Metal Surveys in South African Estuaries
I. Swartkops River

R.J. WATLING and **H.R. WATLING**
**Applied Spectroscopy Division, National Physical Research Laboratory, CSIR, P.O. Box 395, Pretoria 0001*

Abstract

Water, surface sediment and sediment core samples were collected from sites in the Swartkops River up to 15 km from the mouth and analysed for up to sixteen elements. The results indicate the presence of four main areas of contamination in the river, at Redhouse, Swartkops, the brickworks and Amsterdam Hoek. The accumulation of zinc, copper, lead and nickel by oysters grown at the mouth of the river confirms the presence of greater than normal metal concentrations in the river. Fishwater Flats outfall contributes metals to the nearshore marine environment, but the strong tidal sweep disperses the effluent relatively quickly so that metal build-up in the area is minimal. In general, metal levels in the Swartkops River are low and, as yet, the area cannot be described as "polluted" in the true sense of the word.

Introduction

The Swartkops River is joined by the Eland River soon after entering the coastal plain. It flows into Algoa Bay, some 10 km north-east of Port Elizabeth, through the marine clays and marls of the Cretaceous Uitenhage Series. The Eland River is, for the majority of its course, entrenched in Bokkeveld Shales while the Swartkops River has its upper reaches in Table Mountain Sandstone (Macnae, 1957 a, b).

In the upper reaches of the coastal plain the Uitenhage Series forms banks and the river bed is composed of fine silt, while in the lower reaches, the banks disappear and gravel is replaced by sand and mud as the river enters the sea. The banks may attain a height of four metres, but below the town of Redhouse, these are replaced by a broad flood plain with associated levées. These levées are eroded almost entirely below Swartkops village where salt marshes predominate. The mouth of the river has never closed in recorded history and the distribution of sandbanks has been relatively constant over the last eighty years.

This paper describes the results of a detailed trace-metal survey of the Swartkops River. Oysters *(Crassostrea margaritacea)* growing at the mouth of the river were found to contain considerably more zinc, copper and lead than had been determined for the same species growing at other locations on the South African coast (Table 1). This prompted the collection of surface water and sediment samples and of sediment cores from the river up to 15 km from the mouth. At the same time, oysters from the Knysna estuary were transferred to the mouth of the Swartkops River in order to obtain a measure of their rates of metal uptake.

The data obtained from this survey will serve as a baseline for future monitoring surveys should further industrialization or urban development take place along the Swartkops River.

TABLE 1
METAL CONCENTRATIONS IN *CRASSOSTREA MARGARITACEA* COLLECTED ALONG THE SOUTH AFRICAN COAST DURING 1977—1978
(Watling and Watling, 1979)

Location	Wet mass (g)	μg metal per g wet tissue		
		Zn	Cu	Pb
Knysna Heads	3,55	329	4	0,08
Keurboomstrand	3,19	141	3	0,02
Jeffreys Bay	2,31	94	5	0,01
Maitland River	5,19	77	3	0,01
Swartkops River	10,77	574	8	0,15
Cannon Rocks	9,02	157	1	0,03

Materials and Methods

Surface Water Samples

Surface water samples were collected in 2,5 ℓ high-density polyethylene bottles. Three subsamples were separated from each bulk. These were

(a) a 100 mℓ sample, acidified with 1 mℓ nitric acid, for the determination of calcium, magnesium, sodium and potassium;

(b) a 500 mℓ sample, acidified with 2 mℓ nitric acid, for the determination of mercury; and

(c) a 1 000 mℓ sample for the determination of zinc, cadmium, copper, lead, iron, manganese, nickel and cobalt. Ten millilitres of a buffered solution of sodium-diethyldithiocarbamate were added immediately to this sample which was then shaken for 5 min.

On returning to the laboratory, the chelated metals were extracted into chloroform. The organic phase was then separated, acidified with 2 mℓ nitric acid and evaporated to dryness (Watling and Watling, 1976). This organic residue was dissolved in 10 mℓ 1 N nitric acid for atomic absorption analysis.

Ten millilitres of a 25% (m/v) low-mercury potassium permanganate solution and 2 mℓ of concentrated sulphuric acid were added to the 500 mℓ acidified sample and the mixture left for 24 h to oxidise all organically-bound mercury to inorganic mercury.

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*Authors present address: Zoology Department, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000

Surface Sediment Samples

Surface sediment samples were collected using an aluminium scoop which was towed on the end of a nylon rope behind a boat. Three towing traverses were made at each site and a composite sample mixed from the three bulk samples. Approximately 500 g of each composite sample were air-dried between filter-paper sheets, disaggregated in a porcelain mortar and sieved through a 210 μm nylon screen. The fraction which passed through the screen was reserved for analysis.

Samples of 2 g each were transferred to 50 mℓ conical flasks and 10 mℓ concentrated nitric acid added. The samples were allowed to stand at room temperature until the effervescence associated with the breakdown of shell debris had ceased. The solutions were then evaporated to dryness. Ten millilitres of a 4:1 nitric-perchloric acid mixture were added and these solutions were fumed to dryness at 140°C. After cooling, the residue was dissolved in 10 mℓ 1 N nitric acid for flame atomic absorption analysis.

Samples were also prepared for mercury analysis using a simple oxidation procedure. Portions (2 g) of each sample were weighed into a ceramic boat which was then placed inside a combustion tube in a tube furnace preheated to 700°C. Oxygen was passed over the sample at a rate of 650 mℓ/min. The exhaust gases were bubbled through a solution containing 25 mℓ of 5% potassium permanganate and 50 mℓ of 14% sulphuric acid until combustion was complete (about 3 min). All the mercury evolved from the sample was absorbed by this solution (Watling, 1978a).

Sediment Core Samples

Sediment core samples of up to 600 mm in depth were collected using a stainless steel corer with PVC liners. The corer was pushed into the sediment to its full length or until an obstruction was encountered and a rubber stopper inserted into the top. The corer was then withdrawn and the PVC liner containing the sample removed. The inner tube was then sealed using polythene-covered corks and the whole sample frozen to −20°C. Frozen cores had to be stored for up to eight weeks but no changes in the nature of the sediment were observed during this period. Each core was cut longitudinally using a band-saw and both halves cleaned with a stainless steel knife. One half was reserved as a reference sample, resealed in polythene and refrozen. The other half was measured and catalogued sedimentologically before sampling.

Samples weighing approximately 4 g were taken at 20 mm intervals and also on obvious sedimentary boundaries, and oven-dried at 90°C for 24 h. Samples were then leached using the method described for surface sediments.

After sampling the core at 20 mm intervals for the trace metal determinations, the remainder was divided into 50 mm blocks. The final sample at the top (surface) of each core varied between 10 and 40 mm in length. Each block was air-dried between filter paper sheets, disaggregated and sieved through a 1 mm screen to remove large particles and plant debris. Samples (3 g) were oxidized in the tube furnace as described for the surface sediments and the evolved mercury trapped in acidified permanganate solution

Biological Samples

Numbers of *Crassostrea gigas* and *C. margaritacea* were transferred from Knysna to Port Elizabeth. These individuals were weighed and measured before being secured in plastic mesh cages supported on concrete blocks approximately 300 mm above the sandy bottom of the Blue Hole (Fig. 1, site 20). Six-month old *C. gigas* were used for this experiment which was terminated within one year, so that this exotic species would not mature and spawn in the bay. Samples were collected after four

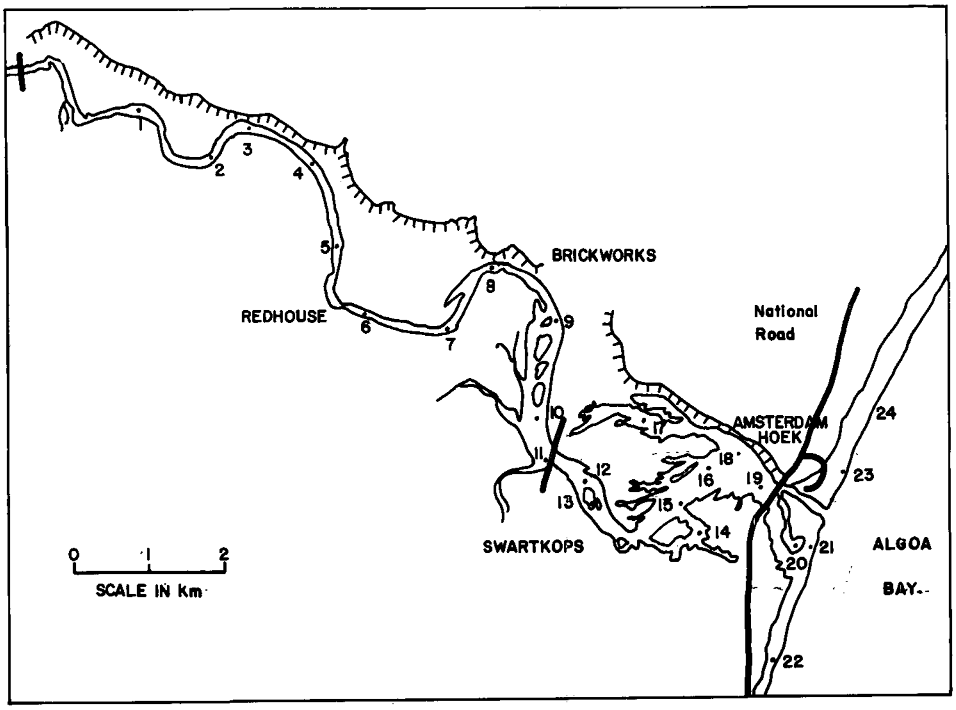

Figure 1
Map of the Swartkops River showing sample sites

and seven months. Individual wet tissues were removed carefully from their shells, washed, drained and frozen in a glass vial to await analysis.

The frozen specimens were thawed, weighed into clean dry flasks and oven-dried at 90°C for 24 h. The dried samples were reweighed, dissolved in 25 mℓ of redistilled analar-grade nitric acid and the sample solution boiled and evaporated to near dryness. The residue was dissolved in 25 mℓ of a 4:1 nitric-perchloric acid mixture. This solution was fumed to dryness at about 120°C. The white residue was redissolved in 10 mℓ v/v nitric acid and the metal concentrations in this solution determined by atomic absorption spectrometry.

Sample Analysis

A Varian-Techtron AA5 with AA6 readout module and BC6 background corrector was used for all measurements. Background correction was employed for the determination of zinc, lead, cadmium, cobalt and nickel, and the slotted tube (Watling, 1978b) was used for the determination of lead and cadmium.

Composite standards were prepared for each group of samples and contained major and trace elements at concentrations similar to those of the sample solutions. In the case of the water samples, sodium, potassium, calcium and magnesium were determined directly or on serial dilutions of the 100 mℓ acidified sample. Zinc, cadmium, copper, lead, iron, manganese, nickel and cobalt were determined on the prepared extracts using standards which had already undergone the extraction procedure (Watling and Watling, 1976). The concentrations of up to fifteen elements were determined in the acid-leach solutions of both surface sediments and sediment core samples, and on the dissolved oysters.

The excess permanganate in the prepared mercury-absorbing solutions was reduced using 10% (m/v) hydroxylammonium chloride in 20% v/v hydrochloric acid. Mercury concentrations in these samples were determined using an amalgamation trap and cold-vapour atomic absorption (Watling, 1978a).

Results and Discussion

Metals in Water

Eighteen samples of surface water were collected in the Swartkops River and estuary, and from Algoa Bay at sites adjacent to the river mouth during a survey of the area in April 1977 (Fig. 1). Element concentrations in these samples are listed in Table 2.

The distribution of sodium, potassium, calcium and magnesium (Fig. 2) indicates that there is a significant marine influence as far up the river as site 1, an area of shallow water adjacent to a causeway across the river. The sea-water contribution becomes progressively greater towards the mouth with tidal lag being approximately 70 min at Swartkops. Levels of copper, lead, zinc, iron, manganese, cobalt, nickel, cadmium and mercury are generally low although there are definite indications of metal input in the vicinity of Redhouse (site 6), Swartkops (site 13), Amsterdam Hoek (sites 18 and 19) and the Fishwater Flats sewage outfall (site 22) (Fig. 2). It is a little surprising that there is no apparent increase in metal load at the site of the warm water effluent input from the Swartkops Power Station.

Metals in Surface Sediments

Eighteen surface sediment samples were collected in the Swartkops River and estuary. Sample sites are coincident with those of the surface waters (Fig. 1). Element concentrations in these samples are listed in Table 3.

TABLE 2
METAL CONCENTRATIONS IN SURFACE WATER SAMPLES

Site	concentration (μg/ℓ)												
(refer Fig. 1)	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Hg	Na	K	Ca	Mg
1	4,8	1,1	1,7	139	75	<0,1	2,3	0,3	<0,005	7 600	199	296	990
2	5,0	0,4	1,6	154	62	<0,1	1,9	0,3	<0,005	8 200	240	309	1 050
3	3,8	0,8	1,7	137	46	0,1	2,1	0,2	<0,005	8 400	250	318	1 130
4	4,4	1,2	4,3	213	56	<0,1	1,9	0,2	<0,005	8 300	250	317	1 090
5	3,8	0,4	1,5	181	46	0,1	1,8	0,3	<0,005	8 900	270	329	1 130
6	4,8	1,2	3,0	256	51	0,1	1,7	0,3	<0,005	8 700	280	335	1 170
7	4,4	2,2	8,0	319	49	0,2	2,0	0,2	<0,005	9 100	240	331	1 140
8	3,6	1,9	2,3	305	34	0,2	1,6	0,3	<0,005	9 200	310	341	1 230
9	3,0	1,6	3,4	314	26	0,1	1,2	0,2	<0,005	9 400	310	371	1 250
11	4,8	1,2	1,9	94	21	<0,1	0,7	0,2	<0,005	10 800	310	399	1 370
13	1,4	2,5	2,5	118	6	0,2	0,9	0,2	<0,005	10 500	340	398	1 330
14	0,6	0,9	1,9	98	7	<0,1	0,6	0,2	<0,005	11 200	320	386	1 370
16	0,6	1,2	1,3	70	4	<0,1	0,3	0,2	<0,005	10 600	330	391	1 370
17	0,1	0,9	7,2	43	4	<0,1	0,4	0,1	<0,005	11 600	330	404	1 390
18	0,1	1,6	1,6	61	4	0,2	0,9	0,2	<0,005	12 900	390	397	1 410
20	1,2	0,6	1,3	19	13	<0,1	0,8	0,2	<0,005	12 900	340	433	1 660
22	1,4	4,7	3,1	155	6	0,5	2,2	0,6	<0,005	11 900	360	462	1 520
24	0,2	0,1	1,0	3	2	<0,1	0,5	0,2	<0,005	11 800	370	463	1 530

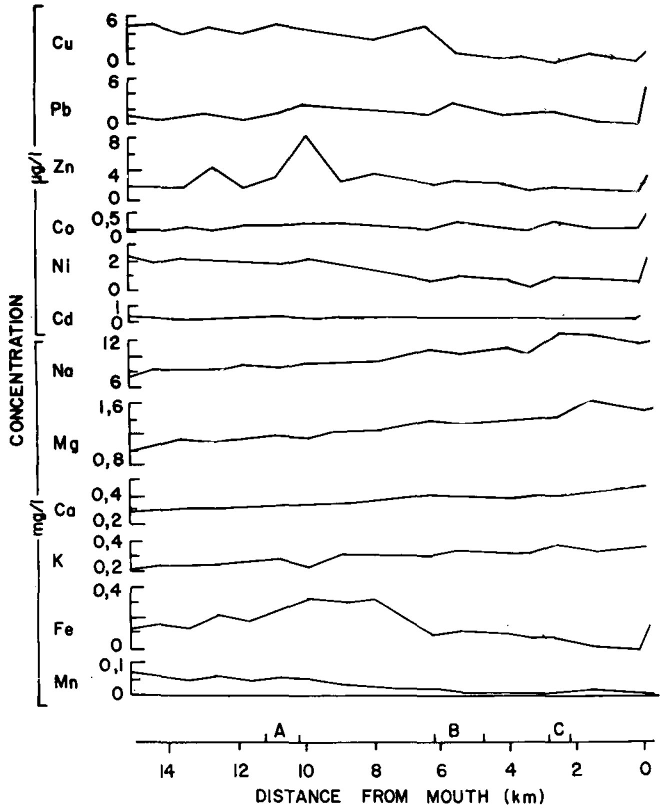

Figure 2
Distribution of metals in water samples along the Swartkops River. A. Redhouse, B. Swartkops, C. Amsterdam Hoek

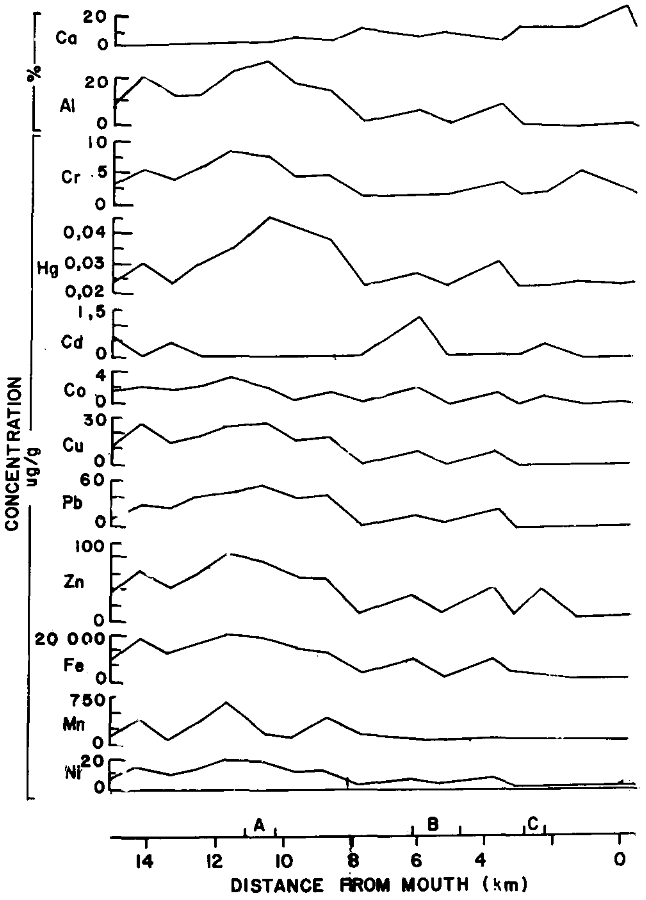

Figure 3
Distribution of metals in surface sediments along the Swartkops River. A. Redhouse, B. Swartkops, C. Amsterdam Hoek

The distribution patterns of copper, lead, zinc, mercury, iron, nickel and cobalt (Fig. 3) are almost identical, there being a broad anomalously high region associated with Redhouse. This may represent local metal input from the towns of Perseverence and Uitenhage, both of which discharge effluent into the Swartkops River. Downstream of the brickworks channel, Swartkops town, Moddersspruit, Tippers Creek and Amsterdam Hoek all show locally elevated metal distribution patterns. However, metal concentrations have once again dropped to background levels once the lower estuary and sea are reached.

TABLE 3
METAL CONCENTRATIONS IN SURFACE SEDIMENT SAMPLES

Site (refer Fig. 1)	concentration (µg/g) Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Hg	Na	K	Ca	Mg	Sr	Al	Cr
1	12,4	10,0	36,8	14 000	130	1,6	8,0	0,6	0,008	9 600	5 600	10 000	452	600	134 000	3,0
2	26,2	27,4	63,8	28 000	400	2,0	14,0	<0,2	0,020	16 400	12 500	6 000	916	600	312 000	5,2
3	14,6	23,8	41,2	18 000	50	1,6	10,0	0,4	0,006	15 740	7 000	10 000	562	600	190 000	3,6
4	18,0	38,4	59,6	24 000	300	2,0	13,4	<0,2	0,019	14 800	10 600	8 000	816	800	192 000	5,4
5	24,8	43,0	84,6	30 000	700	3,2	19,4	<0,2	0,029	14 200	10 600	12 000	972	1 400	340 000	8,2
6	27,0	53,2	73,4	28 000	150	2,0	17,6	<0,2	0,050	21 800	13 600	18 000	1 136	1 200	386 000	7,0
7	16,8	38,6	57,2	22 000	100	0,4	12,4	<0,2	0,044	11 400	9 200	38 000	752	3 600	260 000	4,0
8	18,4	17,8	52,2	18 000	400	1,2	12,0	<0,2	0,035	8 800	8 550	180 000	688	2 600	206 000	4,2
9	1,6	1,4	5,8	6 000	140	<0,2	2,2	<0,2	0,005	2 000	620	104 000	306	7 200	24 000	1,0
11	9,6	16,6	30,2	14 000	60	1,8	5,6	1,2	0,013	4 800	3 160	59 200	372	3 400	98 000	1,2
13	1,8	6,0	9,4	2 000	40	<0,2	2,8	<0,2	0,005	2 000	1 020	84 000	270	4 400	16 000	1,2
14	8,6	24,0	42,6	14 000	70	1,2	6,8	<0,2	0,021	6 200	5 900	38 000	488	3 000	132 000	3,2
16	1,4	0,8	6,8	6 000	30	<0,2	2,2	<0,2	0,005	3 200	660	122 000	310	6 400	18 000	1,6
17	3,4	11,0	25,0	4 000	500	1,2	5,0	<0,2	0,035	5 000	2 460	86 000	412	4 800	66 000	1,8
18	1,4	0,8	38,2	4 000	40	0,8	1,6	0,4	0,006	2 600	620	138 000	352	9 000	16 000	2,0
20	1,4	2,1	3,4	700	20	<0,2	0,4	<0,2	0,009	2 500	470	131 000	2 470	1 340	1 090	5,3
22	1,5	2,0	3,4	700	20	<0,2	0,4	<0,2	0,008	2 400	580	136 000	322	10 400	4 000	1,8
24	1,6	3,0	5,0	900	30	0,2	0,6	<0,2	0,007	2 600	1 620	260 000	492	23 400	28 000	2,4

The distribution of the major sediment facies shows a dramatic change in the vicinity of Swartkops as clay assemblages give way downstream to a true silicate-carbonate sequence. A general correlation matrix for the surface sediments (Table 4) indicates a series of extremely good inter-element relationships. Concentrations of copper, lead, zinc, nickel and chromium have a strong dependence on both iron and clay minerals, suggesting initial transport of metals in solution and co-precipitation with iron hydroxides and flocculated clay minerals in areas of high salinity.

Note: Scatter plots were prepared and a correlation coefficient calculated for each of the possible metal/metal relationships; significant relationships are underlined. It will be noticed that certain relatively high correlation coefficients have not been underlined. This is because localized grouping of data points may tend to give erroneously high values. This situation can be established by referring to the scatter plots. Conversely, certain low correlation coefficients have been indicated to be significant. For example, in the case of magnesium, a single anomalously high magnesium value is sufficient to make otherwise strong relationships appear weak. The correlation coefficients which were computed in the absence of this anomalous value are shown in parentheses in Table 4.

Metals in Sediment Cores

Eighteen sediment cores were collected in the Swartkops estuary from convenient sites in the immediate vicinity of surface sediment sampling sites. Metal concentrations in every core sample, together with a scale drawing of the core and an interelement correlation matrix, have been detailed elsewhere (Watling and Watling, 1979).

A general correlation matrix for metal concentrations in core samples is shown in Table 5, the sample sites referred to being shown in Figure 1. It can be seen that there is an independent build-up of the carbonate facies, as indicated by the strong correlation between strontium and calcium. This facies is unrelated to the clay facies, and the two sedimentary types also show a strong antipathetic relationship, a situation already identified in the surface sediments.

The geometric means for the concentrations of all the study elements in each core are listed in Table 6. While this is not an ideal way to display core data, it does serve as an easy method for identifying anomalous areas. These results confirm that the main areas of metal input to the Swartkops River are associated with the towns of Redhouse, Swartkops and Amsterdam Hoek and with the brickworks.

The core collected from site 12 (Fig. 1), adjacent to

TABLE 4
CORRELATION MATRIX FOR SWARTKOPS RIVER SURFACE SEDIMENTS

	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr	Hg
Cu		0.897	0.928	0.974	0.575	0.810	0.972	0.038	0.936	0.981	0.778	0.245 (0.941)	0.567	0.979	0.803	0.663
Pb			0.898	0.916	0.467	0.735	0.934	0.105	0.897	0.927	0.704	0.241 (0.915)	0.514	0.934	0.784	0.763
Zn				0.941	0.620	0.850	0.954	0.021	0.861	0.924	0.759	0.160 (0.895)	0.549	0.934	0.776	0.690
Fe					0.555	0.824	0.972	0.007	0.915	0.963	0.810	0.175 (0.907)	0.597	0.960	0.761	0.622
Mn						0.685	0.652	0.240	0.430	0.537	0.466	0.100 (0.550)	0.338	0.579	0.549	0.513
Co							0.831	0.247	0.756	0.761	0.708	0.107 (0.712)	0.537	0.781	0.674	0.427
Ni								0.094	0.917	0.963	0.799	0.197 (0.933)	0.588	0.976	0.811	0.711
Cd									0.076	0.135	0.127	0.227 (0.728)	0.129	0.102	0.305	-0.252
Na										0.948	0.740	0.248 (0.911)	0.557	0.935	0.774	0.604
K											0.760	0.236 (0.956)	0.536	0.972	0.796	0.702
Ca												0.085 (0.564)	0.899	0.740	-0.506	-0.476
Mg													0.338 (0.418)	0.228 (0.957)	0.655 (0.953)	0.225 (-0.270)
Sr														0.526	0.460	0.339
Al															0.802	0.752
Cr																0.570
Hg																

TABLE 5
GENERAL CORRELATION MATRIX FOR SWARTKOPS RIVER CORES

	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr
Cu		0,790	0,899	0,648	0,121	0,754	0,833	0,427	0,602	0,848	−0,261	0,247	−0,216	0,879	0,876
Pb		-	0,817	0,435	0,017	0,542	0,648	0,493	0,578	0,724	−0,136	0,262	−0,157	0,779	0,728
Zn				0,708	0,061	0,759	0,869	0,583	0,701	0,934	−0,265	0,284	−0,242	0,947	0,935
Fe				-	0,186	0,776	0,822	0,339	0,421	0,761	−0,476	0,105	−0,325	0,682	0,748
Mn					-	0,444	0,373	−0,261	−0,241	0,048	−0,439	−0,173	−0,261	0,071	−0,012
Co						-	0,955	0,133	0,296	0,788	−0,663	0,024	−0,423	0,815	0,755
Ni							—	0,287	0,438	0,890	−0,582	0,104	−0,401	0,897	0,848
Cd								—	0,678	0,547	0,248	0,374	0,025	0,474	0,548
Na									—	0,678	0,304	0,410	0,098	0,634	0,693
K										—	−0,286	0,259	−0,241	0,952	0,928
Ca											—	0,290	0,601	−0,336	−0,241
Mg												—	0,131	0,253	0,296
Sr													—	−0,272	−0,196
Al														—	0,914
Cr															—

TABLE 6
GEOMETRIC MEANS FOR METAL CONCENTRATIONS IN SEDIMENT CORES

							concentration (μg/g)									
Site	Hg	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr
1	0,001	2,7	4,4	6,9	3 768	210	1,2	2,7	<0,01	1 753	685	139	685	12	2 377	3,9
2	0,003	1,9	4,4	7,5	3 799	156	1,0	2,2	<0,01	1 778	620	140	678	4	2 459	4,2
3	0,003	2,5	5,6	10,7	6 007	46	1,1	2,1	0,02	2 840	933	239	1 004	5	3 139	7,5
4	0,005	2,7	4,2	10,5	5 702	27	0,9	2,4	0,02	2 448	880	597	1 132	6	3 165	9,8
5	0,010	3,9	6,8	17,6	13 000	33	1,3	3,5	0,04	2 922	1 719	1 028	2 159	5	5 749	16,5
6	0,003	2,1	5,1	9,0	2 762	77	0,9	1,7	<0,01	2 107	779	2 284	855	8	2 996	6,2
7	0,011	3,0	6,9	11,0	3 330	15	0,8	1,9	0,03	2 298	1 026	3 058	903	15	4 341	10,5
8	0,012	6,3	12,4	30,2	8 333	57	2,1	5,2	0,03	3 816	2 504	2 519	2 892	15	12 205	25,6
9	0,025	5,7	13,4	25,2	5 632	41	1,2	3,1	0,05	3 516	1 798	51 349	5 131	411	8 395	19,9
10	0,023	3,0	10,6	12,8	2 600	19	0,5	1,4	0,05	3 134	909	81 703	3 579	648	4 383	8,2
12	0,035	3,7	12,0	22,9	3 699	26	0,8	2,7	0,06	3 404	1 817	53 889	3 094	440	7 611	14,1
15	0,005	1,6	4,2	6,0	1 170	14	0,1	0,4	0,04	2 921	593	90 031	2 804	737	2 240	4,9
18	0,057	3,6	8,5	21,9	6 506	31	0,6	2,1	0,11	4 225	1 655	86 865	3 963	740	5 554	17,8
19	0,005	1,2	2,9	1,6	741	12	0,4	0,2	0,03	2 869	426	102 152	2 859	883	867	3,3
20	0,003	1,7	2,6	4,0	617	29	0,1	0,4	0,02	2 980	589	109 758	2 391	1 187	1 110	4,9
21	0,001	1,8	2,5	3,6	584	29	0,1	0,3	0,02	2 382	535	125 515	2 516	1 902	1 077	4,6
22	0,001	1,7	3,4	2,8	680	13	0,2	0,3	0,01	2 851	308	111 485	2 144	1 099	681	2,8
23	0,003	1,2	3,8	2,3	754	17	0,2	0,2	0,01	2 597	290	72 654	2 158	1 363	708	3,8

Swartkops town, is particularly interesting with respect to metal build-up with time. The core is 56 cm long and consists of a series of dark grey medium sands and associated shell debris, (sample 1 was taken at the sediment/water interface). The sands become progressively finer as the surface is approached. Two distinct metal concentration sub-populations exist within this core (Table 7). Between samples 19 and 20, 36 cm below the sediment/water interface, there is a sharp increase in trace metal concentrations although the sedimentary facies remains constant. In many cases the interelement relationships in the "high-metal" sub-populations are not as strongly developed as in the low metal sequence (Table 8). Six distinct distribution patterns can be identified.

The first type of interelement relationship is represented by that of zinc with nickel (Fig. 4 a). The sub-populations are spatially separated from each other and an excellent relationship exists between these two elements. Regression lines drawn for each population are almost parallel to each other. The relationship between copper and zinc is shown in Figure 4 b. Here the sub-populations are spatially separated from each other with an excellent inter-element relationship for the low concentration population but a weaker correlation in the high concentration population. Both populations have the same regression line. In the case of iron and aluminium (Fig. 4 c) there is no spatial separation of the two populations and there is a strong inter-element relationship between both variables. The fourth

TABLE 7
METAL CONCENTRATIONS (µg/g) IN SWARTKOPS TOWN CORE

Sample	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr
1	4,0	19,3	27,0	3 430	30	0,9	2,8	0,060	2 720	1 890	56 400	3 050	423	7 670	14,1
2	4,2	16,2	25,9	4 080	29	0,9	2,8	0,064	3 510	1 820	59 900	3 040	482	7 710	17,4
3	4,6	19,5	29,8	4 010	40	0,9	3,1	0,056	4 470	2 060	52 400	3 530	391	8 270	20,0
4	4,7	17,7	29,8	4 580	40	1,1	3,3	0,064	4 330	2 190	57 500	3 500	429	9 170	21,5
5	5,1	19,7	33,8	4 310	41	1,0	4,5	0,068	4 400	2 210	48 800	3 670	389	9 070	21,0
6	4,5	17,1	29,3	4 160	28	0,9	3,1	0,059	4 050	2 050	54 400	3 440	421	8 650	17,9
7	4,1	18,5	25,3	3 570	23	0,7	2,6	0,058	3 460	1 720	52 500	3 010	420	7 410	15,0
8	4,3	14,9	27,4	3 970	23	0,8	2,9	0,067	3 640	1 830	59 300	3 140	475	8 040	17,6
9	3,6	12,3	23,6	3 280	26	0,7	2,5	0,061	3 090	1 510	50 000	2 720	389	7 020	14,5
10	4,8	20,9	34,4	3 770	32	0,9	3,5	0,079	3 770	2 290	52 900	3 570	392	3 320	17,9
11	4,5	18,8	30,9	3 890	35	0,9	3,2	0,064	3 760	2 040	49 800	3 380	416	8 390	17,4
12	4,6	11,8	27,5	4 060	39	0,9	3,0	0,060	3 430	1 760	48 900	3 070	373	8 150	19,3
13	3,9	11,4	25,1	3 190	26	0,7	2,6	0,055	3 190	1 870	51 700	3 060	413	7 160	12,8
14	4,6	11,7	28,7	3 790	29	1,0	3,2	0,068	3 250	1 840	47 800	3 080	398	8 030	15,9
15	5,0	12,6	28,1	4 030	26	1,0	3,1	0,067	3 380	2 030	50 900	3 140	400	8 830	17,1
16	5,3	12,2	30,6	4 350	32	1,0	3,3	0,075	3 550	2 130	47 400	3 250	383	9 540	19,1
17	4,4	9,9	24,5	3 990	31	0,9	2,8	0,061	2 990	1 450	44 300	2 730	396	7 680	17,9
18	4,5	11,1	26,6	3 870	25	0,8	2,9	0,068	3 130	1 930	49 000	3 140	408	8 130	18,2
19	5,2	12,1	31,2	4 370	33	1,0	3,5	0,079	4 090	2 470	53 000	3 720	451	9 770	18,4
20	1,9	5,0	9,8	2 470	11	0,3	1,4	0,049	2 210	1 080	43 800	2 070	384	4 780	8,4
21	2,4	6,9	13,6	3 450	22	0,6	2,1	0,063	3 250	1 700	58 200	2 950	491	6 820	10,5
22	2,3	7,0	12,8	3 090	13	0,7	2,0	0,058	3 090	1 560	61 800	2 980	515	6 690	7,9
23	2,6	6,6	15,2	3 600	21	0,8	2,4	0,056	3 280	1 800	61 600	3 170	521	7 380	7,6
24	2,3	5,8	12,4	3 020	21	0,5	1,9	0,047	2 820	1 590	5 300	2 740	460	6 220	7,4
25	3,0	8,2	17,4	3 980	26	0,8	2,6	0,057	3 610	2 020	65 200	3 480	535	7 960	9,8
26	2,3	5,9	12,2	3 650	18	0,7	2,1	0,050	3 170	1 700	58 500	3 010	500	6 990	8,3
27	1,7	4,7	9,0	2 420	11	0,4	1,5	0,041	2 810	1 200	54 800	2 440	479	5 070	5,7
28	2,6	5,8	11,3	3 250	16	0,4	1,9	0,055	3 010	1 590	58 000	2 840	542	6 090	7,5
29	2,1	5,1	10,4	2 790	18	0,4	1,8	0,052	2 990	1 400	59 500	2 820	526	5 750	4,9

TABLE 8
INTERELEMENT CORRELATION MATRIX FOR SWARTKOPS TOWN CORE DATA

	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr
Cu	—	0,786	0,975	0,842	0,843	0,879	0,961	0,809	0,689	0,780	−0,434	0,691	−0,655	0,908	0,951
Pb		—	0,878	0,618	0,761	0,719	0,801	0,562	0,675	0,672	−0,208	0,645	−0,540	0,680	0,811
Zn			—	0,793	0,862	0,870	0,967	0,784	0,711	0,794	−0,399	0,719	−0,670	0,879	0,944
Fe				—	0,815	0,906	0,892	0,722	0,807	0,831	−0,076	0,812	−0,310	0,948	0,835
Mn					—	0,851	0,876	0,597	0,759	0,746	−0,306	0,734	−0,573	0,825	0,867
Co						—	0,930	0,714	0,708	0,799	−0,163	0,767	−0,469	0,937	0,852
Ni							—	0,824	0,778	0,882	−0,270	0,829	−0,536	0,955	0,911
Cd								—	0,546	0,763	−0,229	0,658	−0,378	0,809	0,728
Na									—	0,828	0,057	0,900	−0,191	0,800	0,716
K										—	0,034	0,955	−0,220	0,914	0,696
Ca											—	0,174	0,886	−0,152	−0,459
Mg												—	−0,089	0,865	0,623
Sr													—	−0,403	−0,709
Al														—	0,849
Cr															

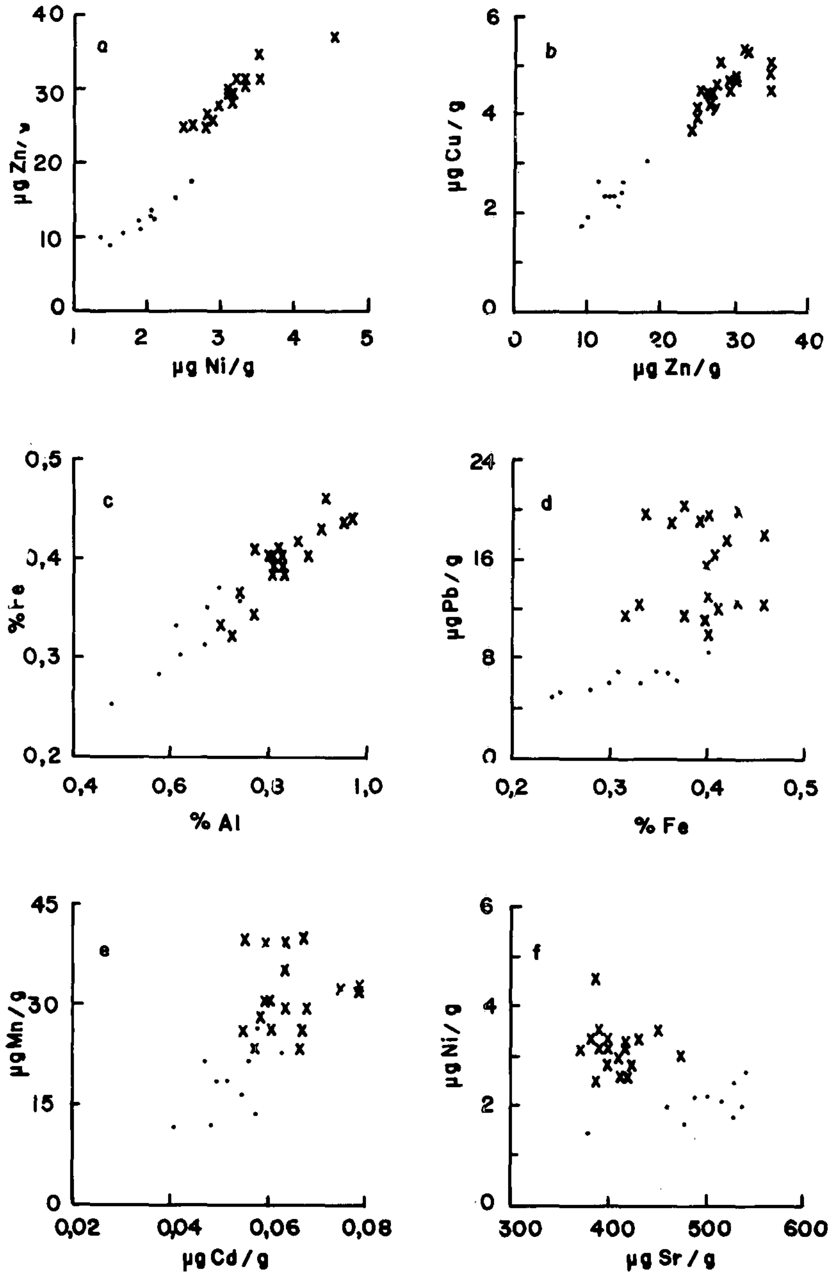

Figure 4
Interelement relationships (illustrated by scatter plots) for the Swartkops town sediment core.
x *Samples 1—19;* ● *Samples 20—29*

type of inter-element relationship is illustrated in the iron-lead scatter plot (Fig. 4 d). Here, there is no spatial separation of the two sub-populations. However, the inter-element relationship in the low-concentration population is excellent while that in the high-concentration population is very weak. The manganese-cadmium scatter plot (Fig. 4 e) is an example of the complete absence of a relationship between two metals. Not only is there no apparent inter-element relationship but thee is also no spatial separation of the sub-populations. However, in the case of nickel and strontium (Fig. 4 f), while there is no significant inter-element relationship there is still a spatial separation of the two sub-populations. In addition, there is an indication that the regression line representing this inter-element relationship has a negative slope.

From these relationships it is apparent that there has been a swift increase in toxic metal input to the upper section of the core, relative to that in the lower section, while the sedimentary facies has not changed significantly. Consequently, this input must be associated with the growth of Swartkops town itself, and hence be classed as man-derived rather than as the result of changing geological provenance. Although cores from three other sites, at Redhouse, the brickworks and Amsterdam Hoek, also exhibit evidence of increased metal loading of the sediment as a result of human activities, none of these cores present as clear a picture as that from Swartkops.

Accumulation of Metals by Oysters

The ability of molluscs to accumulate metals has been used with varying degrees of success to indicate the presence of, and even to monitor the extent of, metal pollution in the marine environment (Darracott and Watling, 1975). However, in most cases these studies have only involved the collection and analysis of samples from a number of sites, followed by a discussion relating the results to natural or man-made sources of metals. Such studies are valuable in that they provide useful background information about a particular area but if molluscs are going to be used to monitor low-level chronic pollution or the intermittent addition of pollutants to water, a more systematic method must be adopted. It is not sufficient that metal accumulation can be demonstrated in laboratory studies, where the metals being tested are necessarily present in much greater than normal concentrations in order to achieve measurable accumulation in a suitably short period. Such studies must be complemented by a

TABLE 9
METAL ACCUMULATION BY *CRASSOSTREA GIGAS* GROWN IN THE BLUE HOLE, COMPARED WITH ACCUMULATION BY THE SAME SPECIES GROWN IN KNYSNA ESTUARY DURING THE SAME PERIOD (1977)

		Wet mass (g)	Concentration (μg/g) in wet tissue								
			Zn	Cd	Cu	Pb	Fe	Mn	Ni	Co	Cr
BLUE HOLE											
Initial Sample	April	4,58	122	0,88	11,3	0,05	16	1,4	0,05	0,03	0,17
Site A*	August	5,91	286	0,28	25,4	0,33	87	3,6	0,13	0,05	0,65
Site B*		6,86	186	0,24	19,4	0,20	68	3,1	0,09	0,02	0,47
Site A*	November	10,68	305	0,14	30,3	0,34	72	4,7	0,19	<0,01	0,25
Site B*		11,00	223	0,14	28,8	0,31	63	3,6	0,16	0,01	0,32
KNYSNA	March	6,36	112	1,03	10,5	0,07	22	1,6	0,04	0,02	0,29
	April	4,58	122	0,88	11,3	0,05	16	1,4	0,05	0,03	0,17
	May	5,49	99	1,10	9,6	0,04	7	1,0	0,06	0,02	0,20
	June	10,29	125	0,42	11,8	0,12	81	2,2	0,05	0,02	0,35
	July	9,59	113	0,28	7,8	0,06	58	2,8	0,08	0,03	0,24
	August	7,67	150	0,50	13,5	0,16	75	2,9	0,08	0,04	0,39
	September	13,32	122	0,26	8,3	0,04	43	2,0	0,03	0,02	0,14
	October	10.14	121	0,28	11,5	0,07	54	2,1	0,10	<0,01	0,16
	November	6,96	224	0,41	29,4	0,07	71	5,1	0,10	0,04	0,24
	December	7,22	166	0,26	21,9	0,06	51	3,0	0,08	0,02	0,08

*Sites A and B in the Blue Hole were approximately 500 m apart, site B being closer to the mouth of the Swartkops River

TABLE 10
METAL ACCUMULATION BY *CRASSOSTREA MARGARITACEA* GROWN IN THE BLUE HOLE, COMPARED WITH ACCUMULATION BY THE SAME SPECIES GROWN IN KNYSNA ESTUARY DURING THE SAME PERIOD (1977)

		Wet mass (g)	Concentration (μg/g) in wet tissue								
			Zn	Cd	Cu	Pb	Fe	Mn	Ni	Co	Cr
BLUE HOLE											
Initial Sample	April	7,93	96	0,84	1,4	0,10	5	0,4	0,02	<0,01	0,51
Site A*	August	4.46	176	0.61	2,6	0,07	24	0,6	0,05	0,02	0,46
Site B*		5,56	226	0,58	5,7	0,09	17	0,6	0,09	0,04	0,56
Site A*	November	3,96	260	0,28	6,7	0,32	39	1,0	0,19	0,02	0,67
Site B*		3,82	244	0.34	8,5	0,20	26	0,8	0,09	<0,02	0,25
KNYSNA	March	4,96	109	1,15	1,1	0,09	7	0,5	0,05	0,04	0,48
	April	7.98	96	0,84	1,4	0,10	5	0,4	0,02	<0,01	0,51
	May	5,42	94	1,26	1,0	0,06	11	0,8	0,04	0,03	0,27
	June	9,12	106	1,98	2,0	0,06	14	1,1	0,01	0,01	0,37
	July	8,90	82	1,07	1,4	0,04	12	0,7	<0,01	0,02	0,30
	August	6,36	155	1,15	6,0	0,14	19	0,5	0,04	0,02	0,44
	September	8.55	150	1,00	4,0	0,06	17	0,5	0,07	0,02	0,17
	October	6,54	160	0,96	3,4	0,05	17	0,5	0,03	<0,01	0,23
	November	7,39	132	0,94	4,1	0,05	16	0,9	0,04	0,01	0,38
	December	5.14	139	0,60	2,0	0,05	14	0,3	0,04	0,02	0,25

*Sites A and B in the Blue Hole were approximately 500 m apart; Site B being closer to the mouth of the Swartkops River demonstration that the same species will accumulate metals under natural conditions.

The method which was investigated in the present study was the introduction of individuals containing near base-line metal concentrations into an area suspected of being contaminated by metals. *C. margaritacea* collected from the Blue Hole at the mouth of the Swartkops River (Fig. 1, site 20), were found to contain higher zinc, copper and lead concentrations than have been determined for the same species growing at other locations on the South Africa coast (Table 1). It was decided that this site afforded an opportunity to test the ability of this species to accumulate metals under natural conditions, as opposed to laboratory trials, and to compare the rates of metal uptake with those achieved by the Pacific oyster *C. gigas*, a known bioaccumulator (Darracott and Watling, 1975).

Metal concentrations in *C. gigas* and *C. margaritacea* collected during this experiment are shown in Tables 9 and 10 respectively and the results are compared with those obtained from a similar experiment carried out in the Knysna estuary.

Considerable accumulation of zinc, copper, lead and nickel by *C. gigas* occurred during the seven months that these oysters were in the Blue Hole. The accumulation of these metals is expected in view of the results of the water and sediment analyses already described. However, some accumulation of zinc and copper is also observed for *C. gigas* growing in the Knysna estuary, an "unpolluted" area, and the concentrations achieved are of the same order as those found in the Blue Hole oysters. The possibility therefore exists that these concentrations may be a seasonal phenomenon. Zinc, copper and, to a lesser extent nickel concentrations tend to increase during the spring and summer months. Such seasonal concentration variations have been reported for other molluscs. Bryan (1973) thought such changes were related to food supply while Phillips (1976) suggested that seasonal fluctuations were at least partly due to the variation of wet mass (water content) with season.

Cadmium concentrations, which are suspected to be slightly above background in Knysna oysters, have become lower during the seven-month experiment at the Blue Hole. Nevertheless, the variation in concentrations which has been observed may be seasonal, cadmium concentrations being higher during the autumn and winter months. The results obtained for lead and nickel are unambiguous and clearly indicate the accumulation of these elements by *C. gigas* at the mouth of the Swartkops River.

Considerable accumulation of zinc, copper, lead and nickel by *C. margaritacea* occurred during the seven months these oysters were in the Blue Hole (Table 10). In all cases the seasonal concentration variations in the Knysna oysters are smaller. These results clearly indicate that *C. margaritacea* is being subjected to greater than normal amounts of these metals, which are presumably derived from the Swartkops River.

Both *C. gigas* and *C. margaritacea* are acting as bioaccumulators. However, for the purposes of monitoring rates of metal uptake with time, the use of the indigenous species yields more useful results.

Conclusions

On the basis of metal concentrations, the Swartkops estuary near Port Elizabeth exhibits clear indications of man-derived contamination. The build-up of metals is, however, closely associated with the sources of input and consequently there is little chance of widespread pollution. The towns of Redhouse, Swartkops and Amsterdam Hoek, together with the brickworks, are the areas most affected. The Swartkops area may obtain a contribution from the power station effluent and Uitenhage and Despatch effluents probably contribute to the contamination of the Redhouse area.

The Fishwater Flats sewer outfall appears to be a further source of contaminants, although metal levels are only elevated in the water column and not in the sediment. This source may not be significant in terms of metal build-up, as tidal sweep disperses the effluent relatively quickly.

Oysters grown at the mouth of the river have accumulated zinc, copper, lead and nickel, thus indicating the presences of greater than normal metal concentrations in the estuary. These results corroborate the sediment and water data.

In general, the metal levels determined for the Swartkops estuary should not be a cause for concern at this stage. Nevertheless, specific sites of input have been identified and these will be monitored closely in the future in order to establish long-term trends. On the basis of such monitoring data it should be possible to minimise future increases in metal levels by instituting suitable control measures.

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References

BRYAN, G.W. (1973) The occurrence and seasonal variation of trace metals in the scallops *Pecten maximus* (L) and *Chlamys opercularis* (L). *J. mar. biol. Ass. U.K.* 53 145.

DARRACOTT, A. and WATLING, H. (1975) The use of molluscs to monitor cadmium levels in estuaries and coastal marine environments. *Trans. R. Soc. S. Afr.* 41 325.

MACNAE, W. (1957a) The ecology of the plants and animals in the intertidal regions of the Zwartkops estuary near Port Elizabeth, South Africa. Part I. *J. Ecol.* 45 113.

MACNAE, W. (1957b) The ecology of the plants and animals in the intertidal regions of the Zwartkops estuary near Port Elizabeth, South Africa. Part II. *J. Ecol.* 45 361.

PHILLIPS, D.J.H. (1976) The common mussel *Mytilus edulis* as an indicator of pollution by zinc, cadmium, lead and copper. I. Effects of environmental variables on uptake of metals. *Mar. Biol.* 38 59.

WATLING, H.R. and WATLING, R.J. (1976) Preconcentration techniques for the determination of trace elements in water. 1. Sodium diethyldithiocarbamate chloroform. CSIR Special Report FIS 83, Pretoria, National Physical Research Laboratory, CSIR.

WATLING, R.J. (1978a) A simple oxidation procedure for biological material prior to analysis for mercury. *Anal. chim. Acta* 99 357.

WATLING, R.J. (1978b) The use of a slotted tube for the determination of lead, zinc, cadmium, bismuth, cobalt, manganese and silver by atomic absorption spectrometry. *Anal. chim. Acta* 97 395.

WATLING, R.J. and WATLING, H.R. (1979) Metal surveys in South African estuaries. I. Swartkops estuary. CSIR Special Report FIS 183, Pretoria, National Physical Research Laboratory, CSIR.