

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 $\mu\text{g}\cdot\text{g}^{-1}$ and 107 $\mu\text{g}\cdot\text{g}^{-1}$. Lead concentrations below 34 $\mu\text{g}\cdot\text{g}^{-1}$ were found in all six sediment types from Klerkskraal Dam, while Potchefstroom Dam had the highest lead levels (range: 34 - 62 $\mu\text{g}\cdot\text{g}^{-1}$) for the six sediment fractions and also for all the fish tissue types (range: 38 - 79 $\mu\text{g}\cdot\text{g}^{-1}$). 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 $\mu\text{g}\cdot\text{g}^{-1}$ to 59 $\mu\text{g}\cdot\text{g}^{-1}$. 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 $\mu\text{g}\cdot\text{g}^{-1}$ to 36 $\mu\text{g}\cdot\text{g}^{-1}$, 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.

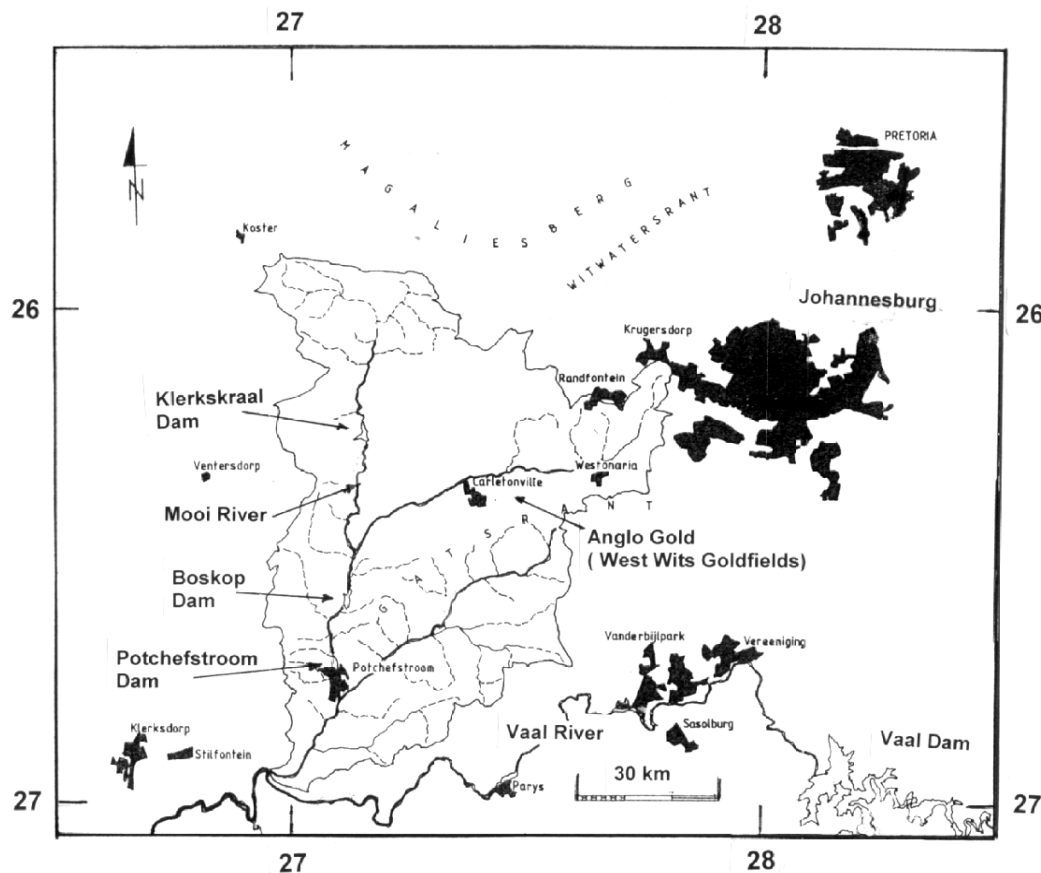


Figure 1
Map of the Mooi River catchment, indicating the three dams and associated towns and cities

TABLE 1
The mean and standard deviation (\pm) 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
(\pm)	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
(\pm)	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
(\pm)	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 $\text{NH}_4\text{H}_2\text{PO}_4$ (25 $\text{mg}\cdot\text{L}^{-1}$). For Pb, a combination of 1% ascorbic acid and palladium (0.2 $\text{g}\cdot\text{L}^{-1}$ $\text{Pd}(\text{NO}_3)_2$ 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% HNO_3 and one mL 65% HClO_4 were added. The open vials were placed in an 80°C 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 $\text{mmol}\cdot\text{L}^{-1}$) by atomic absorption spectrophotometry (Varian, Australia); Fe, Mn, Cu, Zn, B (in $\mu\text{mol}\cdot\text{L}^{-1}$) 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 4°C and dissected to remove one-gram samples (wet mass) of gonads, liver, kidney, intestine (jejunum), 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 from *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 70°C. 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 $\mu\text{g}\cdot\text{g}^{-1}$ 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 $\mu\text{g}\cdot\text{L}^{-1}$, 14 $\mu\text{g}\cdot\text{L}^{-1}$, 6 $\mu\text{g}\cdot\text{L}^{-1}$ and 20 $\mu\text{g}\cdot\text{L}^{-1}$ 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 ($< 2\mu\text{g}\cdot\text{g}^{-1}$) 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%),

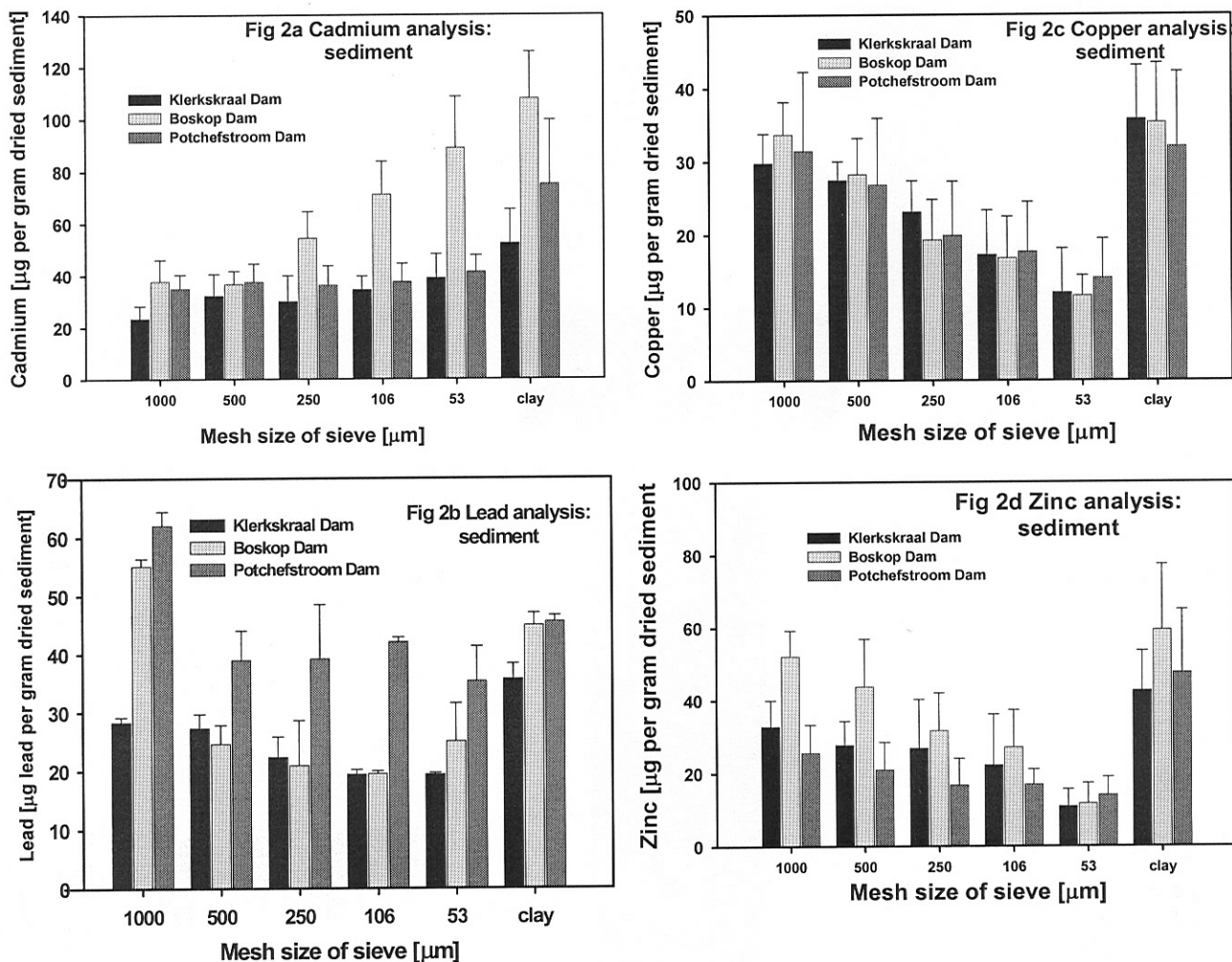


Figure 2

Analysis from 27 sediment cores for lead, cadmium, copper and zinc obtained from the three dams in the Mooi River catchment. Metal concentrations ($\mu\text{g g}^{-1}$ dried sediment) are from six mesh sizes collected from the top 50 mm - layer from nine samples from each dam. Vertical bars denote the standard deviation from the mean. Mesh size of clay is $< 53 \mu\text{m}$.

Dam	Macro-elements in sediment after water extraction (mmol l^{-1})									
	Ca	Mg	K	Na	P	SO ₄	NO ₃	NH ₄	Cl	HCO ₃
Klerkskraal	31.9	40.6	3	5.3	0.1	10.9	3.5	20.9	3.0	42.6
(\pm)	9.0	9.4	0.7	1.2	0.0	5.1	4.3	10.3	1.9	10.7
Boskop	141.	158	3.5	6.0	0.1	95	8.2	26.8	14.7	23.6
(\pm)	97	100	2.6	4.5	0.0	73	6.4	29.6	7.7	6.5
Potchefstroom	88.3	130	3.9	6.7	0.1	60.6	10.2	9.7	22.8	29.6
(\pm)	38.8	39	1.6	2.8	0.0	26.1	9.2	6.2	8.4	9.5

uranium, ($9.0 \pm 2.1\%$) zinc ($3.8 \pm 0.7\%$) and cadmium ($1.0 \pm 1.3\%$) were present, but this does not exclude other metals because the detection limit for this analytical method was 1%. The lithostratigraphy beneath Klerkskraal Dam consists mainly of dolomitic and calcareous-rocks. Boskop Dam, however, is situated

on porous consolidated and unconsolidated sedimentary rocks and basic lavas. Potchefstroom Dam lies above the same consolidated and unconsolidated sedimentary rocks found under Boskop Dam. (Midgley et al., 1990). A large part of the Mooi River that feeds the three dams drains a dolomitic area.

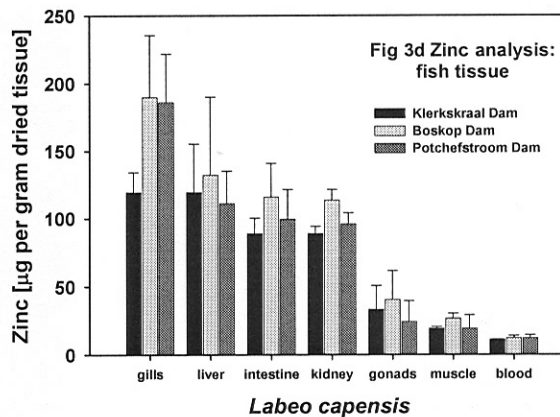
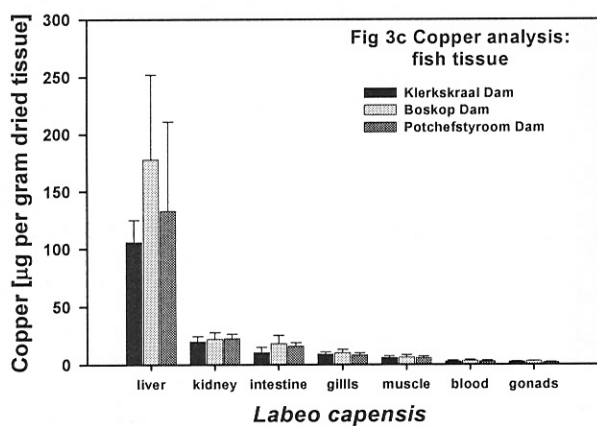
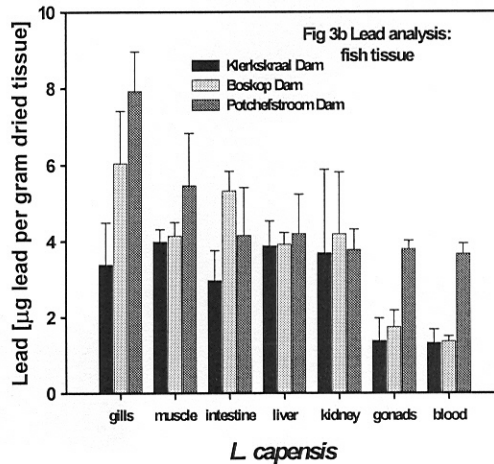
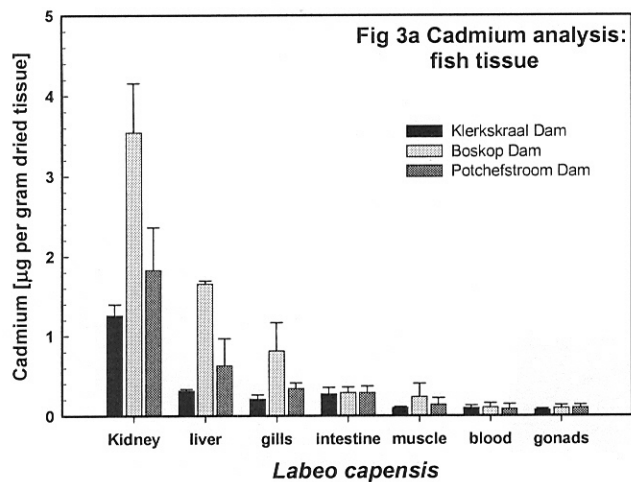


Figure 3

Fish tissue analysis of lead, cadmium, copper and zinc obtained from the three dams in the Mooi River catchment. Metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ dried tissue) are from 80 fish samples from each dam. Vertical bars denote the standard deviation from the mean.

The high iron, lead and zinc levels are in close accordance with similar findings by Wittmann and Förstner (1977a) in sediments in close proximity of mine slimes dams in the Mooi River catchment.

Metal levels in dam sediment fractions

The concentration of Cd in the different sediment fractions in the three dams ranges from about $20 \mu\text{g}\cdot\text{g}^{-1}$ dried sediment (1 000 mesh size) to more than $100 \mu\text{g}\cdot\text{g}^{-1}$ in the dried clay fraction (Fig.2a) with a mean of $60 \pm 9.5 \mu\text{g}\cdot\text{g}^{-1}$. A study by Wittmann and Förstner (1977a) on the pelitic or clay sediments of the mine drainage area of the Mooi River catchment at West Wits Goldfields shows that Cd concentration varied between 0.08 and $0.86 \mu\text{g}\cdot\text{g}^{-1}$. These values are much lower, compared to this study on the clay fraction (range 61 to $107 \mu\text{g}\cdot\text{g}^{-1}$) - range for Po River (Italy) sediment from $0.20 \mu\text{g}\cdot\text{g}^{-1}$ to $1.44 \mu\text{g}\cdot\text{g}^{-1}$ (Vigano et al., 2003); for the Kromme Rijn River (The Netherlands) sediments with a mean Cd concentration of $5.62 \mu\text{g}\cdot\text{g}^{-1}$ (Buykx et al., 2002), and a mean of $30 \mu\text{g}\cdot\text{g}^{-1}$ in the Odiel river sediment in Southwest Spain (Santos Bermejo et al., 2003). The worldwide range for virgin soils is between $0.06 \mu\text{g}\cdot\text{g}^{-1}$ and $10 \mu\text{g}\cdot\text{g}^{-1}$, with an average of $0.4 \mu\text{g}\cdot\text{g}^{-1}$ (Laegreid et al., 1999). The Cd concentrations in the different sediment profiles (Fig. 4a) of the three dams were on much the same levels with the six individual sieved sediment fractions if they were added and compared. As an example (Fig.4a), the three profiles from Boskop

dam were above the $400 \mu\text{g}\cdot\text{g}^{-1}$ Cd level. This gives about the same concentration if the six sediment fractions in Boskop Dam are combined and added. From this analysis it can be deduced that in the Boskop Dam sediment and, to a lesser extent the sediments from the other two dams, the Cd content was about ten times higher compared to other polluted areas world wide, referred to above. A possible reason for the low Cd values for the pelitic sediments at West Wits Goldfields could be the low pH of the effluents dissolving and washing out the Cd from the soil.

The lead concentrations in the different sediment fractions of the three dams were the lowest for Klerkskraal Dam but in comparison, were nearly twice as high for Potchefstroom Dam in the sandy ($62 \pm 4.2 \mu\text{g}\cdot\text{g}^{-1}$) and other fractions. All six mesh size fractions from Potchefstroom Dam were significantly higher than that of either the Boskop or Klerkskraal Dam. The pelitic sediments from eight mine drainage localities analysed in the Mooi River catchment for lead by Wittmann and Förstner (1977a) yielded between 140 and $642 \mu\text{g}\cdot\text{g}^{-1}$. This is an enrichment factor of 17 for lead compared to a standard shale of $20 \mu\text{g}\cdot\text{g}^{-1}$ lead (Wittmann and Förstner 1977a). For the Po River sediments in Italy, the highest value found was $1.44 \mu\text{g}\cdot\text{g}^{-1}$ (Vigano et al., 2003) and for the Kromme Rijn River, (The Netherlands) $5.62 \mu\text{g}\cdot\text{g}^{-1}$ (Buykx et al., 2002). Analysis of the metal concentrations has shown that cadmium, copper and zinc (lead was not analysed) concentrations in each of the three 5 cm sediment profiles did not differ significantly.

TABLE 3
Sample localities and physical measurements of dam sediments from three dams in the Mooi River catchment.
 \pm , standard deviation from the mean;
 c.mol, centimol; CEC, cation exchange capacity;
 EC, electrical conductivity

Dam	Locality	pH	EC ($\mu\text{S}\cdot\text{cm}^{-1}$)	CEC ($\text{cmol}\cdot\text{kg}^{-1}$)
Klerkskraal	26 13' 745"S 27 09' 063"E	7.67	510.0	42.6
		(\pm) 0.26	(\pm) 115.4	(\pm) 4.0
Boskopop	26 31' 531"S 27 07' 348"E	7.49	2720.0	42.3
		(\pm) 0.12	(\pm) 111.0	(\pm) 10.0
Potchefstroom	26 39' 714"S 27 05' 328"E	7.62	1490.2	39.8
		(\pm) 0.03	(\pm) 340.0	(\pm) 7.9

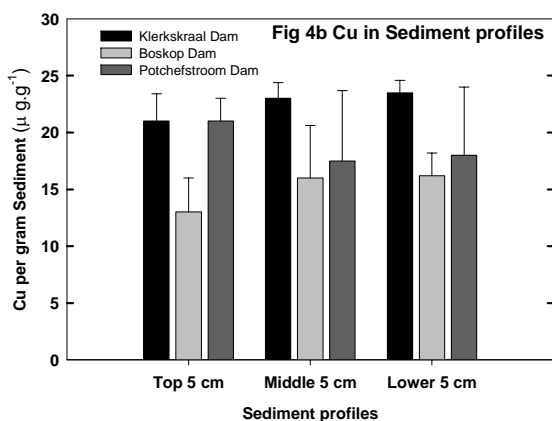
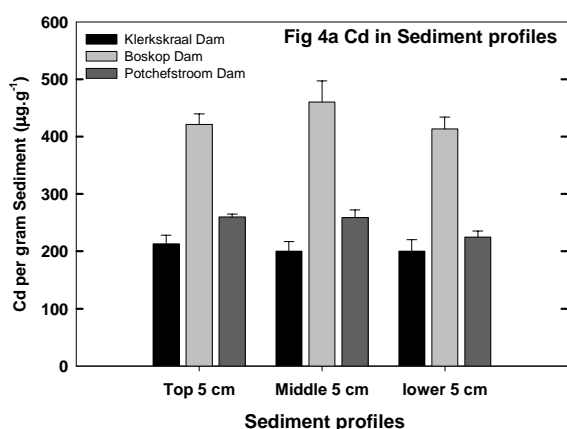


Figure 4

Heavy metal concentrations in three different sediment profiles from the three dams in the Mooi River catchment. 4a, cadmium; 4b, copper. Vertical bars denote the standard deviation from the mean.

Apart from mining activities, a possible explanation for the high lead content in the Potchefstroom Dam is that powerboats using leaded fuel are allowed there, but not on the other two dams. If the mean tetraethyl lead content per litre fuel is $0.54 \text{ mL}\cdot\text{L}^{-1}$ (Fieser and Fieser, 1963), it can be calculated that the combustion of 1 L of fuel releases about 480 000 μg of lead into the water.

Tetraethyl lead is insoluble in water and could accumulate in the sediment. This lead source may enter the food chain for detritus feeders like mudfish (see below).

Copper concentrations in the different sediment fractions decreased sharply from the largest mesh sizes to the smaller sizes, except for the clay fractions which were nearly three times higher compared to the 53 μm fraction (mean concentration $13.5 \mu\text{g}\cdot\text{g}^{-1}$ with a standard deviation of 3.6). The three profiles investigated for Cu (Fig.4b) for the three dams had nearly the same Cu levels for each dam, with a range between $14 \mu\text{g}\cdot\text{g}^{-1}$ and $23 \mu\text{g}\cdot\text{g}^{-1}$ with a mean of $19 \mu\text{g}\cdot\text{g}^{-1}$. Copper levels for the six sediment fractions had a mean value of $24 \mu\text{g}\cdot\text{g}^{-1}$ dried sediment. This value is only about 14 % compared to the Cu concentrations obtained by Wittmann and Förstner (1977a) on eight sampling sites in sediments draining the West Wits Goldfields area. These results indicate that large amounts of heavy metals (but not Cd) are lost between the highly polluted localities investigated by Wittmann and Förstner (1977a) and the recent survey of the three Mooi River Dams in this study.

In comparison with the Kromme Rijn River sediment in The Netherlands, $93.3 \mu\text{g}\cdot\text{g}^{-1}$ copper was found (Buykx et al., 2002).

On average, the Zn concentrations for Boskop Dam sediment fractions were significantly higher compared to the other two dams (Fig.2d). This applied to five of the six sediment fractions analysed (range for the six fractions: 11.5 to $59.3 \mu\text{g}\cdot\text{g}^{-1}$). From the eight sediment localities investigated by Wittmann and Förstner, 1977a, the zinc concentrations at the drainage sites near the West Wits Goldfields were higher (range: $56 \mu\text{g}\cdot\text{g}^{-1}$ to $6440 \mu\text{g}\cdot\text{g}^{-1}$) compared to the analysis in this study. By comparison, the Po River (Vigano et al., 2003) and Kromme Rijn River (Buykx et al., 2002) Zn sediment concentrations were on average $244 \mu\text{g}\cdot\text{g}^{-1}$ and $836.8 \mu\text{g}\cdot\text{g}^{-1}$ respectively.

Generally, the clay fractions from the three dams in the Mooi River catchment had, on average, the highest metal concentrations when compared to the other five sediment types investigated. This is in accord with the knowledge that clays, including pelitic sediments have high adsorption values for metals (Yoshida et al, 1993). Furthermore, the four metals investigated were greatly reduced in their sediment concentration levels compared to the high levels found by the earlier investigators (Wittmann and Förstner, 1977a) near the respective slime dams at the West Wits Goldfields. These mines were recently renamed as Anglo Gold.

For the metal concentrations in sediment profiles, the highest Cd concentration ($429 \pm 37 \mu\text{g}\cdot\text{g}^{-1}$) was found in Boskop Dam (Fig. 4a), and the highest copper levels in Klerkskraal Dam (Fig.4b). These differences were statistically significant. No significant differences in the Zn concentrations ($23.0 \pm 2.2 \mu\text{g}\cdot\text{g}^{-1}$) between the sediment profiles for the three dams could be found.

Cation exchange capacity (CEC) of dam sediment (Table 3)

Of the 27 sediment samples collected, three samples from Boskop Dam and three samples from Potchefstroom Dam were obtained from sandy areas near the dam inflow. The sand samples had CEC values (not included in Table 3) of less than $20 \text{ centimol}\cdot\text{kg}^{-1}$ dried sediment, compared to the mean value of $42 \text{ centimol}\cdot\text{kg}^{-1}$ dried sediment for the other samples obtained from sediment samples with mesh sizes below $250 \mu\text{m}$.

The most important chemical processes affecting the behaviour and availability of heavy metals in sediments are the adsorption of heavy metals from solution to the solid phase. Of the three mechanisms used in adsorption, namely CEC, organic complexation and co-precipitation, CEC is the most important. The adsorption of cadmium, lead, copper and zinc (existing as cations in the sediment solution) onto the negatively charged solid phase of the sediment colloid depends on the density of negative charges on the surface of the sediment colloids. High CEC values indicate a high capacity of sediments to adsorb metals. In this regard the CEC values found for sediments from the three dams indicated that there was a mean exchange capacity of 41.5 ± 7.3 centimol·kg⁻¹ (Table 3). This is about 66% compared to the highest value of 60 centimol·kg reported for mineral soils (Yoshida et al., 1993). This value, however, is much less than the 200 centimol·kg⁻¹ measured for organic soils (Alloway, 1990). For the three dams, the high calcium and magnesium levels (Table 2) found in the sediment could, as cations, play a major part in promoting cationic exchange capacity in dam sediment.

Metal analysis of fish tissues

No significant concentration differences were found when the fish tissues, sampled in the four seasons, were analysed and compared for cadmium. This also applied for copper and zinc. Lead was not seasonally analysed.

The highest Pb (range 3.4 to 7.9 µg·g⁻¹, Fig. 3b) and Zn (range 119.0 to 188.0 µg·g⁻¹, Fig. 3d) concentrations for all three dams were found in the gills of *L. capensis*. Compared to all the other seven tissues, liver tissue (106 µg·g⁻¹ to 178 µg·g⁻¹) had the highest Cu levels. In a 17 month study (Nussey et al., 2000) on *L. umbratus* at the upper reaches of the Olifants River (Witbank Dam), the Pb in dried tissues were 14.0, 6.9, 8.0 and 5.6 µg·g⁻¹ for gills, liver muscle and skin respectively, while the sediment averaged 22.9 µg·g⁻¹. The Pb concentrations in tissues were significantly higher compared with Mooi River Pb levels in *L. capensis*. The combined six sediment fractions (Fig. 2b), if added, gave Pb concentrations not significantly different for the Pb values found in the Olifants River. Although the pH of the water at Witbank Dam was not measured, it is known (Nussey, 1998) that relatively low water pH values (range 6.10 to 8.61) and soft water are encountered in the upper reaches of the Olifants River (Steenkool Spruit), compared to the high pH values (range 8.14 to 8.76) and hard water (230 mg·L⁻¹, as CaCO₃) found in Mooi River water (Van Aardt and Booyen, 2004). This difference in pH and hard water could, in part, explain why the Pb levels in *L. capensis* were much lower in the Mooi River catchment. Precipitation or chelation of Pb to the sediment in hard water with pH above eight has been demonstrated (Van Aardt and Venter, 2004).

Generally low levels of Cd, Pb and Cu were present in blood, muscle and gonad samples (Fig. 3a; b; c), also found for *L. umbratus* (Nussey et al., 2000)

As was expected for Cd, this metal accumulated mainly in kidney tissue (range 1.2 µg·g⁻¹ to 3.5 µg·g⁻¹). The Cd levels in *L. capensis* kidney were about the same, compared to levels in beef kidney, with a range of 0.2 µg·g⁻¹ to 1.6 µg·g⁻¹ wet mass (Fridberg et al., 1979). Sulphide ore minerals that harbour high cadmium concentrations of between 0.2 and 0.4% (Jinadasa et al., 1997; Alloway, 1990), do not occur in Witwatersrand ore deposits

Table 4
Statistical analysis between sediment fractions in the three dams in the Mooi River catchment. K, Klerkskraal Dam; B, Boskop Dam; P, Potchefstroom Dam. Bold capital letters indicate statistical significant differences between dams; † highest concentration between dams; ‡ lowest concentration between dams.

Sediment fractions (µm)	Heavy metals analysed in dam sediment fractions			
	Pb	Cd	Cu	Zn
1000	K, B, P	‡ K, B, P	K, B, P	K, † B, P
500	K, B, † P	K, B, P	K, B, P	K, † B, P
250	K, B † P	K, † B, P	K, B, P	K, B, P
106	K, B, † P	K, † B, P	K, B, P	K, B, P
53	K, B, † P	K, † B, P	K, B, P	K, B, P
clay fraction	† K, B, P	K, † B, P	K, B, P	K, B, P

(Wittmann and Förstner, 1977a).

It is interesting to note that the higher lead concentrations found in Potchefstroom Dam sediment when compared with the other two dams were also reflected in fish tissue sampled from Potchefstroom Dam. Significantly higher concentrations of lead were found in gill tissue, gonads and blood compared with the other dams (Fig 3b). From this finding it can be stated that the mudfish, *L. capensis*, a detritus feeder living from the muddy substrate in Potchefstroom Dam, acquires the high tissue lead through uptake by the gills and also by sucking in and digesting the relatively high lead load in mud sediment. The lead originates from alkyl lead after fuel combustion when lead bromides are formed. In a soil environment these compounds change chemically to insoluble Pb carbonates, oxycarbonates and oxides (Davies, 1990).

Lead concentrations in fish tissue obtained from mudfish (*L. umbratus*) from other catchment areas in South Africa (Heath and Claassen, 1999) were significantly higher (range: 14 µg·g⁻¹ to 454 µg·g⁻¹). The analyses in this study has shown lower lead levels (range: 1.3 to 9.1 µg·g⁻¹; mean: 7.9 µg·g⁻¹) when compared with *Labeo rosae* (range: 3.4 µg·g⁻¹ to 879.1 µg·g⁻¹; mean: 497 µg·g⁻¹) (Heath and Claassen, 1999).

Analysis of metals with low vapour pressures such as lead and cadmium, can be more accurately analysed using electro-thermal AAS (Fridberg et al., 1979). In optimal conditions, sensitivity (Willard et al., 1974) can be improved hundredfold with electro-thermal AAS. This, in part, could explain the different analytical results from investigators analysing the same Cd and Pb samples with or without electro-thermal AAS analytic methods (Ure 1990; Fridberg et al., 1979; Wittmann and Förstner, 1977a).

An important conclusion from this study is that higher values prescribed by national and international standards (Wittmann and Förstner, 1977b) for metal concentrations were found in Boskop Dam sediments. This could be ascribed to mining activities in the vicinity of Boskop Dam, especially when considering that Klerkskraal Dam, acting as a control dam, had significantly lower metal concentrations. The high levels of heavy metals found in the sediments in the close vicinity of the West Wits Goldfields (Anglo Gold) in the late seventies by Wittmann and Förstner (1977a or b), and similar findings in this study regarding sediments and fish tissue in the Mooi River dams should be evaluated jointly. In this regard it is fortunate that the high pH, high alkalinity and hardness of the dolomitic water in the Mooi River prohibits the dissolution

of these potentially toxic metal compounds from the dam sediment where they are deposited. However, a drastic change of the physical properties of the water such as lowering of the pH below 6.5, together with a physical disturbance of not only dam sediment, but sediments in the Mooi River, could potentially release large amounts of toxic metals from the sediment colloids' surface into the water column.

Acknowledgements

We wish to thank the Research Focus Area: Environmental Sciences and Management, for financial assistance, and the School of Environmental Sciences and Development, Potchefstroom University for CHE, Potchefstroom, South Africa, for providing the research facilities

References

ALLOWAY BJ (1990) Soil processes and the behavior of metals. In: BJ Alloway (ed.) *Heavy Metals in Soils*. Blackie, Canada: Halsted Press. 7-28.

BUYKX SEJ, VAN DEN HOOP MAGT and LOCH JPG (2002) Dissolution kinetics of heavy metals in Dutch carbonate- and sulfide-rich freshwater sediments. *J. Environ. Qual.* **31** 573-580.

DAVIES BE (1990) Lead. In: BJ Alloway (ed.) *Heavy Metals in Soils*. Blackie, Canada: Halsted Press. 177-196.

DAY PR (1965) Physical and mineralogical properties, including statistics of measurement and sampling. In: CA Black, DE Evans, JL White LE Esminger, FE Clark (eds.) *Methods in Soil Analysis*. Agronomic Monographs 9, Part 1: American Society of Agronomy, Madison, Wisconsin.

DU PREEZ H, HEATH GM, SANDHAM L and GENTHE B (2003). Methodology for the assessment of human health risks associated with the consumption of chemical contaminated freshwater fish in South Africa. *Water SA* **29** 69-90.

FEATHER CE and KOEN GM (1975). The mineralogy of the Witwaters Rand Reefs. *Miner. Sci. Eng.* **7** 189-224.

FIESER LF and FIESER M (1963) *Organic Chemistry*. Reinhold Publishing Corp. NY.

FRIBERG L, KJELLSTROM T, NORDBERG G AND PISCATOR M (1979) Cadmium. In: L Fridberg, GF Nordberg and VB Vouk (eds.) (1979) *Handbook on the Toxicology of Metals*. Elsevier, Amsterdam.

HARDING JPC and WHITTON BA (1978) Zinc, cadmium and lead in water, sediment and submerged plants of the Derwent Reservoir, Northern England. *Water Res.* **12** (1) 307-316.

HEATH RGM and CLAASSEN M (1999) An Overview of the Pesticide and Metal Levels Present in Populations of the Larger Indigenous Fish Species of Selected South African Rivers. Water Research Commission Report 428/1/99. Pretoria: Water Research Commission.

JINADASA KBPN, MILHAM PJ, HAWKINS CA, CORNISH PS, WILLIAMS PA, KALDOR CJ and CONROY JP (1997) Survey of cadmium levels in vegetables and soils of gGreater Sydney, Australia. *J. Environ. Qual.* **26** 924-933.

KELLY M (1988) *Mining and the Freshwater Environment*. Elsevier Applied Science, London.

LAEGREID M, BOCKMAN OC and KAARSTAD EO (1999) *Agriculture, Fertilizers and the Environment*. CABI Publishing, UK.

MIDGLEY DC, PITMAN WV and MIDDELTON BJ (1990) Surface Water Resources of South Africa, Book of Maps. Vol. II, Drainage Region C Vaal. WCR Report no 298/2.2/94 Map no. 03 and 6.2. Pretoria: Government Printer.

NUSSEY G (1998) Metal Ecotoxicology of the Upper Olifants River at Selected Localities and the Effect of Copper and Zinc on Fish Blood Physiology. Thesis: Ph.D, Faculty of Natural Sciences, Rand Afrikaans University, Johannesburg, South Africa.

NUSSEY G, VAN VUREN JHJ and DU PREEZ HH (2000) Bioaccumulation of chromium, manganese, nickel and lead in the tissues of moggel (Cyprinidae) from Witbank Dam, Mpumalanga. *Water SA* **26** (2) 269-284.

QUEK SY, WASE DAJ and FORSTER CF (1998) The use of sago waste for the sorbtion of lead and copper. *Water SA* **24** (3) 251-256.

OCHSENBEIN U, DAVISON W, HILTON J and HAWORTHHEY (1983) The geochemical record of major cations and trace elements in a productive lake. *Arch. for Hydrobiol.* **98** 463-488.

PEECH M (1965) Lime requirement. In: CA Black, DE Evans, JL White, LE Esminger and FE Clark (eds.) *Methods of Soil Analysis*. Agronomic Monographs 9, Part 2 927-932 American Society of Agronomy, Madison, Wisconsin.

SANDERS MJ (1997) A Field Evaluation of the Freshwater River Crab, *Potamonautes warreni*, as a Bioaccumulative Indicator of Metal Pollution. Thesis, M.Sc. Faculty of Natural Science, Rand Afrikaans University, Johannesburg, South Africa.

SANTOS BERMEJO JC, BELTRÁN R and GOMEZ ARIZA JL (2003) Spatial variation of heavy metals contamination in sediments from Odiel river (Southwest Spain). *Environ. Int.* **29** 69-77.

SONNEVELD C and VAN DEN ENDE J (1971) Soil analysis by means of a 1:2 volume extract. *Plant and Soil* **35** 505-516.

URE AM (1990) Methods of analysis for heavy metals in soils. In: BJ Alloway (ed.) *Heavy Metals in Soils*. Blackie, USA, Halsted Press. 40-80.

VAN AARDT WJ and BOOYSEN J (2004) Water hardness and the effects of Cd on oxygen consumption, plasma chlorides and bioaccumulation in *Tilapia sparrmanii*. *Water SA* **30** (1) 57-64.

VAN AARDT WJ and VENTER LCR (2004) The effects of lead, water hardness and pH on the oxygen consumption, plasma chlorides and bioaccumulation in the freshwater fish *Tilapia sparrmanii*. *Afr. J. Ag. Sci.* **29** 37-46.

VIGANO L, ARILLO A, BUFFAGNI A and CAMMUSSO M (2003) Quality assessment of bed sediments of the Po River (Italy). *Water Res.* **37** 501-518.

WADE PC, WOODBORNE S, MORRIS WM, VOS P and JARVIS NV (2000) Tier 1 Risk Assessment of Selected Radionuclides in Sediment of the Mooi River Catchment. WCR Project number K5/1059.

WILLARD HW, MERRITT LL and DEAN JA (1974) *Instrumental Methods of Analysis*. D van Nostrand Company, New York.

WITTMANN GTW and FÖRSTNER U (1977a) Heavy metal enrichment in mine drainage: III. The Klerksdorp, West Wits and Evander Goldfields. *S. Afr. J. Sci.* **73** 53-57.

WITTMANN GTW and FÖRSTNER U (1977b) Heavy metal enrichment in mine drainage: IV. The Orange Free State Goldfields. *S. Afr. J. Sci.* **73** 374-378.

YOSHIDA H, OKAMOTO A, YAMASAKI H and KATAOKA T (1993) *Fundamentals of Adsorption*. Kodansha, Tokyo.