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Heavy metals pollution profiles in streams serving the Owabi reservoir

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Water samples from five sampling points on four rivers, Owabi, Akyeampomene, Pumpunase and Sukobri, representing the main streams serving the Owabi reservoir were analysed for some pollution indicators using standard methods. Heavy metals (Zn, Cu, Mn, Cu, Pb and As) concentrations and some physical parameters of the water samples were determined. Electrical conductivity and pH of waters from all the streams were found to be within the acceptable limits of the World Health Organization (WHO). All the streams showed high turbidity values above WHO limits. Of the heavy metals determined in the water samples, Fe, Mn, Zn and Cu concentrations in all the streams were within the acceptable WHO limits, whiles Pb and As appeared to be higher than the acceptable limits in all the streams. The highest concentrations of most of the heavy metals were recorded at the Kronum site on Owabi stream. There was a statistically significant positive correlation between pH and some metals at all the sample points (p = 0.05). The results showed that all the streams were polluted and must be treated before consumption. It was also recommended that, human activities within the catchments should be monitored closely to minimise their polluting impacts on the water quality.

Key words: Heavy metals, Owabi, pollution, water quality, WHO.

INTRODUCTION

Heavy metal contamination in rivers is a major water quality issue in many fast growing cities. This is because improvements in water and sanitation infrastructure have not kept pace with population growth and urbanization in most developing countries (Mintz and Baier, 2000). Metals enter rivers and lakes from a variety of sources, such as rocks and soils directly exposed to surface waters, decomposing dead organic matter, fallout of atmospheric particulate matter, and from man's activities, including the discharge of various treated and untreated liquid wastes into the water body (Olayinka, 2004).

Heavy metals such as Cr, Mn, Co, Cu, Fe and Zn play biochemical roles in the life processes of aquatic plants and animals, and their presence in trace amounts in the aquatic environment is essential. However, at high con-centrations, these trace metals become toxic (Nurnberg,

1982). A further special feature of toxic metals is that they are not biodegradable. Instead, they undergo a biogeo-chemical cycle with substantially different residence times in the various spheres and compartments of the environ-ment. Within this cycle they will be taken up also by man, predominantly from food and drinking water. In this respect, toxic metals constitute a particular risk. They have the tendency to accumulate in vital organs (Nurn-berg, 1982). Thus, they will exert progressively growing toxic actions over long periods of the lifespan depending on the cumulative magnitude of the dose as a function of the long term exposure of the individual to its particular environment and the particular metal.

The Owabi reservoir provides drinking water to part of Kumasi metropolis and its environs. The functions of the Owabi catchment which include; maintenance of water quality and flow, water storage, water recharge, repro-duction area for fish a nd other aquatic organisms and climate, control can adversely be affected by high popula-tion and associated increase in human activities (Okurut

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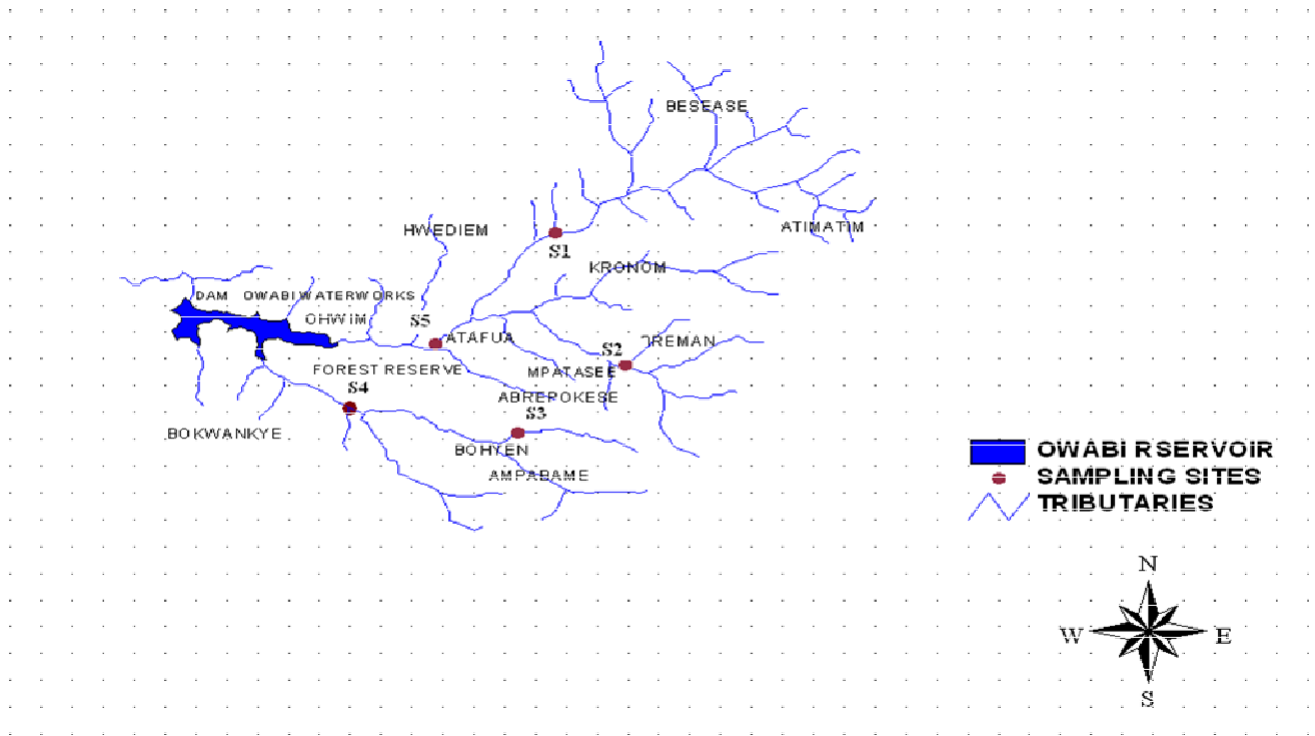*Corresponding author. E-mail wofakmann@yahoo.com.

Figure 1. Map of the study site showing the watershed and the five collection sites.

et al., 2000; Kansiime et al., 2003). Human activities within the catchment are likely to impact negatively on the water quality and the quality of other resources such as fish and food derived from the area.

Human activities found within this area include metal fabrication, auto garages, residential, farming, road construction as well as municipal waste disposal. These activities are sources of toxic metals and other chemicals which pollute ecosystems. For sustainable development of the natural resources in the catchment, it is necessary to study how these activities impact on them.

The objectives of this research are to characterize the distribution of heavy metals in surface water within the Owabi catchment in order to assess the potential public health and ecosystem impact from dissolved metals contaminations found within the Owabi catchment.

MATERIALS AND METHOD

The study area

The Owabi reservoir is designed to produce 20% of the total potable water requirement in the Kumasi metropolis and nearby villages. The streams which serve the Owabi reservoir have been encroached with various human activities due to the high population density within the catchment area. Many steams drain the catchment area of the Owabi reservoir. Some of the streams are main stream in the catchment is River Owabi which flows through agricultural land close to the village of Maase, upstream of Kumasi, River Owabi, Sukobri, Akyeampomene, Pumpunase, and Afu. The and then, joins other tributaries from the urban area at Atafoa a

rapidly-urbanizing agricultural village (McGregor et al., 2002). The streams were selected based on size, popularity and the human activities they are exposed to. The sites are shown in Figure 1. River Akyeampomene flows through Bremang and Suame townships. Human and other developmental activities are sited very closely to the banks. In the Bremang township all the drain and gutters in the entire township are channel into the stream. River Pumpunase originates from the range near Ampabaame and flows north-westwards through Bohyen township, joined by other streams before empting into the reservoir (Figure 1). Five sampling sites were chosen. These were from different community locations. The descriptions of the sampling locations are shown in Table 1.

Sampling and procedure

Five sampling points were selected within the Owabi catchment. The sampling points are indicated in Figure 1. Sampling was done once every month from the month of December, 2006 to April, 2007 (dry season). Samples were collected into sterile screw capped plastic containers. Prior to sample collection, all bottles were washed with dilute nitric acid followed by distilled water and were dried in an oven. Before taking water samples, the bottles were rinsed three times with the water to be collected. The sampling bottles were labeled with dates and sampling source. Collected water samples were stored in a cooler at 4°C. Temperature, conductivity and pH of the samples were measured on site. All the analyses were done by standard methods according to APHA, AWWA (1992).

Digestion of samples for Fe, Cu, Zn, Pb, Mn and As determination

Digestion of the samples was done using concentrated nitric acid

Table 1. Names of sampling sites, sample-collection streams and their geographical locations.

Sample location and code	Name of stream	GPS reading
Kronum (S1)	Owabi	N:06.75838, W:001.64526
Bremang (S2)	Akyeampomene	N:06.73532, W:001.63704
Ampabaame (S3)	Pumpunase	N:06.722582, W:001.65160
Abrepo (S4)	Sukobri	N:06.71186, W:001.64004
Atafoa (S5)	Owabi	N:06.73911, W:001.66418

Table 2. Results for the physical parameters of the water samples; including the means, SDs and ranges of the values.

Parameter/ Site	Temperature (^{o}C)	pH	Conductivity (Scm^{-1})	Turbidity (NTU)	Colour (PtCo)
S1 range	22.1 - 27.48	6.75 – 7.40	233 - 418	21.1 - 83.6	75 - 288
mean + SD	25.41 ± 2.72	7.08 ± 0.24	317 ± 54.76	51 ± 21.54	151 ± 54.97
S2 Range	26.2 – 30.4	7.22 – 7.90	377-830	81.5-157	56-812
Mean + SD	28.62 ± 1.69	7.55 ± 0.29	684 ± 82.98	133. 23.22	309 ± 112.56
S3 Range	28.1 - 33.9	7.1 - 8.81	804-1817	95.3-244	79-482
Mean + SD	30.51 ± 2.21	7.88 ± 0.61	1370 ± 221.32	205 ± 32. 59	301 ± 76.92
S4 range	25 - 29.1	7.35 – 7.93	540-1137	53.8-812	85-1882
mean + SD	27.16 ± 1.76	7.55 ± 0.22	955 ± 67.93	227 ± 43.84	672 ± 122.05
S5 range	23.3 – 28.44	7.32 – 7.76	280-550	36.5-60	30-153
mean + SD	26.58 ± 2.33	7.56 ± 0.14	465 ± 54.21	48 ± 3.96	89 ± 32.76
Natural background	22-29	7	50-300	-	5

according to (Zhang, 2007). Concentrated nitric acid (5 ml) was added to 50 mL of sample of water in a 100 mL beaker. This was heated on a hot plate to boil until its volume reduced to 20 mL. Another 5 mL of concentrated nitric acid was added and then heated for another 10 min and allowed to cool. About 5 mL of nitric acid was used to rinse the sides of the beaker, the solution was quantitatively transferred into a 50 mL volumetric flask and made up to the mark with distilled water. A blank solution was similarly prepared. Heavy metal analysis was done using Atomic Absorption Spectrophotometer (Model; Unicam 969) Calibration curves were drawn for each metal by running suitable concentrations of their standard solutions, from which the concentrations of the elements were obtained by extrapolation. Average values of three replicates were taken for each determination. The absorbance of the blank was taken before the analysis of the samples.

Statistical analysis

Statistical analysis of the results at each site were carried out using both Microsoft Excel (2003 Edition) and Statistical Package for Social Science (SPSS) software. The relationships between the elemental concentrations in water samples at each site were evaluated by linear regression and the determination of Pearson correlation coefficients. All errors were calculated at 95% confidence level.

RESULTS AND DISCUSSIONS

The result obtained for all the parameters analyzed are summarized in Tables 2 and 3. The temperatures of the water samples were normal. The average temperature ranged from 25.41 ± 2.27^{o}C at River Owabi (S1) to 30.51 ± 2.21^{o}C at River Pumpunase (S3) (Table 2). Samples from S1 and S5 showed noticeable variation in temperature. All the water samples showed alkaline pH. Their mean pH values varied from 7.08 ± 0.24 at S1 to 7.88 ± 0.61 at S3. The lowest pH of 6.75 was obtained for the S1 samples; while the highest pH of 8.81 was obtained for the S3 samples. No significant difference was noticed in the observed pH ranges at each site and the variation in pH due to change in sampling location was also not significant. The WHO range for drinking and potable water is 6.5 to 8.5 (WHO, 2003). All the mean values of pH obtained for the streams fell within this range but were slightly above the natural background level of 7.0. This

Table 3. Results for heavy metal analyses; including their means, SDs, and averages

Parameters/Sites	Fe (mg/L)	Zn (mg/L)	Pb (mg/L)	Cu (mg/L)	Mn (mg/L)	As (mg/L)
S1						
Range	1.27 – 1.69	0.1 – 0.3	0.01 – 0.02	0.01 –0.08	0.02 – 0.2	0.05 – 0.1
Mean ± SD	1.43 ± 0.15	0.23 ± 0.07	0.02 ± 0.01	0.04 ± 0.03	0.121 ± 0.05	0.09 ± 0.02
S2						
Range	0.11 – 0.16	0.01 – 0.03	0.01 – 0.02	0.01 – 0.03	0.02 – 0.24	0.07 – 0.1
Mean ± SD	0.14 ± 0.01	0.02 ± 0.06	0.02 ± 0.01	0.02 ± 0.01	0.14 ± 0.12	0.09 ± 0.01
S3						
Range	0.23 – 0.28	0.01 – 0.02	0.01 – 0.03	0.01 – 0.02	0.05 – 0.24	0.0 – 0.06
Mean ± SD	0.26 ± 0.02	0.01 ± 0.01	0.02 ± 0.01	0.014 ± 0.01	0.13 ± 0.09	0.01 ± 0.02
S4						
Range	0.15 – 0.18	0.01- 0.03	0.02 – 0.03	0.01 – 0.04	0.01 – 0.2	ND – 0.05
Mean ± SD	0.16 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.022 ± 0.01	0.10 ± 0.08	0.011 ± 0.02
S5						
Range	0.01 – 0.03	0.01 – 0.02	0.01 – 0.03	0.01 – 0.03	0.01 – 0.17	ND – 0.01
Mean ± SD	0.02 ± 0.006	0.02 ± 0.005	0.017 ± 0.01	0.02 ± 0.007	0.099 ± 0.05	0.004 ± 0.001
Natural Background	0.670	0.030	0.005	0.005	0.120	-

§ ND = Not Detectable.

increase in pH of the water samples above the normal background levels may be due to the presence of dissolved carbonates and bicarbonates present in the water, which are known to affect pH of almost all surface water (Chapman, 1992).

Electrical conductivity (EC) is the numerical expression of an aqueous solution to carry electrical current and is a useful indicator of the mineralization in a water sample (Jain et el. 2005). The lowest EC of 233 was obtained for the S1 samples; while the highest EC of 1817 was obtained for the S3 samples. The ECs varied between 233 - 418 Scm^{-1} (with a mean of 317 ± 54.76 Scm^{-1}) at S1 and 804 - 1817 Scm^{-1} (with a mean of 1370 ± 221.32 Scm^{-1}) at S3 (Table 2). The WHO limit for EC for drinking and potable water is 700 Scm^{-1} (WHO, 2003). This limit was exceeded in S3 and S4 samples. Based on this parameter, these two rivers are not suitable for domestic use. Health effects in humans for consuming water with high EC may include disturbances of salt and water balance; and adverse effect on certain myocardic patients and individuals with high blood pressure (Fatoki and Awofolu, 2003).

The mean turbidity values ranged from a minimum of 48.0 ± 3.96 NTU, in S5, to a maximum of 227 ± 48.84 NTU. These values were recorded for S5 and S4 respectively. There were significant differences (p<0.05) in all the sampling points with point (S3) showing a tremendous variation. The observed mean turbidity values for all the streams were well above the safe limit for drinking water (WHO, 2003). It has been realized that the type and concentration of suspended solids in a water body controls the turbidity of the water (Chapman, 1992). Over-cultivation along the river banks leaves the soil bare and hence susceptible to erosion during the raining season.

In the whole study area, the highest average concentra - tions of the analyzed trace metals equaled (in decreasing order) 1.43 ± 0.15 mg/L for iron at S1, 0.23 ± 0.07 mg/L for zinc at S1, 0.14 ± 0.12 mg/L for manganese at S2, 0.09 ± 0.12 mg/L for arsenic at S2 0.04 ± 0.03 mg/L for cupper at S1 and 0.03 ± 0.01 mg/L for lead at S4. Table 3 reports the range of values and mean concentrations of heavy metals in our study area. Background reference concentrations (BRC) are also reported in order to give an idea of the concentrations that would be expected to be found in surface water in the absence of any human activity. The concentration of essential nutrients (Zn, Fe, Mn and Cu) are similar to the values measured in the main tributaries of the Densu River and some selected streams in the Brong Ahafo region of Republic of Ghana (Akpabli and Drah, 2001; Akoto and Adiyiah, 2007) . Besides, the presences of two toxic metals Pb and As found in the Dansu river are relatively lower than concen- tration measured in this study. From the results in table 3, the mean level of Zn ranged from 0.01 ± 0.01 mg/L for S3 to 0.23 ± 0.017 g/L for S1. The tolerance limit for Zn in water for domestic supply is 5 mg/L (US EPA, 2003) . Therefore, Zn concentration is adequate if the water is used for only domestic purposes. However, Zn could be a problem in water for other uses, for example, for the use of the aquatic ecosystem. The range for Zn in water for the use of aquatic ecosystem is

Table 4. Correlations of different heavy metals, pH and EC of the water samples at S5.

	pH	EC	Fe	Zn	Pb	Cu	Mn	As
pH	1.000							
EC	-0.320	1.000						
Fe	0.329	-0.160	1.000					
Zn	-0.293	-0.060	0.068	1.000				
Pb	0.252	0.279	0.364	-0.383	1.000			
Cu	-0.352	0.675*	0.050	-0.185	0.659*	1.000		
Mn	0.073	0.634*	-0.078	0.325	-0.109	0.006	1.000	
As	0.723*	0.284	0.298	-0.183	0.349	0.000	0.607	1.000

*Correlation is significant at the 0.05 level (2-tailed).

is 0 to 0.02 mg/L. This limit was exceeded in the Owabi at S1. Thus, water from this river is unsuitable for use for the aquatic ecosystem as it could be detrimental to fish and other aquatic lives.

It is remarkable that some of these metals exceeded the levels stipulated by WHO for water sources utilized for various purposes. Noticeable among them are Pb and As with recommended values for drinking water, fisheries, and aquatic life given as 0.007 - 0.01 mg/L for Pb and 0.001- 0.01 mg/L for As (Committee for fisheries, 1993). Pb had a mean range of 0.017 ± 0.01 mg/L for the S5 samples to 0.03 ± 0.01 mg/L for the S4 samples and As had the range of 0.004 ± 0.001 mg/L to 0.09 ± 0.01 mg/L for the S5 and S2 samples respectively. Each ele-ment had values comparatively higher than acceptable limits set by WHO, and WHO's published recommended limits for these metals are not supposed to be exceeded. The amount of these toxic metals in all the water samples did not show any significant variations.

The mean concentration range of Fe, Mn and Cu in all the water samples varied from 0.02 ± 0.006 -1.43 ± 0.15 mg/L, 0.099 ± 0.08 - 0.14 ± 0.12 mg/L, and 0.014 ± 0.01-0.04 ± 0.03 mg/L respectively. Of all the sampling sources, the highest mean concentrations of Fe (1.43 ± 0.15 mg/L) and Cu (0.04 ± 0.03 mg/L) were observed for the S1 samples and Mn (0.14 ± 0.12 mg/L) for the S2 samples. Whereas Fe (0.02 ± 0.006 mg/L) and Mn (0.099 ± 0.08 mg/L) were at minima in the S5 samples, minimum Cu (0.014 ± 0.01 mg/L) was observed in the S3 samples. The highest concentrations of most of the heavy metals (Fe, Zn, Cu and As) were obtained in the S1 samples.

The concentrations of most of the metals in the Owabi stream at Kronum (S1) which is upstream generally showed higher values as compared to samples from the same stream at Atafoa (S5), which is downstream and closer to the reservoir. This may be due to the dilution effect from other tributaries that join the river before the sampling point at S5. In addition, in warmer season metal levels are likely to be reduced by biochemical processes. In Ghana, temperatures are high in the dry season and this increases the biochemical activities in the stream.

Since there were no runoffs into the streams, the concentrations of the metals are reduced the more.

Furthermore, of all the heavy metals investigated, Mn and to a lesser extent, Pb showed the most even distribution throughout the study area and a relatively restrict-ted range of concentration variability. This is because the major source of Pb in the catchment is from atmospheric inputs. Correggiari et al. (1989) found that riverine and terrestrial inputs represented negligible sources of Pb and Cd as compared with atmospheric deposition. On the contrary, heavy metals Fe, As and Cu showed a clear trend in distribution in the study area. In general, all the water sources had high concentrations of toxic metals (Pb and As) and low concentrations of Fe, Zn and Cu (micro-nutrients).

Possible metal-metal, metal-pH and metal-EC relation-ships were investigated using the Pearson correlation coefficient, r, $p < 0.05$ and 0.01 significant levels. At S1 pH-Fe and As-Zn are significantly correlated with r values of 0.662 and 0.754 respectively. There was no significant correlation observed in the heavy metals with the ECs. At S2 Mn and Zn exhibited a significant correlation with pH with r values of 0.932 and -0.764 respectively and inverse correlation (Fe-EC) with r value of -0.704 was observed. Pb exhibited significant positive correlation with Zn with r value of 0.667 at S3. Mn significantly correlated with pH, EC and Fe with r values of 0.647, 0.702 and 0.799 respectively. Fe and Pb also exhibited positive significant correlation with r value of 0.795. At S4, pH correlated sig-nificantly with EC (r = -0847) and Zn (r = 0.722). There was inter-elemental significant correlation between Zn and Pb (r = 0.66). At S5 EC correlated significantly with Cu and Mn, Pb showed significant correlation with Cu and As had a significant positive correlation with pH (Table 4) . These significant correlations of metals are indicative of a common source of pollution in the rivers.

Conclusion

The results showed that, the water is unfit for drinking purposes. Once pollution trends set into a water body, it

generally accelerates to cause greater deterioration of the watershed. It is therefore recommended that close monitoring of the various human activities within the Owabi watershed be established to minimize their impact on the ecosystem.

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