

OCCURRENCE OF ALUMINIUM AND BERYLLIUM IN THE OKAVANGO DELTA BOTSWANA: HUMAN HEALTH RISKS

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ABSTRACT

The Okavango River runs through 3 countries; Angola, Namibia and Botswana and is a major source of water for drinking and other domestic uses for the basin communities in the riparian states. Developments in the 3 countries, e.g. agriculture, tourism, mining, power generation industries, etc., are putting pressure on the river's water quality which threatens both human and overall ecosystem health. Data is therefore needed to monitor changes of water quality as a result of both natural and anthropogenic sources. The objective of this study was to quantify the concentration levels of aluminium (Al) and beryllium (Be) at three sites (Mohembo East, Sepopa and Guma) of the Okavango Delta's panhandle, study the influence of water discharge and pH on concentration of these metals and evaluate the human health risks associated with their occurrence. Surface water samples were collected in triplicates every three weeks from 3 sampling sites between July 2014 and October 2015. Samples were preserved with nitric acid and stored in the laboratory before analysis. Direct analysis with ICP-OES was used to determine their concentrations. Al values ranged from 0.032 – 0.305mg/L at Mohembo East; 0.005 – 0.333 mg/L at Sepopa and 0 – 0.151mg/L for Guma. Be concentrations ranged between 0 – 0.008mg/L at all three sites. There were no significant differences ($P>0.05$) between the three sites in concentrations of these metals. Seasonal variations in metal concentrations were observed for both metals, with the highest concentrations occurring around October, coinciding with lowest water levels. In accordance with the WHO regulatory limits for drinking water, the mean concentrations of both Al and Be, and the calculated hazard quotient(HQ) which was less than 1, do not pose any long term human health threats. However, both metals need to be monitored because concentrations above 200 μ g/L for Al and 4 μ g/L for Be (WHO acceptable limits) were exceeded at times at these sampling sites, which may cause acute toxicity to humans and aquatic organisms. From this study, we concluded that both aluminium and beryllium exist in the Okavango River at concentrations comparable to world river values. We recommend a more comprehensive monitoring programme for toxic metals in the Okavango River to ensure protection of both human and ecosystem health.

Keywords: Aluminium, Beryllium, Okavango, Water quality, Human health

1. INTRODUCTION

The Okavango River in Botswana (one of two perennial rivers in the country) is considered a pristine water source by the people of North West District (Mazvimavi and Mmopelwa, 2006) and some scientists who have studied or reviewed the water quality of the river system (Mackay et al., 2011; Masamba and Mazvimavi, 2008; Masamba and Muzila, 2005; Mmualefe and Torto, 2011; West et al., 2015). Most studies however, have based these conclusions on levels of basic water quality parameters such as electrical conductivity, pH, turbidity, dissolved oxygen, nitrogen, phosphorus, microbiological indicators and a few metal ions. The few studies that investigated toxic metals in the delta (e.g. Masamba and Mazvimavi, 2008; Masamba and Muzila, 2005), focussed on the common toxic metals (lead, chromium, cadmium and mercury) and evaluated their effects on ecosystem health. Monitoring of metals in aquatic environments is critical for both human and ecosystem protection (Batayneh, 2011; Genthe et al., 2013; Muhammad et al., 2011). Ecotourism is the major income earner around the Okavango Delta, and prudent ecosystem management is therefore important. The river is a source of water for domestic use, including drinking, for 8.7% of the people living in the area around the delta (CSO, 2011). Therefore the river requires protection from pollutants, especially toxic metals which have not received much attention yet. Data on concentration levels of toxic metals, their mobility, sources and health risks in the Okavango River is scarce, as mentioned, especially for aluminium and beryllium. These metals have not been studied well in the Okavango River, but they have a fascinating hydrochemistry and pose serious human health risks, if present at high concentrations. Aluminium and Beryllium have a similar chemistry in the aquatic environments, probably because of their small ionic size and ease of hydrolysis (Neal, 2003). Aluminium is ubiquitous in the environment, amphoteric in nature and exists in different chemical forms. The monomeric form, which is predominant in acidic and near neutral pH waters is toxic to aquatic organisms (Guibaud and Gauthier, 2003; Ščančar and Milačič, 2006). Toxicity of aluminium to humans is associated with long term exposures (chronic), and manifests in the nervous system as Parkinson's dementia and Alzheimer's diseases (Dzulfakar et al., 2011).

Beryllium is one of the most toxic elements to humans as well as aquatic organisms (Armiento et al., 2012; Calabrese et al., 1985; Neal, 2003). It is also known to be a group 1 carcinogen (IARC, 1993).

Relatively, little attention in terms of research has been given to beryllium probably because of its low concentrations in the environment. In aquatic systems, acidic conditions enhance the mobility of beryllium, and the concentrations are influenced by pH, hydroxides of aluminium, organic matter and fluorides (Armiento et al., 2012; Neal, 2003; Veselý et al., 2002). Exposure to beryllium is associated with respiratory diseases such as chemical pneumonitis, chronic beryllium disease, and cancer (Gordon and Bowser, 2003).

Monitoring of metals in the environment is thus very important for protection of human health and maintenance of ecological systems. The objective of this study was to assess the concentrations of aluminium and beryllium in three locations of the Upper Okavango River in Botswana. The relationship between concentrations of these metals with each other and with discharge was also investigated. An evaluation of the human health risks, calculated as hazard quotients (HQ), associated with these two metals through drinking river water, was carried out for adult population.

2. MATERIALS AND METHODS

2.1 Study area

The Okavango River, the fourth longest river in southern Africa, has its headwaters in the Angolan highlands and traverses through 3 countries; Angola, Namibia and Botswana. It is one of the two perennial rivers in the Botswana and is part of the famous Okavango delta, a Ramsar site and a UNESCO World Heritage site. This makes it a very important river in the country and calls for its protection and management. The upper region of the delta, with its meandering channels, is known as the Panhandle and the lower part is the alluvial fan.

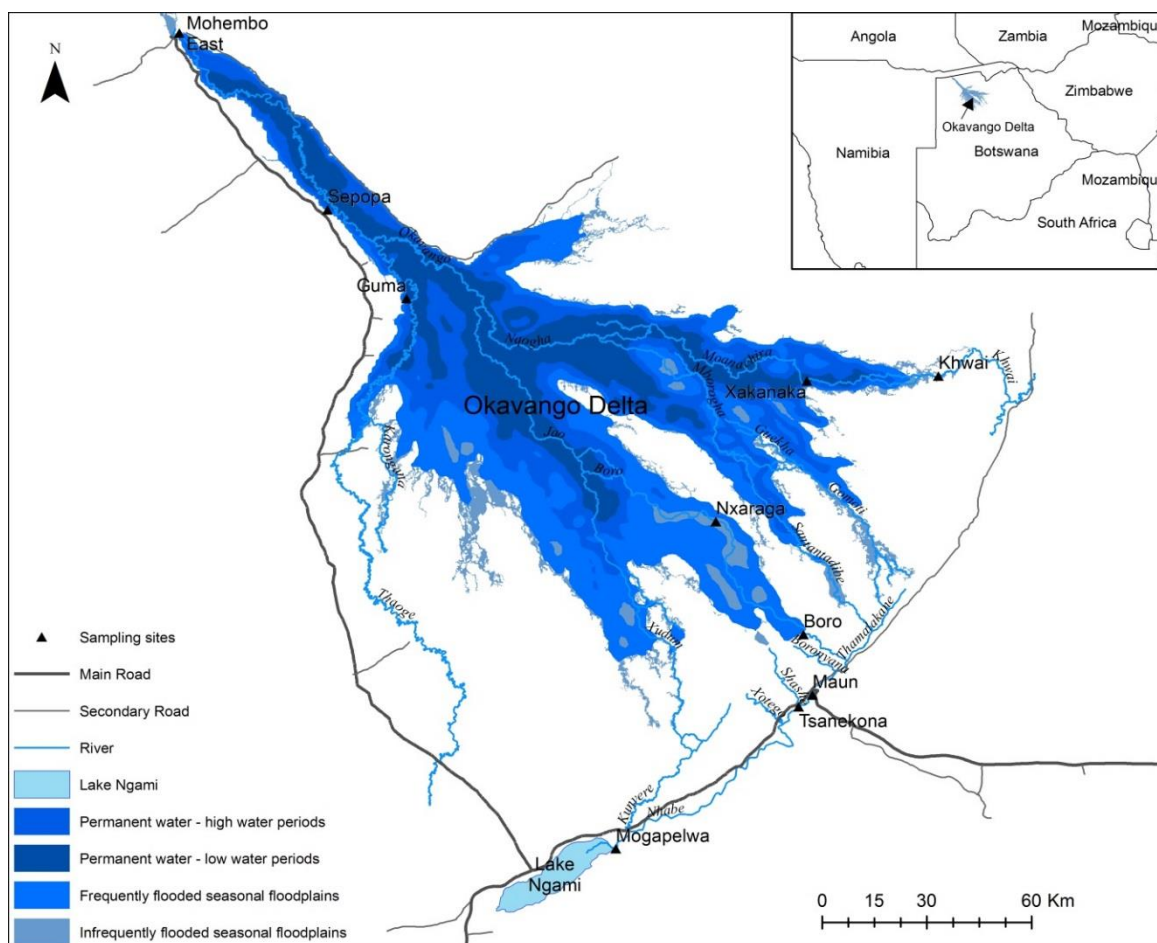


Figure 1. The Okavango Delta in north western Botswana. The panhandle comprises the graben from Mohembo East to Guma

The river serves as major water source for communities living in and around the Okavango delta system and provides water for drinking and other domestic activities; livestock, crop farming and ecological

maintenance (CSO, 2011). Since the water is used without treatment for these purposes, it is important to know its quality for protection of human health and for environmental management. The current study is part of a larger water quality and quantity project which is covering most of the Okavango delta, from the panhandle through the alluvial fan areas, to the terminal Lake Ngami, as shown in Figure 1. The project, Southern African Science Service Centre for Climate Change and Adaptive Land Management (SASSCAL), funded by the German government, is aims at improving inventory of existing water quality and quantity data, also strengthening water quality monitoring and management systems in Botswana.

2.2 Sampling

Water samples were collected from the Okavango Delta's Panhandle at 3 sampling sites, Mohembo East, Sepopa and Guma. Samples were collected in triplicates, every three weeks for 16 months, starting July 2014 to October 2015. These were collected in 500ml polyethylene bottles which were pre-cleaned, rinsed with nitric acid and then with milli-Q water. The samples were acidified with concentrated nitric acid immediately after collection, closed and transferred to the laboratory in cooler boxes for metal analysis. The hydrogen ion concentration (pH), was measured at sampling sites using a calibrated pH meter while discharge is measured daily by the Department of Water Affairs at Mohembo East.

2.3 Analytical Method

Analysis of metals was performed using U. S. EPA method 200.7, with ICP-OES (Perkin Elmer, Optima 2100DV). Aluminium and Beryllium were analysed at 396.153 and 234.861nm wavelengths respectively with spectrometer set on axial view. A 3-point calibration was used for both metals with correlation coefficient of ≥ 0.995 .

2.4 Quality assurance

All samples were analysed in triplicates, with 2 blanks analysed for each batch. In-house quality control samples were also analysed with each batch for ensuring accuracy and reproducibility. Ultra-pure water was used for rinsing glassware and preparing reagents. All chemicals used were of analytical grade.

2.5 Statistical method

Analysis of variance (ANOVA) was used to test for any significant variations in metal concentrations between locations. Regression correlation analysis was used to establish any relation between aluminium, beryllium, pH and discharge.

2.6 Human health risk assessment

The major entry pathway of heavy metals into the human body is through ingestion; drinking of water and food consumption (Kavcar et al., 2009; Muhammad et al., 2011). Other entry pathways are dermal absorption (bathing, swimming) and inhalation but only water ingestion was used to evaluate the risks for adults associated with the two metals in this study. Using guidelines provided by (U.S. EPA, 1992), the exposure to metal contaminants was calculated according to a modified formula used by Batayneh, (2011) and Muhammad et al. (2011) where,

$$CDI = C \cdot \frac{DI}{BW} \quad (1)$$

CDI is the chronic daily intake of the metal (mg/Kg – day), C is the concentration of the metal contaminant in mg/L, DI is the average daily intake of water and BW is the average body weight of an adult. In this study we used references used by U. S. EPA for water intake, which are 2 litres a day and an adult body weight of 70kg. The non-cancer risk associated with intake of aluminium and beryllium through drinking the river water were also evaluated by hazard quotient, HQ. The hazard quotient is used to evaluate the risk and is calculated according to U.S. EPA (2005) expression;

$$HQ = \frac{CDI}{RfD} \quad (2)$$

Where HQ is the hazard quotient and RfD is the reference dose of the metal or the tolerable daily intake (reference values used in this study were obtained from U.S. EPA (2005)). The population exposed to the contaminant is said to be safe if the HQ is ≤ 1 .

3. RESULTS AND DISCUSSION

3.1 Concentrations of aluminium and beryllium in river water

The concentrations of aluminium and beryllium in the Okavango River at Mohembo East, Sepopa and Guma over a period of 16 months are presented in Table 1.

Table 1. Discharge (m³/s), pH, Al and Be concentrations (µg/L) in the Panhandle, Okavango River Botswana

Sampling date	Discharge	Mohembo			Sepopa			Guma		
		pH	Al	Be	pH	Al	Be	pH	Al	Be
15/07/2014	-	6.79	160.7	3.6	6.33	139.3	3.9	6.76	151.5	4.3
12/08/2014	-	6.45	122.7	5.1	6.77	51.2	5.6	6.70	48.1	5.9
02/09/2014	-	7.03	165.6	6.5	6.60	90.6	6.7	6.63	15.8	6.8
23/09.2014	-	7.14	251.4	6.9	6.70	99.9	7.5	6.72	64.2	7.6
14/10/2014	120.4	6.87	237.0	7.9	6.57	333.1	8.4	6.57	116.9	BDL
04/11/2014	110.6	6.69	168.9	2.3	6.68	56.1	BDL	6.53	-	BDL
26/11/2014	133.8	7.07	305.4	1.7	6.76	61.2	BDL	6.78	104	BDL
15/12/2014	205.7	6.48	164.8	BDL	6.37	176.7	BDL	6.54	114	BDL
20/01/2015	297.8	6.50	108.3	BDL	6.13	42.4	BDL	6.64	11.6	BDL
17/02/2015	421.6	6.40	72.9	2.5	6.15	4.6	BDL	6.33	BDL	BDL
13/04/2015	459.9	6.05	42.4	3.6	6.18	84.2	BDL	6.31	14.9	BDL
12/05/2015	-	6.33	32.4	3.1	5.92	8.6	0.2	6.03	7.9	BDL
09/06/2015	239.9	6.33	133.9	2.5	6.10	4.6	0.5	6.17	3.6	BDL
07/07/2015	187.2	6.72	91.0	2.2	6.24	17.2	0.2	6.05	2.9	BDL
11/08/2015	159.7	6.81	152.9	2.7	6.55	61.3	BDL	6.41	0.2	BDL
01/09/2015	136.2	6.43	185.4	2.2	6.58	104.8	BDL	6.52	16.9	BDL
16/10/2015	104.8	6.74	181.2	2.5	6.67	131.8	BDL	6.46	2.5	BDL

*BDL is concentrations below detection limits. Detection limits were 1.1µg/L for aluminium and 0.002µg/L for beryllium.

3.1.1 Aluminium

Aluminium concentrations in the Panhandle varied with time and space, with a concentration range of

0 – 0.33mg/L. According to WHO (1998), world natural surface waters with pH close to neutral, have aluminium concentration range of 0.001 - 0.1mg/L. In Africa, various ranges of aluminium concentrations in river waters have been documented; 0.02 – 0.17mg/L in the Nile River, Egypt (El Bouraie et al., 2010); 0.03 – 0.80mg/L for Bandama River in Ivory Coast (Sorenson et al., 1974), 0.04 – 3.6mg/L for the Orange River in South Africa (Sorenson et al., 1974); 0.11 – 64mg/L in the Olifants River, South Africa (Genthe et al., 2013), a river considered one of the most polluted rivers in southern Africa. In Germany, Elbe and Saale Rivers were reported to have a range of 0.16 – 0.90mg/L (Sorenson et al., 1974), whereas Guibaud and Gauthier (2005) obtained a range of 0.016 – 0.130mg/L for the River Vienne of Limousin region in France. The maximum aluminium concentrations in the Okavango River, 0.33mg/L is higher than the maximum reported by the WHO (1998) for world values, probably due to poor acid soils in the area which are known

to solubilise aluminium into river waters (Genthe et al., 2013). The highest aluminium concentrations in the Okavango Panhandle were recorded in October/November, when the volume of the river water was at its lowest and temperatures were high, a phenomena that enhance the concentration of salts in the river system. The low concentrations of aluminium were observed during the high flows of the river which may be attributed to dilution effects and the removal of the salts from the study area because of the increased water velocity. In terms of spatial variations, there was no significant difference ($P>0.05$) in concentration levels of aluminium between upstream and downstream locations of the panhandle although the mean concentration values decreased downstream, Mohembo East > Sepopa > Guma (0.147, 0.082, 0.076 mg/L respectively). It is important to compare the aluminium concentrations in the river to drinking water standards because people in this area use this water directly for drinking and other domestic activities (CSO, 2011). The Botswana drinking water standard, BOS 32:2009 and U. S. EPA regulatory limits for aluminium in drinking water is 0.2mg/L. During the course of the sampling period, there were times in Mohembo East and Sepopa when the regulatory limits were exceeded, but the results of most sampling points and mean concentrations were within the limits. However, because the limit was exceeded at times, this means that people drinking and cooking using river water were exposed to unsafe levels of Al. The influence of pH on aluminium concentrations were evaluated by regression analysis (as shown in Figure 2) and the pH vs. aluminium plots gave an r^2 of 0.66 at Mohembo East and 0.43 at Guma, indicating increase of aluminium concentration with increasing pH. It must be noted that this observation was made within the pH range of the Okavango Delta. The plots at Sepopa did not give an appreciable association of pH with aluminium concentration.

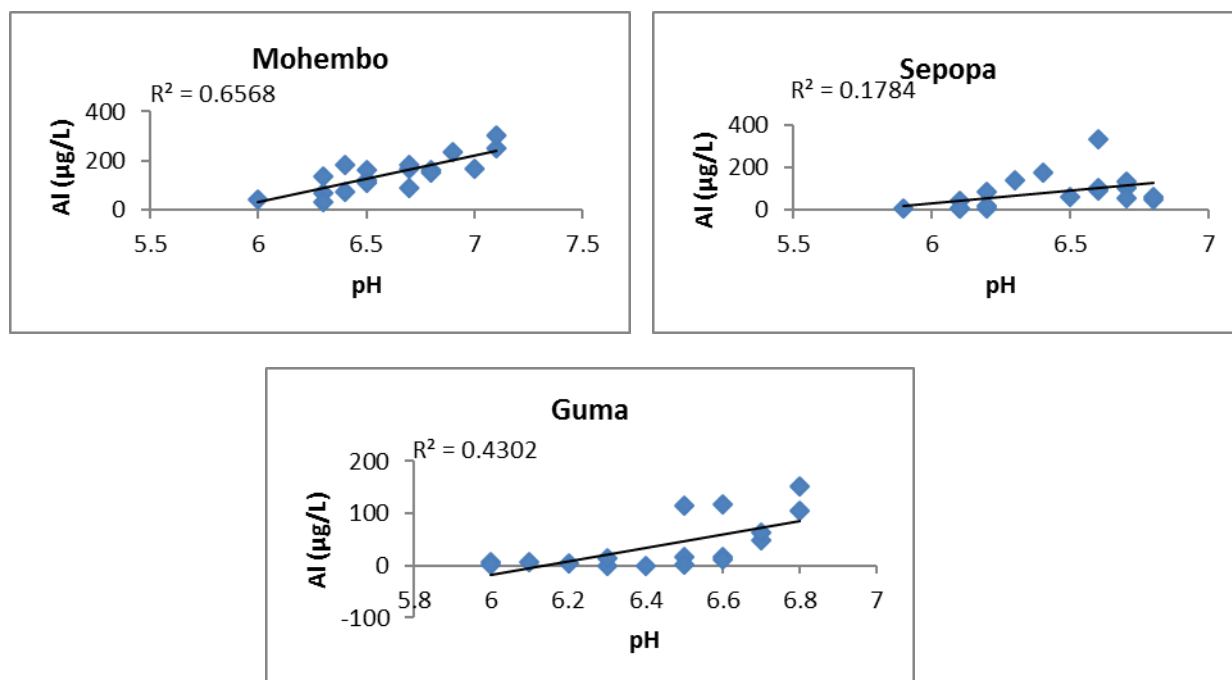


Figure 2. Scatter plots showing relationship between pH and aluminium concentration in the panhandle

3.1.2 Beryllium

Beryllium normally occurs in low concentrations in natural surface waters; typical concentration range varies between a few nanograms to a few micrograms per litre (Vesely et al., 2002). Concentrations in the Okavango Panhandle ranged from 0 – 0.008mg/L with mean concentrations of 0.003, 0.002 and 0.001mg/L for Mohembo East, Sepopa and Guma respectively at the time of sampling. These concentrations are much higher than the values published in studies done elsewhere but in the same range as South Africa's Olifant's River. In eastern United Kingdom rivers, beryllium concentration range from 0.01 – 0.09µg/L (Vesely et al., 2002), United States Rivers have a mean of 0.22µg/L (Calabrese et al., 1985) and the Olifant's River of South Africa has recorded a range of 0.002 – 0.01mg/L (Grobler et al., 1994). In this study, a similar trend with Al was observed, where mean concentrations of Be decreased downstream with no significant differences between the locations ($p>0.05$). This decreasing trend of beryllium concentration downstream was also observed by Vesely et al. (2002), who attributed it to adsorption of beryllium onto solid materials in river waters of neutral pH conditions. In this study, the highest beryllium concentrations of 0.008mg/L were recorded at all 3 sites between the months of September and October, when the river flow was at its lowest.

It seems beryllium concentrations were higher in 2014 in all sampling sites but decreased appreciably in 2015 in all sampling points. Further evaluation to see if there could be a common source of Al and Be was performed by correlation regression analysis and the resulting coefficient was weak, ($r^2 = 0.1$). However conclusions can be made from the occurrence of high concentrations of these metals at the same time (October), that they probably were introduced into the river at the same time. Botswana Bureau of Standards has not set a limit for beryllium in natural waters but U. S. EPA regulatory limit is $4\mu\text{g/L}$. There were some points in the 3 sampling sites when the limits were exceeded, and this becomes a concern for the communities who drink this water because beryllium is very toxic and is a group 1 carcinogen (IARC, 1993). Scatter plots for pH vs. beryllium in the panhandle could not give any appreciable trend.

3.2 Effects of discharge on concentrations of aluminium and beryllium in river water

Data for discharge was sourced from the Department of Water Affairs and the data is from October 2014 to October 2015, all recorded at Mohembo East. The lowest discharge value for the sampling period was $104\text{ m}^3/\text{s}$, obtained in October 2014, and whereas the highest was $459\text{ m}^3/\text{s}$ recorded in April, 2015. The relation between discharge and metal concentrations were evaluated by computing regression correlations and the results show an inverse relation of discharge with aluminium ($r^2 = 0.63$). Beryllium did not show any association with discharge, ($r^2 = 0.01$). This indicates that discharge has a high influence on aluminium concentration, high floods resulting in low concentrations probably due to dilution effects; low floods resulting in high concentrations which can be attributed to high evapotranspiration rate in the delta, which is well documented. The influence of discharge on beryllium concentration was very weak, indicated by a low correlation coefficient, an observation contrasting with previous studies (Vesely et al., 2002).

3.3 Human health risk assessment

The human health risk is expressed here as Hazard Quotient (HQ), and is calculated for the mean concentrations of each metal contaminant at each sampling site. The U. S. EPA acceptable risk level is $\text{HQ} < 1$, therefore any contaminant that gives a hazard quotient of more than 1 will probably have negative health effect on the human population. The U.S. EPA (2005) RfD values are 1mg/Kg for aluminium, and 0.002mg/Kg for beryllium and these were used to calculate the HQ. The calculated values for chronic daily intake show that adults in the Okavango panhandle who drink river water were not exposed to dangerous levels of aluminium and beryllium at the time of sampling, as shown by low CDI values, Table 2.

Table 2. Mean concentrations (mg/L), Chronic Daily Intake (CDI, mg/Kg day) and Hazard quotients for Al, Be

Sampling site	Al	CDI	HQ	Be	CDI	HQ
Mohembo East	0.147	0.0042	0.0042	0.0032	9.14×10^{-5}	0.046
Sepopa	0.082	0.0023	0.0023	0.0018	5.14×10^{-5}	0.026
Guma	0.076	0.0022	0.0020	0.0014	4.00×10^{-5}	0.020

The risks (HQ) associated with aluminium and beryllium ingestion through drinking Okavango river water was also negligible, below 1 at all sampling points. This study demonstrates that the riparian population of the Okavango delta who use river water for drinking are not at any chronic health risks from aluminium and beryllium toxicity, but high concentrations which were above recommended limits may pose acute health problems.

4. CONCLUSION

The mean concentrations of aluminium and beryllium in the Okavango Panhandle were comparable to world river water values, within the BOS 32: 2009 and U. S. EPA drinking water quality standards. However, the highest concentrations of both aluminium and beryllium recorded in the panhandle during the study period exceeded the international drinking water limits, which may pose acute toxicity. Aluminium concentrations were strongly influenced by discharge and pH at Mohembo, but beryllium did not show any strong association. This study is the first attempt to assess human health risks arising from ingestion of trace metals (aluminium and beryllium) present in the Okavango River, and the assessment indicated that riparian communities living in and around the Okavango are not at risk from long term toxicity of these two metals.

It is recommended that the study be expanded to include other toxic metals which are likely to be present in the river for the protection of human health and ecosystem balance.

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