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ICP-MS determination of toxic heavy metals from Lotsane river and nearby boreholes in Botswana

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Abstract

The study was performed on water samples along Lotsane river and nearby boreholes close to Palapye in the central district of Botswana which provide drinking water for some inhabitants. The concentrations of toxic heavy metals in water were measured using inductively coupled plasma-mass spectrometry (ICP-MS) in order to determine the quality of water from this area. The mean toxic heavy metal concentrations for water samples in mg/L from the various locations presented in descending order are Zn > Cu > Ni > Pb > Cr > Co > As. The ranges of these toxic heavy metals in mg/L were: Zn (0.036 to 5.271, averaging 0.871); Cu (0.031 to 1.362, averaging 0.451); Ni (0.001 to 0.212, averaging 0.056); Pb (0.001 to 0.083, averaging 0.029); Cr (0.000 to 0.025, averaging 0.006); Co (0.000 to 0.004, averaging 0.002); As (0.000 to 0.002, averaging of 0.001) respectively. The average As, Cr, Cu, Co and Ni drinking water concentrations were lower than the recommended international limits while Pb and Zn had higher values than the recommended international limits. The high concentrations of toxic heavy metals Pb and Zn might be attributed to elevated levels of acid mine drainage from the study [Winde et al., 2004]. This pilot study will provide drinking water quality awareness to residents in the area.

Keywords

ICP-MS; toxic heavy metals; drinking water; water quality; acid mine drainage

1 Introduction

Humans have been exposed to toxic heavy metals for a very long time. Anthropogenic and natural activities have resulted in toxic heavy metals being found in all places [Wang et al., 2017]. Toxic heavy metals are generally characterised by a specific gravity larger than 5 $g.cm^{-3}$, high atomic number and weight. This classification type covers some lanthanides, actinides, transition metals, metalloids, basic metals and metals from groups III to V of the Periodic Table. Examples of toxic heavy metals include cadmium (Cd), copper (Cu), arsenic (As), cobalt (Co), lead (Pb), selenium (Se), chromium (Cr), zinc (Zn), manganese (Mn), nickel (Ni) and mercury (Hg) [Tchounwou, 2012]. Generally, organic pollutants decompose to slowly produce water and carbon dioxide, whereas toxic heavy metals are not normally broken down and will therefore mostly bio-accumulate. This results in toxic heavy metals remaining in the natural environment

and being moved from one medium to another. They are consumed on a daily basis by humans through food, air, water or soil [Atieh et al., 2017]. The toxicity level and symptoms on humans vary based on the metal, the absorbed dose and whether the exposure was chronic, acute or not. Some toxic heavy metals are detrimental to human body tissues and organs. Toxic heavy metals may be toxic to humans as well as animals even if present in very small quantities [Kamunda, 2017]. The combustion of coal at the nearby Morupule coal power station has potential to release elevated amounts of toxic heavy metals into the surrounding water bodies which have the potential to result in health effects for the surrounding population.

Certain metals including copper and iron are essential for human life due to their unique functions in body organs. Each living organism requires different toxic heavy metal amounts. At high concentrations, heavy metals become toxic to living organisms [Lane and Morel, 2009]. Toxic heavy metals including lead, mercury and arsenic have no value to human and numerous additional living organisms. These types of heavy metals may possibly be toxic even at low concentrations. Arsenic, lead and mercury are ranked first, second and third most hazardous respectively on the priority list of toxic heavy metal [ATSDR, 2007]. Anthropogenic activities such as mining might lead to toxic heavy metal contamination of water bodies, land and the general environment. This could in turn result in the extreme toxic heavy metal accumulation in agricultural land, potentially leading to higher heavy metal uptake in plants [Kamunda, 2017]. Unintentional toxic heavy metal intake could also happen via food and drink.

Arsenic is a carcinogen to humans from very low levels of exposure [ATSDR, 2007]. After absorption into the human body, arsenic mostly spreads in the spleen, skin, kidneys, liver, lungs and aorta. Extreme arsenic exposure to arsenic or its compounds might result in nausea, abdominal pain, vomiting, diarrhoea, muscle cramps as well as burning in the throat and mouth [NRC, 1999]. Ongoing exposure to smaller arsenic quantities results in rare skin hyper-pigmentation, peripheral nerve damage, diabetes and tingling [Kamunda, 2017; UNEP, 2002]. Lead is a human mutagen and potential carcinogen [Tchounwou, 2012]. It causes renal tumours, chronic damage to the central and peripheral nervous system, lowers cognitive development, lowers haemoglobin synthesis, surges blood pressure for adult humans as well as disrupting normal functions of the cardiovascular system, reproductive system and kidneys [Ogwuegbu and Muhanga, 2005]. Acute ingestion of mercury salts could induce gastrointestinal disorders like haemorrhage, abdominal pain, vomiting and diarrhoea [Kamunda, 2017]. Chromium (III) is an vital element while chromium (VI) compounds are toxic, carcinogenic as well as mutagenic [Wang et al., 2017]. Chronic exposure might cause skin irritation, nervous disorders, circulatory disorders and damage to the liver or kidney [NRC, 1999].

1.1 Description of study area

The study area includes the upper catchment area of the Lotsane river, an ephemeral river that drains eastwards to Limpopo river. Lotsane river rises from Spring lines originating at the base of the sandveld escarpment and to the west is where the Lotsane river begins. The study area lies on an altitude of approximately 950m above level [Shumba Energy, 2017], located at the GPS coordinates 22.522˚S 27.050˚E and lies approximately 280km to the north of Gaborone.

2 Materials and methods

2.1 Sampling and sample preparation for analysis

A total of eight (8) representative water samples were taken from the study area through the random sampling method at points shown in Figures 1-1 and 1-2 into polyethylene bottles. Figure 1-1 shows the water sampling points in Lotsane river while Figure 1-2 shows the water sampling points near A14 road from Palapye to Serowe. The polyethylene bottles, each of approximately 2 L volume, were then tightly sealed with a lid. All the polyethylene bottles had been previously rinsed using a 0.1M dilute hydrochloric acid (HCl) to reduce contamination. Any suspended sediments and coarse material were removed by filtering the samples through a 0.45 µm filter paper. The collected water samples were then spiked with 1M HNO_3 before being sealed to prevent the adsorption of radionuclides onto the internal surface of the polythene container walls [Martin and Hancock, 1992; Moulton-Meissner et al., 2015]. Each sample was properly labelled with a unique sample code and the respective GPS coordinates recorded in a logbook. All samples were transported to the CARST laboratory for additional processing. Heavy metal analysis was subsequently performed at Eco-Analytica Laboratories in Potchefstroom, South Africa.

Fig. 1 - 1: Water sampling points in Lotsane river [http://www.earth.google.com, Accessed March 16, 2019]

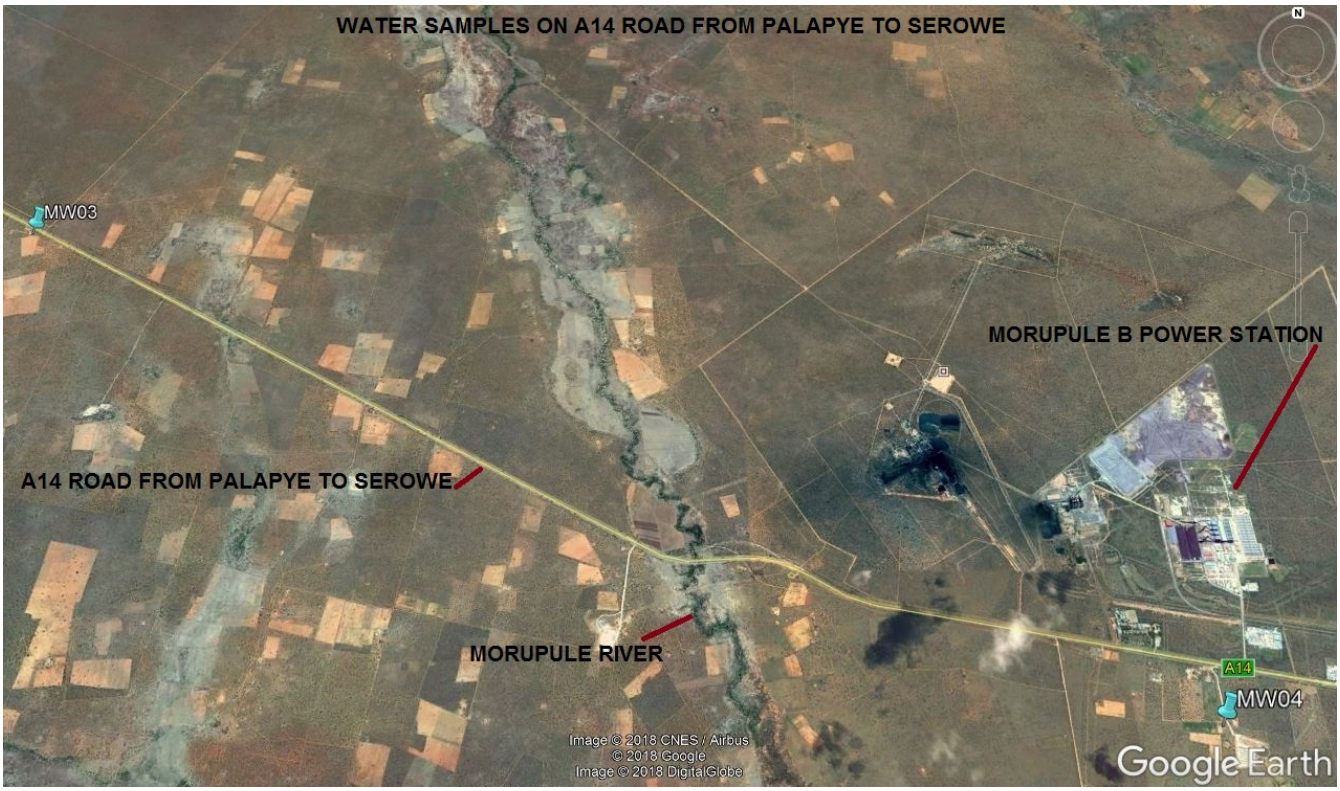

Fig. 1 - 2: Water sampling points on A14 road from Palapye to Serowe [http://www.earth.google.com, Accessed February 22, 2019]

2.2 Inductively Coupled Plasma-Mass Spectrometry

ICP-MS analysis was utilized to perform toxic heavy metal analysis for water, bottom ash, soil, coal and fly ash. ICP-MS is useful in the quantitative determination several elements [Helaluddin et al., 2016]. Prior to being analyzed by the ICP-MS system, the soil, bottom ash, coal and fly ash samples were initially digested by means of a microwave system as explained in the next section. Digestion is performed so as to extract the toxic heavy metals from the soil, fly ash, coal and bottom ash samples. A gram of individually measured dry soil samples as well as 9 mL hydrochloric acid and 3 mL nitric acid were all mixed in a rotor container, with approximately 1 mL hydrogen peroxide being subsequently added to the reaction vessel. The contents were subsequently digested for 45 minutes at 120 ^{o}C. After cooling, the digested contents were then added into 100 mL volume volumetric flasks containing 2 % nitric acid. Distilled water was subsequently utilized in topping up the 100 mL volumetric flask [Kamunda, 2017; Mathuthu et al., 2016]. After sedimenting overnight, the digested contents were sieved using No. 40 Whatman filter paper. Each 5 mL nitric acid, 1 mL hydrochloric acid as well as 5 mL water sample were poured into a rotor vessel containing 1 mL hydrogen peroxide [Kamunda, 2017]. The mixture was again digested following the same procedure as that of fly ash, coal, soil and bottom ash samples.

The TotalQuant method was utilized in enabling drift and contamination detection while also simultaneously increasing the results accuracy. The Perkin Elmer Pure Plus NexION Dual Detector Calibration Solution standard was used. The TotalQuant calibration was attained utilizing 200 micrograms per litre of Ce, Cu, Mn, Al, Ba, Co, U, Ni, In, Li, Mg, Zn, Tb, and Pb [Kamunda et al., 2016]. The standard, blank solution and replicate samples were analyzed simultaneously in adherence to the quality control process. Arsenic, lead, mercury, cadmium,

chromium, cobalt, nickel, copper and zinc were the toxic heavy metals of interest. With the use of equation 1.0, the ICP-MS heavy metal concentration results of mg/L were subsequently changed to mg/kg for solid samples [Kamunda et al., 2016].

$$\frac{(a-b)*v}{w} mg/L \quad (1.0)$$

where

a = toxic heavy metal concentration for the sample in mg/L;
b = toxic heavy metal concentration for the blank in mg/L;
v = total volume of the digest in mL
w = weight of soil sample (g)

3 Results and discussion

3.1 Toxic heavy metal concentrations in water samples

The mean toxic heavy metal concentrations for water samples in mg/L from various locations in the vicinity of the power station are shown in Table 1-1. The mean toxic heavy metal concentrations in water from the power station vicinity presented in descending order are Zn > Cu > Ni > Pb > Cr > Co > As. Toxic heavy metal concentrations below the detection limit were written as 0.000. The ranges of these toxic heavy metals in mg/L were: Zn (0.036 to 5.271, averaging 0.871); Cu (0.031 to 1.362, averaging 0.451); Ni (0.001 to 0.212, averaging 0.056); Pb (0.001 to 0.083, averaging 0.029); Cr (0.000 to 0.025, averaging 0.006); Co (0.000 to 0.004, averaging 0.002); As (0.000 to 0.002, averaging of 0.001) respectively.

Table 1 - 1: Heavy metal concentrations in water samples

Sample Code	**Toxic heavy metals concentration (mg/L)**						
	As	**Pb**	**Cr**	**Cu**	**Zn**	**Co**	**Ni**
MW01	0.000	0.025	0.004	0.853	0.459	0.000	0.125
MW02	0.000	0.083	0.000	1.362	0.137	0.000	0.078
MW03	0.000	0.040	0.000	0.570	5.721	0.000	0.003
MW04	0.000	0.060	0.000	0.658	0.451	0.000	0.212
MW05	0.002	0.007	0.025	0.044	0.036	0.004	0.011
MW06	0.001	0.003	0.010	0.039	0.066	0.003	0.008
MW07	0.001	0.013	0.005	0.054	0.054	0.004	0.012
MW08	0.001	0.001	0.000	0.031	0.047	0.001	0.001
Average	0.001	0.029	0.006	0.451	0.871	0.002	0.056
Minimum	0.000	0.001	0.000	0.031	0.036	0.000	0.001
Maximum	0.002	0.083	0.025	1.362	5.721	0.004	0.212

The results were then compared to the available South African as well as international guidelines of acceptable limits of toxic heavy metals in drinking water shown in Table 1-2.

Table 1 - 2: Recommended toxic heavy metal limits for drinking water [DOH, 2004; USEPA, 2011b; WHO, 2004]

Country	Concentration limit of toxic heavy metals (mg/l)								
	As	Pb	Hg	Cd	Cr	Cu	Zn	Co	Ni
WHO	0.010	0.010	0.006	0.003	0.050	2.000	n.a	n.a	0.070
South Africa	0.010	0.010	0.001	0.003	n.a	1.000	n.a	n.a	n.a
USEPA	0.010	0.015	0.002	0.005	0.100	1.300	0.500	0.100	n.a

n.a: not available

The results indicated that the average As, Cr, Cu, Co and Ni drinking water concentrations were lower than the recommended international limits while Pb and Zn had higher values than the recommended international limits. The high concentrations of toxic heavy metals Pb and Zn might be attributed to elevated levels of acid mine drainage from the study [Winde et al., 2004].

4 Conclusion

The aim of this study was to determine the levels of toxic heavy metals from Lotsane river and nearby boreholes using ICP-MS. The mean toxic heavy metal concentrations for water samples in mg/L from various locations in the study area presented in descending order were such that Zn > Cu > Ni > Pb > Cr > Co > As. Toxic heavy metal concentrations below the detection limit were written as 0.000. The actual ranges of these toxic heavy metals in mg/L were: Zn (0.036 to 5.271, averaging 0.871); Cu (0.031 to 1.362, averaging 0.451); Ni (0.001 to 0.212, averaging 0.056); Pb (0.001 to 0.083, averaging 0.029); Cr (0.000 to 0.025, averaging 0.006); Co (0.000 to 0.004, averaging 0.002); As (0.000 to 0.002, averaging of 0.001) respectively. The results were then compared to the available South African as well as international guidelines of acceptable limits of toxic heavy metals in drinking water [DOH, 2004; USEPA, 2011b; WHO, 2004].

The results indicated that the average As, Cr, Cu, Co and Ni drinking water concentrations were lower than the recommended international limits while Pb and Zn had higher values than the recommended international limits. The excess concentrations of toxic heavy metals Pb and Zn might be attributed to elevated levels of acid mine drainage from the study [Winde et al., 2004]. Excess lead is a human mutagen and potential carcinogen [Tchounwou, 2012]. It also results in damage to the nervous system, brain disorder as well as blood disorder in mammals [Ogwuegbu and Muhanga, 2005]. Excess zinc results in fumes that have a corrosive effect to the skin and also damage nervous membrane [Singh et al., 2011]. Results from this study show that the government should adopt and implement certain treatment technologies in order to minimize the excess heavy metals from waters in Lotsane river and nearby boreholes in order to make it safer for public consumption.

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