



Physico-chemical characteristics and pollution levels of heavy metals in the rivers in Thohoyandou, South Africa

Jonathan O. Okonkwo*, M. Mothiba

Department of Environmental Sciences, Faculty of Natural Sciences, Tshwane University of Technology, 175 Nelson Mandela Avenue, Private Bag X680, Pretoria 0001, South Africa

Received 19 September 2003; revised 19 October 2004; accepted 29 October 2004

Abstract

In this study, trace metal analysis of the surface waters from river Dzindi, Madanzhe and Mvudi in Thohoyandou, South Africa, were conducted with a view to obtain a baseline data of their levels. The physico-chemical forms of the metals as a means of assessing their availability and non-availability for toxicity to aquatic organisms was also investigated. Surface water samples were collected randomly from selected sites in the rivers aforementioned. The samples were analysed for Cd, Cu, Pb and Zn using a Varian flame atomic absorption spectrometer. The concentration range of the metals were: 1.6–9.3, 2.0–3.0, 10.5–20.1 and 2.1–2.5 $\mu\text{g l}^{-1}$ for Cd, Cu, Pb and Zn, respectively. The concentration ranges of all the metals measured were found to be below the international guidelines and acceptable concentrations for drinking water except the values for Cd and Pb. Also, when compared to the world average of trace elements for unpolluted rivers, the three rivers considered were polluted by Cd and Pb. With the speciation studies, Pb was found predominantly in the particulate fraction, while Cu and Zn were dominant in the non-labile fraction. However, Cd was found in equal distribution between the labile and non-labile fractions. The non-labile fractions of Cd, Cu and Zn were considered unavailable to cause any serious danger to aquatic organisms. However, the labile Cd was considered to be bio-available and therefore, can pose a danger to aquatic organisms.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Speciation; Heavy metals; Rivers; South Africa

1. Introduction

In heavy metal analysis, the total concentrations of the metals are most often determined (Kapoor and Virarghavan, 1998; Nkono et al., 1995; Okonkwo et al., 1999, 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 physico-chemical 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 (Davidson and Ure, 1995).

According to Roux et al. (1994) there is inadequate knowledge and data on heavy metal concentrations in

* Corresponding author.

E-mail address: okonkwoj@techpta.ac.za (J.O. Okonkwo).

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.

In the present study we report the analysis of selected heavy metals in the chosen rivers with a view of establishing a baseline data of their levels.

2. Materials and methods

2.1. Apparatus and materials

A Varian Spectra AA 220 atomic absorption spectrophotometer equipped with a single slot burner was used. Measurements were carried out in triplicate. All glass and propylene ware used were first soaked in dilute HNO_3 , thoroughly washed with liquid soap and then rinsed with double distilled de-ionised water and acetone. Thereafter, 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 reagent stock solutions: 1000 mg l^{-1} of the metals Cd, Cu, Pb and Zn used were of analytical reagent grade supplied by BDH.

2.2. Sampling site

Tohoyandou lies between latitudes $20^\circ50'$ and $23^\circ45'$ South and longitudes $29^\circ50'$ and $30^\circ30'$ East, located in Limpopo Province, South Africa. The area is characterised by relatively hilly to undulating slopes with a combination of flatlands. The area receives large amount of rainfall during summer period. The study area has several rivers that include, Dzindi, Madanzhe and Mvudi Rivers. These rivers are the major ones in the study area and are located just outside Tohoyandou town centre and they cross some of the major roads leading to the town centre and are intensively used in most agricultural areas in Tohoyandou. Although Tohoyandou is not known for its large-scale industrial activities, potential sources of pollution particularly that of heavy metals still exists along the selected rivers. For example, Madanzhe and Mvudi Rivers run pass a sewage treatment plant and a waste-dumping site, respectively. The location of Tohoyandou and the sampling points are shown in Fig. 1.

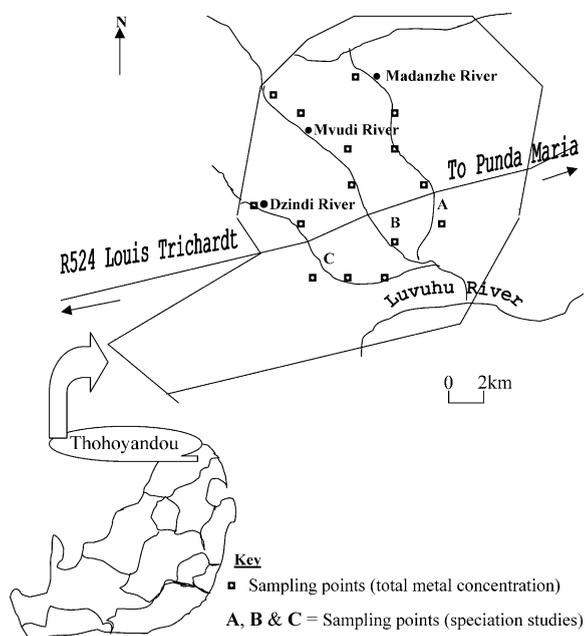


Fig. 1. A sketch map of South Africa (bottom left) and Tohoyandou (top right) showing the sampling points.

Water samples were collected randomly on a weekly basis from the rivers as indicated in Fig. 1, in November 2000 and April 2001, representing wet and dry seasons, respectively. The propylene containers were used for sample collection. Before use the propylene containers (500 ml) were first rinsed with the water samples and thereafter 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), while total suspended solids was determined in the laboratory the same day. The samples for total metal concentrations were acidified in the field with grade HNO_3 , while samples for speciation studies were taken to the laboratory and filtered under pressure through acid washed $0.45\ \mu\text{m}$ cellulose nitrate membrane filters.

3. Sample treatment procedure

3.1. Total, chelex-100 labile and non-labile metal concentrations

The digestion method employed for the total metal concentration is similar to that described by VanLoon

(1985). This 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 transferred to a clean 5 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. (1995). Particulate matter left on the 0.45 μm filter was digested in the fume cupboard as described by Nkono (1995). The solution obtained was carefully transferred into a 50 ml volumetric flask and made up to the mark with double distilled de-ionised water for analysis.

The chelex-100 resin used in this study is similar to that of Florence (1977). The resin (in Na form) was washed in 2 M HNO_3 and then packed into a 2 cm diameter straight glass column. The resin was further washed with 30 ml 2 M HNO_3 and double distilled de-ionised water until the pH of the effluent was greater than 4.0. About 50 ml 2 M NH_4OH was then passed through the column followed by washing with double distilled de-ionised water until the pH of the effluent was about 8.5. Thereafter 400 ml of the filtered water sample was then buffered using 2 M 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 then leached out with 10 ml 2 M 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-100 resin separation process was transferred into a 50 ml volumetric flask and made up to the mark and then analysed without further pretreatment.

The analytical quality control performed included daily analysis of standard and replicate 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. 100 ml double distilled de-ionised water was measured and transferred into a clean 500 ml beaker and then spiked with metal standard solutions at fortification levels of 5 $\mu\text{g l}^{-1}$ (Cd, Cu) and 15 $\mu\text{g l}^{-1}$ (Pb, Zn). The procedure as described in the aforementioned sample treatment, were then repeated. After the analysis the percentage recoveries of the metals were then 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 of each of these concentrations were prepared and analysed. The detection limits were determined from $3d$ (d =standard deviation) of the replicate determinations for each of the element (Miller and Miller, 1998).

4. 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 98.5 ± 5.73 , Pb 96.8 ± 6.30 and Zn $102 \pm 3.29\%$. The calibration values gave correlation coefficient ranging from 0.95 to 0.97. The detection limits obtained for the elements analysed were: Cd 1.0, Cu 2.0, Pb 10.1 and Zn 2.0 $\mu\text{g l}^{-1}$.

4.1. Total particulate associated metal

The mean total concentrations levels ranged between 1.60–9.30, 2.0–3.0, 10.5–20.1 and 2.1–2.5 $\mu\text{g l}^{-1}$ for Cd, Cu, Pb and Zn as can be seen in Table 1. The concentration values for the wet season

Table 1
Mean total concentration ($\mu\text{g l}^{-1}$) of heavy metals in the rivers in Thohoyandou, South Africa

Rivers	November 2000 (wet season)				April 2001 (dry season)			
	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.

Table 2

Mean heavy metal concentration ($\mu\text{g l}^{-1}$) in the rivers in Thohoyandou compared 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	1000	2000	1400	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	2000	–	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 Meybeck and Helmer (1989) and Schiller and Boyle (1987). Numbers in parenthesis represent dry season mean values.

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 may be the oxides of the metals. The nature of these suspended particulates may be the oxides of the metals. The Pb concentrations 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 next to the rivers especially during precipitation. Other investigations (Quinche et al., 1969; Chow, 1970; Motto et al., 1970; Fatoki and Hill, 1994) have demonstrated that Pb emissions from motor vehicles produce elevated concentrations of the element in roadside vegetation and soil. Recent study (Okonkwo et al., 2003) has shown high levels of Pb on vegetation and soil as a result of the use of leaded petrol in Thohoyandou. The high concentrations of Pb in Madanzhe and Mvudi Rivers, may have been influenced by the effluent from a nearby sewage treatment plant and a waste dumping site, respectively. The observed high levels of Pb is followed by that of Cd, particularly in Mvudi River. Again the sewage effluent and the leaching of Pb from the dumping site may have contributed to the observed values. Also the 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 and in metal-based pesticides and compost and manure. With respect to Cd, contribution from roadside contamination is very unlikely since the contamination of roadside soil and vegetation by Cd is usually less anomalous than that of Pb and Zn. The values shown by Cu and Zn are fairly similar. It is possible that the low cost houses roofed with Zn corrugated sheets may have contributed to the level of Zn determined. It is possible

that Zn may have been leached out into the surrounding environment from the roofs, since the pH of the rivers measured were marginally within the acidic range of 6.4–6.9.

The Cd and Pb exceed the WHO and South African water quality guidelines of 3.0 and 5, respectively as shown in Table 2 (WHO, 1991; SADWAF, 1996). 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). This comparison is important since the rivers are used daily by the locals for domestic purposes without further treatment. There is therefore, cause for concern. The water quality parameter for the water samples used for the speciation studies is shown in Table 3. It can be seen from Table 3 that there is no significant difference between the wet and dry season pH values. Also the pH values from the sampling points are more or less the same (6.4–6.9). However, the conductivity and the total suspended solids values for the wet season are significantly higher than that of the dry season. During the wet season, urban run off may have introduced high load of suspended matter into water system.

Table 3

Mean values of water quality parameters in the water sample for speciation study

Date	Season	Sampling point	pH	Conductivity (mS/m)	TSS (mg l^{-1})
Novem-ber	Wet	Dv	6.4	182.5	82.3
		Ma	6.6	66.8	30.0
		Mv	6.4	157.5	139.3
April	Dry	Dv	6.8	81.3	16.3
		Ma	6.7	45.0	14.7
		Mv	6.9	75.8	52.8

Table 4

Heavy metal concentrations ($\mu\text{g l}^{-1}$) in the different speciation fractions in the rivers in Thohoyandou, South Africa

Metal		Sampling points					
		November 2000			April 2001		
		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.

Generally all the metal concentrations for the wet season are higher than the values for the dry season, particularly the value for Pb as shown in Table 4. It can also be observed that all the other metals except Pb show low concentrations in the particulate fraction. This can be attributed to the dominant forms of metals such as Pb that are usually adsorbed or co-precipitated as hydroxides of basic salts (Benes and Steinnes, 1975). Cu and Zn were found more in the 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 of Cu agrees with the findings of other researchers (Sholkovitz, 1975; Florence et al., 1992). On the other hand, Cd showed an almost consistent distribution pattern between the non-labile and labile fractions in both the wet and dry seasons. The labile fractions (materials retained on the chelex-100 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 hazard to humans and aquatic organisms considering the health implications of the metal.

In the present study, 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 $\mu\text{g l}^{-1}$ for Cd, Cu, Pb and Zn, respectively. These concentrations are significantly higher than those reported on the toxicity of these metals on algae (Florence et al., 1992). The present report is part of an ongoing research programme on heavy metal speciation in surface water and sediments within Thohoyandou in South Africa.

Acknowledgements

The authors are indebted to the National Research Foundation (NRF) for their financial support. The technical assistance of Dr Nana Agyei and Ms Flecia Lefawane are highly appreciated.

References

- Benes, P., Steinnes, E., 1975. Migration forms of trace elements in natural fresh waters and the effect of the water storage. *Water Res.* 9, 741–747.
- Castro Dantos, T.N., Dantos Neto, A.A., Moura, M.C.P.A., Barros Neto, E.I., Forte, K.R., Leite, R.H.L., 2003. Heavy metals extraction by microemulsion. *Water Res.* 37, 2709–2717.
- Chow, J.J., 1970. Lead accumulation in roadside soil and grass. *Nature* 255, 295–296.
- Christie, S.L., 1995. Speciation, in: Fitfield, F.W., Haines, P.J. (Eds.), *Environmental Analytical Chemistry*. Chapman and Hall, UK.

- Davidson, C.M., Ure, A.M., 1995. *Chemical Speciation in the Environment*, first ed Chapman and Hall, UK.
- Fatoki, O.S., Hill, S.J., 1994. Speciation studies of tetraalkyllead and inorganic PbII in polluted roadside vegetation and soil samples. *Int. J. Environ. Stud.* 46, 289–301.
- Florence, T.M., 1977. Trace metal species in fresh water. *Water Res.* 11, 681–687.
- Florence, T.M., Morrison, G.M., Stauber, J.L., 1992. Determination of trace element speciation and the role of speciation in aquatic toxicity. *Sci. Tot. Environ.* 125, 1–13.
- Kapoor, A., Viraraghavan, T., 1998. Removal of heavy metals from aqueous solutions using immobilized fungal biomass in continuous mode. *Water Res.* 32, 1968–1977.
- Meybeck, M., Helmer, R., 1989. The quality of water from pristine stage to global pollution. *Palaeogr. Palaeoclimatol. Palaeoecol. (Global and planetary change section)* 75 (283), 309.
- Miller, J.C., Miller, J.N., 1998. *Statistics for Analytical Chemistry*, second ed. Ellis Horwood, Chichester.
- Motto, H.L., Daines, R.N., Chilko, D.M., Motto, C.K., 1970. Lead in soil and plants: its relationship to traffic volume and proximity to highways. *Environ. Sci. Technol.* 4, 231–234.
- Nkono, N.A., Asubiojo, O.L., Ogunsua, O.A., Oluwole, F., 1995. Levels, sources and speciation of trace elements in the surface waters of the Lagos lagoon. *Int. J. Environ. Stud.* 56, 215–230.
- Okonkwo, J.O., Lwenje, S.M., Mtetwa, V.S.B., Mkhweli, T.B., 1999. Measurement of lead concentration in the hair of school children in the Manzini region, Swaziland. *Int. J. Environ. Stud.* 56, 419–428.
- Okonkwo, J.O., Lwenje, S.M., Mtetwa, V.S.B., Gumedze, P.N., Shilongonyane, M.M., 2001. Determination of urinary lead in school children in Manzini, Swaziland, southern Africa. *Environmentalist* 21, 205–209.
- Okonkwo, J.O., Ndou, L.W., Marais, P.J.J.G., 2003. Lead concentration in roadside soils and vegetation: a measure of motor vehicle pollution in Thohoyandou town, South Africa. *Int. J. Environ. Stud.* 60, 2–3.
- Quinche, P.J., Zuber, R., Bovay, E., 1969. Lead pollution of highway roadside vegetation. *Phytopathol. Z.* 66, 259–274.
- Roux, D.J., Badenhorst, J.E., du Preez, H.H., Steyn, G.J., 1994. Note on the occurrence of selected trace metals and organic compounds in water, sediments and biota of the Crocodile River, Eastern Transvaal, SA. *Water SA* 20, 333–339.
- Schiller, A.M., Boyle, E.A., 1987. Variability of dissolved trace metals in the Mississippi river. *Geochim. Cosmochim. Acta* 51, 3273–3277.
- Sholkovitz, E.R., 1975. The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. *Earth Planet Sci. Lett.* LS41, 77–86.
- South African Department of Water Affairs and Forestry (SADWAF) Water Quality guidelines, 1996. Domestic Use. vol. 1, second ed.
- VanLoon, J.C., 1985. *Selected Methods of Trace Metal Analysis—Biological and Environmental Samples, Chemical Analysis*, vol. 80. Wiley, New York pp. 94–96.
- WHO, 1991. *Guidelines for Drinking Water Quality, Recommendations*, vol. 1. WHO, Geneva.