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HEAVY METAL ANALYSIS OF FRESH WATER SUPPLIES AND WASTEWATERS: A CASE OF CHINHOYI AND HARARE, ZIMBABWE

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ABSTRACT

Heavy metals are of significant bioimportance as trace elements. However, the biotoxic effects of heavy metals to man and his environment are of great concern. The study was conducted to assess the levels of physico-chemical parameters and heavy metals in both fresh water supplies and wastewaters. Fresh water supplies and wastewater samples from Chinhoyi (n=7) and Harare (n=8) were collected and analysed for the presence and concentrations of heavy metals: Atomic absorption spectra (ZF-9, Japan) was employed to analyse trace elements of cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe) and lead (Pb). Analyses of elements were done following calibration and equilibration of the equipment by known standard procedures. Temperature and pH were determined during sampling using Mettler Toledo universal Pocket Meter (USA). The mean concentrations of samples from each of these two cities were computed using simple descriptive statistics. The characteristics for samples from Chinhoyi were pH ranged between 5.78-8.08 with a mean of 6.78, temperature ranged between 25.97-29.63 °C with a mean of 28.08 °C, Fe concentration ranged between 0.03-8.85 mg^{-l} with a mean of 2.21 mg^{-l}, Pb concentration ranged between 0.00-0.05 mg^{-l} with a mean of 0.02 mg^{-l} and Cu concentration ranged between 0.06-0.25 mg^{-l} with a mean of 0.11 mg^{-l}. The profiles of samples from Harare were pH ranged between 2.86-7.01 with a mean of 4.65, temperature ranged between 23.40-29.90 °C with a mean of 26.69 °C, Fe concentration ranged between 0.05-16.35 mg^{-l} with a mean of 3.08 mg^{-l}, Pb concentration ranged between 0.00-0.07 mg^{-l} with a mean of 0.03 mg^{-l} and Cu concentration ranged between 0.06 -0.16 mg^{-l} with a mean of 0.09 mg^{-l}. However, the mean levels of pH from Harare and Fe from both cities were not within the legally recommended limits for water and wastewater disposal of the Government of Zimbabwe. Effective pre-treatment of wastewater at industrial sites and strict enforcement of regulations regarding their disposal could minimise environmental and health hazards in freshwaters. The role of both small scale to commercial agriculture and extensive mining operations is also highly implicated in this study.

Keywords: Heavy metals; trace; concentration; detection

1. INTRODUCTION

Water is an absolute requirement of life on our planet. The distribution, quality, quantity and availability of freshwater rivers, lakes and ground water are the major drivers for development of agriculture, industry, rural, urban and municipal use (Vandas *et al*., 2002). The addition of persistent and recalcitrant xenobiotics is now gradually polluting our ground and surface water resources (Kamusoko and Musasa, 2012). The increased water pollution has been largely assigned to rapid urbanization and industrialization (Mishra and Bhatt, 2008). Streams and rivers which collect impurities from surface run off, municipal and industrial effluents act as feeder streams of major rivers, lakes or reservoirs that supply our drinking water (Salem *et al*., 2000). The problem of water pollution by toxic heavy metals has recently become a major cause concern in most metropolitan cities (Prabu, 2009). Heavy metals are toxic even at low concentration to both humans and aquatic biota. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements (Duruibe *et al*, 2007). Generally heavy metal bioaccumulate during metabolic processes and yet their biotoxic effects in human biochemistry are hugely unexplored (Duruibe *et al.*, 2007). Interestingly, some heavy metals like iron, copper, zinc, nickel and other trace elements are needed for proper functioning of biological systems. Deficiencies of these trace elements may lead to a number of disorders (Prabu, 2009). Their potential accumulation in biosystems and food chain has been documented. Thus a better understanding of heavy metal contamination profiles and their effect in water, soil and plant systems has attracted a lot of research interest (Prabu, 2009).

Biotoxicity of heavy metals refers to the harmful effects to the body when consumed especially above the bio-recommended limits (Duruibe *et al.*, 2007). In humans such elevated levels may lead from simple changes to lethal body disorders. Excessive heavy metal levels in natural waters may cause the following sub-lethal effects in aquatic organisms: histological or morphological change in tissues; changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation; change in biochemistry, such as enzyme activity and blood chemistry; change in behaviour; and changes in reproduction (Connell and Millar, 1984). Heavy metal toxicity in form of sulphides, phosphates and carbonates are very insoluble in hard waters and usually travel with sediment. However the availability of these metals in biosystems is determined by precipitation-dissolution reactions which are strongly affected by pH. Therefore, at a lower pH, metallic ions are more available and more reactive. More importantly, most of heavy metals then undergo methylation as they bioaccumulate in microorganisms. Excessively high and low pH values can also be detrimental for the use of water. High pH causes a bitter taste, water pipes and water-using appliances become encrusted with deposits, and it depresses the effectiveness of the disinfection of chlorine, thereby causing a high chlorine demand during water treatment. Low pH water will corrode or dissolve metals and other substances. In addition, excessive PH extremes lead to increased chlorine demand during water treatment processes.

Freshwater supplies and wastewaters are known to have a high degree of variability in terms of physico-chemical quality, heavy metal concentration, microbial quality and other factors which affect human health, urban agriculture and industrial production. Currently, Lake Chivero, the largest water supply to the City of Harare has experienced problems of pollution and eutrophication. It is suspected that pollution in the lake is caused by nutrients, and chemicals introduced by disposal of not properly treated sewage effluent on land or into rivers feeding the lake (Moyo, 1997). Chinhoyi is part of Mashonaland West Province located 120 km away from Harare, the national capital. It has also experienced problems of pollution in some of its major water supplies. At one time, the municipality of Chinhoyi was charged by Environmental Management Agency (EMA) for discharging raw sewage in Cold stream which feeds Hunyani River. The importance of maintaining good water quality highlights the increasing need for advanced technologies to help monitor and manage water quality. Traditional methods have been used to determine the concentration of heavy metals in water and wastewater and they are is still important today. However, these methods are expensive, less sensitive and time consuming. Biosensors are now becoming popularly important tools used in many civilian areas including environment and habitat monitoring as emergence technology. A combination of potable biosensors and field spectroscopy offer an efficient and cost-effective way of in situ determination of heavy metal and physico-chemical levels in aqueous solutions. Therefore, the present study has been undertaken to assess the profiles of heavy metals and physico-chemical parameters in fresh water supplies and wastewaters. This was an initial step towards development of biosensor from low cost maize tassel biomaterial for detection of heavy metals in aqueous solutions.

2. EXPERIMENTAL

2.1 MATERIALS

Concentrated nitric acid, perchloric acid, griffin beakers of assorted sizes, qualitative filter paper and filter funnels, graduated cylinder, electric hot plate, deionised water (double distilled water with a resistance of 20).

2.2 INSTRUMENTATION

Atomic absorption spectrophotometer (ZF-9, Japan) was employed to analyse trace elements of Cr, Cu, Pb, Fe, and Cd and Mettler Toledo Universal pocket meter (USA) was employed to determine both the pH and temperature at the sampling point. The determination was done following calibration and equilibration of the equipment using the standard procedure from the manufacturer.

2.3 PROCEDURES

2.3.1 SAMPLING

Sampling had been carried out during November 2010. The locations selected for the investigation in Chinhoyi were Chinhoyi University of Technology (CUT) farm dam, CUT dam (Nutrichem side), Hunyani River, Cold stream, Angwa River (Golden Kopje), Chinhoyi caves, and Angwa River (Alaska). In Harare, Glenlorne stream (Mutoko Road), Cleveland dam, Zimphos stream, Mukuvisi River (Magaba), Prince Edward dam, Marimba River and Lake Chivero were selected for sampling. Analysis of pH and temperature were done at the point of collection. Grab fresh water and wastewater samples (Chinhoyi, n=7; Harare, n=8) were collected in clean polyethylene containers that were rinsed by the sample at the sampling point. These were then transported in ice cool boxes to the Standard Association of Zimbabwe (SAZ) for further characterization within 24 hrs.

2.3.2 HEAVY METAL ANALYSIS

Samples were first filtered prior to acidification for heavy metal analysis. Following this was digestion in nitric acid and perchloric acid to reduce the volume. The digestate was diluted to volume and the concentrations of heavy metals were determined using an atomic absorption spectrophotometer (AAS) (JF-9, Japan). Temperature and pH were measured on site, with Mettler Toledo universal Pocket Meter (USA).

2.4 DATA ANALYSIS

Data pertaining to the above parameters were subjected to statistical analysis. The observations were treated by simple descriptive statistics using GraphPad Prism 6 software program.

3. RESULTS AND DISCUSSION

The research has presented physicochemical and heavy metal analysis of some fresh water supplies and wastewaters of samples collected from different sources from Chinhoyi and Harare.

3.1 PHYSICO-CHEMICAL PARAMETERS

The mean pH of 6.78 reported from Chinhoyi was close to neutral and was within the recommended limits (6-9) of the Government of Zimbabwe. The pH ranged from acidic to alkaline conditions between 5.78 and 8.08. Chinhoyi caves reported the minimum pH of 5.78 and it was below the recommended range while CUT dam (Nutrichem side) recorded the maximum pH of 8.08. On the other hand, the pH profiles from most research sites in Harare were very low with a mean of 4.65 below the recommended limits. The minimum pH of 2.86 was reported in Zimphos stream and the maximum pH of 7.01 in Marimba River. The possible reason for very low pH may be acidic process wastewaters from industrial and mining activities. For example, Zimphos, a fertilizer manufacturing company discharges process wastewaters containing sulphuric acid that may result in reduction of pH in its stream. Extremes of pH of water and wastewater are generally not acceptable as they pose problems to survival of aquatic life (Kavitha *et al*., 2012). In addition, acidic pH also increases the solubility (availability) and reactivity of heavy metals often leading to their subsequent bioaccumulation in bacteria. Microbial metabolic processes of bioaccumulated heavy metals lead to their conversion into toxic organometallic compounds (Connell and Millar, 1984; Kavitha *et al*., 2012). The pH of water also determines the solubility and bioavailability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon). For instance, Lake Chivero is now eutrophic due to high levels of plant nutrients, probably a result of low pH from its feeder streams. Low pH in water is also corrosive to metals and other materials when used for domestic purposes. In a study conducted by Kashyap (2008), low pH conditions were found to be highly aggressive in corrosion of concrete.

The mean temperatures of samples from Chinhoyi and Harare were 28.08 °C and 26.69 °C respectively. The maximum temperature of 29.63 ˚C was reported from Angwa R. (Golden kopje) and Angwa River (Alaska) showed the minimum temperature of 25.97 ˚C in Chinhoyi. In Harare, Zimphos stream and Mukuvisi River reported the maximum temperature of 29.90˚C while the minimum temperature of 23.40˚C was noted in Marimba River. The temperatures of all the samples from Harare and Chinhoyi fell within the acceptable limits (<35 ˚C) of the Government of Zimbabwe, a signal of minimal hazards of thermal pollution. It is known that severely depressed or elevated temperature regimes affect the speciation levels of pollutants in water. The data for pH and temperature profiles for Chinhoyi and Harare research sites are shown in table 1 and 2 respectively.

3.2 HEAVY METALS

The general trend showed that the profiles of average concentrations for heavy metals were higher in Harare than Chinhoyi. As a result Harare residents and surrounding community are more exposed to health risks than those from Chinhoyi since they are more likely to consume water with high levels of heavy metals. A comparison of heavy metal concentrations for Chinhoyi and Harare is shown in Figure 1.

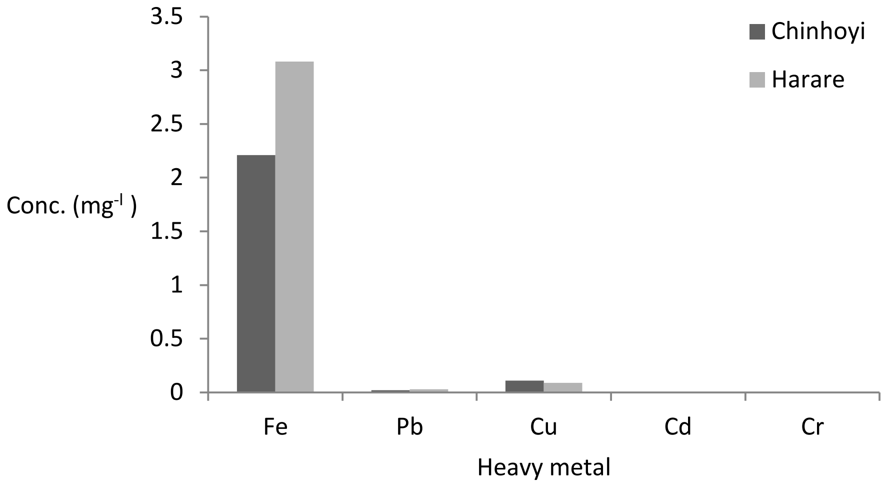

Fig. 1. Comparison of mean heavy metal concentrations for Chinhoyi and Harare.

The mean Fe concentration of 2.21 mg^{-l} from Chinhoyi exceeded the acceptable limits (≤0.3 mg^{-l}) of the Government of Zimbabwe. Chinhoyi Caves reported the minimum Fe concentration of 0.03 mg^{-l} while the maximum Fe concentration of 8.85 mg^{-l} was observed in Cold stream. However, samples collected from Harare reported a characteristically high mean Fe concentration of 3.08 mg^{-l} that was also above the legally acceptable limits. Town House reported a minimum Fe concentration of 0.08 mg^{-l} and Zimphos stream had a maximum Fe concentration of 16.35 mg^{-l}. Sulphuric acid, a raw material for production of fertilisers such as superphosphate of lime and ammonium sulphate at Zimphos is manufactured using Fe as catalyst, a probable reason for such elevated levels in Zimphos stream. The other possible sources for the Fe could be galvanising, electroplating and polishing industries as well as agricultural and mining activities. Fe is known to promote the growth of iron bacteria in drinking water and also makes water distasteful. It also forms rust in water and cause clogging and staining of pipes (Kurup *et al*., 2010). High levels of Fe in drinking water may also cause Fe overload in the body despite its recommendation for formation of functional molecules such haemoglobin (Casiday and Frey, 2000).

Cd was not detected under experimental conditions from all the research sites. Interestingly, Cd is well known to have some profound toxic effects to human body systems even at extremely low levels. Some trace amounts of Cr that were reported from Glenlorne stream and CUT dam (Nutrichem side) may be a result of alloys, preservatives, dying and tanning activities, and metal coatings from industrial activities. Chinhoyi had a mean Pb concentration 0.02 mg^{-l} and ranged between 0.00 and 0.05 mg^{-l}. T he mean Pb concentration of samples from Harare was 0.03 mg^{-l}. The maximum Pb concentration of 0.07 mg^{-l} from L. Chivero exceeded recommended limits (≤0.05 mg^{-l}). Pb is the most significant toxin of the heavy metals. These high levels of Pb can pose serious threat to the public health given that Lake Chivero is the major supplier of water to greater Harare area and surrounding communities. Such elevated levels of human exposure may lead to damage of almost all organs, most importantly the CNS, kidneys and blood, culminating in death at excessive levels (Tong *et al*., 2000). It will be more interesting to determine the current Pb pollution in communities which currently consumes water from Lake Chivero. Furthermore, this lake is famous for fish supplies to Harare and Norton towns. A lot more, Pb contamination may remain unreported and would continue to kill people in these areas. The possible sources of Pb may be the discharge of industrial wastes from leaded gasoline, tire wear, pigments, lubricating oil and grease, bearing wear, lead acid batteries, solder, alloys, cable sheathing, rust inhibitors, ammunition, glazes and plastic stabilizers (WHO, 2011), into feeder streams of the lake. Mean Cu concentrations of 0.11 and 0.09 mg^{-l} from Chinhoyi and Harare respectively were within the acceptable limits (≤1.0 mg^{-l}) of the Government of Zimbabwe. According to Prabu (2009), Cu is essential in trace amounts for human life, but high doses may lead to anaemia, liver and kidney damage, stomach and intestinal irritation also induces hypertension, coma and sporadic fever. The mean concentrations of heavy metals in samples from Chinhoyi and Harare are shown table 1 and 2 respectively.

Table 1. Mean levels of temperature, pH and heavy metals in samples from Chinhoyi

Parameter	Unit	Range of values	Mean (± standard deviation)
pH	pH units	5.78-8.08	6.78±0.83
Temperature	°C	25.97-29.53	28.08±1.27
Iron	mg^{-l}	0.03-8.85	2.21±3.23
Lead	mg^{-l}	0.00-0.05	0.02±0.02
Copper	mg^{-l}	0.06-0.25	0.11±0.06
Cadmium	mg^{-l}	*nd	*nd
Chromium	mg^{-l}	0.00-0.01	0.001±0.004

***Table 2**.* Mean levels of temperature, pH and heavy metals in samples from Harare

Parameter	Unit	Range of values	Mean (± standard deviation)
pH	pH units	2.86-7.01	4.65±0.57
Temperature	°C	23.40-29.90	26.69±0.81
Iron	mg^{-l}	0.08-16-35	3.08±2.00
Lead	mg^{-l}	0.00-0.07	0.03±0.01
Copper	mg^{-l}	0.06-0.25	0.09±0.01
Cadmium	mg^{-l}	*nd	*nd
Chromium	mg^{-l}	0.00-0.03	0.004±0.004

***nd**: non-detectable

4. CONCLUSION

The study concluded that wastewaters distributed in Chinhoyi and Harare need more effort in limiting the levels of heavy metals released into freshwater supplies. The mean level of pH from Harare and Fe from both cities exceed the legal regulatory framework suggesting that some agricultural, mining, municipal and industrial activities are increasing contaminant concentrations in freshwater resources. Effective pre-treatment of wastewater at industrial sites should be a pre-requisite prior to disposal into freshwater resources. Failure to comply with the legal regulatory framework would imply that the regulations that govern the disposal of wastewaters should be strictly enforced by responsible authorities in order to minimise contamination of freshwater supplies. Awareness campaigns should be held to the public regarding the ecological and health effects of polluting freshwater resources. This would help to minimise the contribution of human-made activities in deteriorating the quality of water. The results from this study may form a baseline survey for the determination of profiles of heavy metals towards development of sensor for detection of heavy metal in aqueous solutions. Normally sensors have the capacity to detect concentrations of heavy metals that are lower than the heavy metal profiles obtained in this study.

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