Heavy metal levels in water, catfish (*Clarias gariepnus*) and African fish eagle *(Haliaeetus vocifer)* specimens from the municipal waste water fed Modimola dam outside Mafikeng city, North West province, South Africa.

Mathew Nyirenda, Precious D Itumeleng, Blessing M Dzoma, Lebogang E Motsei, Rendani V Ndou, Francis R Bakunzi.

Centre of Animal Health Studies, North West University (Mafikeng Campus), Private Bag X2046, Mmabatho, 2735, South Africa. Email:- *mathew.nyirenda@nwu.ac.za*

Abstract: Ten composite samples each of water, sediment, catfish (*Clarias gariepnus)* and African fish eagle (*Haliaeetus vocifer*) from the Modimola dam on the outskirts of Mafikeng city were analysed for concentrations of Pb, Cd, As and Cr using atomic absorption spectophotometry. The mean recoveries in water and catfish samples revealed the following trends: Pb > As > Cd> Cr and Pb > As > Cr> Cd respectively. The highest Pb, As, Cd and Cr concentrations in water of 250, 10, 9 and 0.7ppm respectively were obtained nearest to the inlet from the waste water facility while the lowest were from samples in the middle of the dam. The sampling point near the dam wall, where the water reticulation works are also situated had the second highest concentrations of Cd, As and Cr. The concentrations of Pb, Cd, As, and Cr in the water samples were 125 000, 1 872, 204 and 7 times higher than the EC/WHO maximum threshold for water while that of Pb was 28 times higher than that recommended for fish. Sediments generally had higher concentrations of metals than those in water, although a reverse trend was noted for Pb. Specimens from catfish and the fish eagle birds also had varying levels of heavy metals. The unacceptably high levels of Pb, Cd, As and Cr in the dam and the bioaccumulation of the metals in the food chain calls for urgent intervention measures, that should also focus on the municipal water supplies.

[Mathew Nyirenda, Precious D Itumeleng, Blessing M Dzoma, Lebogang E Motsei, Rendani V Ndou, Francis R Bakunzi. **Heavy metal levels in water, catfish** (*Clarias gariepnus*) **and African fish eagle** *(Haliaeetus vocifer)* **specimens from the municipal waste water fed Modimola dam outside Mafikeng city, North West province, South Africa.** Life Science Journal. 2011;8(S2):47-52] (ISSN: 1097 – 8135). http://www.lifesciencesite.com.

Keyword: Heavy metal levels in water, catfish (Clarias gariepnus) and African fish eagle**.**

Introduction

Contamination of freshwater bodies with a wide variety of pollutants has been a matter of great concern over the last few decades, not only because of the threat to public water supplies, but also the damage caused to aquatic life (Canli *et al.*, 1998). Municipal waste water, mining and industrial processing are some of the commonest anthropogenic activities that cause heavy metal contamination in the environment (Lee and Stuebing, 1990). Heavy metals like copper, zinc, and iron are essential for metabolism in animals while others such as mercury, cadmium, and lead have no known role in biological systems. The accumulation of heavy metals in tissues is mainly dependent upon the water concentration of metals and exposure period, while environmental factors such as salinity, ph, hardness and temperature also play significant roles in metal accumulation. Under certain environmental conditions heavy metals can accumulate up to toxic concentrations and cause ecological damage. Heavy metal discharges to the marine environment are therefore of great concern all over the world and have a great ecological significance due to their toxicity and accumulative behaviors (Guven *et al.*, 1999). Through bioaccumulation, pollutants have a realistic chance of moving up the food chain and be of public health significance. The presence of heavy metals in different foods constitutes a serious health hazards depending on their relative levels (Mansour and Sidky, 2002). The Modimola dam hosts the Mafikeng city municipal sewerage and waste water works as well as the water reticulation plant. The dam also boasts of high local economic activities, mainly involving subsistent fisherman who sell fish, catfish and fish eagles to both rural and city inhabitants, as well as provision of water to communal livestock. Heavy metals such as Cd, Cu, Pb and Zn have been associated with mixtures of wastewater and sewage sludge (Muchuweti *et al.*, 2006; Mapanda *et al.*, 2007), and are also known to be toxic at high concentrations (Jarup, 2003, Rana *et al.*, 2008).

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

Materials and methods

a. Study area

The study was conducted using samples from the Modimola dam on the outskirts of Mafikeng (25° 52' 0S and 25° 38' 60E), in the North West province of South Africa. The dam receives effluent from the near by municipal sewerage and waste water works. Water and sediment samples were collected from the dam while catfish and birds were purchased from local fishermen at the dam.

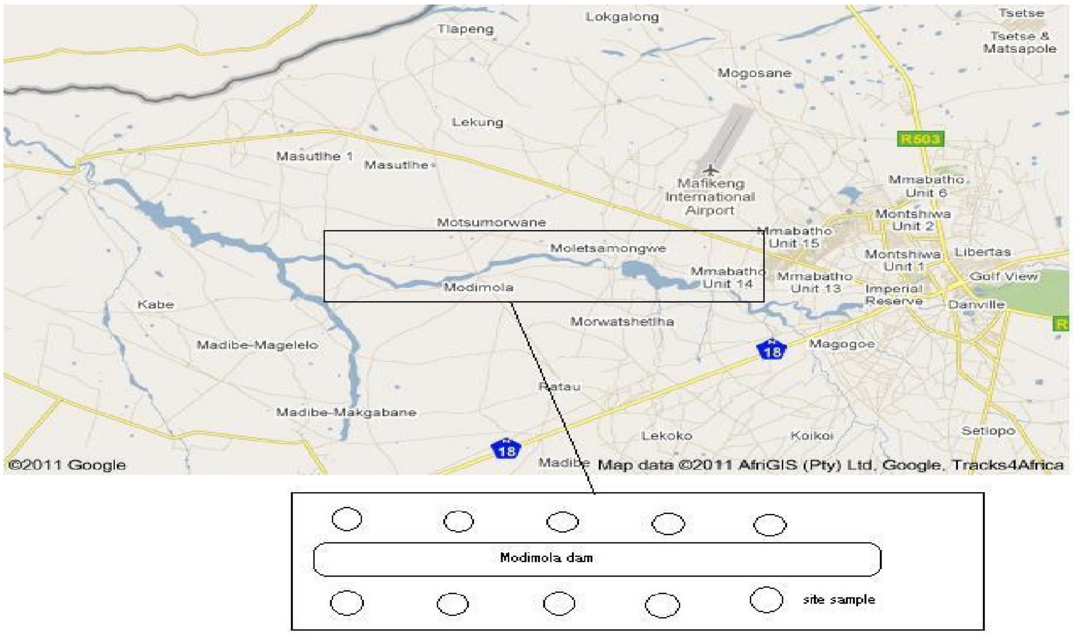

Fig 1. Location map and sampling map of the study area.

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.

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

Parameter	Temperature	pH
Unit	^{0}C	
Count	5	5
Average	20.0	7.3

b. Sample collection

i. Sediment and water samples

TEN composite sediment and water samples were collected from a 1 km stretch of the dam. 500g sediment samples were collected at various distances from the banks of the dam, at a depth of about 10cm. The samples were transported to the laboratory in clean plastic bags. In the laboratory, these samples were combined to make a composite sample that was then well mixed and made into ten 1kg duplicate samples. 500 ml each of water was collected from similar points as sediment, and made into similar composite samples to produce 10 one litre duplicate samples.

ii. Catfish and bird tissues

These were purchased from local fisherman at the modimola dam.

c. Sample preparation

i. Water

Each water sample was filtered through a 0.45 micron microspore membrane filter in order to avoid clogging of the burner capillary.

ii. Sediment

Sediment samples were put in aluminum plates and left to air dry for 7 days. They were then refined through a 2 mm screen prior to digestion.

iii. Tissue samples

Catfish and bird specimens were stored in insulated boxes, transferred to the laboratory and then frozen at -21°C until processing for metal analysis. The samples were freeze-dried for 10 days to a constant weight for the determination of metal content**.**

d. Digestion of samples

i. Equipment preparation

All laboratory equipments 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. A desiccator was used for 6 hours to cool crucibles.

ii. Sediment

5g each of sieved soil and sediments were mixed with 10 ml of distilled water and shaken for 30 minutes. The aqua regia digestion method (Mapanda *et al.*, 2007) was performed for complete dissolution of soil samples. The solution was filtered through Whatman filter paper no 42 into a suitable container. The extracts were used for analysis.

iii. *Water*

Digestion was performed to ensure the removal of organic impurities from the samples and thus prevent interference (Momodu and Anyakora, 2010). The samples were digested with concentrated nitric acid, where 10ml of nitric acid was added to 50ml of water in a 250ml conical flask. The mixture was evaporated to half its original volume on a hot plate after which it was allowed to cool and then filtered through Whatman filter paper No.42.

iv. Tissue samples

All glassware were previously soaked in diluted nitric acid for 24 hours and rinsed with deionised water. The method of Agemian *et al.* (1980) was used. Ten grams (fresh weight) of samples were digested in 15ml of freshly prepared nitric acid-hydrogen peroxide. The beakers were covered with a watch glass and set aside for 15 minutes in order to allow the initial reaction to subside. The samples were then heated at 160°C for 30 minutes after which a reduction in volume was noted. The contents of the beaker were transferred into a 25ml volumentric flask and diluted to the mark with deionised water.

(v). Estimation of heavy metals in acid digested samples

All the acid digested samples of water, sediment, catfish and birds were analyzed for Cd, Cu, Pb and Zn using the Atomic Absorption Spectrophotometer (AAS) 777S, using approved methods from the Perkin Elmer release Version E (2000). Values were expressed in parts per million (ppm), reflecting recovery rates of the metals in specimens.

Results

Composite samples, each constituted from 20 individual samples each of water, sediment, catfish and predator birds were collected from the Modimola dam and analysed for 4 heavy metals. The mean recoveries in water samples revealed the following trends: Pb > As > Cd> Cr respectively, while those in catfish samples were Pb > As > Cr> Cd respectively. Table 2 shows the concentrations of heavy metals in the various specimens. The highest concentrations of Pb, As, Cd and Cr obtained in the water samples were 250.23, 10.20, 9.36 and 0.7 ppm respectively obtained nearest to the inlet from the waste water facility and lowest in the middle of the dam. The sampling point near the dam wall, where the water reticulation works are also situated had the second highest concentration levels for Cd, As and Cr. The sediments generally had higher concentrations of metals than those in water, although the trend was different for Pb and As. Concentrations were highest at the wastewater inlet followed by the dam wall site. Specimens from catfish and birds also had varying levels of heavy metals.

Table 2. Concentrations (ppm) of 4 heavy metals in water, sediment, catfish (*Haliaeetus vocifer)* and African fish eagle from the Modimola dam outside of Mafikeng.

	As (ppm)	**Cr (ppm)**	**Cd (ppm)**	**Pb (ppm)**
Water next to sewage	10.20±0.112	0.7±0.022	9.36±02.22	250.23±21.32
Water upstream	9.63±0.00121	0.73±0.01	8.72±01.23	115.00±10.23
Water midstream	9.36±0.0021	0.36±0.02	11.63±0.23	80.50±02.12
Water lower stream	11.23±0.010	0.77±0.00	15.32±2.30	100.23±12.33
Sediment upperstream	5.3±0.0019	5.9±0.07	16.32±2.35	60.32±6.33
Sediment midstream	3.00±0.0009	0.6±0.01	17.22±03.20	50.42±5.22
Sediment lower	3.6±0.0010	6.5±0.06	10.69±2.51	50.60±5.26
Catfish liver	0.3±0.0000035	0.13±0.01	0.0023±0.00001	5.73±0.05
Catfish kidney	1.2±0.0025	0.11±0.03	0.013±0.001	3.66±0.03
Bird liver	0.022±0.000001	0.01 ± 0.01	0.0012±0.00000001	0.007±0.00001
Bird kidney	0.2±±0.000002	0.002 ± 0.00	0.0010±0.0000011	0.002±0.000002
Bird muscle	0.003±0.000003	0.001± 0.00	0.0000±0.0000001	0.36±0.000005

DISCUSSION

The Modimola dam is central to human and livestock communities around Mafikeng, the capital city of the North West province of South Africa. The analysis of water and other specimens from the dam therefore becomes mandatory from public and animal health perspectives. Fish, like other marine organisms, accumulate contaminants from the aquatic environment and are therefore extensively used in pollution monitoring systems of the aquatic environment (Henry *et al.*, 2004). The levels of contaminants, especially heavy metals in fish, are of particular interest because of the potential risk to humans who consume them (Ashraf, 2005). To the best of our knowledge, no biomonitoring studies have been carried out at the Modimola dam despite the strategic importance of the dam. Heavy metals such as Cd, As, Pb and Cr have been associated with mixtures of wastewater and sewage sludge (Muchuweti *et al.*, 2006; Mapanda *et al.*, 2007). On the other hand, these trace metals are known to cause various forms of public (Jarup, 2003) and animal health problems (Rana *et al.*, 2008).

The recovery rates in water, sediment and catfish samples show that Pb was the most abundant contaminant, followed by Cd and As. The water levels of Pb, As, Cd and Cr at the most polluted site were 250, 10.2, 9.4 and 0.7ppm respectively. The most polluted site also happened to be the nearest to the sewerage works, pointing to a point source contamination. The high concentrations at the dam wall could have been a result of the concentrating factor as water stagnated as a result of the dam wall.
The levels in catfish specimens were 1.2ppm As in kidney, 1.1ppm Cr in liver, 0.013ppm Cd in kidney and 5.7ppm in liver. Different tissues have varied accumulating capacities of metals, which may be due to the different metabolic roles of metals and functions of organs (Ashraf, 2005). The values in the current study are several magnitudes above the EU threshold values for water and fish (table 3), possibly, putting the human and livestock population dependent on the dam at risk. For example, the Pb level in fish liver is 28.6 times the recommended threshold.

Table 3. Recommended safe metal concentrations (ppm) as stipulated by the EC Regulation (2005).

Metal	EU Water threshold (ppm)	No of times above threshold	EU fish threshold (ppm)	No of times above threshold
Pb	0.001 – 0.007	125000	0.2	28.7
Cd	0.005	1872	0.05	Normal
As	0.05	204	*NA	-
Cr	0.1	7	*NA	-

***NA- not available**

Lead poisoning is generally ranked as the most common environmental health hazard (Yildirim *et al.*, 2009). Excessive consumption of cadmium (Cd) and lead (Pb) could result in neurological, bone and cardiovascular diseases, renal dysfunction and various cancers, even at relatively low levels (Gulser and Erdogan, 2008; Mansour and Sidky, 2002; Calderon, 2000; Jarup, 2002). Young animals are particularly susceptible to Pb exposure due to high gastrointestinal uptake and permeable blood brain barrier (Jarup, 2003). The adverse health effects of cadmium exposure may occur at lower levels than previously anticipated, primarily in the form of kidney damage but possibly also bone effects and fractures (Jarup, 2003). Long-term exposure to arsenic in drinking water is mainly related to increased risks of skin cancer, but also some other cancers, as well as other skin lesions such as hyperkeratosis and pigmentation changes. Chromium can cross placenta, and may lead to excessive chromium exposure and influence the development of the fetus if blood chromium levels of mothers are raised by environmental pollution and in addition chromium can lead to DNA damage, which may result in cancer causing gene mutations (Dingbang *et al.*, 1995).

Sediment generally had higher concentrations of metals, except for Pb. The general trend was not surprising since it is known that sediments serve as a sink for various anthropogenic pollutants (Peijnenburg *et al.* 2005; Davies and Abowei, 2009).

With respect to bird eating fish, Pb and As were the most cumulative contaminants. The bioaccumulation presents some challenges regarding the health of the community members feeding on fish and birds from the area (Ashraf, 2005). It would be recommendable to include tape water reticulated from the dam in future studies to check the efficiency of the process with regards to heavy metals.

Conclusion

The dam contains unacceptably high levels of Pb, Cd, As and Cr. The metals are bioaccumulating in catfish and fish eating birds, showing a likely hood of the same trend in humans feeding on fish and birds from the dam. Further studies need to focus on heavy metals in tap water reticulated from the dam. It is recommended that measures be put in place to continually biomonitor the dam with a view of prescribing intervention methods.

References

1. **Agemian H, Sturtevant DP, Austen KD** 1980. Simultaneous Acid Extraction of Six Trace Metals from Tissues by Hotblock Digestion and Determination by Atomic Absorption Spectrometry. *Analyst*, **105**: 125.

2. **Ashraf W 2005**. Accumulation of heavy metals in kidney and heart tissues of Epinephelus microdon fish from the Arabian Gulf. *Environ Monit Assess*, **101(1-3)**: 311-316.
3. **Calderon RL** 2000. The epidemiology of chemical contaminants of drinking water. *Food Chem Toxicol*, **38:** S13-S20.
4. **Canli M, Ay O, Kalay M** 1998. Levels of heavy metals (Cd, Pb, Cu, Cr and Ni) of C*uprinus carpio, Barbus Capito and Choudrostrome* regium from the Seyhan River, turkey, Tubitak. *Turk J Zool*, **22:** 149-157.
5. **Davies OA, Abowei JFN** 2009. Sediment quality of lower reaches of Okpoka Creek, Niger Delta, Nigeria. *Eur J Sci Res*, **26(3)**: 437- 442.
6. **Dingbang C, Jiaming H, Renqiu H** 1995. Whole blood trace element content study of 170 pair neonate and lying-in woman. *Guangdong Trace Elements Science*, **2**: 55–59.
7. **EC- European commission Regulation** 2005. Commission Regulation (EC) No: 78/2005 of 16 January 2005 amending Regulation EC No: 466/2001 as regards heavy metals. *Official Journal of the European Union: Legislation Series*, **16**(43):43-45.
8. **Gulser F, Erdogan E** 2008. The effects of heavy metal pollution on enzyme activities and basal soil respiration of roadside soils. *Environ Monit Assess*, **145(1-3)**: 127-133.
9. **Guven K, Ozbay C, Unlu E, Satar A** 1999. Acute lethal toxicity and accumulation of copper in *Gammarus pulex* (L.) (Amphipodal). *Turk J Biol*, **23**: 510-521.
10. **Henry F, Amara R, Courcot L, Lacouture D, Berthon ML** 2004. Heavy metals in four fish species from the French coast of the Eastern English Channel and Southern Bight of North Sea. *Environment International*, **30**: 675–683.
11. **JARUP L** 2002. Cadmium overload and toxicity. *Nephrol Dial Transplant*, **17(2):** 35-39.
12. **Jarup L** 2003. Hazards of heavy metals contamination. *Br Med Bull*, **68**: 167-182.
13. **Lee YH and Stuebing RB** 1990. Heavy metal contamination in the River Toad, juxtasper (Inger), near copper mine in East Malaysia. *Bull Environ Contam Toxicol*, **45**: 272-279.
14. **Mansour SA and Sidky MM** 2002. Ecotoxicological studies 3: Heavy metals contaminating water and fish from fayoum Government of Egypt. Food Chem, **78**: 15-22.
15. **Mapanda F, Mangwaya EN, Nyamangara J, Giller KE** 2007.
16. Uptake of heavy metals by vegetables irrigated using wastewater and the subsequent risks in Harare, Zimbabwe. *Phys Chem Earth*, **30**: 1399–1405.
17. **Momodu MA, Anyakora CA** 2010. Heavy metal contamination of ground water: the surulere case study research. *J Environ Earth Sci*, **2(1)**:39-43.
18. **Muchuweti M, Birkett JW, Chinyanga E, Zvauya R, Scrimshaw MD, Lester JN** 2006. Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health. *Agric Ecosyst Environ*, **112(1)**: 41-48.
19. **Peijnenburg W, De Groot A, Jager T, Posthuma L** 2005. Short-term ecological risks of depositing contaminated sediment on arable soil. *Ecotoxicol Environ Safety*, **60(1):** 1-14.
20. **Rana T, Sarkar S, Mandal, TK, Batabyal S** 2008. Haematobiochemical profiles of affected cattle at arsenic prone zone in Haringhata block of Nadia District of West Bengal in India. *Internet J Hematol*, **4(2).**
21. **Yildirim Y, Gonulalan Z, Narin I, Soylak M** 2009. Evaluation of trace heavy metal levels of some fish species sold at retail in Kayseri, Turkey. *Environ Monit Assess*, **149**: 223–228.

6/20/2011