Levels of Cd, Hg and Zn in some surface waters from the Eastern Cape Province, South Africa

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Abstract

Total trace metals levels – Cd, Hg and Zn, which may affect human health and the "health" of the aquatic ecosystem, were determined in the Umtata, Buffalo, Keiskamma and Tyume Rivers and in the Sandile and Umtata Dams. These elements were also determined in sediment samples from some of these surface waters. Normal levels of the metals were detected in water samples from the Umtata River and the Umtata Dam but samples from Buffalo, Keiskamma and Tyume Rivers contained elevated levels of Cd. Generally the levels of Hg and Zn were normal in samples from all the surface waters. The probable sources of the metals in the rivers are diffuse, originating from rural and urban runoff and from agricultural runoff in the catchments although there could be contribution from natural and point sources.

Keywords: heavy metals, water, sediments, atomic absorption spectrometry

Introduction

The accumulation of metals in an aquatic environment has direct consequences to man and the ecosystem. Interest in a metal like Zn, which is required for metabolic activity in organisms, lie in the narrow "window" between their essentiality and toxicity (Skidmore, 1964; Spear, 1981). Its study is also important because of its synergistic reaction with cadmium in the aquatic systems. Other metals like Cd and Hg exhibit extreme toxicity even at trace levels (Merian, 1991; DWAF1996a-c).

Cd, Hg and Zn are common environmental pollutants, which are widely distributed in the aquatic environment. Their sources are mainly from weathering of minerals and soils (Merian, 1991); atmospheric deposition from non-ferrous metal mines, smelters and refineries, coal combustion, refuse incineration and iron and steel industries (Merian, 1991); industrial effluents (Asami, 1974; Prater, 1975); domestic effluents (Preuss and Kollman, 1974); urban storm-water runoff (Field and Lager, 1975) and spoil heaps (Heitfield and Schottler, 1973).

Extensive literature on the aquatic toxicity of Zn and especially its toxicity to fish has been reviewed by Alabaster and Lloyd (1980) and by Spear (1981). Zn is unusual in that it has low toxicity to man, but relatively high toxicity to fish (Alabaster and Lloyd 1980).

Cd has been found to be toxic to fish and other aquatic organisms (Rao and Saxeena, 1981; Woodworth and Pascoe, 1982). Effect of Cd toxicity in man includes kidney damage (Friberg, et al., 1986a; Herber et al., 1988) and pains in bones (Itai-itai disease) (Tsuchiya, 1978; Kjellstroem, 1986). Cd also has mutagenic, carcinogenic and teratogenic effects (Fischer, 1987; Friberg et al., 1986b, Kazantzis, 1987).

Hg is a metal of major concern because of its potentially harmful effects on human health and the environment. Its major pathway to man is commonly accepted to be ingestion of aquatic organisms, particularly fish. Hg is the only metal, which indisputably magnifies through the food chain. In addition, unlike most other metals, Hg is efficiently transformed into its most toxic form (methyl mercury) in the aquatic environment. These facts make Hg exposure to the target population potentially serious, even in remote areas. All of the above observations suggest that the effects of environmental exposure to Hg may be insidious, difficult to detect, and potentially widespread (Harrison, 1983). Hg is a potential cellular toxin and is known to decrease neurotransmitter production, disrupt important processes within the nerve cells, and decrease important hormones such as thyroid and testerone. In the aquatic system, it may affect the fitness of fish species in terms of health and behaviour and in terms of the fitness of the fish flesh for human consumption (DWAF, 1996d).

The pH of a water body determines the chemical species of many metals and thereby alters their availability and toxicity in aquatic environment (DWAF, 1996b). Metals like Cd and Zn are most likely to have increased detrimental environmental effects as a result of lowered pH (DWAF, 1996b).

Temperatures at which a sample is collected and at which physico-chemical measurements are made are important for data correlation and interpretation purposes. For domestic use high temperature may increase the toxicity of many substances such as heavy metals in waters. In addition to microbial activities within an aquatic medium, temperature and pH are two important factors that govern the methylation of elements such as Pb and Hg (Van Loon, 1982; Dojlido and Best, 1993).

Electrical conductivity (EC) is a useful indicator of the mineralisation in a water sample. It correlates with the total dissolved solids (TDS) of that sample. The SA guideline for EC in water for domestic use is 70 mS/m but health effects of EC occur only at levels above 370 mS/m. The effects of high EC may include disturbances of salt and water balance, adverse effects on certain heart patients and individuals with high blood pressure, adverse effects on individuals with renal disease and laxative effects where elevated concentrations of sulphate are present (DWAF, 1998).

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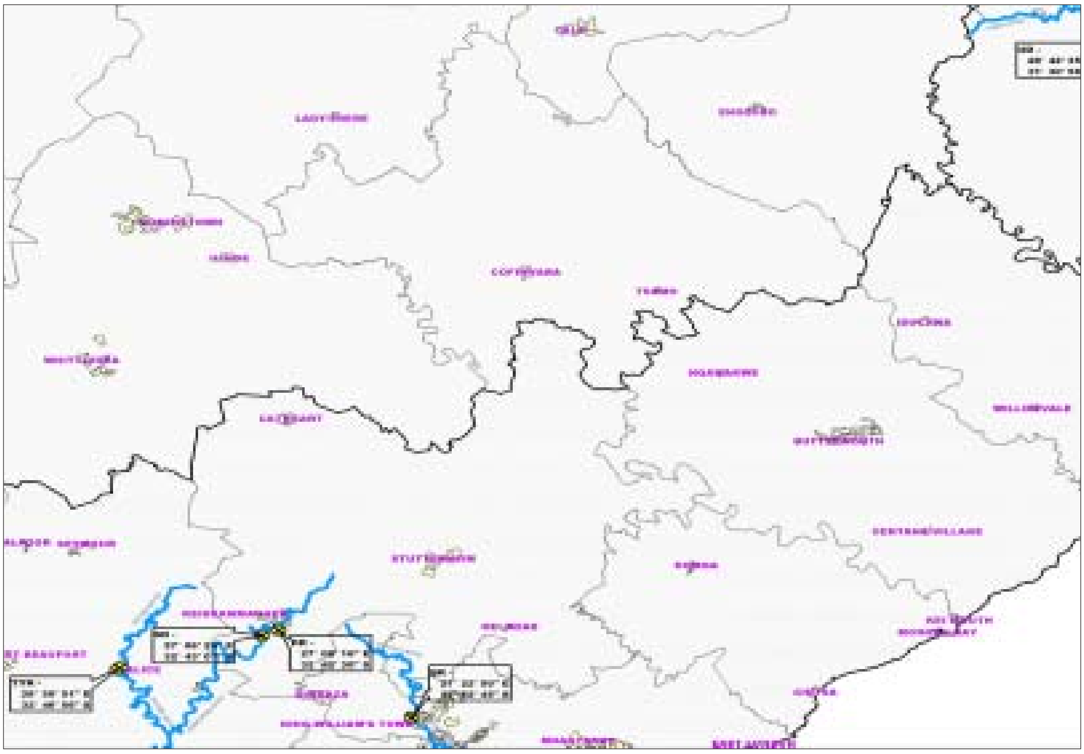

Figure 1
Map of the sample sites
BR = Buffalo River, KR = Keiskamma River, SD = Sandile Dam, TYR = Tyume River, UD = Umtata Dam

This study reports the levels of Cd, Hg and Zn in water and sediment samples from the Umtata, Keiskamma, Buffalo and Tyume Rivers and from the Umtata and Sandile Dams with the associated pH and electrical conductivity values of the water bodies. These catchments support rapidly growing populations and there are concerns regarding the water quality of the surface waters.

Materials and methods

Calibration curves and blank determinations for metal analysis in water samples

Cd: Normal concentration of Cd in freshwater is 0.005 mg/ℓ (DWAF, 1996a). However concentration as high as up to 0.1 mg/ℓ could be found where there is contamination. Calibration standards in the range of 0 to 0.1 mg/ℓ Cd were therefore prepared using 1000 mg/ℓ Cd standard solution with Cd $(NO3)_2.4H_2O$, supplied by BDH laboratory, England and diluted to the required concentrations with doubly distilled water. Blank determination was done using the doubly distilled water, which gave a clean background.

Zn: Normal concentration of Zn in freshwater sources is 3 mg/ℓ (DWAF, 1996a) but concentration up to 10 mg/ℓ is not uncommon. Therefore calibration standards in the range 0 – 10 mg/ℓ Zn was prepared from 1000 mg/ℓ Zn stock standard solution using standard $ZnCl_2$ with doubly distilled water. This initial concentration was suitably diluted with the distilled water. Blank determination was also performed with the doubly distilled water, which gave a clean background.

Hg: Normal concentration of Hg in freshwater sources is 0.001 mg/ℓ (DWAF, 1996a). Therefore calibration standards in the range of 0 – 0.03 mg/ℓ Hg were prepared using doubly distilled water with $HgSO_4$. Solution of the $HgSO_4$ was made to mark with 1% H_2SO_4 for cold vapour analysis. Blank determination was performed using 1% H_2SO_4 solution, which gave a clean background.

Detection limits and the determination of % recoveries of the elements from spiked water and sediment samples for quality assurance

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 by the flame AAS for Cd and Zn and cold vapour AAS for Hg (DAWF, 1992). Six replicates each of these concentrations were prepared and analysed. The detection limits were determined from 3δ (δ = standard deviation) of the replicate determinations for each element (Miller and Miller, 1998).

The quality assurance studies were performed with distilled water samples by spiking method at fortification levels of 0.005 mg/ℓ for Cd, 10 mg/ℓ for Zn and 0.02 mg/ℓ for Hg. The open beaker digestion method (DWAF, 1992) was initially employed for Cd and Zn before employing the comparative extractive concentration method with amino pyrolidine dithiocarbamate (APDC) as complexing agent and methyl isobutyl ketone (MIBK) as the extracting solvent (Van Loon, 1982) for the metals (Cd and Zn). Determination was by flame AAS. The cold vapour AAS method (hydroxylamine sulphate and potassium permanganate method) (DWAF, 1992) was used to determine Hg in water samples. Recovery experiments were done in triplicate for each of the elements. The recovery experiments with pre-extracted sediment were performed again by spiking method, using both the aqua regia (DWAF, 1992) and perchloric acid digestion methods (Fatoki et al., 2001) for Cd and Zn. Recoveries were calculated from the ratio of the amount of the elements recovered after spiking to the amount added. Three replicate analyses were done for each element for each of water and sediment samples collected.

Sampling sites

The sampling sites along the rivers and the dams are shown in Fig. 1. The sites were chosen due to easy accessibility and they also reflect different activities in the catchments, which may affect the quality situation in the river. Samples were taken between October 2002 and March 2003.

Before sampling for chemical analysis, sample bottles were cleaned by soaking in detergent for 24 h, followed by rinsing several times with tap water until free of detergent, rinsed with 5% nitric acid and then thoroughly rinsed with distilled-deionised water (DWAF, 1992; DWAF, 1999).

Water and sediment samples were collected in clean plastic bottles from the Buffalo River, the Keiskamma River, the Sandile Dam, the Umtata River, the Umtata Dam and the Tyume River (water samples were collected only in Sandile Dam), according to the standard procedures described in the sampling guide (DWAF, 1992; DWAF, 1999). Samples for metal analyses were preserved with 5 mℓ concentrated HNO_3. The samples after collection were kept at about 4°C until analysed.

Analyses of water and sediment samples for Cd, Hg and Zn

Total metal contents (Cd and Zn) of water samples were analysed by the open beaker digestion method (DWAF, 1992) as it gave better recoveries and better repeatability than the extractive concentration method (Van Loon, 1982). Sediment samples were analysed by perchloric acid digestion method (Fatoki and Mathabatha, 2001) for total Cd and Zn. The cold vapour AAS method (hydroxylamine sulphate and potassium permanganate method) was used to determine total Hg in water samples only (DWAF, 1992). Three replicate analyses were done for each element for each of the water and sediment samples collected. Temperature was determined on site and pH (with un-acidified water samples) was determined using the Merck (Pty Ltd) 330-pH meter while electrical conductivity was determined by the Merck (Pty Ltd) LF 330 conductivity meter.

Results and discussion

The detection limits for the heavy metals by flame AAS were 1 ng/ℓ for Cd and 6 ng/ℓ for Zn. The detection limit of Hg by the cold vapour method was 3 ng/ℓ (Table 1). The mean percentage recovery of Cd from spiked water samples was 90.67 ± 6.80% and for Zn, 90.47 ± 0.29% by open beaker digestion method (DWAF, 1992) and 83.33 ± 5.73% for Cd and 88.17 ± 3.09% for Zn by extractive concentration method (Van Loon, 1982) (Table 1). Thus the open digestion method gave better recoveries and was therefore tested on environmental water samples for Cd and Zn. The mean percentage recovery of Hg from spiked water samples by cold vapour method was 103.33 ± 6.83 (Table 1). This recovery was deemed to be acceptable and the method was therefore tested on environmental water samples.

The mean percentage recoveries of Cd and Zn from spiked sediment were 66.00 ± 3.27% and 92.00 ± 9.93%, respectively by aqua regia digestion method (DWAF, 1992) and 92.67 ± 2.49% for Cd and 93.40 ± 0.71% for Zn by perchloric acid digestion method (Fatoki and Mathabatha, 2001) (Table 2); thus the latter method was used for the analyses of environmental sediments.

The concentration of Cd in the river water samples ranged from 0.008 ± 0.003 mg/ℓ to 0.011 ± 0.010 mg/ℓ in the Buffalo River, from 0.007 ± 0.001 mg/ℓ to 0.009 ± 0.002 mg/ℓ in the Keiskamma River, from 0.008 ± 0.003 mg/ℓ to 0.017 ± 0.002 mg/ℓ in the Tyume River and from 0.003 ± 0.001 mg/ℓ to 0.007 ± 0.001 mg/ℓ in the Umtata River. The concentration of Cd in water samples from the Sandile Dam varied between 0.003 ± 0.040 mg/ℓ and 0.015 ± 0.002 mg/ℓ while in the Umtata Dam the levels ranged from trace to 0.007 ± 0.003 mg/ℓ (Table 3).

TABLE 1
Detection limits (ng/ℓ) and % recoveries for Cd, Zn and Hg from water samples

Element	Detection limit	^{a}% Recoveries ±S.D*	^{b}% Recoveries ±S.D*
Cd	1	90.67 ± 6.80	83.33 ± 5.73
Zn	6	90.47 ± 0.29	88.17 ± 3.09
Hg	3	103.33 ± 6.83	

a - Open beaker digestion method (DWAF, 1992)
b - Extractive concentration method (van Loon, 1982)
S.D. - Standard deviation
* - Average of 3 replicate analyses

TABLE 2
% Recoveries for Cd and Zn from sediment

Element	^{c}% Recoveries* ±S.D.	^{d}% Recoveries ±S.D.*
Cd	66.00 ± 3.27	92.67 ± 2.49
Zn	92.00 ± 9.93	93.40 ± 0.71

c - Aqua regia digestion method (DWAF, 1992)
d - Perchloric acid digestion method (Fatoki and Mathabatha, 2001b).
S.D. - Standard deviation
* - Average of 3 replicate analyses

The levels of Cd detected in the water samples from the other rivers and the dam were higher than the SA guideline of 0.005 mg/ℓ (DWAF, 1996a) in water for domestic use, except for the Umtata River and the Umtata Dam where the levels of Cd appeared normal (Table 3). The levels of Cd detected in the Umtata River and the Umtata Dam in this study were much lower than the levels detected in previous study between May 1999 and April 2000 (Fatoki et al., 2002). The reduced levels of Cd recorded in this new study might be due to the intervention programme embarked upon by the authors (a workshop with all the stakeholders on water quality situation in the catchment to discuss ways of preventing or reducing pollution in the river catchment).

In view of the fact that major use of water in the catchments is domestic, the high levels of Cd in the other rivers and in the Sandile Dam are of great concern. Cd is extremely toxic and the primary use of water high in Cd could cause adverse health effect to consumers (Friberg et al., 1986a; Kjellstroem, 1986; DWAF, 1998). The SA guideline for Cd in water to be used for livestock watering is 0.01 mg/ℓ (DWAF, 1996c). This level was also exceeded in water samples from the Buffalo and Tyume Rivers and from Sandile Dam. The use of water from these sources to feed livestock may lead to chronic Cd metal poisoning in the livestock. The water

TABLE 3
Levels of heavy metals (mg/l)* in fresh water samples from the Eastern Cape Province of South Africa with other physical parameters

Sampling sites	Sampling dates	Cd	Zn	Hg	pH	Temperature °C	Conductivity (mS/m)
UD	29/10/02	0.003 ± 0.001	0.161 ± 0.060	trace	7.12	23.5	27.2
UR	,,	0.003 ± 0.001	0.053 ± 0.010	trace	6.54	20.4	38.2
BR	,,	0.011 ± 0.010	0.043 ± 0.009	trace	6.73	23.6	407.0
KR	,,	0.009 ± 0.002	0.092 ± 0.010	trace	6.02	20.8	223.0
SD	,,	0.015 ± 0.002	0.120 ± 0.030	trace	6.90	22.9	146.0
TYR	,,	0.017 ± 0.002	0.028 ± 0.010	trace	6.20	21.5	309.0
UD	23/11/02	0.007 ± 0.003	0.196 ± 0.10	trace	5.88	21.5	46.5
UR	,,	0.007 ± 0.002	0.090 ± 0.07	trace	6.04	21.8	22.7
BR	12/12/02	0.008 ± 0.003	0.031 ± 0.001	trace	7.18	23.5	46.0
KR	,,	0.001 ± 0.001	0.009 ± 0.010	trace	6.90	23.2	25.3
SD	,,	0.006 ± 0.003	0.045 ± 0.004	trace	6.75	23.7	124.7
TYR	,,	0.008 ± 0.003	0.026 ± 0.010	0.003 ± 0.001	6.87	22.8	251.4
BR	27/01/03	0.006 ± 0.020	0.150 ± 0.030	trace	6.81	21.8	136.0
KR	,,	trace	0.070 ± 0.021	trace	6.50	24.2	86.2
SD	,,	0.003 ± 0.040	0.094 ± 0.010	trace	7.15	24.3	225.3
TYR	,,	0.016 ± 0.002	0.010 ± 0.005	trace	6.79	23.7	142.0
UD	15/02/03	trace	0.085 ± 0.120	trace	6.91	22.5	720.0
UR	,,	0.004 ± 0.005	0.073 ± 0.050	trace	6.35	23.2	129.0
BR	,,	0.011 ± 0.010	0.043 ± 0.009	trace	7.10	24.4	276.0
BR	01/03/03	0.009 ± 0.002	0.280 ± 0.008	0.003 ± 0.001	6.80	23.5	185.1
KR	,,	0.006 ± 0.003	0.152 ± 0.005	trace	6.54	24.3	154.2
SD	,,	0.006 ± 0.001	0.372 ± 0.004	0.004 ± 0.001	6.95	23.8	96.0
TYR	,,	0.007 ± 0.001	0.324 ± 0.002	trace	6.87	24.5	211.4

BR = Buffalo River, KR = Keiskammahoek River, SD = Sandile Dam, TYR = Tyume River, UD = Umtata Dam, and UR = Umtata River

*Values are mean of triplicate analyses

criteria for Cd in water for use in the ecosystem are 0.015 mg/l in soft water and 0.025 mg/l in moderately soft water (DWAF, 1996b). These guidelines were exceeded in water samples from the Tyume River and the river would not be suitable for aquatic ecosystem use.

The levels of Cd in sediments varied between 0.008 ± 0.004 mg/kg and 0.017 mg/kg in the Buffalo River, between 0.008 ± 0.003 mg/kg in the Keiskamma River, between 0.012 ± 0.003 mg/kg and 0.063 ± 0.01 mg/kg in the Tyume River and between 0.006 ± 0.15 mg/kg in Umtata River. The level in sediment sample from the Umtata Dam was 0.003 ± 0.01 mg/kg (Table 4).

The probable sources of Cd in the catchments are from natural sources due to the geology of the catchment soil (DWAF, 1996b), and from runoffs from agricultural soils that use phosphate fertilizers (Cd is a common impurity in phosphate fertilizers) (Stoeppler, 1991). Other probable sources include leachates from disused Ni-Cd based batteries and Cd-plated items (Hutton et al., 1987; Stoeppler, 1991) from the rural communities that are disposed in the refuse dumps in the settlements.

The results for Zn analyses in water samples are also shown in Table 3. The levels of Zn ranged from 0.009 ± 0.01mg/l in Keiskamma River to 0.324 ± 0.002 mg/l in Tyume River and from 0.085 ± 0.120 mg/l to 0.372 ± 0.004 mg/l in the dams. The SA guideline for Zn in water for domestic supply is 3 mg/l (DWAF, 1996a, DWAF, 1998). Therefore, Zn is not supposed to be a problem in the river catchments if the water is used for domestic purposes. However, Zn could be a problem in water for other uses, for example, for the use of the aquatic ecosystem (DWAF, 1996b). The SA Target Water Quality Range for Zn in water for the use of aquatic ecosystem is 0 to 0.02 mg/l. This limit was exceeded in the Buffalo and the Tyume Rivers and in the Sandile Dam. Thus waters from these rivers and the dam are unsuitable for use of the aquatic ecosystem and could be very detrimental to fish.

The levels of Zn in sediment (Table 4) varied between 0.026 ± 0.01 mg/kg in the Tyume River and 0.350 ± 0.005 mg/kg in the Buffalo River. The levels of Zn in water samples from the Umtata Dam was 0.003 ± 0.01 mg/l. The probable sources of Zn in the catchment are natural (due to geology of the catchment) and from domestic sewage and diffuse sources.

The levels of Hg detected in water samples form the rivers ranged from trace to 0.003 ± 0.001 mg/l in the Buffalo River, were trace in the Keiskamma and Umtata Rivers and varied between trace and 0.003 ± 0.001 mg/l in the Tyume River. The levels of Hg detected in water samples from the dams varied between trace and 0.004 ± 0.001 mg/l in the Sandile Dam and was trace in the Umtata Dam. The South African guideline for Hg in water for domestic use, use of ecosystem and aquaculture use is 0.001 mg/l (DWAF, 1996a,b&d)). Based on this guideline, the levels of Hg are considered generally low in the rivers and dams and would not pose a problem in water for the above uses.

The pH values of water samples from the rivers and the dams varied between 5.88 and 7.26. The SA Target Water Quality Range for pH in water for domestic use is 6 to 9 (DWAF, 1996a). All of the values of pH obtained for the rivers and most for the dams fell within this range. The levels of electrical conductivity varied between 18.4 mS/m and 407.0 mS/m. The SA guideline for electrical conductivity in water for domestic use is 70 mS/m (DWAF, 1996a; DWAF, 1999). This level was exceeded in the rivers and the dams and based on this parameter the rivers and the dams are not suitable for domestic use (DWAF, 1996a, DWAF, 1999). The temperatures of the water samples were normal.

TABLE 4
Levels of heavy metals (mg/kg)* in sediment samples from freshwater sources in the Eastern Cape Province of South Africa

Sampling sites	Sampling dates	Cd	Zn
BR	29/10/02	0.009 ± 0.03	0.030” 0.004
KR	,,	0.058 ± 0.001	0.033” 0.06
SD	,,	ND	ND
TYR	,,	0.063 ± 0.01	0.141 ± 0.02
BR	12/12/02	0.017 ± 0.001	0.040 ± 0.01
KR	,,	0.008 ± 0.003	0.029 ± 0.01
SD	,,	ND	ND
TYR	,,	0.018 ± 0.001	0.026 ± 0.01
BR	27/01/03	0.012 ± 0.12	0.05 ± 0.03
KR	,,	0.004 ± 0.001	0.110 ± 0.01
SD	,,	ND	ND
TYR	,,	0.022 ± 0.01	0.029 ± 0.03
UD	15/02/03	0.003 ± 0.01	0.052 ± 0.08
UR	,,	0.006 ± 0.15	0.150 ± 0.03
BR	01/03/03	0.008 ± 0.004	0.350 ± 0.005
KR	,,	0.008 ± 0.004	0.252 ± 0.003
SD	,,	ND	ND
TYR	,,	0.012 ± 0.003	0.225 ± 0.006

BR = Buffalo River, KR = Keiskammahoek River, SD = Sandile Dam and TYR = Tyume River, UD = Umtata Dam and UR = Umtata River
*Values are mean of triplicate analyses,
ND = Not determined

Conclusion

The levels of total trace metals, namely Cd, Hg and Zn were determined in the Buffalo, Keiskamma, Tyume and Umtata Rivers and in the Sandile and Umtata Dams. Generally excessive levels of Cd were observed in the rivers and the dams (except in the Umtata River and the Umtata Dam), which may affect the "health" of the aquatic ecosystem. Also, the excessive level of Cd may affect the health of the rural community that uses the river water for direct domestic use without prior treatment. The levels of Zn and Hg appeared generally to be normal in all the rivers and the dams. Probable sources of the metals pollution in the catchment appear to be diffuse and include rural and urban runoff and agricultural runoff in the catchment. There could be a contribution from natural (i.e. from the geology of the catchment) and point sources in the catchment (i.e. the towns' sewage works).

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