A comparative study of the levels of heavy metals in dam water, borehole water and cattle serum around the Modimola dam of the Mafikeng, North West province, South Africa.

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Abstract: Ten composite samples each of dam water, borehole water and cattle blood from the Modimola dam and surrounding livestock farms on the outskirts of Mafikeng city were analysed for concentrations of Pb, Cd, As, and Cr using induced coupled plasma mass spectrometer (ICP-MS). The mean recoveries in the dam water, borehole water and bovine blood samples revealed the following trends: Pb> As> Cd> Cr, Pb> As> Cr> Cd, Pb> As> Cr> Cd respectively. The highest Pb, As, Cd and Cr concentrations in dam water and borehole were in the same range with means: 55.13 vs 55.53 Pb, 3.71 vs 3.22 As, 0.67 vs 0.33 Cd and 0.41 vs 0.33 Cr ppb respectively were obtained. The closeness of the values could indicate a lateral contamination of the ground streams by the contaminated dam hence the values. The mean concentrations of blood samples collected from bovines drinking from the dam were 2.46 Pb, 1.34 As, 0.90 Cr and 0.55 Cd ppb. The dam and borehole water values lie within the recommended safe concentrations (ppb) as stipulated by the WHO/EPA and the EC regulation (2005).
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1. Introduction

Water is one of the essentials that support all forms of plant and animal life (Vanloon and Duffy, 2005). It is generally obtained from two principal natural sources; surface water such as fresh water lakes, rivers, streams, etc. and ground water such as borehole water and well water (McMurry and Fay, 2004). In nature, water is not pure as it acquires contaminants from its surroundings and those arising from humans and animals as well as other biological activities (Mendie, 2005).

Heavy metals are elements having atomic weights between 63.546 and 200.590 and a specific gravity greater than 4.0 i.e. at least 5 times that of water. They exist in water in colloidal, particulate and dissolved phases (Adepoju-Bello et. al. 2009).

Heavy metals are environmentally stable and non-biodegradable, toxic to the living beings and tend to accumulate in plants and animals causing chronic adverse effects on human health. Heavy metals are introduced to the environment through a variety of sources such as combustion, extraction, agricultural runoff and transportation. Heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic and industrial application. Though some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micro nutrients for plants and microorganisms, many other metals like Cd, Cr and Pb are proved detrimental beyond a certain limit (Vijaya et. al. 2009).

Despite these risks, only one preliminary study by Nyirenda et. al. (2011) had been made to determine the levels of pollution in the Modimola dam, and the possible implications on live stock and public health.

The aims of this study were therefore to investigate the levels, potential for bioaccumulation and lateral cross contamination between borehole and dam water sources of 4 heavy metals in the Modimola dam of the North West province, South Africa.

2. Materials and Method

2.1 Study area

The study was conducted using samples from the Modimola dam on the outskirts of Mafikeng (25° 52' 0S and 25° 38' 60E), altitude 1278m above sea level, in the North West province of South Africa. The dam receives effluent from the nearby municipal sewerage and waste water works. Water samples were collected from the dam and bore holes from the homesteads surrounding the dam. Fourteen blood samples were collected from bovines of both sexes and different ages ranging from 6months – 2 years, 3-5 years and 6-8 years which were randomly selected from a communal herd that grazes around and drinks from the Modimola dam.

Stream water parameters

The first step in analysing the temporal dynamic of hydrochemical parameters in the Wonderfontein was focused on their variation over the sampling sites. This gives an overview of the range of possible hydrochemical conditions at the time of sample collection. The number of measurements (counts) and selected statistical parameters are compiled in Table 1.

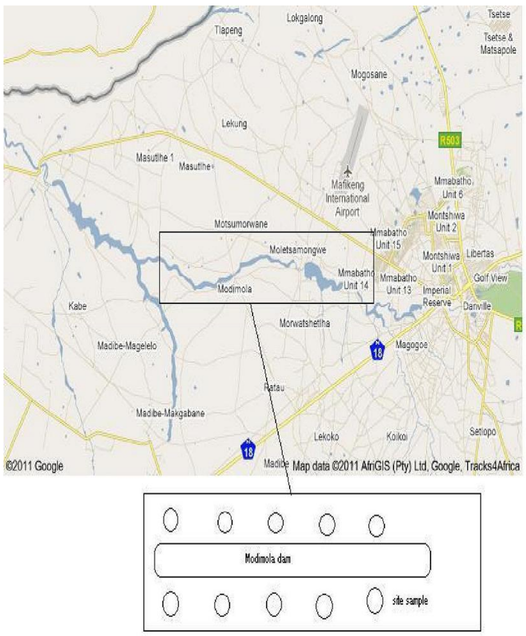

Fig 1: Location map and sampling map of the study area.

Table 1. Stream water parameters measured in the Wonderfontein in 5 – 10 minutes interval between sampling sites.

Parameter	**Temperature**	**pH**
Unit	**°C**	
Count	**5**	**5**
Average	**24**	**7.6**

i. Water samples

Ten composite water samples were collected from a 1 km stretch of the dam. Five hundred ml each of water collected at various distances from the banks of the dam. And five hundred ml each of borehole water were also collected from the area around Modimola dam.

i. Blood samples

Blood samples were collected from cattle which were restrained in crush pens. Blood was collected from either the jugular or coccygeal veins of the cattle using sterile 18gauge needles and vacutainer sleeves. The blood samples were directly collected into the red stopper tubes and left at room temperature over night. The serum was separated after centrifugation which was done at 2500rpm for 10minutes and stored at 20^0C until analysis.

c. Sample *preparation*

***i.* Water samples**

Each water sample was filtered through a 0.45 micron microspore membrane filters. 2mls of hydrochloric acid (HCL) and 6mls of concentrated nitric acid (HNO_3) were added to every 5mls of each water sample. The samples were then digested as in d.ii.

ii. Blood

Blood samples were left over night at room temperature to allow clotting and centrifuged at 2500rpm for 10min. The serum was then stored in clean plastic tubes and then immediately frozen at 20^0C until the day of analysis.

d. *Digestion of samples*

***i.* Equipment preparation**

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

***ii.* Water**

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

iii. Serum

Ten grams of Tetra Acetic Chlorine Acid (TCA) was diluted with 100mls of distilled water inside volumetric flasks. 0.7ml of serum was then diluted in 7ml of the TCA solution and then centrifuged at 2500rpm for 10minutes. The supernatant was then extracted and analysed using the ICP Mass Spectrometer NexION 300Q machine.

e. *Estimation of heavy metal level concentrations in acid digested Sample.*

All the acid digested samples of water and blood serum were analyzed for Cd, Cu, Pb and As using the ICP Mass Spectrometer NexION 300Q machine. Values were expressed as parts per billion (ppb), reflecting recovery rates of the metals in specimens.

f. *Statistical analysis*

Statistical analysis of the data was performed using ANOVA following the general linear model 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-tests.

3. Results & Discussion

Ten composite samples each of dam water and borehole water were collected from the Modimola dam and surrounding areas. Blood samples from 14 randomly selected bovines were also collected. The mean recoveries of the metal concentrations of heavy metals in dam and borehole water samples revealed the following trends in table 2.

Table 2: mean concentrations (ppb) of Cr,As,Cd and Pb in dam water samples.

	Water treatment plant	Water Up stream	Water Midstream	Water Down stream
Cr	0.43	0.33	0.39	0.48
As	3.18	2.45	4.00	5.20
Cd	0.95	0.31	1.08	0.33
Pb	54.85	51.58	51.51	62.68

The mean recoveries in dam water samples revealed the following trends: Pb> As> Cd> Cr. The concentrations of Cr, As and Pb were highest downstream. This the part of the dam where the dam wall is built thus accounting for heavy metal accumulation because of water being stagnant. The Cd concentrations were highest mid stream. The second highest concentrations of Cr, As, Cd and Pb were noted closest to the water treatment plant. This was as a result of the direct disposal of waste water from the water treatment plant.

The lower concentrations of the Cr, As and Pb were observed up stream and mid stream respectively. This could be as a result of the dilution effect in the dam water at these points. The Cd lower concentrations were recorded upstream and downstream. The concentration levels of heavy metals in Modimola dam water is represented in table 3 below.

Table 3: mean concentrations (ppb) of Cr,As,Cd and Pb in borehole water samples.

	Water treatment plant	Water Up stream	Water Midstream	Water Down stream
Cr	0.39	0.32	0.34	0.30
As	3.58	3.47	2.58	3.51
Cd	0.30	0.36	0.43	0.23
Pb	57.49	51.37	55.75	52.08

The mean recoveries in borehole water samples revealed the following trends: Pb> As> Cr> Cd>. Concentrations of Cr, As and Pb were higher next to the water treatment plant. Cadmium concentrations were recorded highest mid stream. The second highest heavy metal concentrations of Cr, As and Pb were recorded mid stream whilst that of Cd was noted closest upstream.

The lower concentrations of the Cr, As and Pb were observed up stream and mid stream respectively. Cadmium lower concentrations were observed next to the treatment plant and closest downstream. Table 4 below compares the heavy metal concentrations of dam water and borehole water around the Modimola dam.

Table 4: mean concentrations (ppb) of Cr,As,Cd and Pb in dam(D) and borehole (B) water samples.

		Water treatment plant	Water up stream	Water mid stream	Water down stream
D	Cr	0.43	0.33	0.39	0.48
B	Cr	0.39	0.32	0.34	0.30
D	As	3.18	2.45	4.00	5.20
B	As	3.58	3.47	2.58	3.51
D	Cd	0.95	0.31	1.08	0.33
B	Cd	0.30	0.36	0.43	0.23
D	Pb	54.85	51.58	51.51	62.68
B	Pb	57.49	51.37	55.75	52.08

The concentration levels of chromium in the dam water were higher than in the ground water. Concentration levels of arsenic were also higher in the dam water than in the ground water except for the concentration in the ground water collected from areas next to the water treatment plant and up stream. These concentrations could be because arsenic compounds absorb strongly to soils and thus travel short distances in groundwater and surface water (Evanko and Dzombak, 1997).

The cadmium concentration levels were also higher in the dam water than in the ground water excluding the concentration of the ground water collected from areas close to the dam up stream. Lastly the concentration levels of lead were high in the ground water than in dam water samples except for the dam water collected upstream and downstream which had higher concentration levels.

Table 5 below represents the comparison between the EU recommended safe metal concentrations and the metal concentrations found in the Modimola dam water samples. According to the WHO/EPA represented in table 5, the heavy metal concentrations of dam and borehole water in this research were below the toxic levels except for lead. The lead concentrations were above the WHO/EPA recommended safe metal concentrations. Although Cd, As, and Cr concentrations in dam and borehole water samples were below the limits and standards of the WHO, there was however, a relationship between dam and borehole water samples, with higher metal concentrations in the dam samples that led to higher metal concentrations in borehole water samples, suggesting lateral cross contamination between water sources.

Table 5: Recommended safe metal concentrations (ppb) as stipulated by the EC Regulation (2005).

	EU threshold	Dam values	Times above threshold
Cr	100	1.treatment plant (0.43)	Normal
		2.up stream (0.33)	Normal
		3.mid stream (0.39)	Normal
		4.downstream(0.48)	Normal
As	500	1.next to treatment plant(3.18)	Normal
		2.up stream (2.45)	Normal
		3.mid stream (4.00)	Normal
		4.downstream(5.20)	Normal
Cd	5	1.next to treatment plant(0.95)	Normal
		2.up stream (0.31)	Normal
		3.mid stream (1.08)	Normal
		4.downstream(0.33)	Normal
Pb	1-7	1.next to treatment plant(54.85)	Exceeds by 7.84
		2.up stream (51.48)	Exceeds by 7.35
		3.mid stream (51.51)	Exceeds by 7.36
		4.downstream(62.68)	Exceeds by 8.95

Previous studies by Nyirenda et. al. (2011) reported that the Modimola dam contained unacceptable high levels of Pb, Cd, As, Cr. The number of times above the EU water threshold values for Pb,Cd, As and Cr were 12500, 1872, 204,7 respectively. In our current study, the water threshold values were within the normal limits except for lead whose average value exceeded the water threshold by 7.88. Table 6 below represents the heavy metal concentrations in serum collected from bovines that drink from the Modimola dam.

Table 6. Average of concentrations (ppb) of heavy metals in all blood samples collected from bovines drinking from Modimola dam.

Age Range	Cr	As	Cd	Pb
6mnt-2yrs	0.87	0.80	0.54	1.96
3yrs-5yrs	0.88	1.55	0.51	2.42
6yrs-8yrs	0.95	1.56	0.61	2.90
AVERAGE	**0.90**	**1.34**	**0.55**	**2.46**

The mean concentrations for the various metals are shown in table 6. Generally heavy metal concentrations were lower in the 6months – 2years age group and significantly higher in the 6-8years age group

The age of the animal which simultaneously determines how long the animal has been drinking from the dam and the duration of exposure is a major contribution to the varying concentration levels. These results imply that the animals with higher concentration levels were those that had being exposed for a longer time compared to those with less concentration levels.

Conclusion

The Modimola dam heavy metal concentrations appear to fluctuate with time but are mainly normal. There appears to be lateral contamination of heavy metals from the dam to the borehole water. Serum metal values were higher in older animals than in younger animals, thus indicating cumulative bioaccumulation.

Further studies are needed on specific aspects of production, health and reproduction in order to determine the impact of the heavy metals on the ecosystem including humans.

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