen in a tropical lake as an indicator of biodegradable organic pollution. *The Science of the Total Environment 231 1999. 145 - 158.*
2. American Public Health Association (APHA, 1998). "Standard Methods for the Examination of Water and Wastewater," 20th Edition, Washington DC, 1998.
3. Artiola, J. F., Pepper, I. L. and Brusseau, M. L., 2004. Environmental Monitoring and Characterization. Academic Press. P 410.
4. Asante – Duah, D. K., 1996. Managing contaminated sites. Problem diagnosis and development of site restoration. John Wiley, West Sussex.
5. Asante – Duah, D. K., 2002. Public health risk assessment for human exposure to chemicals. Kluwer Academic Publishers. The Netherlands.
6. Darko, H.F., Ansa-Asare, O., Paintsil, A., 2013. A Number Description of Ghanaian Water Quality—A Case Study of the Southwestern and Coastal Rivers Systems of Ghana. *Journal of Environmental Protection, 4, 1318-1327.*
7. Jesper, G.D. 2010. Handbook of Water Quality Assessment, DHI – Water, Environment & Health, 8th Edition, Horlshom, Denmark.
8. Kollunu, R.V., Bartell, Pitablado, R. M., Stricoff, R. S., 1996. Risk Assessment and Management Handbook. McGraw-Hill, New York.
9. Obiri, S., Dodoo, D. K., Essumang, D. K. and Armah, F. A. (2010): Cancer and non – cancer risk assessment from exposure to arsenic, copper and cadmium in borehole, tap and surface water in the Obuasi Municipality, Ghana. *Hum. Ecol. Risk Assess. 16(3): 651 – 665.*
10. Obiri, S., Dodoo, D. K., Essumang, D. K., Okai – Sam, F. and Adjorlolo – Gaskpoh, A., 2006. Cancer and non – cancer health risk from eating cassava grown in some mining communities in Ghana. *Environ. Monit. Assess. Vol. 118, pp 37 – 49.*
11. Paustenbach, J., 2002. Human and Ecological Risk Assessment: Theory and Practice. John Wiley and Sons, New York.
12. Pierre-Yves, A., Gavin, L., Gillian D. L. 2013. Metal concentrations in stream biofilm and sediments and their potential to explain biofilm microbial community structure. *Environmental Pollution, 173, 117-124.*
13. US Environmental Protection Agency (EPA, 1999). EPA Guidance Manual. Turbidity Provisions. Washington D.C.
14. US Environmental Protection Agency (USEPA, 2001). Integrated risk information system (IRIS). National Centre for Environmental Assessment, Office of Research and Development, Washington.
15. US Environmental Protection Agency (USEPA, 2004). National Wadeable Stream Assessment: Water Chemistry laboratory Manual. EPA 841 – B – 04 – 008. US Environmental Protection Agency, Office of Water and Office of Research and Development, Washington.
16. US Environmental Protection Agency (USEPA, 2008): Child – Specific exposure factors handbook. General Factors, Office of Research and Development, Washington.
17. Water Resources Commission (WRC, 2003a). Ghana Raw Water Quality Criteria and Guidelines, Volume 1, Domestic Water –Use. Water Resources Commission, Accra, Ghana.
18. Water Resources Commission (WRC, 2003b). Ghana Raw Water Quality Criteria and Guidelines, Volume 5, Aquaculture Water –Use. Water Resources Commission, Accra, Ghana.