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Levels and Speciation of Heavy Metals in Some Rivers in South Africa

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In heavy metal analysis, the total concentrations of the metals are most often determined (El-Sammak and Aboul-Kassim, 1999, Nkono *et al*; 1999, Okonkwo *et al* 1999 and 2001, Castro Dantos *et al*, 2003). However, total concentration provides no information concerning the fate of the metal in terms of its interaction with sediments, its bio-availability, or its resultant toxicity (Christie, 1995). In order to understand the environmental chemistry of a metal, it is necessary to include the different forms of the metal, especially the amount of free metal ions and very labile complexes under the diverse range of conditions possible in natural systems.

According to Roux *et al* (1994) there is inadequate knowledge and data on heavy metal concentrations in South African waters. This has been attributed to relatively few studies that have been undertaken in South Africa dealing with levels of heavy metals particularly their speciation in surface waters. The situation is even exacerbated in the remote parts of the country where pollution monitoring is given little or no attention. The present study reports the analysis of selected heavy metals in some rivers in Thohoyandou, South Africa, with a view of establishing a baseline data of their levels. Also speciation studies of the metals were investigated in order to establish the different forms of the metals within the water system studied. A simple but rapid scheme has been developed to separate the metals into different fractions.

MATERIALS AND METHODS

A Varian Spectra AA 220 atomic absorption spectrophotometer equipped with a single slot burner was used, while analytical signals were recorded using a program for data handling controlled by a microprocessor. All glass and propylene ware used were first soaked in dilute HNO_3, thoroughly washed and then rinsed with double distilled de-ionized water and acetone. After washing, all the glassware were dried in the oven at 100°C for 24 h, while the plastic ware were left to dry at room temperature and later used for water sample collection. All reagents used in the present study were of analytical grade. 1000 mg^{-1} stock solutions of the metals (Cd, Cu, Pb and Zn) were purchased from BDH chemicals.
Standard working solutions were prepared from the stock of each metal from which lower concentrations were prepared.

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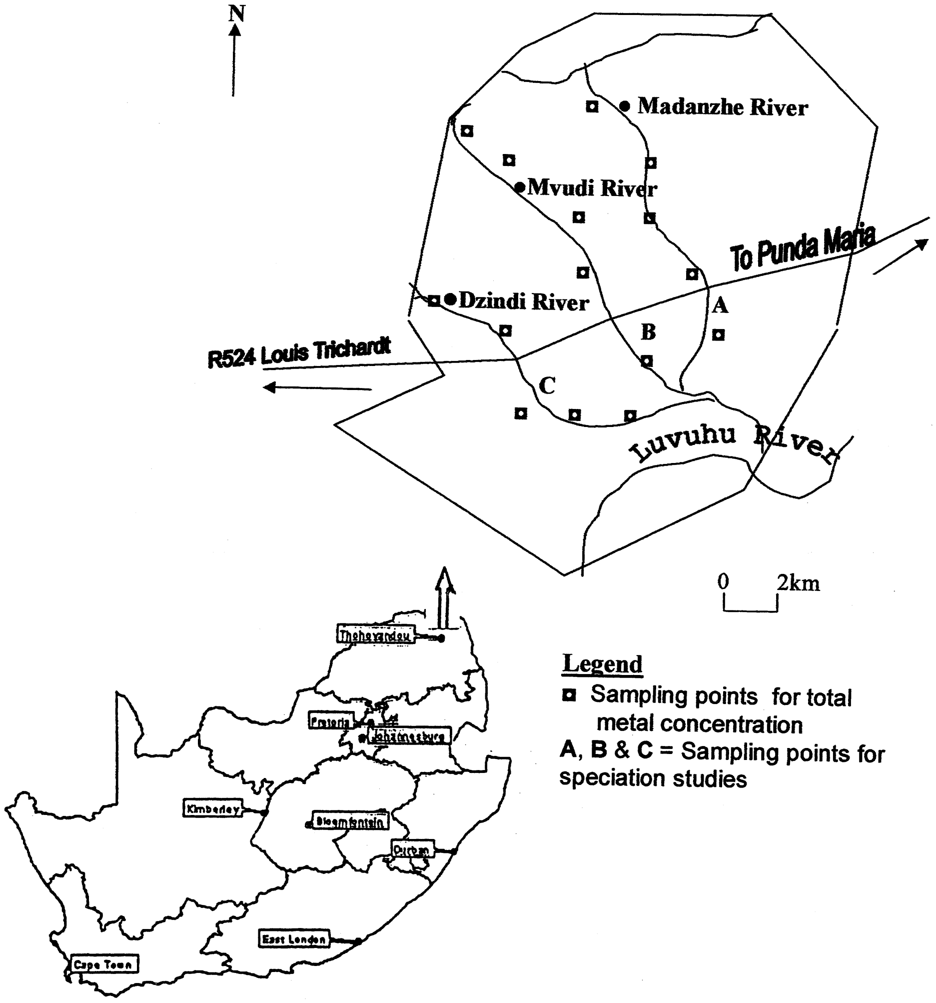

Figure 1. A sketch map of South Africa (bottom left) and Thohoyandou (top right) showing the sampling points along the various rivers studied

Normal linear fit working calibration curve of each metal was prepared for metal determination. All measurements were carried out in triplicate.

Water samples were collected from the five sites per river as indicated in Figure 1, in November 2002 and April 2003, representing wet and dry seasons respectively.

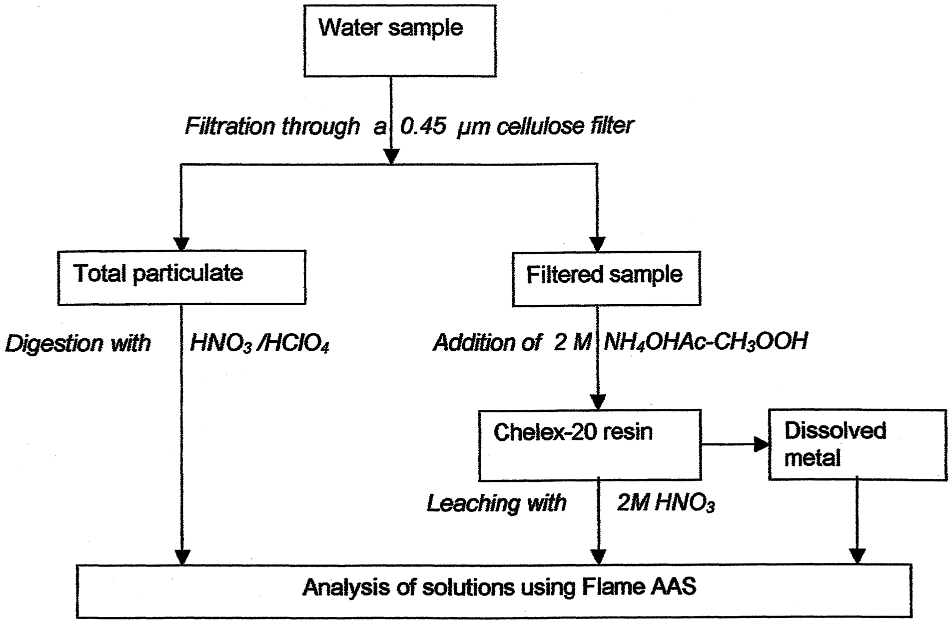

Figure 2. Scheme for the classification of metal species in the rivers in Thohoyandou.

The propylene containers were used for sample collection. Before use the propylene containers (500 ml) were first rinsed with the water samples and then immersed about 15 cm below the surface. After collection, pH and conductivity were determined in the field using portable measuring and data recording equipment (IQ scientific Instruments, USA). The samples for total metal concentrations were acidified in the field using analytical grade HNO_3, while samples for speciation studies were taken to the laboratory and filtered through acid washed 0.45 µm cellulose nitrate membrane filters. The digestion method employed for the total metal concentration involved gently heating known quantity of water sample (in this case 100 ml) with concentrated HNO_3 and $HClO_4$ on a hot plate for about 30 min. After reduction of the volume to about 5 ml, the digest was then transferred to a clean 50 ml volumetric flask and made up to the volume with de-ionised water.

The analytical speciation scheme used in this study is a slightly modified version of the scheme used by Nkono *et al* (1999), and it is shown in Fig. 2.

Particulate matter left on the 0.45 micron filter was digested in the fume cupboard as described by Nkono (1999). The metals were recovered with 20 ml HNO_3 (1%) centrifuged and decanted. The solution obtained was carefully transferred into a 50 ml volumetric flask and made up to the mark with double distilled de-ionized water for analysis.

The Chelex-20 resin (in Na form) was washed in 2M HNO_3 and then packed into a 2 cm diameter straight glass column. The resin was further washed with 30 ml 2M HNO_3 and double distilled de-ionized water until the pH of the effluent was greater than 4.0. About 50 ml 2M NH_4OH was then passed through the column followed by washing with double distilled de-ionized water until the pH of the effluent was about 8.5. Then 400 ml of the filtered water sample was buffered using 2M ammonium acetate-acetic acid buffer to pH 8.5. The buffered water sample was then passed through the resin in the column at a flow rate of 1.5-2.0 ml min^{-1} The metals retained on the resin in the column were later leached out with 10 ml 2M HNO_3. The solution obtained was transferred into a 50 ml volumetric flask and made to the mark.

The liquid fraction obtained from the chelex-20 resin separation process was transferred into a 50 ml volumetric flask and made up to the mark and then analyzed without further pretreatment. The analytical quality control performed included daily analysis of standards and triplicate analysis of samples and blanks. Due to the unavailability of standard reference materials for heavy metals in water, spiking method was employed for the validation of the analytical method used in this study. 100 ml double distilled de-ionized water was measured and transferred into a clean 500 ml beaker and then spiked with metal standard solutions at fortification levels of 5 µg l^{-1} (Cd, Cu) and 15 µg l^{-1} (Pb, Zn). The fortification experiment as described above was repeated using 100 ml water samples collected from the rivers. The procedures as described in the aforementioned sample treatment were then repeated. After the analysis the percentage recoveries of the metals were calculated.

The detection limits for each of the elements were determined using the lowest concentration of each of the elements that gave the least detectable signal using flame AAS for Cd, Cu, Pb and Zn. Six replicates each of these concentrations were prepared and analyzed. The detection limits were determined from 3δ (δ = standard deviation) of the replicate determinations for each of the element (Miller and Miller, 1998).

RESULTS AND DISCUSSION

The results of the quality control studies showed very good percentage recoveries for the elements investigated: Cd 90.67 ± 6.80%, Cu 98.50 ± 5.73%, Pb 96.8 ± 6.30% and Zn 102 ± 3.29% for spiked de-ionised water and Cd 87.50 ± 5.5%, Cu 95.56 ± 4.82%, Pb 97.45 ± 2.56% and Zn 90.67 ± 8.24% for spiked water samples collected from the rivers. The calibration values gave correlation coefficients ranging from 0.95-0.97. The detection limits obtained for the elements analyzed were: Cd 1.0 µg l^{-1}, Cu 2.0 µg l^{-1}, Pb 10.1 µg l^{-1} and Zn 2.0 µg l^{-1}.

Table 1 shows the total mean concentration values for Cd, Cu, Pb and Zn in the water samples studied. It can be seen from Table 1, that the levels ranged between 1.60-9.30 µg l^{-1}, 2.0-3.0 µg l^{-1} , 10.5-20.1µg l^{-1} and 2.1-2.5 µg l^{-1} for Cd, Cu, Pb and Zn respectively. From Table 1, the concentration values for the wet season are generally higher than that of the dry season. This can be attributed to runoff from land into the rivers during the wet season. Consequently, the suspended particulate loads in the rivers increased.

Table 1. Total mean concentration ($\mu g\ l^{-1}$) values of heavy metals in the rivers in Thohoyandou, South Africa.

	November 2002 (wet season)				April 2003 (dry season)			
Rivers	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Dz	3.3±0.2	2.6±1.2	12.3±2.3	2.1±3.8	1.6±0.4	2.1±0.5	10.5±2.4	ND
Ma	4.8±0.5	2.5±0.1	20.1±1.5	2.3±1.2	4.6±1.0	2.0±0.6	12.0±0.5	2.1±0.5
Mv	9.3±0.6	3.0±1.0	15.7±3.2	2.5±0.1	3.4±0.8	2.8±1.3	11.6±0.3	2.4±0.2

Dz =Dzindi River, Ma = Madanzhe River, Mv = Mvudi River.
ND =Not detectable

The nature of these suspended particulate may be the oxides of the metals. Comparing the concentration levels of the metals investigated, Pb concentration in water samples from all the rivers were significantly higher than the values for the other metals in both the wet and dry seasons.

The high levels shown by Pb may be attributed to the deposition of Pb particulates on the roads close to the rivers through vehicle exhaust. The deposits may have easily been washed into the rivers especially during precipitation. Other studies (Quinche *et al*; 1969, Chow, 1970, Motto *et al*, 1970, Fatoki and Hill, 1994) have shown that Pb emissions from motor vehicles produce elevated concentrations of the element in roadside vegetation and soil. Also in a recent study (Okonkwo *et al*; 2003) high levels of Pb on vegetation and soil as a result of the use of leaded petrol in Thohoyandou, has been reported. The presence of a sewage treatment plant and waste dumping site near Rivers Madanzhe and Mvudi, may have influenced the level of Pb and Cd obtained in this study. Also the ongoing small scale agricultural activities around the rivers may have contributed to the observed high levels of Pb and Cd levels, since these metals can occur as impurities in fertilizers, in metal-based pesticides, compost and manure. The farmers within Thohoyandou are known to use fertilizers, compost and manure as well as metal-based pesticides to enrich the soil and kill pests respectively.

With respect to Cd, contribution from roadside contamination is very unlikely since the contamination of roadside soil and vegetation by Cd is usually irregular than that of Pb and Zn. The concentrations shown by Cu and Zn are very similar. It is possible that the low cost houses roofed with Zn corrugated sheets may have contributed to the level of Zn determined. Where the pH of rain is acidic, the leaching of metals such as Zn into the surrounding environment from the roofs is highly possible. The pH of the rivers measured were marginally within the acidic range of 6.2-6.5. Likewise, elevated Zn concentrations have been shown in roadside plants (Lagerwerff and Specht, 1970; Connor *et al*; 1971, Ward *et al*; 1977; Nyagababo and Hamya, 1986). This contamination of roadside vegetation by airborne Zn is considered to arise from motor traffic tyre wear. Once deposited on roadside vegetation or soil, it can easily be washed into water bodies during precipitation.

Table 2 shows a comparison of the values obtained in the present study with some international guidelines for drinking water. It can be seen from Table 2, that Cd and Pb exceed the WHO and South African water quality guidelines of 3.0 µg l^{-1} and 5 µg l^{-1} respectively (WHO, 1991; SADWAF 1996).

Table 2. A comparison of the mean heavy metal concentration (µg l^{-1}) in the rivers in Thohoyandou to international guidelines for drinking water.

Metal	SA	WHO	WA	Dz	Ma	Mv
Cd	5	3	1	3.3(1.6)	4.8(4.6)	9.3(3.4)
Cu	1,000	2,000	1,400	2.6(2.1)	2.5(2.0)	3.0(2.8)
Pb	10	10	4.0	12.3(9.5)	20.1(12.0)	15.7(11.6)
Zn	2,000	-	200	2.1(ND)	2.3(ND)	2.5(ND)

SA = South Africa (Department of Water and Forestry) guideline for drinking water
WHO = World Health Organisation guideline for drinking water
WA = World Average of trace elements in unpolluted rivers: From Schiller and Boyle (1987)
Numbers in parenthesis represent dry season mean values

Since the rivers are used daily by the locals for domestic purposes without further treatment there is therefore, cause for concern with respect to the levels of Pb and Cd obtained in the present study. The values shown by Cu and Zn are well within the guidelines of WHO and South African Department of Water Affairs and Forestry (WHO, 1991; SADWAF 1996).

Table 3 contains the concentrations of the speciation fractions of the metals in the water samples investigated. Generally all the metal concentrations for the wet season are higher than the values for the dry season, particularly the value for Pb. It can also be observed that all the other metals except Pb show low concentrations in the particulate fraction. This is not surprising since dominant forms of metals such as Pb are usually adsorbed or co-precipitated as hydroxides of basic salts. Cu and Zn were found more in the non-labile fraction, while Cd was evenly distributed between the labile and non-labile fractions. This suggests that Cu and Zn may have existed in form of metal complexes that did not dissociate on the column and these are more likely to be associated with colloidal materials and therefore not available.

The result on Cu agrees with those reported by other researchers (Florence *et al*, 1992). On the other hand, Cd showed nearly a consistent distribution pattern between the non-labile and labile fractions in both the wet and dry seasons. The labile fractions, i.e., materials retained on the chelex-20 column, would consist of hydrated metal ions and metal complexes that dissociated on the column.

Since the second highest proportion of Pb is in this fraction, it is therefore bio-available. Consequently, this may pose a health risk to humans and aquatic organisms considering the health implications of the metal.

Table 3. Concentrations (µg l^{-1}) of the speciation fractions of heavy metals in the rivers in Thohoyandou, South Africa.

Metal		Sampling points					
		November 2002			April 2003		
		A	B	C	A	B	C
Cd	Particulate	3.9	4.0	3.8	2.2	2.3	3.5
	Labile	6.2	5.4	5.5	3.2	4.5	5.2
	Non-labile	5.0	6 .0	7.1	2.8	3.1	4.2
Cu	Particulate	2.1	2.2	2.3	2.0	2.1	2.3
	Labile	2.3	2.1	2.5	2.0	1.9	3.1
	Non-labile	4.0	4.2	5.1	3.5	3.1	3.3
Pb	Particulate	23.6	17.5	19.2	12.4	12.7	11.6
	Labile	12.4	11.3	11.1	10.2	10.3	10.5
	Non-labile	10.5	13.2	12.5	ND	ND	ND
Zn	Particulate	2.0	ND	ND	ND	ND	ND
	Labile	2.2	2.0	2.2	ND	ND	ND
	Non-labile	3 .0	3.5	4.1	2.4	2.7	2.4

Dz = Dzindi River; Ma =Madanzhe River; Mv=Mvudi River
ND = not detectable

This study has shown that the concentration of metals that can be considered to be bio-available to the aquatic system ranges between 3.2-6.2, 1.9-2.5, 10.3-12.4 and ND-2.2 µg l^{-1} for Cd, Cu, Pb and Zn respectively. Compared to the toxicity of these metals reported on algae (Florence *et al*, 1992), the values obtained in the present study are significantly higher. This is, therefore, reason for concern.

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