Heavy metals (Cd, Pb, Cu, Zn) in mudfish and sediments from three hard-water dams of the Mooi River catchment, South Africa

WJ van Aardt* and R Erdmann
School of Environmental Sciences and Development, Potchefstroom University, Private Bag 6001, Potchefstroom 2520, South Africa

Abstract

Fish tissue from *Labeo capensis* and sediment core samples from three dams in the Mooi River catchment area were collected and analysed for Cd and Pb by electro-thermal AAS, and for Cu and Zn by flame AAS. The highest Cd concentrations were found in the clay fractions in all three dams, with a range between 66.0 $\mu g \cdot g^{-1}$ and 107 $\mu g \cdot g^{-1}$. Lead concentrations below 34 $\mu g \cdot g^{-1}$ were found in all six sediment types from Klerkskraal Dam, while Potchefstroom Dam had the highest lead levels (range: 34 - 62 $\mu g \cdot g^{-1}$) for the six sediment fractions and also for all the fish tissue types (range: 38 - 79 $\mu g \cdot g^{-1}$). Lead alkyls from motorboat exhausts were probably responsible for the high lead concentrations in the sediment of Potchefstroom Dam and in the mudfish tissues. The mean zinc concentrations from five of the six fractions in Boskop Dam were significantly higher compared to the other dams, with a range between 25 $\mu g \cdot g^{-1}$ to 59 $\mu g \cdot g^{-1}$. The combined six fractions were between five and 100 times lower in concentration when compared to the pelitic sediment samples from sediments at the Lebanon and West Driefontein mines in the Mooi River catchment. Copper concentrations in dam sediment from the six fractions for the three dams, ranging between 11$\mu g \cdot g^{-1}$ to 36 $\mu g \cdot g^{-1}$, were higher when compared with copper levels worldwide. The kidneys, gills and liver had the highest levels of Cd, Pb and Cu respectively compared to other tissues from *L. capensis,* while the gills had the highest concentration of Zn. In conclusion, higher than normal metal concentrations were found in Boskop Dam sediments, which could be linked to gold mine operations inside the Mooi River catchment area. Lead, Cd, Cu and Zn concentrations in *L. capensis* tissues were much lower compared to reported data on South African fish, but on par with world levels. The percentage of uranium present in sediment samples (analysed by energy dispersive X-ray spectrometry) from the three dams was 9.0 % (SD 2.1%). In sediment it was found that cation exchange capacity measurements and the dolomitic hard water and high pH of the Mooi River water effectively 'detoxified' Cd and Pb, forming insoluble complexation products buried in the sediment.

Keywords: Cd, Pb, Cu, Zn, dam sediment, fish tissues, CEC, sediment profiles

Introduction

There is an increasing awareness of the potential hazards that exist due to the contamination of freshwater impoundments by toxic metals associated with the mining industry (Kelly, 1988; Du Preez et al., 2003; Quek et al., 1998; Feather and Koen, 1975). The reason is the world demand for minerals, which has intensified the exploitation of natural resources. The water and tailings waste from mining and milling operations are discharged into settlement and treatment dams or tailings ponds. Eroded or disused tailings dams may contain considerable concentrations of toxic metals, usually dissolved in water at pH values as low as 1.7 (Wittmann and Förstner, 1977a) that may be released into the environment. The close proximity of the Mooi River catchment to the West Wits goldfields area near Carletonville, South Africa, and the established release of mine water into a tributary of the Mooi River (Fig. 1) may contribute to enhanced toxic metal levels in the water and sediment (Wittmann and Förstner 1977a; Kelly 1988). In a report (Wade et al., 2000) to the South African Water Research Commission it was found that not only were heavy metals enriched in Mooi River sediments, but radionuclide concentrations in the sediment at a locality in a Mooi River tributary near West Wits gold mines were higher than stipulated by the Nuclear Energy Act of 1993.

Many of the dissolved metals that enter rivers are adsorbed onto colloid particulates. Also at high alkalinity and pH, the metals, particularly lead and cadmium, precipitate by forming complexation products, resulting in an array of chemical speciation of metals that dramatically influence metal toxicity (Van Aardt and Booysen, 2004; Van Aardt and Venter, 2004) Therefore, precipitation and sedimentation of cadmium and lead and, to a lesser extent, copper and zinc in alkaline water bodies could be greater at the dam inlet where sedimentation processes act as a sink for metals (Harding and Whitton, 1978). Heavy metals such as lead, copper, nickel and zinc are usually deposited in sediments not deeper than 15 cm (Ochsenbein et al., 1983; Santos Bermejo et al., 2003).

The mine drainage from gold and uranium recovery operations at the West Wits goldfields has an enrichment factor of 500, 600, 1800 and 2600 respectively for Cd, Pb, Cu and Zn (Wittmann and Förstner, 1977 a or b). The Mooi River catchment and its fish were not included in the report of a national survey on metal accumulation in fish (Heath and Claassen, 1999) on six major river catchments of South Africa.

In this study, we report on the accumulation of four heavy metals in different sediment particle sizes, sediment profiles and different fish tissues in the Potchefstroom Dam and the Boskop Dam, from where the city of Potchefstroom obtains its irrigation and potable water supply. Metal concentration data are compared with sediments and fish tissues in the Klerkskraal Dam (as control dam), situated in the upper reaches of the Mooi River catchment, not affected by mining activities.

---

* To whom all correspondence should be addressed.
☎+2718 299-2376; fax:+2718 299-2370; e-mail: drkwjva@puknet.puk.ac.za
Received 8 July 2003; accepted in revised form 18 February 2004.

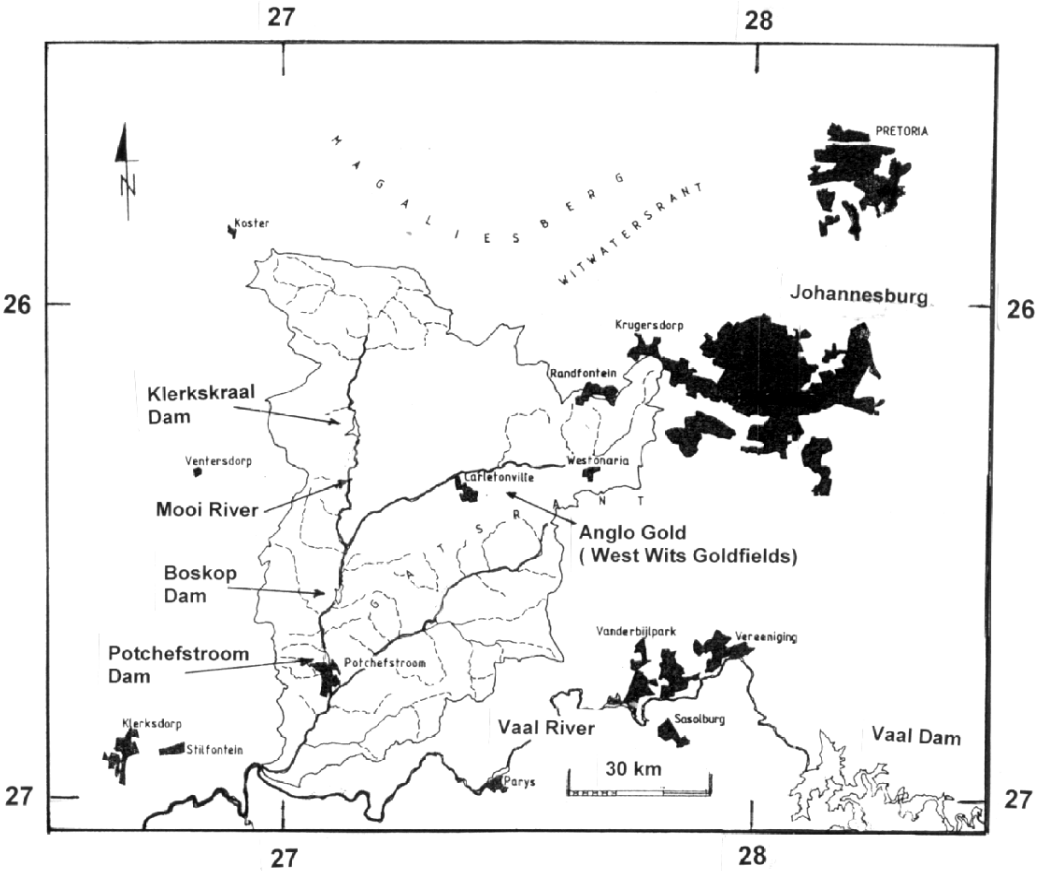

Figure 1
Map of the Mooi River catchment, indicating the three dams and associated towns and cities

TABLE 1
The mean and standard deviation (±) of the percentage particle size distribution in sediment core samples (n = 9) from three dams in the Mooi River catchment.

Dam	% particle size distribution per sediment sample						
	>2000 (µm)	2000-100 (µm)	1000-500 (µm)	500-250 (µm)	250-106 (µm)	106-53 (µm)	<53 (µm)
Klerkskraal Dam(n = 9)	8.70	8.34	9.26	9.36	15.82	10.94	46.31
(±)	2.77	7.05	5.16	4.69	3.76	2.77	16.37
Boskop Dam(n = 9)	6.60	6.13	6.56	9.34	20.93	15.23	42.80
(±)	2.54	1.07	0.73	3.38	7.15	1.64	11.14
Potchefstroom Dam(n = 9)	6.02	3.62	4.93	11.84	16.03	7.37	55.76
(±)	2.93	1.13	1.95	1.94	1.29	1.86	2.36

Materials and methods

Collection of sediment samples

Between July 1996 and April 1997, samples were collected from the three dams (Klerkskraal Dam; Boskop Dam; Potchefstroom Dam) in the Mooi River catchment (Fig. 1). Three sites per dam, about 50 m apart, were selected to collect the sediment. The sites were situated near the inflow of each dam as indicated by GPS localities (Table 3).

For each locality, six core samples were taken, using a specially made stainless steel core sampler with a mechanical valve, cutting face, and hammer action. The sampler was operated from a boat and could sample sediments from about two meters below the water surface. Each core sample was dried in its PVC jacket in a vertical position for 24 h. With the two halves of the jacket still in position, each core was cut lengthways into two halves by a wire cutter and allowed to dry horizontally in the jackets for 12 h. Usually not less than 500 g and up to 1 200 g dried sediment per core sample could be harvested from each of the nine cores per dam.

Core preparation: particle size distribution

For each locality, the top 50 mm sediment layer was removed from the two halves of the PVC jacket. Fifty grams from this layer were prepared according to Day (1965) and then sieved to produce six sediment particle-size fractions, starting with particles smaller than 2 mm in diameter. The percentage of a given particle size in the sample, on a mass basis, was then calculated (Table 1). For each particle size fraction, 1 g was taken for heavy metal analysis. Cadmium and lead were determined by electro-thermal analysis in combination with an atomic absorption spectrophotometer (AAS) from Varian (Varian SpectraAA –250, GTA 97). Zinc and copper were determined by flame analysis, using AAS (Varian SpectraAA –250).

Sediment profiles

From each dam, one core sample from each locality was used. The top 150 mm layer was removed and divided into three 50 mm layers, namely the top profile, middle profile and lower profile. With the aid of a swing mill (Siebtechnik, Mühlheim, Germany), each profile containing about 70 g sediment was separately pulverised for 15 s.

Core analysis

A 1 g sample from the pulverised core was taken for cadmium and lead determinations by electro-thermal analysis using AAS (Varian SpectraAA-225, GTA97, Australia) for Cd and AAS (GBC, Australia) for Pb. The matrix modifier used for Cd determinations was $NH_4H_2PO_2$ (25 mg·ℓ^{-1}). For Pb, a combination of 1% ascorbic acid and palladium (0.2 g·ℓ^{-1} $Pd(NO_3)_2$ in 15% nitric acid) was used. Copper and zinc were determined by flame analysis at 324.8 nm and 213.9 nm respectively, using an AAS (Varian, SpectraAA-225).

One gram dried, sieved particle size or pulverised core samples were placed separately in clean 20 mℓ glass vials and one ml de-ionised water, two ml 70% HNO3 and one mℓ 65% $HClO_4$ were added. The open vials were placed in an 80ºC water bath for 12 h. (VarianAAS analytical procedures, Australia). All chemicals used in the metal analysis were from Merck (*pro analisi)*, usually with heavy metal concentrations below 0.0005 %. The digested samples were diluted and filled up with de-ionised water to a total volume of 10 mℓ before the metals were analysed. Marine Sediment Reference Materials (Mess-2) from the National Research Council, Canada were used to calibrate and check the digestion method. One-gram samples from the pulverized cores were taken for energydispersive X-ray spectrometric analysis, using a Phillips EDAX-analyser (EDAX, CDU LEAP Detector) and electron microscope (XL30 Phillips Dzi). Three buttons for each sample were prepared using a sticking film. Sediment was lightly pressed onto the film and covered with a layer of carbon (Emscope TB 500).

Water: sediment extraction

The chemical composition of the sediment cores was determined by using a water extracting technique (Sonneveld and Van den Ende, 1971). After the extraction procedure, using 75 mℓ of dried homogenous core sample in 150 mℓ de-ionised water, the following chemicals were analysed: (chemical/element; analytical method; manufacturer): NH_4 (Ion selective electrode; Orion, USA); HCO_3 (Titerometry; Radiometer, Denmark); SO_4, NO_3 (Capillary electrophoresis; Quanta, USA); Ca, Mg, K, Na, (in mmol.ℓ^{-1}) by atomic absorption spectrophotometry (Varian, Australia); Fe, Mn, Cu, Zn, B (in μmol ℓ^{-1}) by AAS, (Varian, Australia); P (Liquid chromatography; Skalar, The Netherlands); Cl , SO_4 (Capillary electrophoresis; Quanta, USA); pH (Orion, USA) and electrical conductivity (in microSiemens; TetraCon 325, WTW, Germany). Cationic exchange capacity (CEC) was determined using the method as described by Peech (1965) and the sodium was analysed by means of flame AAS (Varian 250, Australia).

Fish tissue

Mudfish *(L. capensis)* were caught by gill netting at the beginning of July (winter) and October (spring) 1996 and also at the beginning of January (summer) and April (autumn) 1997 at the Klerkskraal, Boskop and Potchefstroom Dams (Fig.1). For each of the four seasons, and for each dam, 20 fish (body mass range: 451g to 1211 g) were caught. Immediately after netting, a 1 mℓ blood sample was taken from each fish by heart puncture with syringes (containing heparin). The fish were transported to the laboratory, kept at 4ºC and dissected to remove one-gram samples (wet mass) of gonads, liver, kidney, intestine (jejenum), gills and muscle (on the lateral body wall). From each tissue type 1g tissue was weighed and placed into clean glass vials. The fish tissue was digested for 12 h as described for sediment material. One gram of dried reference material serving as an international certification reference material (Dogfish Muscle and Liver Certified Reference Materials (Dorm-2)) from the National Research Council, Canada was used for calibration; one mℓ de-ionised water was added with 2 mℓ HNO_3 plus 1 mℓ $HClO_4$ (*pro analisi*, Merck).

To express the metal concentrations obtained form *L. capensis* per gram dried tissue mass, the percentage of water for each of the seven tissue types was determined by drying the tissue on aluminium foil for 12 h at 70ºC. The following mean water percentages were found: gonads, 8.11 %; liver, 73.90%; kidney, 72.0%; intestine, 77.2%; gills, 77.3%; muscle, 75.72%. The standard deviation (SD) from the mean for all tissues weighed was below 0.03%.

Statistica 5 was used to analyse the data. Normal distribution was calculated using the Shapiro Wilk test. A one-way analysis of variance (Anova) was performed and the Tukey test was used to indicate statistically significant differences. Differences in mean values were accepted as being statistically significant if $P< 0.05$.

Results and discussion

No differences in the metal concentrations in mudfish tissue or metal accumulations in sediment for the three respective dams were found between samples collected at different seasons; between October 1996 and April 1997. Data from male and female fish were combined, since no significant differences in metal concentration between the sexes were found.

The electro-thermal atomic absorption spectrometry analysis for Cd, Pb and flame absorption spectrometry for Cu and Zn done on the reference material from Canada were respectively within 5% and 5.5% of certified values. The detection limit of 0.24, 0.9, 2.0, and 3.1 μg·g^{-1} for dried sediment or tissue mass was found for Cd, Pb, Cu and Zn respectively. Except for Cd, a linear relationship between absorbance and metal concentration was achieved for the standard curves.

Metal analysis of the water was not determined in this study but flame atomic absorption analysis of cadmium, lead, copper and zinc (Sanders, 1997) from Potchestroom Dam water gave values of 5 μg·ℓ^{-1}, 14 μg·ℓ^{-1}, 6 μg·ℓ^{-1} and 20 μg·ℓ^{-1} water respectively. In previous studies, however, Cd (Van Aardt and Booysen, 2004) and Pb (Van Aardt and Venter, 2004) were not detectable in Mooi River water, or exhibited very low values (< 2μg·g^{-1}) compared to soft water bodies (Heath and Claassen, 1999).

Metal analysis by the EDAX-method for dam sediment

The percentage occurrence of metals by Edax-analysis in the three sediment profiles for each dam did not differ significantly. Iron (66.3±2.9 %), followed by copper (10.0 ±1.7%), lead (9.4±3.4%),