Heavy metal levels in water, catfish (*Clarias gariepnus*) and riparian grass specimens from the municipal waste water fed Hex River outside Rustenburg city, North West province, South Africa.

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Abstract: Ten composite water samples, fish and grass from the Hex River were collected to analyse the concentration of Arsenic (As), Lead (Pb), Chromium, (Cr) and Cadmium, (Cd) using the induced coupled plasma mass spectrometer (ICP-MS). The mean recoveries in the Hex River samples revealed the following trends: As>Pb>Cr>Cd, (water), Pb>Cr (fish) and Pb>Cd (grass) respectively. High concentration of As, Pb and Cr in the water samples were noted next to the water treatment plant while Cd concentrations were normal. Water concentration of As, Pb, and Cr were 1132, 108.57 and 8.8 times higher than the WHO/EPA recommended threshold for safe water. Highest concentrations of lead were 99.45ppm followed by chromium at 34.73ppm in fish times higher than the WHO recommended threshold in fish. High concentrations of Pb in grass were noted next to the water treatment plant while Cd concentrations were high midstream, There is lateral contamination between surface and ground water hence high concentrations of heavy metal were noted in grass along the banks of the dam.
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1. Introduction

Rustenburg is a city situated at the foot of the Magaliesberg mountain range in North West Province of South Africa. It is also reported to be the fastest growing city in South Africa. Rustenburg is home to the two largest platinum mines in the world and the world's largest platinum refinery which processes around 70% of the world's platinum. As a result of the mining activity in the area, surface water (fresh water lakes, rivers, streams, etc.) and ground water (borehole and wells) can get contaminated. (McMurry and Fay, 2004; Mendie, 2005).

Water is one of the essentials that supports all forms of plant and animal life (Vanloon and Duffy, 2005) that has unique chemical properties due to its polarity and hydrogen bonds which means it is able to dissolve, absorb, adsorb or suspend many different compounds (WHO, 2007), thus, in nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities. (Mendie, 2005).

Ground water contamination is one of the most important environmental issues today (Vodela et al., 1997) and between the wide diversity of contaminants affecting water resources; heavy metals receive particular concern considering their strong toxicity even at low concentrations. (Marcovecchio *et al.,* 2007).

Heavy metal pollution in the freshwater continues to attract attention as these metals are capable of bioaccumulation in tissues of aquatic biota and can also affect the composition, distribution and diversity benthic organisms. (Geydu- Ababio *et al,* 1999).

Toxic metals accumulate in water, sediments, soil, plants, and organisms along the food chain (Miranda *et al.*, 2004). Heavy metal contamination may therefore have shocking effects on the ecological balance of the recipient environment (Farombi *et al.*, 2007).

Among animal species, fishes as inhabitants of the more vulnerable aquatic environments, cannot escape the detrimental effects of these pollutants (Olifa *et al.*, 2004). Fish are therefore commonly used as bio-indicators of aquatic environment pollution in many bio-monitoring schemes (Rashed, 2001; Farkas *et al.*, 2002; Birungi *et al.*, 2007).

Studies carried out on various fishes have shown that heavy metals may alter the physiological activities and biological parameters both in tissues and blood (Basa and Usha, 2003). In aquatic ecosystems fishes are regarded as good representative indicators of overall system health due to their high position in the food chain (Adams *et al.*, 1992). They are therefore widely used to assess the health of the aquatic ecosystem, where their samples are considered vital in the estimation of metal pollution levels (Rashed, 2001; Farkas *et al.*, 2002).

Despite these risks, no studies have been carried out to determine the levels of pollution in the Hex River, and the possible implications on livestock and public health. The aims of this study were therefore to investigate the levels of 4 heavy metals in the Hex River of the North West province, South Africa.

2. Material and Methods

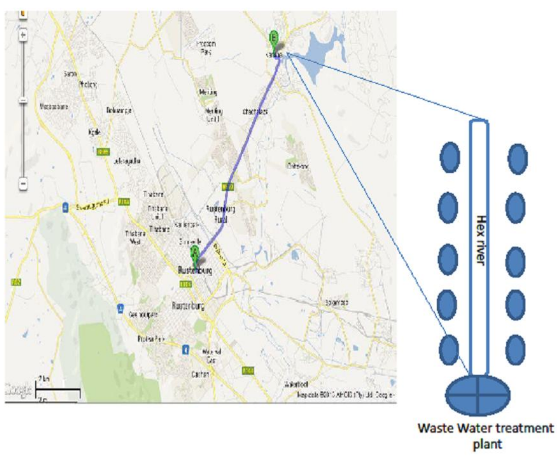
Study area

The research was conducted using samples obtained from Hex River on the outskirts of Rustenburg (S 25° 39′ and E 27° 18′) in the North West province of South Africa. The dam receives effluents from the nearby Riool werke municipal sewerage and waste water works. Water and grass was collected from the dam and the fish was bought from the local fisherman.

Sample collection

Water sample

Ten composite water samples will be collected from a 1 km stretch of the river. Five hundred ml each of water was collected at various distances from the banks of the river.



Grass sample

Grass was collected next to the treatment plant, midstream and upstream of the Hex River, and placed on the sterile containers.

Fish samples

Fish was purchased from the local fisherman fishing from the Hex River.

Sample preparation

Water samples

Each water sample was filtered through a 0.45 micron microscope membrane filters. 6.0mls of hydrochloric acid (HCL) and 2.0mls of concentrated nitric acid (HNO3) were added to every 5mls of each water sample.

Grass samples

The plant samples were first dried at 105°C for 6 to 8 hours. 0.5 gram of the dry material was decomposed in a quarts vessel using 8mls of HNO3 and 2mls of HCL.

Fish samples

Fish muscle was dried overnight in a way that they can be crushed to be fine. 0.5 gram of dry fine crushed fish muscle was added to 5mls of HNO3 and 0.5mls of HCL.

Equipment preparation

The pipette tips, funnels, glass beakers and 100ml volumetric flask were autoclaved. Some laboratory equipment's that were used for sample digestion and analysis was soaked in 32% HCI overnight. They were rinsed with distilled water 3 times and dried in a hot air oven for 16 hours at 106° C.

Digestion

Digestion was performed to ensure the removal of organic impurities from the samples and thus prevent interference (Nyirenda *et al* 2013, Momodu and Anyakora, 2010). The prepared mixture of each sample was digested using the Anton Paar Multiwave 3000 microwave.

Estimation of heavy metal level concentrations in acid digested sample.

All the acid digested samples of water, grass and fish were analyzed for K, Fe, Cu, Zn, Hg, Pb, As, and Se using the ICP Mass spectrometer NexION 300Q machine. Values were expressed as parts per billion (ppb), reflecting recovery rates of the metals in specimens.

Statistical analysis

Statistical analysis of the data was performed using ANOVA following the general linear models of the SPSS program (version 17.0). The results were expressed as means and pulled SE of mean (SEM). The means were compared using independent t-test.

3. Results

Ten composite samples of dam water, two fish and grass were collected from the Hex River. The mean recoveries of the metal concentration of heavy metals from the dam revealed the following trends in tables 1, 2 and 3. The mean recoveries in the dam water samples revealed the following trends: As> Pb>Cr>Cd. Heavy metals were found highest next to the treatment plant. This was the point where waste water was being released into the dam.

As, Pb, and Cr, concentrations were found to be the highest midstream and was normal for Cd. The concentration of heavy metals midstream did not differ that much from the concentration of water next to the treatment plant. This could be because of high intake volume of pollutants into the dam.

As, Pb, and Cr, concentrations were high upstream while that of Cd was normal. High concentrations could be the results of stagnant water in the upstream.

Recommended safe metal concentration as regulation (2005) stipulated by the WHO/EPA and the EC

Table 1 (water from Hex River)

WATER	VALUE	WHO/EPA	NUMBER OF TIMES ABOVE WHO/EPA THRESHOLD	EC	NUMBER OF TIMES ABOVE EU THRESHLOD
NEXT TO TREATMENT PLANT (As)	5.66	0.005	1132	0.05	113.2
(Pb)	0.76	0.001-0.007	108.57	0.05	15.2
(Cr)	0.88	0.1	8.8	0.1	8.8
(Cd)	0.003	0.05	NORMAL	0.005	NORMAL
MIDSTREAM (As)	4.59	0.005	918	0.05	91.8
(Pb)	5.16	0.001-0.007	737.14	0.05	103.2
(Cr)	0.54	0.1	5.4	0.1	5.4
(Cd)	0.002	0.05	NORMAL	0.005	NORMAL
UPSTREAM (As)	7.02	0.005	1404	0.05	140.4
(Pb)	1.35	0.001-0.007	192.85	0.05	27
(Cr)	1.06	0.1	10.6	0.1	10.6
(Cd)	0.005	0.05	NORMAL	0.005	NORMAL
DOWNSTREAM (As)	6.47	0.005	1294	0.05	129.4
(Pb)	0.0008	0.001- 0.007	NORMAL	0.05	NORMAL
(Cr)	1.14	0.1	11.4	0.1	11.4
(Cd)	0.006	0.05	NORMAL	0.005	1.2

High concentrations of As>Cr>Cd were also seen downstream and Pb was normal. This could also be because of stagnant water in the downstream since the concentrations of this stream do not differ much from the concentrations of upstream.

Recommended safe metal concentration as stipulated by the WHO/EPA and the EC regulation (2005)/ WHO (1993) REVISION OF WHO GUILDLINES FOR WATER QUALITY. WHO, GENEVA.

Table 2 (Fish from the Hex River)

FISH	VALUE	WHO	NO OF TIMES ABOVE WHO THRESHOLD	EC	NO OF TIMES ABOVE EU THRESHOLD
As	0.27	NA	NA	2	NORMAL
Pb	19.89	1.5	13.26	0.2	99.45
Cr	5.21	0.15	34.73	NA	NA
Cd	0.05	0.2	NORMAL	0.05	NORMAL

NA= NOT AVAILABLE

Table 3 (grass from Hex River) WHO/FAO 2007 and EUROPEON UNION STANDARS (EU 2006)

GRASS	value	WHO/FAO	NUMBER OF TIMES ABOVE WHO/FAO THRESHOLD	EU	NUMBER OF TIMES ABOVE EU THRESHOLD
NEXT TO TREATMENT PLANT					
As	0.85	NA	NA	NA	NA
Pb	2.21	5.0	NORMAL	O.30	7.36
Cr	4.70	NA	NA	NA	NA
Cd	0.009	0.2	NORMAL	0.2	NORMAL
MIDSTREAM					
As	0.66	NA	NA	NA	NA
Pb	6.33	5.0	1.2	0.30	21.1
Cr	4.13	NA	NA	NA	NA
Cd	0.16	0.2	0.8	0.2	0.8
UPSTREAM					
As	0.71	NA	NA	NA	NA
Pb	4.55	5.0	NORMAL	0.30	15.16
Cr	4.21	NA	NA	NA	NA
Cd	0.01	0.2	NORMAL	0.2	NORMAL

NA-NOT AVAILABLE

The mean recoveries in the fish from the dam revealed the following trends: Pb>Cr>Cd>As. Concentration of Pb and Cr were found to be high in fish, Cr found to be normal. These values show a relationship between the high concentration of Pb and Cr in fish and water in the Hex River and indicated fish as bio indicator for metal contamination in the dam. While Cd and As were normal and acceptable by the WHO/EU standards. The mean recoveries of the grass revealed the following trends: Pb>Cd>Cr>As. Pb concentrations of grass were the highest next to the treatment plant and Cd concentrations were normal. Absorption of Pb in high quantities in grass could be because of the closets range of the grass next to the treatment plant and it is at the point of disposal into the dam, that's why high concentrations were noted.

Pb concentrations of grass were much higher in the midstream accompanied by Cd concentrations; this could be because of stagnant of water around the banks thus giving rise to high absorption of heavy metals by the grass.

Concentrations of Pb of grass in the upstream were high but dropped by 5.94ppm and the Cd concentrations were normal. This could be as a result of dilution effect in the dam water; this was influenced by the movement of water from one region to the other and loss metal strength of concentration. There is lateral contamination between surface and ground water. Concentrations of Cd were normal and acceptable as stipulated by the WHO/EU standards while As and Cr standards were not available.

Conclusion

The Hex River contains unacceptably high concentration levels of As, Pb, Cr, and Cd. Fish from Hex River contained high heavy metal levels of Pb and Cr respectively. The grass along the banks of the dam contained heavy metal levels of Pb, and Cd in that order. Heavy metals from Riool werke waste water treatment plant might have contaminated Hex River water, fish and grass along its banks on which the community and livestock of Kanana, Rustenburg depended on. Further research on environmental, public health and livestock health need to be investigated.

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