Metal surveys in South African estuaries IX. Buffalo River

RJ Watling*, MMJ-F Talbot, EB Branch and SA Marsland
Zoology Department, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa

Abstract

Surveys to study the distribution of selected metals in the Buffalo River, Mzoniana and Ncabanga streams were carried out in the period August 1982 to August 1983. Surface sediment and water samples and sediment cores were analysed for up to fifteen elements using atomic absorption spectroscopy. Inter-element relationships as well as absolute metal concentrations were examined before interpreting the data obtained. Changes in the primary geochemistry of the catchment from acidic to basic igneous and metamorphic rocks are reflected in the sediment by variations in the clay mineral assembly and inter-element ratios.

Results indicate widespread anthropogenic input of copper, lead, zinc, cobalt, nickel, cadmium, chromium and mercury throughout the study area, with concentrations reaching one hundred times those of equivalent background samples.

Introduction

The Buffalo River drains a catchment of approximately 1300 km² and enters the sea at East London (Fig. 1). The catchment is short and steep, descending from 1 400 m at its source to sea level in 40 km. During the dry season the flow is made up largely of seepage water from rocks of the Lower Beaufort Series and is consequently highly mineralized.

Approximately 400 000 people live in the catchment and of these 57% are concentrated into four cities, East London, Mdantsani, Zwelitsha and King Williams Town. All these cities are on the banks of the Buffalo River. The urban areas, however, occupy only 9% of the total catchment with forestry and agriculture occupying a further 75%. Agriculture is pastural except for 10% allocated to pineapple farming. Considerable impact is being made on the environment by the urban developments of Mdantsani, Potsdam and East London.

Rainfall occurs as storms of high intensity and consequently flooding incidents commonly punctuate prolonged droughts causing high erosion rates. Five dams have been built on the river and these at present fully exploit the freshwater input to the area. The methods of dispersion of domestic and industrial effluents are grossly ineffective and result in heavy contamination of the Buffalo River (Tow, 1981).

The purpose of this study was to establish the current distribution of selected metals in the Buffalo River. This data would provide a baseline for future studies in the area and give an indication as to the present status of the Buffalo River with respect to metal contamination.

Materials and Methods

Unfiltered surface water samples were collected in 250 ml high density polythene bottles, acidified with 1 ml concentrated redistilled nitric acid and stored for the determination of copper, lead, zinc, iron, manganese, cobalt, nickel, cadmium, sodium, potassium, calcium, magnesium, strontium and chromium. An additional 500 ml sample was collected for mercury analysis. Concentrated nitric acid (10 ml) was added to this sample as a preservative.

Copper, lead, zinc, iron, manganese, cobalt, nickel, cadmium and chromium were determined using a Varian Techtron AA875 with GTA95 graphite furnace. Mercury concentrations were determined using cold vapour atomic absorption. The samples were analysed for sodium, magnesium, potassium, calcium and strontium using standard flame conditions.

Methods used for the collection, preparation and analysis of surface sediments and sediment cores have already been detailed (Watling and Watling, 1982a).

Results and Discussion

Metals in surface waters

Major, minor and trace elements concentrations in surface water

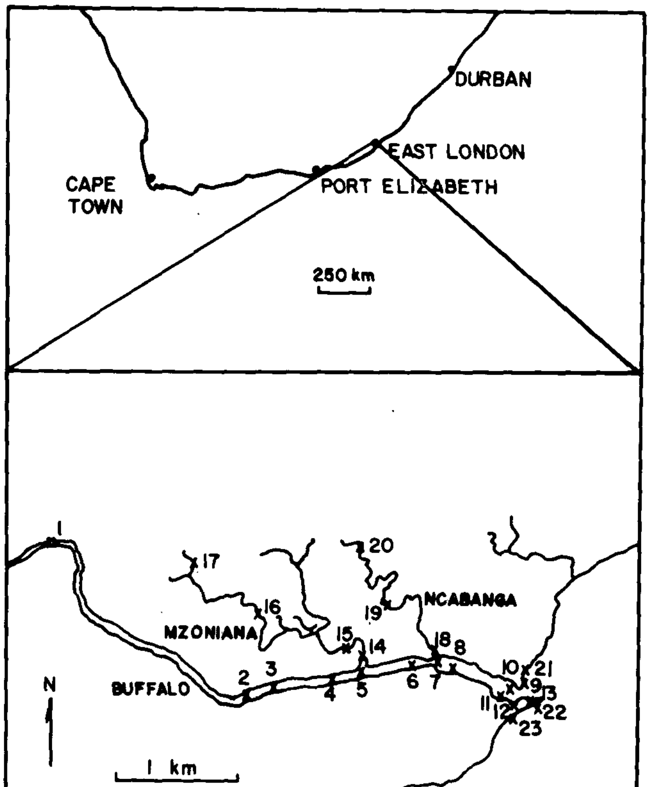

Figure 1
Distribution of sample sites in the Buffalo, Mzoniana and Ncabanga Rivers, East London.

*Current address: Council for Mineral Technology, Private Bag X3015, Randburg 2125, South Africa. To whom all correspondence should be addressed.
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samples collected from sites shown in Fig. 1 are listed in Table 1 The distribution of sodium, potassium and magnesium confirms a significant marine influence on the Buffalo River as far as station 2. However, marine waters did not significantly penetrate the Mzoniana or Ncabanga streams.

Trace metal concentrations were generally high throughout the study area, with the exception of copper, cobalt, cadmium and chromium which, at some sites in the estuary, were only slightly elevated above background and of the same order of magnitude as those reported for the Swartkops estuary (Watling and Watling, 1982a). In water samples from the Ncabanga stream and the Buffalo estuary, lead concentrations ranged from 13 $\mu g/\ell$ to 207 $\mu g/\ell$ and in the middle reaches of the Buffalo River nickel values reached 132 $\mu g/\ell$. These levels are up to one hundred times higher than the average values reported for Eastern Cape estuaries (Watling 1981). Zinc, nickel and chromium concentrations increased downstream in the Mzoniana and Ncabanga streams while copper and cadmium concentrations decreased. Cadmium levels in the streams ranged from 0,14 to 1,12 $\mu g/\ell$ while those typical of Eastern Cape estuaries are $<0,01$ $\mu g/\ell$ (Watling, 1981).

Mercury levels in estuarine water samples were excessively high, ranging from 1,45 $\mu g/\ell$ to 1,80 $\mu g/\ell$. These values were three times higher than those found in the Knysna Lagoon which

TABLE 1
CONCENTRATION OF METALS IN SURFACE WATERS

Site	Cu	Pb	Zn	Fe	Mn ($\mu g/\ell$)	Co	Ni	Cd	Cr	Hg	Na	K	Mg (μg/ml)	Ca	Sr
1	2,4	<0,1	1,4	460	30	<0,1	1,9	0,07	<0,1	0,12	114	1,5	22	132	0,2
2	0,2	27	0,4	177	13	0,1	2,3	<0,02	<0,1	1,68	11 200	370	1 420	420	11
3	1,6	50	0,1	9	9	0,2	2,6	<0,02	<0,1	1,60	11 400	360	1 480	430	11
4	2,5	28	2,1	200	14	0,2	2,2	<0,02	<0,1	1,40	10 900	300	1 300	430	11
5	7,9	207	16,0	231	22	1,4	132,0	0,07	0,2	1,45	10 900	300	1 280	430	10
6	7,2	34	2,0	27	24	0,4	2,3	<0,02	0,3	1,40	11 400	320	1 470	440	11
7	29,0	10	62,0	540	210	0,6	13,1	<0,02	10,3	1,68	11 200	310	1 400	430	10
8	1,3	13	2,6	54	10	0,2	6,1	<0,02	0,1	1,71	11 800	370	1 480	450	11
9	7,3	1,4	2,0	360	14	<0,1	1,8	<0,02	<0,1	1,21	11 400	320	1 460	390	10
10	7,5	1,0	2,0	350	5	<0,1	1,0	<0,02	0,1	1,20	11 300	310	1 440	380	10
11	6,2	26	1,6	120	14	0,1	1,3	<0,02	1,1	1,43	11 400	320	1 470	380	11
12	6,1	37	1,3	27	5	0,1	1,9	<0,02	1,9	1,46	11 500	340	1 460	380	12
13	4,3	100	0,8	19	2	<0,1	5,6	<0,02	2,8	1,80	12 000	360	1 490	410	13
14	4,1	1,2	28,0	250	604	1,1	33,9	0,14	0,2	1,76	190	12	18	31	1,4
15	9,1	9,6	26,3	272	442	1,6	47,6	0,14	5,2	2,86	190	13	19	31	1,2
16	15,3	1,0	21,0	217	74	1,1	4,6	0,42	2,7	2,91	160	14	15	25	1,2
17	2,2	12,0	12,3	191	31	1,7	106,0	0,04	0.4	1,53	90	4	13	21	1,1
18	5,3	15	10,7	205	55	6,9	8,9	0,48	7,2	1,32	8 200	290	900	320	8
19	4,4	64	21,7	263	610	0,2	4,8	0,14	5,4	1,31	140	10	19	28	1,3
20	5,0	8,1	14,7	259	440	2,4	68,0	1,12	1,0	1,79	160	4	22	31	1,1
21	5,9	1,1	1,1	7	1	<0,1	20,3	<0,02	0,1	1,50	13 000	360	1 200	420	12
22	4,4	78	0,7	11	4	<0,1	15,7	0,04	3,1	8,12	11 400	390	1 530	490	12
23	15,0	118	2,1	11	<1	0,1	0,4	0,02	0,1	1,47	11 300	360	1 290	530	11

TABLE 2
METAL CONCENTRATIONS IN SURFACE SEDIMENTS

Site	Cu	Pb	Zn	Mn	Co (μg/g)	Ni	Cd	Cr	Sr	Na	K	Ca (mg/g)	Mg	Al	Fe
1	50	74,0	109	520	13,2	21,3	2,9	73	57	7,4	1,6	5,8	5,6	19,5	36,0
2	26	7,0	26	170	6,0	14,3	1,2	26	26	5,2	2,2	3,3	3,1	19,8	27,0
3	15	1,1	31	110	6,7	18,5	1,9	47	34	5,4	3,2	4,5	4,2	25,5	24,5
4	16	2,0	36	120	6,0	12,4	0,11	46	32	5,4	3,0	3,9	2,6	27,2	22,5
5	37	6,8	56	170	4,6	12,3	0,12	38	30	2,8	1,5	3,1	1,6	22,0	28,0
6	190	20,0	460	445	29,0	135,0	0,53	16	24	3,9	1,3	3,9	2,1	44,5	85,0
7	109	55,0	150	135	9,5	20,5	0,19	50	135	3,5	1,9	4,1	4,4	34,0	29,0
8	845	32,0	720	790	43,5	19,0	0,36	18	73	3,5	1,5	2,6	2,4	44,0	89,0
9	530	36,0	110	173	14,2	27,0	0,10	34	500	5,0	1,7	18,8	4,2	26,0	21,5
10	127	45,0	105	165	7,3	16,1	0,14	47	490	6,0	3,1	10,5	4,5	32,0	26,0
11	436	127,0	105	160	11,2	30,0	0,16	42	510	6,0	2,0	10,5	4,2	21,7	18,5
12	120	41,0	83	130	6,1	13,0	0,13	44	310	6,1	1,6	14,5	4,0	29,5	23,0
13	6	2,0	13	85	0,4	1,2	0,04	9	126	2,4	0,9	18,0	5,1	4,5	5,5
14	42	1,5	170	350	7,2	20,5	0,10	58	56	0,5	6,1	3,6	4,1	49,5	35,0
15	46	40,0	145	510	8,3	28,5	0,12	31	36	1,0	10,3	2,3	6,7	75,0	12,0
16	25	15,0	72	290	6,9	3,1	0,10	69	25	1,1	8,8	2,1	5,3	80,0	36,0
17	21	12,0	60	290	4,3	8,0	0,07	32	20	1,1	8,0	2,2	5,1	72,0	32,0
18	850	4,3	230	465	9,6	17,0	0,11	57	220	1,0	2,2	22,5	3,2	18,5	36,5
19	8	52,0	21	340	8,0	23,0	0,10	76	20	0,8	3,3	2,0	3,0	22,7	25,5
20	16	27,0	100	175	4,9	6,9	0,06	20	23	0,4	1,6	2,3	1,4	12,0	11,5
21	3	0,4	7	42	0,2	3,0	0,01	19	760	1,9	0,6	9,9	2,9	3,4	3,4
22	2	0,4	5	40	0,1	3,1	0,01	12	840	1,8	0,6	10,2	3,1	3,9	3,0
23	3	0,6	6	40	0,1	3,0	0,01	16	900	1,6	0,6	11,0	3,3	3,2	2,6

is an area influenced by urban mercury contamination (Watling and Watling, 1982b) and one hundred times above background (0,025 $\mu g/\ell$) for rivers in the South-eastern Cape (Watling, 1981).

Metals in surface sediments

The distribution of elements in surface sediment samples is given in Table 2. All sites sampled during the survey had elevated levels of copper, lead, zinc, cobalt, nickel, cadmium and chromium. The highest concentrations were found in the area associated with sites 6, 8 and 18. These sites are situated opposite the confluence of the Mzoniana and the Ncabanga streams in the middle reaches of the estuary where the piston-like circulation of the estuarine water may result in maximum deposition. The elevated levels of trace metals found in samples collected at site 3 indicate that water with high trace metal loads from the streams and harbour, reach the upper reaches of the estuary during high tide.

The entire Buffalo estuary together with the Mzoniana and Ncabanga streams are contaminated to a greater or lesser extent by anthropogenic inputs of heavy metals. Copper, lead and zinc are the most ubiquitous contaminants with concentrations in excess of one hundred times the background level for Eastern Cape estuaries (Watling, 1981). The concentrations in the Mzoniana stream were highest at sites 14 and 15 where raw and partially treated sewage enter the stream.

Metals in core material

Eleven cores were collected in the Buffalo estuary and four in the Mzoniana stream at the sites shown in Figure 1. Only one core could be obtained from the Ncabanga stream as dolerite outcrops occur throughout the middle reaches and the stream is canalised below this.

Metal concentrations in every core sample, together with a scale drawing of the core and an inter-element correlation matrix have been detailed elsewhere (Watling *et al.*, 1983). A general correlation matrix for metal concentrations in core samples from the Buffalo River and one from the two streams are shown in Tables 3 and 4, with sampling sites referred to being shown in Figure 1. The geometric means for the concentrations of each element in each core have been calculated and are listed in Table 5. While this is not the ideal way to display core data, it does serve as an easy method for identifying anomalous areas (Watling and Watling, 1982b).

The relationship between potassium and aluminium, characteristic of clay minerals in the rivers between Mossel Bay and the Great Fish River (Watling, 1983) was absent in the study area. However, a good correlation exists between magnesium and aluminium in all the core material collected from the estuary and streams. This reflects a change in the primary geochemistry of the catchment from acidic to more basic igneous rocks, and from sandstones to shales and phyllites. The lack of correlation be-

TABLE 3
CORRELATION MATRIX FOR BUFFALO RIVER SEDIMENTS

	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr
Cu	—	0,449	0,326	-0,360	-0,200	0,597	0,742	0,674	0,271	0,278	0,692	0,054	0,865	-0,396	0,190
Pb		—	0,622	-0,108	-0,224	0,532	0,698	0,645	0,262	-0,039	0,373	0,177	0,601	-0,182	-0,040
Zn			—	0,305	-0,349	0,427	0,564	0,573	0,470	0,027	0,129	0,644	0,313	0,383	0,127
Fe				—	0,067	-0,090	-0,051	-0,133	0,181	0,020	-0,437	0,556	-0,416	0,806	0,310
Mn					—	-0,184	-0,331	-0,289	-0,397	-0,163	-0,082	-0,341	-0,185	-0,153	-0,031
Co						—	0,877	0,565	0,163	0,337	0,406	0,292	0,623	-0,216	0,344
Ni							—	0,717	0,398	0,273	0,468	0,375	0,748	-0,132	0,333
Cd								—	0,299	0,337	0,533	0,266	0,704	-0,138	0,343
Na									—	0,098	0,078	0,702	0,231	0,383	0,121
K										—	0,187	0,219	0,189	0,074	0,607
Ca											—	-0,091	0,861	-0,553	-0,029
Mg												—	0,026	0,749	0,310
Sr													—	-0,495	0,053
Al														—	0,257
Cr															—

TABLE 4
CORRELATION MATRIX FOR NCABANGA AND MZONIANA STREAMS SEDIMENTS

	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr
Cu	—	-0,169	0,478	0,134	0,007	-0,092	0,603	-0,210	0,036	-0,715	-0,058	0,163	0,130	0,405	0,306
Pb		—	0,284	0,481	0,575	0,539	0,194	0,646	0,782	0,314	0,510	0,475	0,443	0,486	0,562
Zn			—	0,789	0,697	0,720	0,726	0,659	0,593	-0,046	0,737	0,791	0,650	0,590	0,515
Fe				—	0,821	0,904	0,688	0,782	0,678	0,157	0,736	0,937	0,573	0,676	0,566
Mn					—	0,887	0,543	0,804	0,767	0,346	0,752	0,833	0,574	0,626	0,681
Co						—	0,583	0,872	0,745	0,404	0,804	0,905	0,596	0,566	0,510
Ni							—	0,369	0,512	-0,176	0,401	0,749	0,381	0,698	0,499
Cd								—	0,837	0,444	0,813	0,790	0,582	0,528	0,587
Na									—	0,309	0,646	0,752	0,499	0,698	0,754
K										—	0,411	0,274	0,227	0,016	-0,051
Ca											—	0,756	0,889	0,425	0,424
Mg												—	0,601	0,770	0,579
Sr													—	0,390	0,373
Al														—	0,776
Cr															—

TABLE 5
MEDIAN METAL CONCENTRATIONS FOR SEDIMENT CORES

Site (see Fig. 1)	µg/g									mg/g					
	Cu	Pb	Zn	Mn	Co	Ni	Cd	Cr	Sr	Na	K	Ca	Mg	Al	Fe
2	38,4	14,1	38	97	7,9	15,3	0,09	42,5	35	3,8	2,3	3,0	3,3	35,9	17,6
5	7,0	8,1	37	270	4,4	6,8	0,02	41,3	46	3,3	1,9	3,8	2,6	23,3	19,7
6	24,7	22,0	71	144	7,0	15,0	0,06	46,8	68	7,0	2,4	2,7	4,9	39,1	27,0
7	35,9	44,4	109	137	9,1	17,9	0,10	46,0	97	6,2	2,1	3,3	4,9	40,1	26,7
8	38,8	30,5	97	157	7,3	17,7	0,07	51,0	61	4,8	2,3	2,0	4,8	49,6	38,0
9	235	42,9	104	143	11,7	24,2	0,12	50,0	309	6,5	2,6	7,5	4,8	34,8	26,1
10	131	37,4	91	155	7,2	15,4	0,09	38,0	253	5,9	2,1	7,0	4,4	34,0	24,8
11	232	87,0	99	146	12,1	28,6	0,15	43,9	481	6,2	2,3	10,5	4,2	24,4	20,6
13	82	33,1	78	151	5,8	11,8	0,09	36,0	276	6,1	1,9	11,0	4,1	28,1	23,2
14	60	42,0	92	209	7,6	23,8	0,14	56,0	53	0,8	1,8	2,6	4,1	58,8	31,1
15	53	27,0	76	202	6,9	22,8	0,07	56,0	20	0,7	1,7	1,7	4,0	51,6	32,2
16	27	24,0	44	295	5,7	14,9	0,18	47,0	29	0,7	4,7	2,1	3,1	35,5	18,2
17	9	25,0	29	81	5,6	8,2	0,05	29,0	34	0,3	4,9	2,4	2,3	20,3	12,7
20	5	33,0	23	94	3,5	3,8	0,08	11,0	24	0,3	1,9	1,6	1,3	11,0	10,6

tween concentrations of copper, lead, zinc, cobalt, nickel, cadmium and chromium with iron, aluminium or calcium suggests that there was little or no coprecipitation or association of toxic elements with these facies components.

The lack of any association with these metals with the clay minerals indicates that they are likely to be of anthropogenic origin. The concentrations of copper, lead, zinc, cobalt, nickel and chromium in the Mzoniana and Ncabanga streams, were elevated above background for Eastern Cape estuaries (Watling, 1981) and increased downstream. In the Ncabanga stream with the exception of copper, the concentrations of all these metals were higher than those found in the harbour sediments. This could be attributed to the use of the upper reaches of the Ncabanga as a dump site for building refuse and used motor cars. Both the Mzoniana and Ncabanga streams flow for almost their entire length through urban areas. A sewage works, situated in the lower reaches of the Mzoniana stream, discharges its insufficiently treated effluent about 300 m above site 14 (Fig. 1). From its confluence with the Mzoniana stream, the Buffalo River flows over highly reducing muddy sediments rich in organic matter. High metal levels were recorded throughout this region with highest concentrations being found in the busy part of the harbour (sites 9, 10, 11). Lower, but still elevated, metal levels were found in samples taken at the head of the estuary. These elevated concentrations were not related to the changes in sedimentary facies which indicates that anthropogenic inputs from the harbour and the two study streams reach the upper estuary during high tides.

Conclusion

The results indicate that the Buffalo estuary and the Mzoniana and Ncabanga streams have the highest anthropogenic inputs of heavy metals yet recorded in estuaries of the Eastern Cape. High metal levels are found throughout the study area. The two streams are used as uncontrolled dumpsites for a wide variety of noxious waste materials as well as wastes from poorly serviced dwellings on their banks. High metal levels are consistently found in the water column indicating that metal input is persistent. Concentrations may be further elevated during periods of high rainfall and increased runoff. During these periods river flow rates are also increased and this may result in metals being transported to the lower estuary and harbour before they are precipitated under marine influence and become incorporated in the sediment.

Metal levels, especially copper, are particularly elevated near the busy loading quays in the Buffalo harbour. In this region copper concentrations can reach 800 µg/g. Elevated metal levels are also found in the upper estuary and are probably due to tidal movement of contaminated waters to these regions. Sediment is constantly dredged from the harbour and dumped approximately 2 km offshore. The extent to which this process redistributes metals both within the harbour area and offshore needs further detailed investigation.

The Buffalo River estuary is the most contaminated estuary between East London and Mossel Bay and its continued use as an unrestricted dumpsite for a wide variety of toxic substances must be vigorously discouraged if it is to retain the status of a river rather than an effluent canal.

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