A note on the occurrence of metals in the Olifants River, Eastern Transvaal, South Africa

DF Grobler*, PL Kempster and L van der Merwe
Institute for Water Quality Studies, Department of Water Affairs and Forestry, Private Bag X313, Pretoria 0001, South Africa

Abstract

In order to assess the trace metal status of sediment, water and fish in the middle and lower Olifants River a preliminary investigation into the occurrence of 20 metals was carried out in December 1990. Data collected for the past 8 years on the trace metal content of the Loskop Dam and the Elands River are presented. In general it can be concluded that low levels, representing natural geological background levels, occur in the study area. Elevated levels of some metals do exist at localised points in the study area and warrant further investigation. Arsenic, cadmium, mercury and lead were not detected in any of the aquatic compartments investigated.

Introduction

The Olifants River in the E. Transvaal, South Africa has often been described, without qualification of the sections of the river, nor the pollutants involved, as one of the most polluted rivers in Southern Africa (Batchelor, 1992 and Engelbrecht, 1992). The Loskop Dam has been described as a sink for heavy metals deriving from the upper catchment (Engelbrecht 1992). The fish eagles resident on the Loskop Dam have been found to have the highest pesticide levels accumulated in their eggs (Batchelor, 1992) when compared with data from around South Africa. The results of a pesticide study which coincided with this study are published elsewhere (Grobler, 1993). The question of whether the lower survival rates of crocodile clutches in the Loskop Dam area were pure coincidence or could be linked to the water quality has also been posed (Batchelor, 1992). By implication the whole of the Olifants River has been described as degraded and contaminated with metals and other chemicals.

These concerns have been expressed as a consequence of the large number of agricultural, industrial and mining activities in the catchment. Mining activities consist mainly of coal mining in the upper reaches of the catchment and intensive agricultural activities in the middle and lower catchment and some mining activities on tributaries of the Olifants River in the lower and middle sections of the river.

The catchment area is approximately 54 500 km^2 and constitutes 4.3% of the total surface area of South Africa and 18.9% of the Transvaal. The rivers mean annual runoff is 1 861 x 10^6 m^3. The mean annual rainfall in the catchment is 660 mm/a (DWAF, 1991).

A limited amount of data is available for the middle and lower Olifants River in terms of trace metals, and the data obtained, for an extensive list of metals, from this study can form part of baseline data to be used in future assessment of the pollution status of the Olifants River as a whole.

Materials and methods

Sampling points and techniques

Bottom sediment samples were collected from the Olifants River inflow into the Loskop Dam, Phalaborwa Barrage, 2 sampling points between the 2 impoundments (B5H002 and B7H007) and from the Selati River (Fig. 1). Samples were collected with an Eckman grab sampler, and stored deep-frozen until analysis.

Fish were collected overnight with gill nets from 2 major impoundments in the Olifants River. Two localities were selected in the Loskop Dam (Lombards Bay and the Olifants River inflow) and one at the Phalaborwa Barrage (Fig. 1). For the purpose of trace metal analysis, 3 fish species, representing different trophic levels, and occurring throughout the study area, were selected for analysis (Table 1). Fish were gutted and decapitated, and wrapped in aluminium foil and stored deep-frozen until sample preparation. Individual fish were homogenised (with scales) using an electric meat mincer which had been pre-washed in RBS-35 soap solution and rinsed well with hot soap water. Subsamples (20 g) from individuals of a species, collected at a sampling point, were pooled, homogenised and analysed.

Water samples were collected from 11 sampling points throughout the study area (Fig. 1), including all the major tributaries in the study area. Both dissolved and acid-extractable metals were determined.

Dissolved trace metal data obtained from the raw water sources of the South Ndebele Water Treatment Works (WTW) for the period 1984 to 1992 are presented. These include data from the Renosterkop Dam (B3M10RR) on the Elands River, Loskop Dam irrigation canal (B3M10LR) and Weltevreden Weir (B3M10WR), the direct abstraction point for the WTW on the Elands River (Fig. 1).

Analytical techniques

Sediment samples were oven-dried at 45°C, finely ground with a porcelain pestle and mortar and sieved through an 0.2 mm stainless steel sieve to normalise the particle size distribution. Sediment (0.1 g) was digested with 10 mℓ Aqua regia and 2 mℓ hydrofloric acid in a polyfluor DGI:PTFE digestion vessel in a KIC microwave oven. Boric acid (2 g) was added to the sample after digestion to complex the excess fluoride ions, and the digest then filtered through a No. 42 Whatman filter paper into a 100 mℓ volumetric flask. Sediment samples were analysed in duplicate.

One gram wet homogenised tissue was digested stepwise with a nitric and perchloric acid sequence in a polyfluor DGI:PTFE digestion vessel in a KIC microwave oven. The digested mixture was then filtered through a No. 42 Whatman filter paper into a 100 mℓ volumetric flask and quantitatively diluted with deionised water. Fish tissue samples were similarly analysed in duplicate.

* To whom all correspondence should be addressed.
Received 15 March 1993; accepted in revised form 18 February 1994.

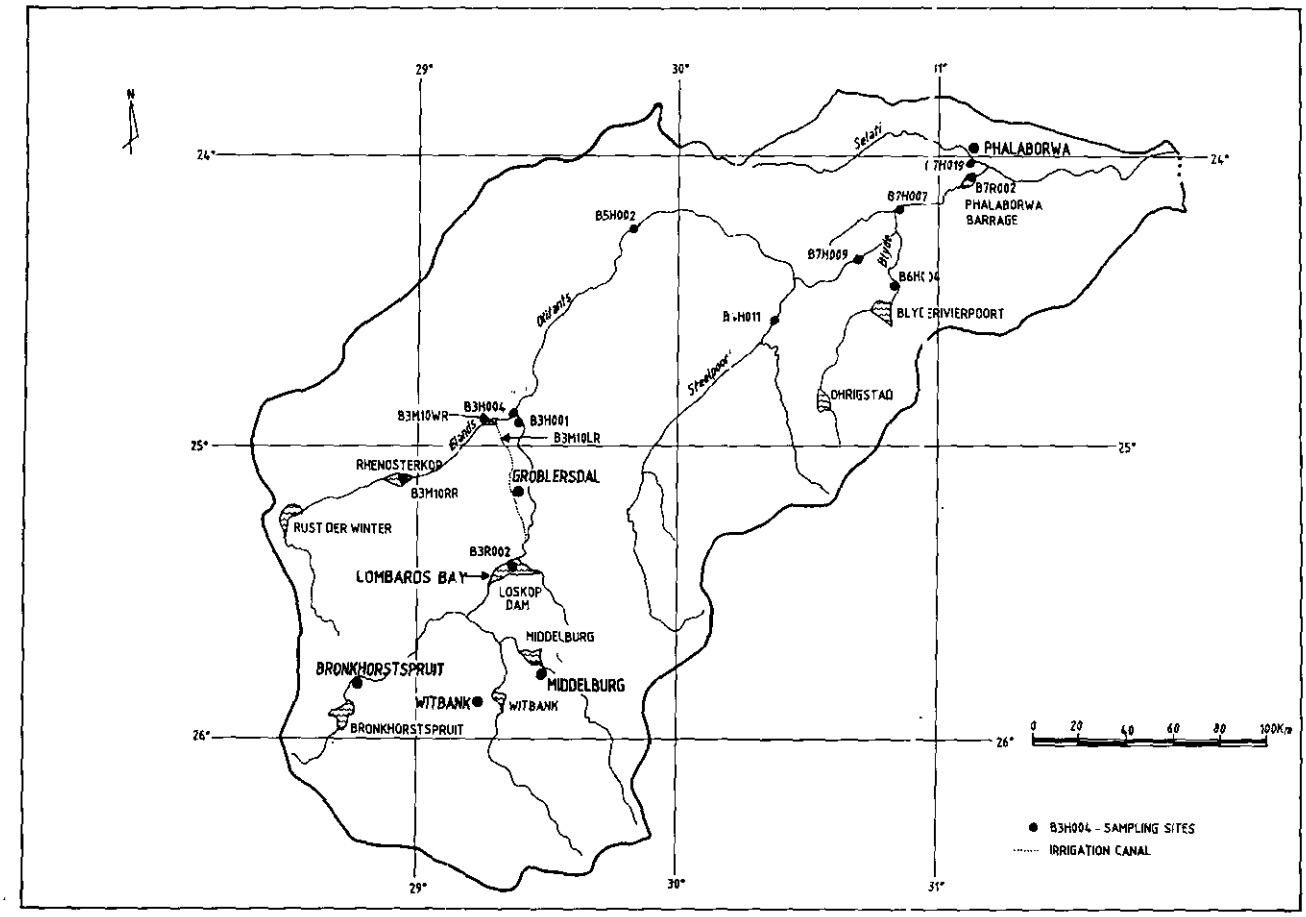

Figure 1
Sampling sites on the Olifants River and its major tributaries

The sediment and fish tissue digestion techniques were tested against standard reference material from the International Atomic Energy Agency i.e., SD-M-2/TM (marine sediment), IAEA 350 (tuna fish flesh) and MA-B-3/TM (fish homogenate). The metal concentrations were determined by inductively coupled plasma emission spectrometry (1978 ARL model 3400 polychromator and a 1983 model ARL 3510 scanning monochromator) (Kempster, 1986). A list of the trace metals, their detection limits and analytical methods that were used are presented in Table 2.

Results

Of the 20 selected metals for the whole study area, 15 were detected in the sediment samples (Table 3), 7 in the fish muscle tissue (Table 4), and 15 and 16 in the dissolved and acid-extractable fractions respectively (Tables 5 and 6). This excludes arsenic, cadmium, lead and mercury which were not detected in any of the sampled compartments.

Sediments

The aluminium concentrations were comparable in all the sediment samples. Concentrations of beryllium, iron, manganese, vanadium and zinc were comparable in the Loskop Dam, Olifants River at Oxford (B7H007), Phalaborwa Barrage and Selati sediments, but were considerably lower in the sediment from the Olifants River at Zeekoegat (B5H002). The highest value for chromium was found in the sediment from the Phalaborwa Barrage, while copper, titanium, strontium and vanadium were highest in the sediment from the Selati River. The Loskop Dam sediment showed the highest values for aluminium, beryllium, iron, molybdenum, vanadium and zirconium. Cobalt and nickel were only detected in one sediment sample from the Phalaborwa Barrage. The highest concentration for barium was found in the Olifants River at Oxford (B7H007) (Table 3).

Water

Large differences exist in the acid-extractable concentration between different sampling points. Cobalt, nickel, copper and zirconium were only detected at a few sampling points. The other metals were detected at almost all the sampling points, the Steelpoort River showing the highest concentrations of 12 of the 16 detected metals. The Selati River showed the highest strontium concentration (Table 5).

Of the 20 metals that were analysed for, 15 were detected in the dissolved fraction (Table 5). Cobalt, copper and zirconium were detected at a few of the sampling points. The strontium concentration was the highest in the Selati River, and the Blyde River showed the highest copper, iron and manganese concentrations (Table 6).

The median pH values for Loskop Dam (B3M10LR), Weltevreden Weir (B3M10WR) and Renoster Kop Dam

TABLE 1
FISH COLLECTED FROM LOSKOP DAM (B3R002) AND PHALABORWA BARRAGE (B7R002) IN DECEMBER 1990

Species	No	Standard length (mm)	Total length (mm)	Gender	Mass (g)	Age (years)
Loskop Dam						
Lombards Bay						
O. mossambicus	1	325	397	♂	1 150	5
	2	310	382	♂	1 125	4
	3	295	369	♂	1 075	3
	4	287	356	♀	900	5
	5	305	376	♂	975	4
E. depressirostris	1	315	375	♀	525	4
	2	274	330	♀	350	4
	3	248	300	♀	225	3
C. gariepinus	1	565	640	-	2 075	4
Olifants River inflow						
O. mossambicus	1	330	405	♂	1 650	4
	2	325	394	♂	1 050	5
	3	290	355	♀	1 150	4
	4	310	375	♀	1 550	3
	5	310	375	♀	1 050	4
E. depressirostris	1	250	300	♀	300	3
	2	210	255	♀	150	2
C. gariepinus	1	460	510	♂	1 100	4
Phalaborwa Barrage						
O. mossambicus	1	180	230	♀	350	3
	2	185	230	♀	350	2
	3	230	290	♂	500	3
	4	175	225	♂	300	2
	5	190	240	♂	350	1
E. depressirostris	1	315	385	♀	500	3
	2	280	342	♀	250	3
	3	280	340	♀	350	2
	4	265	330	♀	350	4
	5	255	313	♀	100	3
C. gariepinus	1	415	475	♀	850	3
	2	485	505	♀	100	4
	3	535	620	♂	1 800	5
	4	428	495	♂	1 000	1

TABLE 6
DISSOLVED TRACE METAL CONCENTRATIONS, EXPRESSED AS mg/l, IN WATER SAMPLES COLLECTED FROM THE OLIFANTS RIVER, E. TRANSVAAL, SOUTH AFRICA, IN DECEMBER 1990

	Sampling sites										
	B3R002	**GROB**	**B3H001**	**B3H004**	**B5H002**	**B4H011**	**B7H009**	**B6E005**	**B7H007**	**B7R002**	**B7H019**
Metal											
pH	7.5	7.9	8.2	8.0	8.1	8.0	8.2	7.9	7.8	8.1	7.8
TAL	46	80	243	124	138	118	180	74	102	151	239
Al	0.130	0.034	0.296	0.101	-	0.068	0.047	0.017	0.007	0.028	-
Ba	0.055	0.071	0.048	0.091	0.073	0.019	0.055	0.027	0.041	0.041	0.094
Bo	0.048	0.100	0.043	0.024	0.035	0.080	0.099	0.024	0.053	0.005	0.170
Be	0.002	-	0.004	0.010	0.009	0.007	0.003	-	0.005	0.004	0.002
Co	-	-	-	-	-	0.021	-	-	-	-	-
Cr	0.025	0.007	0.052	0.098	0.086	0.071	0.027	0.031	0.048	0.038	0.048
Cu	0.024	-	-	-	-	-	-	0.111	0.006	-	0.006
Fe	0.283	0.161	0.375	1.172	0.105	0.133	0.185	1.906	0.063	0.082	0.231
Mn	0.028	0.008	0.028	0.054	0.030	0.030	0.035	0.129	0.020	0.015	0.032
Mo	0.049	0.016	0.096	0.110	0.144	0.087	0.016	0.049	0.071	0.033	0.068
Ti	-	-	0.007	0.007	0.004	0.006	0.002	0.002	0.006	-	-
V	0.023	0.009	0.035	0.033	0.049	0.061	0.024	0.017	0.029	0.023	0.041
Zn	0.368	0.187	0.146	0.297	0.228	0.280	0.196	0.095	0.138	0.104	0.070
Zr	-	-	0.024	-	-	0.022	-	-	-	-	0.022
Sr	0.153	0.266	0.099	0.219	0.285	0.085	0.186	0.029	0.103	0.149	4.252

0.296 - highest observed concentration for a specific metal.
\- concentration below detection limit.
GROB - Olifants River at Groblersdal.
TAl - Total alkalinity as mg/l $CaCO_3$

(B3M10RR) are comparable (Table 7); however, the median total alkalinity concentration was the highest at the Renosterkop Dam and the lowest in the Loskop Dam canal. Cadmium, copper, cobalt, mercury and lead were never detected above the detection limit at any of the 3 sampling points. Arsenic, beryllium, chromium, nickel, titanium, vanadium and zirconium were rarely detected above the detection limit at all 3 sampling points. Aluminium, manganese, molybdenum and zinc were detected more often and/or at higher concentrations at the Weltevreden Weir. The highest maximum concentrations for arsenic, boron, barium, beryllium, nickel and titanium were recorded at the Renosterkop Dam, whereas the highest maximum concentrations for iron and vanadium were recorded at Loskop Dam canal. The order of abundance of the median concentrations of metals, detected above the detection limits, is Mn,Mo>Fe>Sr>Ba>B for Weltevreden weir, Fe>Sr>Ba>B for the Renosterkop Dam and Fe>Sr>Mn for the Loskop Dam irrigation canal.

Yearly summaries of the data, using box-and-whisker plots for boron, iron, manganese and strontium for the 3 sampling points are presented in Fig. 2. Between 1985 and 1992, there is evidence of a decrease in boron and iron concentrations and an increase in strontium concentrations. At Weltevreden Weir manganese shows an increase in concentration from 1985 to 1988, followed by a steady decrease.

Fish

With a few exceptions aluminium, barium, iron, manganese, strontium and zinc were detected in all the fish samples collected in the 2 impoundments. Boron was only detected in 2 samples. The concentrations of aluminium, barium and strontium in fish muscle tissue were the highest in *O. mossambicus*, compared to the other 2 fish species (Table 4). Zinc concentrations were comparable in *O. mossambicus* and *E. depressirostris*, with *C. gariepinus* showing lower concentrations. Nickel and boron were rarely detected, while iron and manganese were found in all samples.

Discussion

In general the levels obtained in this study are surprisingly low. The reasons for this can be attributed to a number of factors operating in the Olifants River. Suspended sediment in the water provides binding sites for metals making them unavailable to aquatic organisms, and imperceptible in the dissolved fraction of metal analyses. This is clearly demonstrated by the differences between the acid extractable and dissolved metal concentrations for the Selati River, Olifants River at Liverpool (B7H009) and the Olifants River at Oxford (B7H007) which were sampled while it was in flood and contained high loads of sediment. The Steelpoort sediment (Table 5) shows some evidence of contamination with many metals.

TABLE 7

A SUMMARY OF THE DISSOLVED TRACE METAL CONCENTRATIONS AT WELTEVREDEN WEIR (B3M10WR), RENOSTERKOP DAM (B3M10RR) AND LOSKOP DAM (B3M10LR) COLLECTED FROM 1984 TO 1992. (CONCENTRATION UNITS mg/ℓ UNLESS OTHERWISE STATED)

	pH	Tal	Al	As	B	Ba	Be	Cr	Fe	Mn	Mo	Ni	Ti	V	Zn	Zr	Sr
B3M10WR n=85 Weltevreden Weir (Elands River)																	
MED	7.4	77.3	-	-	0.0029	0.0093	-	-	-	0.055	0.076	-	-	-	-	-	0.0139
MAX	8.7	133	1.35	0.0062	0.027	0.067	-	0.0127	1.52	0.431	0.431	-	0.0029	0.012	0.0375	0.69	0.143
n > dl			20	4	62	48		7	66	83	83		1	3	33	1	81
B3M10RR n=85 Renosterkop Dam (Elands River)																	
MED	7.68	113	-	-	0.0051	0.0093	-	-	0.062	0.002	-	-	-	-	-	-	0.0152
MAX	8.66	153	0.524	0.0088	0.142	0.102	0.0029	0.0125	1.24	0.117	0.0176	0.0296	0.0163	0.0092	0.0087	0.02	0.139
n > dl			21	3	68	49	2	4	70	49	7	1	3	4	7	1	84
B3M10LR n=89 Loskop Dam irrigation canal																	
MED	7.4	44.6	-	-	-	-	-	-	0.042	0.002	-	-	-	-	-	-	0.0133
MAX	9.63	147	0.767	0.007	0.003	0.0062	-	0.0099	6.26	0.17	0.021	0.02	0.0128	0.024	0.016	0.024	0.126
n > dl			9	3	45	46	-	4	64	50	6	1	2	4	10	2	85

pH - in pH units
Tal - total alkalinity as mg/ℓ $CaCO_3$
\- - below detection limit
n > dl - number of samples above detection limit
MED - median concentration
MAX - maximum observed concentration

The low levels of metals present in the water and sediment of the Loskop Dam and the Phalaborwa Barrage are also reflected by the collected fish in which low levels of the metals were found in the muscle tissue. Only 7 of the 20 metals which were analysed for were detected in the fish muscle tissue. Iron, and zinc can be described as essential trace elements, and can be expected in fish tissue. Bryan (1976) indicated that copper, molyb-denum and zinc were regulated over a range of ambient concentrations in finfish. In general it can be assumed that essential metals are all regulated and that non-essential metals are not regulated. Copper, iron, manganese and zinc are therefore all regulated and indications exist that molybdenum is also regulated. Non-essential metals, cadmium, lead and chromium on the other hand are poorly regulated. According to Phillips (1980), this is particularly evident in the responses of organs such as gills, liver and kidney to low ambient concentrations of these metals. The detection of these metals in muscle tissue will then confirm pollution. The regulation of metals eliminates the possibility of using at least muscle tissue of teleosts as indicator material for regulated metals (Phillips, 1980).

When results for the fish muscle samples are compared with levels reported by Du Preez and Steyn (1992), collected from the Olifants River in the Kruger National Park, similar levels for iron, zinc and manganese are found. In contrast no cadmium, nickel or lead was detected in the collected fish samples, neither in the water. Nickel was, however, detected in the sediment sample collected from the Phalaborwa Barrage. This implies a source of these metals downstream of the Phalaborwa Barrage or a difference in the bioconcentration abilities of the 3 species collected in this study and the tiger fish (*Hydrocynus vittatus*). The Selati River, draining the extensive mining areas around Phalaborwa, has been implicated as a possible source of a number of these metals.

Sequential pH extractions for iron, manganese, copper and vanadium were also carried out on the sediment samples collected from the Loskop Dam, Phalaborwa Barrage, B5H002, B7H007, and B7H019 (Kempster et al., 1991). The results obtained from this sequential extraction stage have not only demonstrated the value of the method but have also indicated that even under the optimum extraction procedures, at

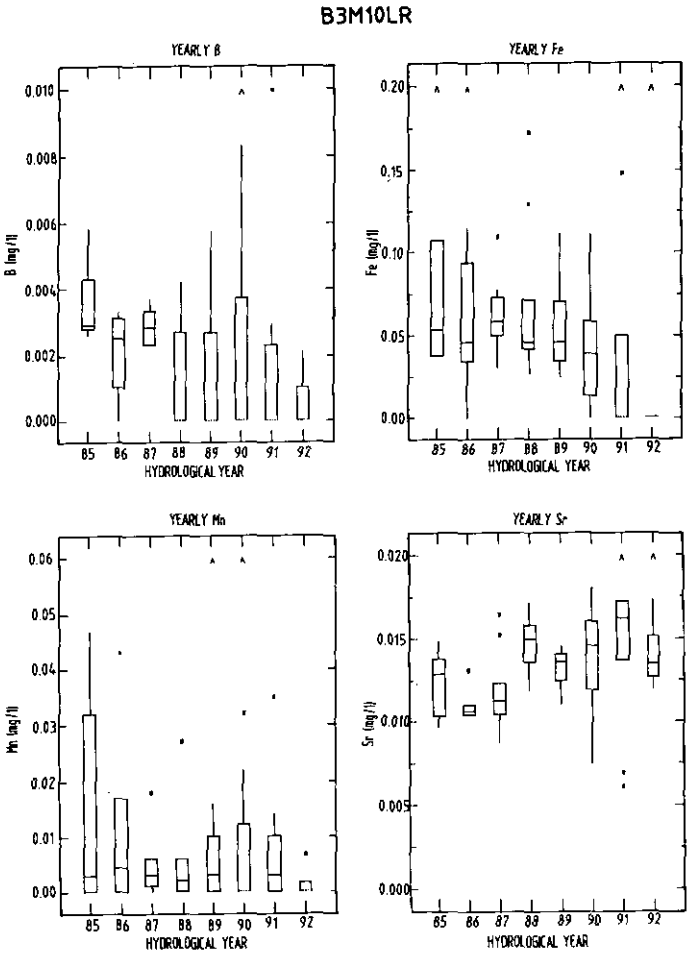

Figure 2a
Yearly box-and-whisker plots for boron, iron, manganese and strontium at B3M10LR

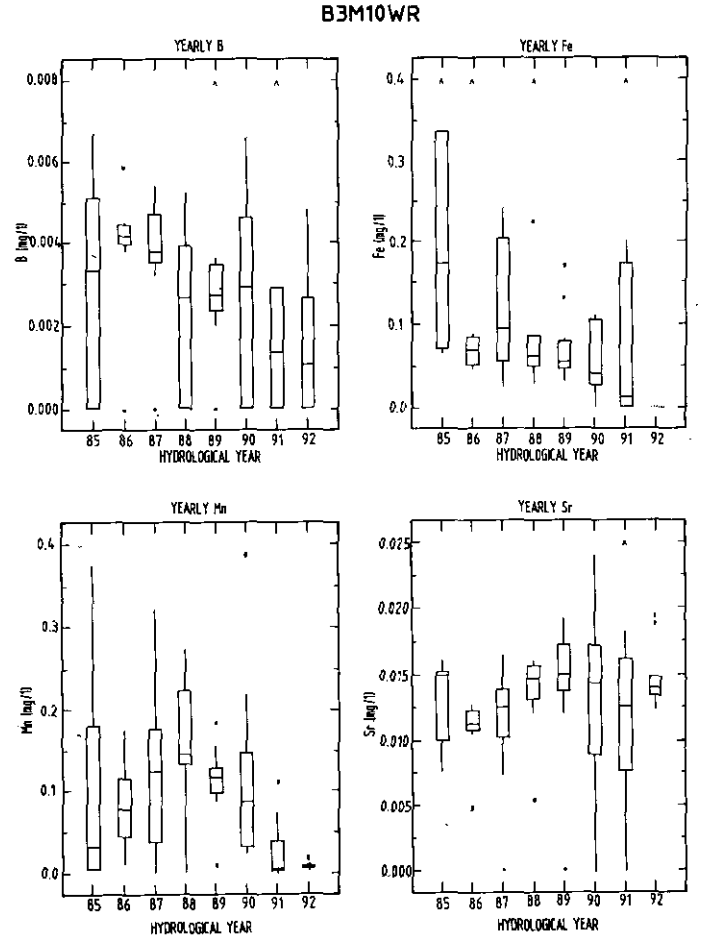

Figure 2b
Yearly box-and-whisker plots for boron, iron, manganese and strontium at B3M10WR

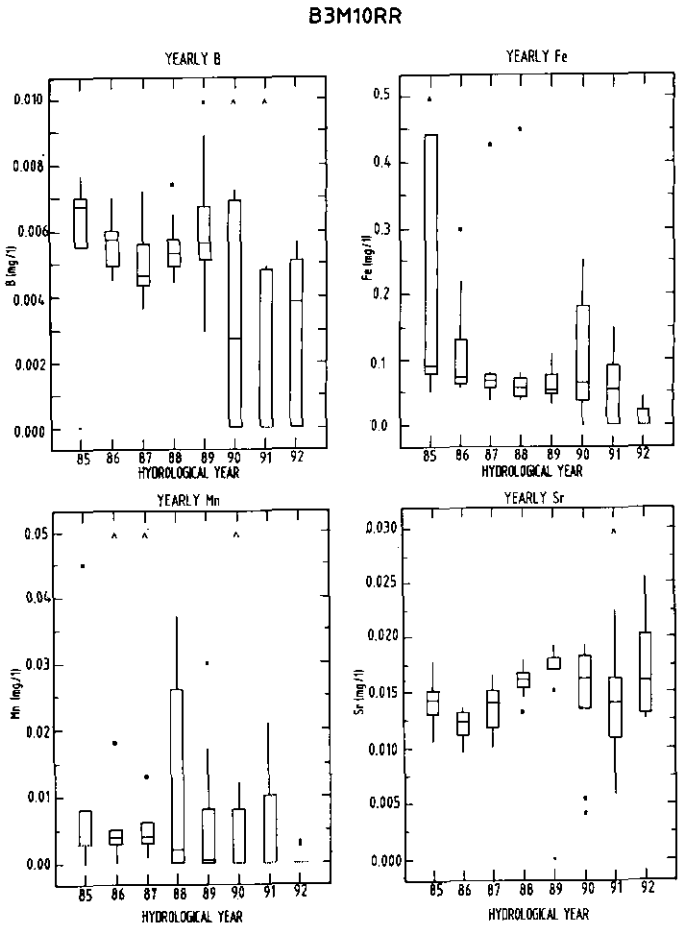

Figure 2c
Yearly box-and-whisker plots for boron, iron, manganese and strontium at B3M10RR

pH 3, no evidence could be found of excessive metal contamination associated with the sediments. The results obtained by Kempster et al. (1991), do not indicate significant differences between the Loskop Dam and the lower sections of the Olifants River for iron, manganese, copper and vanadium.

If the data collected from the Elands River (Renosterkop Dam and Weltevreden Weir) and the Loskop Dam (Loskop Dam canal) are compared, there is no indication that the Loskop Dam's water, abstracted at the dam wall, is different from that of the Elands River. One exception, however, appears to be iron, although there is no difference between the median values, the maximum level of 6.26 mg/l observed in the Loskop Dam appears to be high. The reasons for the difference in the levels found in the Renosterkop Dam, which is situated upstream of the Weltevreden Weir, and the Weltevreden Weir itself are not clear.

Conclusions

Results obtained in this study demonstrated that low levels of metals occur in the middle and lower Olifants River. Of the 20 selected metals, 15 were detected in the sediment samples, 7 in the fish muscle tissue, and 16 in the water phase. Taking the detection limits into account no arsenic, cadmium, lead or mercury were detected in the sediment, water or fish. However, some metals do occur in elevated levels in Selati and Steelpoort tributaries, shown by the acid-extractable concentrations in the water. Future studies will need to distinguish between metals from geological origin and those from anthropogenic origin, and should be extended to the Witbank Dam catchment, known for the low pH water in some of its subcatchments.

Acknowledgements

Mr DJ Roux and Miss JE Badenhorst (Institute for Water Quality Studies) and Mr T Pieterse (Nature and Environmental Conservation) are thanked for assistance during the sampling trip. Mr R Möller is thanked for data processing. This paper is published with the permission of the Department of Water Affairs and Forestry.

References

BATCHELOR, GR (1992) From dammed to damned. *Fauna and Flora* **48** 22-29.

BRYAN, GW (1976) Some aspects of heavy metal tolerance in aquatic organisms. In: Lockwood, APM (ed.) *Effects of Pollutants on Aquatic Organisms*. Cambridge University Press. Cambridge. 193 pp.

DU PREEZ, HH AND STEYN, GJ (1992). A preliminary investigation of the concentration of selected metals in the tissue and organs of the tigerfish (*Hydrocynus vittatus*) from the Olifants River, Kruger National Park, South Africa. *Water SA* **18**(2) 131-136.

DWAF (1991) Water Resources Planning of the Olifants River Basin. Annexure 9. Department of Water Affairs and Forestry, Private Bag X313, Pretoria.

ENGELBRECHT, J (1992) Acid rain and toxic water. *Fauna and Flora* **48** 15-21.

GROBLER, DF (1993) PCBs and Chlorinated Hydrocarbon Pesticides

Residues in Water, Fish and Sediment from the Olifants River. Department of Water Affairs and Forestry, Private Bag X313, Pretoria. Internal Report, NB000/00/REQ/0491.

KEMPSTER, PL (1986) Application of Inductively Coupled Plasma Emission Spectrometry in the Analysis of Environmental samples. Department of Water Affairs and Forestry Technical Report 130.

KEMPSTER, PL, PRETORIUS, L, VAN VLIET, HR and VAN STADEN, JF (1991) Analysis of metals in river sediments as indicators of pollution status. *Proc. of Conf. on Heavy Metals in the Environment.* Edinburgh.

PHILLIPS, DJH (1980) *Quantitative Aquatic Biological Indicators.* Applied Science Publishers LTD, London.