

# Metal surveys in South African estuaries VII Bushmans, Kariega, Kowie and Great Fish Rivers

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## Abstract

Surveys to study the distribution of selected metals in the Bushmans, Kariega, Kowie and Great Fish Rivers were carried out in the period August 1978 – April 1979. Surface sediment and water samples and sediment cores were analysed for up to sixteen elements using atomic absorption spectroscopy. Interelement relationships as well as absolute metal concentrations were examined before interpreting the data obtained.

Metal concentrations in sediment and water samples from the four rivers are normal for unpolluted Eastern Cape rivers and such conditions are likely to be maintained in the absence of further urbanization or industrialization.

## Introduction

The rivers surveyed during this investigation all flow into the Indian Ocean on the south-eastern Cape coast between the two industrial centres of Port Elizabeth and East London. This part of the coast is relatively undeveloped, there being only a few holiday resorts and the small town of Port Alfred.

The Bushmans River rises near Webster, about 60 km south of Somerset East and enters the sea to the east of the town of Bushmans River Mouth, about 24 km west of Port Alfred (Fig. 1). The estuary is about 400 m wide but narrows upstream to a width of about 180 m. The catchment area is about 2700 km<sup>2</sup> (Day,

1981) and the region is fairly dry, which causes problems in the adequate supply of water to the towns of Bushmans River Mouth and Kenton-on-Sea.

The Kariega River rises to the west of Grahamstown and enters the sea 2 km to the east of the Bushmans River (Fig. 1). The estuary is about 370 m wide near the sea but becomes much narrower upstream. The river mouth area is very shallow and the river is tidal for about 24 km (Day, 1981). The river banks are shallow in the lower reaches of the estuary but become steeper and higher upstream. The river catchment area supports some agricultural activities and a large part of it is covered in forest or indigenous bush.

The Kowie River rises to the south of Grahamstown and flows into the sea at Port Alfred (Fig. 1). It has a catchment area of about 580 km<sup>2</sup> with an average rainfall of 640 mm/a (Day, 1981). The estuary extends about 19 km upstream from the mouth; it is relatively narrow in the upper reaches but about 150 m wide near the mouth where the river banks have been canalised. In general, there is a paucity of flora and fauna which could be due to the fast tidal exchange rate and to the canalisation at the mouth which has resulted in a reduced saltmarsh and *Zostera* bed area (Day, 1981).

The Great Fish River is approximately 180 km by road from Port Elizabeth (Fig. 1). Background information about this river is almost non-existent, probably because of its relative remoteness from a major town. The river drains a large area of the Eastern Cape lying between Cradock and Queenstown and supports an

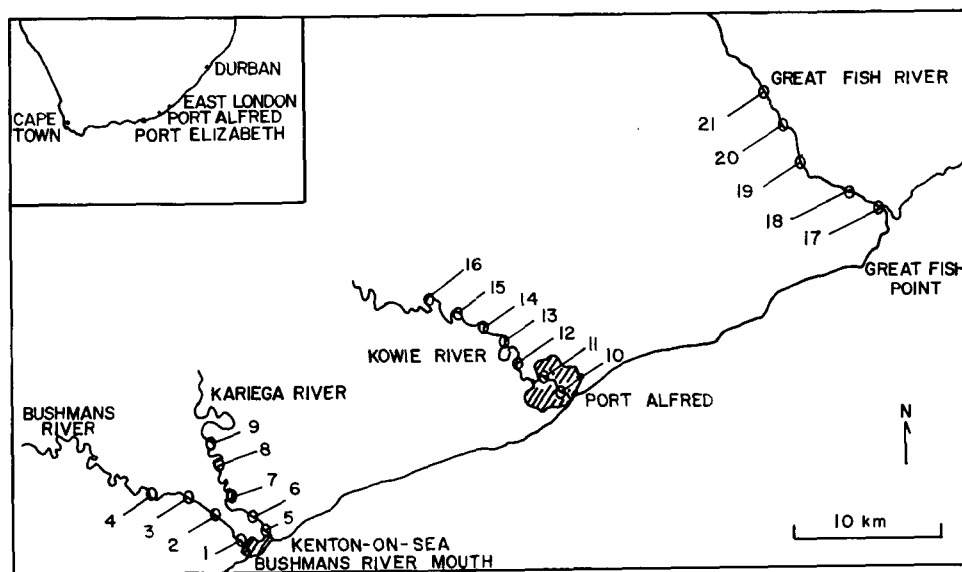


Figure 1  
Location of study area and sampling sites

extensive irrigated agricultural scheme; the catchment area of the river and its tributaries is 30 430 km<sup>2</sup> (Day, 1981). The river mouth has not been closed in recorded history, although the suspended sediment load is particularly great. The northerly limit of the mouth is fixed by an outcrop of calcareous consolidated dune sands of the Ecca Group. The south bank is flat, muddy and low-lying with several creeks draining wide saltmarshes (Day, 1981).

The aim of these preliminary surveys, carried out in the period 1978 - 1979, was to determine the current metal levels in the sediments and water of the four rivers. Situated as they are, in the undeveloped region between Port Elizabeth and East London, the data obtained will not only serve as a baseline for future monitoring surveys of these rivers, but will also provide a useful comparison with the data obtained from the two industrial centres.

### Materials and Methods

The methods used for the collection, preparation and analysis of the water and sediment samples collected during these surveys are detailed by Watling and Watling (1982 a and c).

### Results and discussion

#### Water samples

Metal concentrations in surface water samples are listed in Table 1. Sampling sites are shown in Figure 1.

The low concentrations present in samples from the Bushmans and Kariega Rivers indicate that these rivers are uncontaminated with respect to metals. Metal concentrations in samples from the Kowie River are also low. The relatively high mercury levels at sites 15 and 16 and the high nickel level at site 14 are probably the result of catchment leaching of metal-rich soils.

The higher metal levels present in water samples from the Great Fish River are partly due to the high concentration of suspended material carried by this river. Metal concentrations in filtered and unfiltered water samples collected during two further surveys of this river are compared in Table 2. These results indicate that with the exception of iron and manganese, there are only relatively small differences in the metal concentrations in filtered and unfiltered samples. The levels of iron and manganese are considerably lower in the filtered samples, confirming that these elements are present mainly in the suspended particulate phase.

There are marked differences in the metal contents of those water samples collected in the summer (low flow) and those collected in the winter (high flow) season. The higher copper, cadmium and mercury concentrations found in the summer samples are thought to be due to an increased input of metal-rich seepage water to the river. Even during these periods, the overall metal concentrations are average for Eastern Cape rivers (Watling and Watling, 1982 b and c).

#### Surface sediments

Metal concentrations in surface sediment samples are listed in Table 3.

TABLE 1  
METAL CONCENTRATION ( $\mu\text{g/l}$ ) IN WATER SAMPLES

Site (Refer Fig. 1)	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Cr	Hg
<b>Bushmans River</b>										
1	2,2	0,10	1,10	226	5,4	0,20	0,10	0,10	0,3	0,004
2	1,1	0,20	0,30	350	7,6	0,20	0,20	0,10	0,6	0,004
3	1,5	0,30	0,20	310	11,3	0,30	0,10	0,10	0,3	0,004
4	2,4	0,10	0,40	320	16,4	0,10	0,50	0,20	0,3	0,010
<b>Kariega River</b>										
5	1,9	0,05	0,50	74	1,8	0,10	0,05	0,05	0,3	0,004
6	1,6	0,70	0,40	135	3,3	0,10	0,20	0,05	0,2	0,010
7	1,3	0,05	1,10	164	7,4	0,05	0,10	0,10	0,3	0,001
8	1,4	0,10	0,50	310	10,8	0,20	0,20	0,10	0,2	0,001
9	1,1	0,20	0,05	168	24,2	0,10	0,10	0,05	0,3	0,001
<b>Kowie River</b>										
10	1,4	0,05	0,40	24	0,4	0,10	0,10	0,05	0,3	0,001
11	1,9	0,05	0,60	56	1,7	<0,05	0,05	0,05	0,2	0,010
12	1,8	0,10	0,70	123	8,6	<0,05	0,20	0,05	0,3	0,042
13	1,7	0,30	0,50	219	13,2	0,30	0,30	0,05	0,2	0,002
14	1,6	0,60	0,70	420	21,9	0,20	2,70	0,05	0,2	0,001
15	1,5	0,10	0,30	199	15,6	0,20	0,05	0,05	0,3	0,216
16	1,9	0,40	0,80	460	21,5	0,20	0,40	0,05	0,2	0,131
<b>Great Fish River</b>										
17	1,3	1,6	4,3	242	30	0,6	0,9	0,03	1,3	0,096
18	2,2	0,8	2,1	496	39	0,9	2,1	0,07	2,1	0,132
19	2,5	1,3	2,0	2160	64	1,0	2,0	0,05	2,0	0,017
20	2,9	1,0	3,6	3120	62	0,7	1,6	0,10	2,8	0,024
21	2,1	0,9	2,9	1210	47	0,7	1,6	0,09	1,7	0,036

**TABLE 2**  
**A COMPARISON OF METAL CONCENTRATIONS ( $\mu\text{g/l}$ ) IN FILTERED AND UNFILTERED SURFACE WATER**

Site and Sample	Element									
	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Cr	Hg
<b>Winter 1980</b>										
<b>Unfiltered</b>										
17	1,2	1,4	2,5	278	23	0,3	0,9	0,08	1,0	0,187
18	2,0	0,9	4,0	780	47	0,3	1,7	0,08	2,1	0,168
19	3,9	1,5	8,2	2520	38	0,7	2,7	0,06	5,6	0,020
20	4,0	1,8	6,5	2100	79	0,7	2,5	0,06	4,7	0,113
21	3,6	1,0	6,1	1220	49	0,3	1,6	0,13	2,7	0,058
<b>Filtered</b>										
17	1,5	0,8	5,1	7	23	0,3	0,8	0,09	0,8	0,094
18	2,5	0,4	4,9	12	26	0,3	1,3	0,04	1,2	0,157
19	3,6	0,6	4,6	92	1,8	0,3	1,4	0,07	0,9	0,019
20	4,2	1,0	3,1	18	0,8	0,2	1,5	0,03	1,1	0,058
21	4,5	0,6	2,9	26	0,9	0,1	1,8	0,04	1,8	0,032
<b>Summer 1981</b>										
<b>Unfiltered</b>										
17	4,5	1,1	2,5	114	14	<0,1	0,5	0,48	0,8	0,495
18	4,6	1,9	4,2	460	136	<0,1	1,8	0,55	1,4	0,412
19	5,3	0,6	5,0	600	33	<0,1	1,8	0,54	1,5	0,128
20	5,0	0,7	3,8	1060	28	<0,1	1,7	0,16	2,4	0,263
21	4,4	1,0	3,1	1000	20	<0,1	1,8	0,06	2,5	0,130
<b>Filtered</b>										
17	3,2	0,8	2,1	4,2	3,2	<0,1	0,4	0,26	0,3	0,435
18	3,1	0,4	2,9	4,6	4,6	<0,1	1,3	0,19	1,0	0,400
19	3,7	0,5	3,1	5,3	5,0	<0,1	1,2	0,29	0,9	0,127
20	3,2	0,6	3,0	8,4	5,2	<0,1	1,1	0,10	0,9	0,252
21	2,9	0,9	2,1	8,0	4,1	<0,1	1,1	0,06	1,7	0,121

**TABLE 3**  
**METAL CONCENTRATIONS ( $\mu\text{g/g}$ ) IN SURFACE SEDIMENT SAMPLES**

Site (Refer Fig. 1)	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Cr	Na	K	Ca	Mg	Sr	Al
<b>Bushmans River</b>															
1	1,4	1,3	2	2 700	36	0,2	0,4	0,04	4,2	1 760	109	12 100	2 250	563	840
2	2,4	6,3	11	5 210	47	1,4	5,7	0,06	27,1	5 290	3 980	81 600	4 130	540	17 200
3	3,4	6,4	20	9 210	47	3,2	7,3	0,10	27,3	5 120	2 720	12 400	3 210	58	22 500
4	4,1	7,4	17	12 200	67	3,9	6,9	0,02	28,4	1 720	1 480	2 960	1 710	17	18 600
<b>Kariega River</b>															
5	2,6	4,3	3	2 120	36	0,5	0,5	0,06	8,6	5 130	327	14 200	8 620	840	1 120
6	5,3	6,8	9	8 120	146	1,6	3,7	0,04	22,7	7 120	1 430	109 000	8 960	620	7 410
7	8,6	12,9	34	21 200	220	8,7	10,4	0,04	30,9	13 600	4 120	45 200	9 050	146	16 900
8	10,7	17,4	38	29 200	146	11,7	22,8	0,05	32,7	10 300	3710	22 500	7 140	115	27 300
9	10,2	12,3	51	19 600	109	4,7	12,0	0,04	37,4	8 420	3 690	27 200	6 340	39	21 200
<b>Kowie River</b>															
12	29,3	40,7	190	29 800	400	30,2	30,6	0,10	69,7	8 120	8 000	590	5210	12	38 700
13	12,6	29,7	120	29 000	450	12,9	20,3	0,04	59,6	7 960	6 200	410	4 710	10	40 000
14	9,6	21,3	37	19 200	360	10,6	16,4	0,04	47,6	7 420	4 310	1 320	4 290	17	38 200
15	15,3	30,2	64	39 300	920	17,6	24,3	0,07	43,8	5 720	5 410	900	5 120	6	28 000
16	15,6	27,3	69	44 200	520	18,4	30,2	0,05	96,7	5 730	8 060	2 170	5 770	16	51 300
<b>Great Fish River</b>															
17	2,7	4,0	5	2 140	30	0,4	1,2	0,92	5,3	3 240	660	169 000	2 660	1 620	1 750
18	6,8	10,3	30	12 900	196	5,3	12,7	0,21	12,9	3 000	2 900	6 200	2 910	60	13 900
19	7,3	8,6	37	8 620	84	3,9	8,2	0,23	12,0	3 260	2 860	3 290	3 160	59	12 700
20	4,2	7,4	29	9 900	74	3,4	8,0	0,12	14,1	1 290	1 400	3 920	1 270	27	12 700
21	4,1	7,6	30	10 000	39	2,6	7,4	0,02	9,6	1 410	1 360	2 980	1 160	60	10 900

Concentrations in the surface sediments of the Bushmans River are average for an uncontaminated Eastern Cape river (Watling and Watling, 1982 b and c). The sample collected at the mouth of the river is in no way unusual when compared with other coastal samples (Watling and Watling, 1983). Concentrations in samples collected up-river are consistently low with very little variation along that part of the river surveyed. The only exceptions are a general increase in the levels of iron, aluminium and potassium and a decrease in the levels of calcium and strontium with increasing distance from the river mouth.

Many of the element concentrations determined for the Kariega River samples are higher than those in samples from equivalent sites in the Bushmans River. Levels of copper, lead, zinc, cobalt, nickel and chromium increase significantly in the upstream samples but both the cobalt/nickel and iron/aluminium relationships indicate that the metals are derived from the weathering of catchment rocks (Watling and Watling, 1982 g). These metals are being trapped in the riverine sediments and it is unlikely that they will be released to the water column.

It was not possible to collect sediment samples in the canalised section of the Kowie River as the small amounts of sediment which have been deposited from the fast flowing water have collected between the boulders on the bed of the canal. Concentrations of copper, lead, zinc, cobalt, nickel, cadmium and chromium in surface sediments collected further upstream are higher than would be expected from an unpolluted river (Watling and Watling, 1982 a to c). The high iron and aluminium concentrations are indicative of the presence of clay and hydrated iron minerals. The relative concentrations of iron and aluminium and of cobalt and nickel suggest that for the most part, the trace metals are derived from the leaching of a mineralised catchment (Watling and Watling, 1982 g).

Metal concentrations in the Great Fish River are indicative of an unpolluted river. Some increased metal levels occur in the

sediment from site 18, which is adjacent to a small stream which feeds the main river. The tributary catchment may therefore contain some metal enrichment.

#### Sediment cores

Sediment cores were collected at four sites in the Bushmans River, four sites in the Kariega River, three sites in the Kowie River and five sites in Great Fish River. Sample locations are coincident with those of the water and surface sediment samples but sediment cores were collected from the side of the nearest available mud or sand bank. Consequently, the concentrations measured at the top of each core may not correspond with those for the equivalent surface sediment. Specific metal levels which can vary in the space of metres are not necessarily indicative of pollution. Conclusions should be drawn on the basis of overall trends and metal inter-relationships rather than on absolute levels.

Metal concentrations in every core sample, together with a scale drawing and sedimentological description of the core and an interelement correlation matrix have been detailed elsewhere (Watling and Watling, 1982 d to f). The geometric means for the concentrations of each element in these cores have been calculated and are listed in Table 4. While this is not an ideal way to display core data, it does serve as an easy method for identifying anomalous areas.

The metal concentrations and interelement relationships determined for the sedimentary sequences of each of the four study rivers indicate that the major input of metals to those rivers is derived from the weathering of catchment rocks. Variations in the rates of weathering, either associated with seasonal differences in rainfall or the periodic occurrence of severe flooding, is illustrated by the distribution of metals in the core from Great Fish River site 19 (Table 5). The middle area of this core between 200 to 340 mm below the sediment surface (samples 67 to 61) is

TABLE 4  
MEAN METAL CONCENTRATIONS ( $\mu\text{g/g}$ ) IN SEDIMENT CORE SAMPLES

Site (Refer Fig. 1)	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Cr	Hg	Na	K	Ca	Mg	Sr	Al
<b>Bushmans River</b>																
1	1,2	1,7	2,1	2 450	31	0,1	0,4	0,04	5,7	0,004	2 440	188	112 000	2 740	586	927
2	4,4	7,5	20,2	10 800	72	2,5	7,5	0,06	22,0	0,052	5 110	2 730	90 900	4 610	663	12 900
3	4,5	7,4	20,2	10 700	97	2,7	5,9	0,09	20,1	0,048	4 500	2 730	72 800	4 080	479	13 000
4	4,5	8,9	17,7	12 200	96	4,7	6,9	0,02	32,2	0,019	2 930	2 460	5 590	2 460	56	17 100
<b>Kariega River</b>																
5	3,1	3,2	3,2	2 460	33	0,3	0,5	0,06	8,7	0,008	6 410	375	147 000	8 960	918	1 220
6	5,0	4,9	8,9	6 430	83	1,3	3,1	0,09	16,8	0,088	7 420	1 670	124 000	9 000	837	6 200
7	8,8	11,7	29,6	18 400	176	7,1	10,1	0,13	30,9	0,047	10 400	3 830	39 200	7 490	95	17 300
8	10,8	14,3	51,4	21 600	119	9,5	15,3	0,04	38,8	0,037	9 890	3 850	24 900	6 790	17	22 400
<b>Kowie River</b>																
13	11,1	23,7	46,6	26 700	318	10,2	19,7	0,01	48,5	0,18	6 610	5 250	506	3 730	9	28 700
14	10,5	20,0	40,7	20 900	153	9,9	16,2	0,04	35,9	0,17	9 910	5 210	554	3 720	8	29 600
15	15,0	33,6	68,4	36 200	584	14,7	25,4	0,06	65,8	0,17	4 930	6 800	1 470	4 870	10	48 700
<b>Great Fish River</b>																
17	2,1	3,0	3,4	2 350	55	0,9	0,8	0,03	8,4	0,007	3 000	272	12 000	3 000	874	3 260
18	11,9	12,0	33,1	16 900	322	9,7	14,9	0,04	24,5	0,012	6 110	3 340	5 590	4 220	37	2 220
19	9,9	12,0	28,7	16 100	438	10,1	13,4	0,22	29,4	0,017	2 090	2 530	6 650	3 670	43	22 200
20	5,6	6,3	14,9	8 900	102	3,9	6,4	1,32	22,3	0,015	1 060	1 360	3 960	2 130	286	12 600
21	5,3	6,9	15,4	9 900	99	3,6	8,0	0,22	15,4	0,006	1 110	1 150	4 440	2 030	276	12 500

TABLE 5  
TRACE METAL DISTRIBUTION WITH DEPTH IN GREAT  
FISH RIVER CORE 19 ( $\mu\text{g/g}$ )

Sample	Cu	Pb	Zn	Co	Ni	Cr
77*	5	9	23	8	9	13
76	7	10	29	8	12	16
75	7	7	19	8	7	12
74	4	6	19	6	8	9
73	5	7	19	8	8	11
72	6	9	22	8	9	15
71	7	10	32	8	11	18
70	10	10	25	9	13	18
69	8	11	25	8	12	17
68	9	14	31	11	14	20
67	16	22	33	16	19	24
66	17	19	36	15	19	23
65	15	20	43	13	21	18
64	16	19	41	15	21	24
63	20	23	47	19	24	42
62	14	14	32	11	18	26
61	14	13	36	13	18	27
60	10	11	28	9	12	20
59	9	8	24	8	12	18
58	6	8	23	9	11	19
57	9	8	23	9	12	17
56	7	8	19	6	9	16
55	8	11	32	10	14	23
54	8	13	29	9	11	22

\*\*Sample 77 is at the sediment surface and the core is 600 mm long.

an area of elevated metal levels. This is associated with the increased input of silt and organic material containing relatively high metal concentrations during a flood just prior to the present survey. A series of strong interelement relationships based on the clay minerals facies is present throughout the entire sequence and this indicates that the variations in metal concentrations which have been observed are the result of a greater input of metal-rich suspended matter during the limited flood period. Sedimentation has re-established its equilibrium after the flood, as indicated by the metal concentrations found in samples nearer the sediment surface. The Great Fish River carries the greatest suspended particulate load (cf. Bushmans, Kariega and Kowie Rivers), so that variations due to seasonal rainfall or flood conditions are accentuated.

In general terms, there is no indication of a systematic build-up of metals in any of the sediment cores collected during this survey. Metal concentrations vary considerably between the rivers (Table 4) and, in many cases concentrations increase upstream.

At the same time there is an increase in the clay minerals and organic matter contents of the sediments, with which these metals may be associated. Interelement relationships between metals are relatively constant throughout the survey area which suggests that the metals are derived from the same formational geochemical anomaly. Two exceptions to this generalization are the calcium/strontium and potassium/aluminium ratios in samples from the Great Fish River. The relatively elevated strontium levels in these samples suggest that this element is not only present in shell debris but is also derived partially from catchment runoff. The potassium/aluminium ratio does not fall within the range 1:4 to 1:6 which is usually found when the clay minerals content of the sediment is high. This variation may also be indicative of an additional input of terrigenous material during the flooding which occurred just prior to the survey.

### Summary

Metal concentrations in sediment and water samples from the four study rivers are indicative of unpolluted river catchments. Relatively elevated metal levels are found at sites upstream from the river mouths but interelement ratios for these samples suggest that the metals are not anthropogenic but are derived from weathering of catchment rocks. Metal levels in the sediment do not vary greatly with depth.

Conditions in these rivers are likely to be maintained in the absence of further urbanization or industrialization in the area, and the rivers do not need to be monitored on a routine basis.

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