

# Metal Surveys in South African Estuaries III Hartenbos, Little Brak and Great Brak Rivers (Mossel Bay)

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## Abstract

Surveys to study the metal contents of the Hartenbos, Little Brak and Great Brak Rivers were undertaken. Water samples were analyzed for thirteen elements and surface sediments and sediment core samples for sixteen elements using atomic absorption spectroscopy. Inter-element relationships as well as absolute metal concentrations were examined before interpreting the data obtained.

The results indicate that all three rivers experience some degree of metal contamination. With the exception of the extremely high chromium levels in part of the Great Brak River, these metal concentrations do, however, not present a significant pollution threat.

## Introduction

The largest urban and industrial settlement on the south coast between Port Elizabeth and Cape Town is Mossel Bay. The town has a population of approximately 23 000 and supports diverse industrial concerns. Sewage enters the sea near the harbour at Mossel Bay and also from the three main urban settlements in the Bay *viz.* Hartenbos, Little Brak River and Great Brak River. The three major rivers which enter the bay are also known by the same names (Fig. 1).

The Hartenbos River enters the sea through eolian sands and gravels and late tertiary beach deposits. The river is incised in Cretaceous conglomerates, sandstones and argillaceous material, probably of terrestrial origin, along most of its length, while shales and phyllites of the Cape Group can be found in the upper reaches. The depth of the water varies but is generally between 2–4 m and the river is 5–10 m wide except in the lower estuary where it broadens considerably.

The lower reaches of the Little Brak and Great Brak Rivers are incised in recent alluvial material resting on Cretaceous conglomerates and gravels. The Great Brak River has its origin in the granite-gneiss of the George intrusive and enters the sea just south of its junction with the Alexandra Formation. Both rivers have wide estuarine areas with extensive flood plains and salt marshes just inland from the sea and are contained within reasonably well consolidated bank material. Banks between 5–7 m high are found in the Great Brak catchment. The depth of both rivers varies up to a maximum of 4 m while an average river width of about 15 m is common in the lower reaches.

All three rivers enter the sea after incising the late tertiary raised beaches which are well developed north of Mossel Bay and there is no obvious mineralisation in any of the catchment areas.

The aim of the survey which was carried out in July 1978, was to establish current metal levels in these three rivers. A preliminary survey of the Mossel Bay area, including the three rivers, was undertaken and the results of meiofaunal and chemical analyses (other than for metals) of samples collected during the survey, were reported by Eagle *et al.* (1979). Together these data will serve as a baseline for future pollution monitoring surveys, should further industrialization or urban development take place in this region of the South African coast.

## Materials and Methods

Surface water samples were collected in 2,5 l high-density polythene 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.

Approximately 500 g of a composite surface sediment was collected using an aluminium scoop. These samples were air-dried between filter-paper sheets, disaggregated in a porcelain mortar and sieved through a 210  $\mu$ m nylon screen. The fraction which passed through the screen was reserved for analysis.

Sediment cores were collected by hammering PVC tubes directly into the sediment. Good penetration with very little compaction of the sediment was achieved using this method. The tube was then sealed at the top using a rubber stopper and withdrawn from the sediment. Both ends of the tube containing the sediment core were sealed using polythene-covered corks and the whole sample frozen to  $-20^{\circ}\text{C}$ . Frozen cores had to be stored for eight weeks but no deterioration of the sediment was observed during this period.

Detailed descriptions of the further preparation of these samples and the determination of their metal contents are explained by Watling and Watling (1982).

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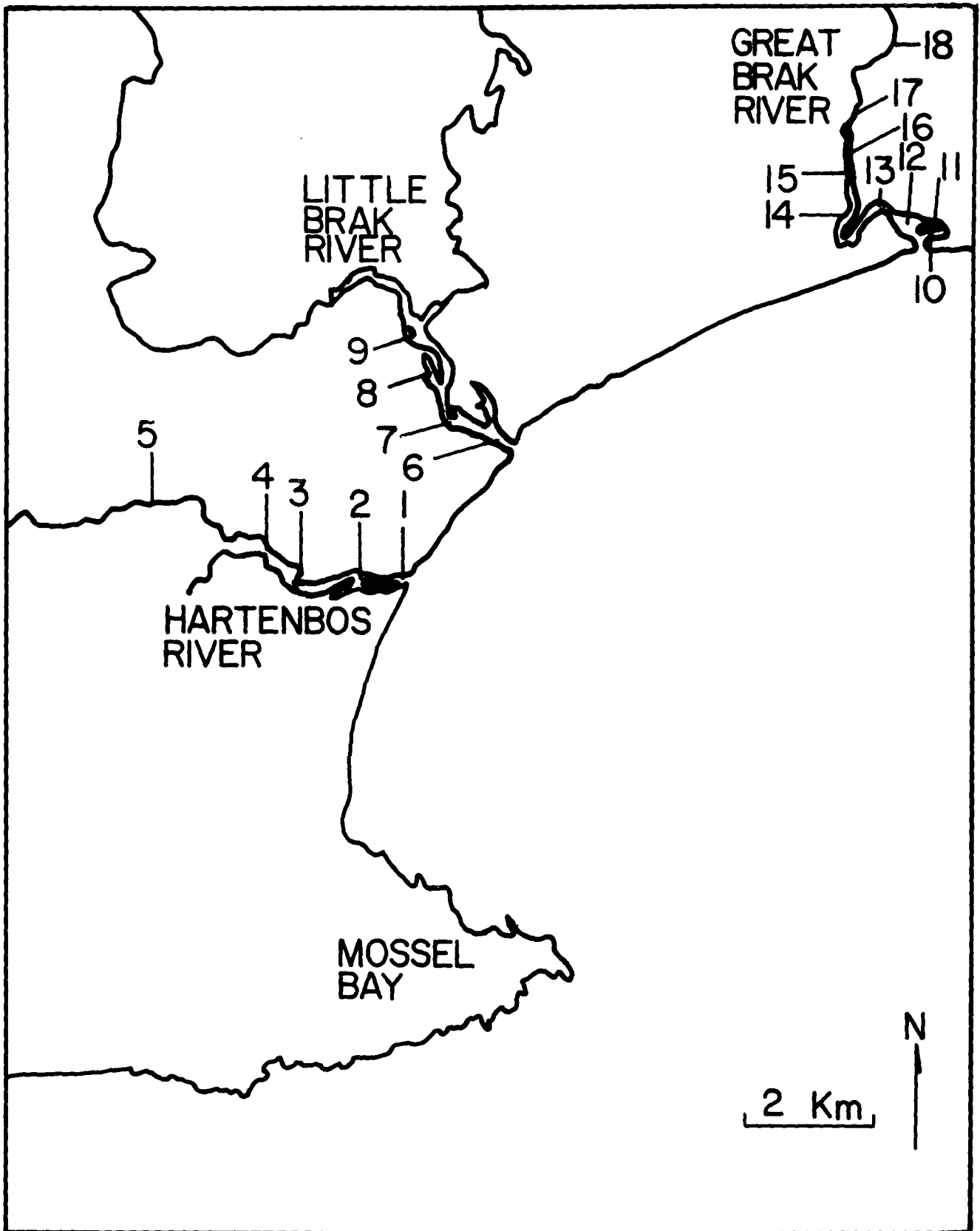


Figure 1  
Study area and location of sampling sites

## Results and Discussion

Samples were collected from five sites in the Hartenbos River, four sites in the Little Brak River and nine sites in the Great Brak River (Fig. 1).

### Metals in Water

Trace and minor element concentrations in surface water samples are listed in Table 1.

The mouths of the Hartenbos and Great Brak Rivers were closed by sand bars at the time the water samples were collected. Consequently the effect of marine water on the river water salinity was limited. Salinities for the Hartenbos River range from 33 mg/ml near the mouth to <0,03 at site 5 (station 22, Eagle *et al.*, 1979). The minor element concentrations reflect this trend strongly, the influence of fresh water being particularly evident above site 3. The salinity of the Great Brak River was in the region of 23 mg/ml downstream from the town of the same name, while upstream of the town salinity levels decreased to about 10 mg/ml at site 18 (station 8, Eagle *et al.*, 1979). The changes in salinity are followed closely by variations in the minor element composition although concentrations are greater than those found in the Hartenbos River.

The Little Brak River was open to the sea and the marine influence on water salinities is evident even at site 9, furthest upstream. Minor element concentrations follow the salinity gradient although the potassium and magnesium concentrations appear to be elevated relative to those determined for water samples of equivalent salinity from the other two rivers.

Trace element concentrations are generally low in the Hartenbos River when compared with those determined for some other south-eastern Cape rivers (Watling and Emmerson, 1981; Watling and Watling, 1980b; 1982a; 1982b), although iron, manganese, zinc, copper, cadmium and nickel are elevated locally at site 3 near the road causeway and at site 4 near a farm track. Cadmium and copper levels are higher in the Little Brak River than in either of the other rivers, although nowhere do they attain significance. Water samples from the Great Brak River have trace element levels which are approximately average for rivers of the south-eastern Cape. Iron attains some significance downstream of the town, but the highest concentrations of this element are upstream and do not indicate a pollutant source. Mercury levels in the three rivers reach levels above background (0,025 µg Hg/l) for rivers in the south-eastern Cape, but they are much lower than the 0,400 µg Hg/l found in Knysna Lagoon which was considered to be indicative of urban contamination (Watling and Watling, 1982b).

### Metals in Surface Sediments

The metal concentrations found in the surface sediments of the Hartenbos, Little Brak and Great Brak Rivers are listed in Table 2.

In general, metal levels in the surface sediments of all three estuaries may be considered as average for rivers of the south-eastern Cape. The only exceptions that do occur are those at site 4 (Hartenbos River) where lead, cobalt, nickel, chromium and mercury levels are considerably elevated above background; and sites 8 and 9 (Little Brak River) where cobalt,

TABLE 1  
METAL CONCENTRATIONS (µg/l) IN WATER SAMPLES

Site	Zn	Cd	Cu	Pb	Fe	Mn	Ni	Co	Hg	Na	K	Ca	Mg
HARTENBOS RIVER													
1	0.8	0.4	1.1	0.2	58	8	0.1	<0.1	0.038	11 200	290	460	1 450
2	0.9	0.3	0.9	<0.1	79	58	0.2	<0.1	0.038	10 400	250	420	1 350
3	2.2	0.6	0.9	0.4	245	115	0.4	<0.1	0.038	10 200	220	410	1 280
4	1.3	0.5	0.7	0.5	39	250	0.5	0.4	0.001	1 370	16	124	193
5	0.9	0.3	0.6	0.4	160	18	1.0	<0.1	0.004	610	7	57	86
LITTLE BRAK RIVER													
6	1.8	0.7	2.6	0.2	44	5	<0.1	<0.1	0.046	12 600	380	450	1 540
7	1.1	0.8	2.4	0.3	100	9	<0.1	<0.1	0.028	11 400	360	440	1 450
8	1.0	0.6	2.4	0.1	115	15	<0.1	<0.1	0.042	10 700	310	400	1 420
9	1.3	1.3	3.1	0.4	86	13	<0.1	<0.1	0.066	10 300	310	400	1 330
GREAT BRAK RIVER													
10	2.0	0.4	1.5	0.3	70	20	<0.1	<0.1	0.025	9 600	200	360	1 050
11	1.7	0.5	1.5	0.3	95	22	<0.1	<0.1	0.023	6 500	190	310	890
12	2.6	0.1	1.0	0.4	27	13	<0.1	<0.1	0.012	8 300	200	320	1 020
13	3.2	0.4	2.2	0.2	80	23	0.5	0.1	0.018	7 900	210	310	1 030
14	2.4	0.4	2.6	<0.1	116	27	<0.1	<0.1	0.020	8 100	190	300	1 010
15	2.9	0.4	3.2	<0.1	142	31	<0.1	<0.1	0.018	7 600	190	300	990
16	2.1	0.3	2.2	<0.1	144	30	0.1	<0.1	0.024	7 200	190	300	960
17	2.6	0.6	2.6	<0.1	240	40	0.2	<0.1	0.051	4 600	110	170	570
18	4.3	0.5	2.7	1.1	71	32	0.1	<0.1	0.016	2 030	53	80	260

TABLE 2  
METAL CONCENTRATIONS ( $\mu\text{g/g}$ ) IN SURFACE SEDIMENTS

Site	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr	Hg
HARTENBOS RIVER																
1	1,9	10,3	6,0	1 400	33	0,8	1,6	0,03	2 140	880	81 200	2 260	27	2 410	1,6	0,010
2	5,1	12,6	15,3	2 500	186	0,9	3,2	0,03	2 000	750	75 200	2 150	32	2 400	1,5	0,009
3	4,1	10,2	11,7	698	52	1,5	4,9	0,01	1 380	1 920	1 780	2 130	1	12 700	6,0	0,046
4	8,5	37,5	22,6	16 100	304	7,0	11,4	0,07	2 660	350	4 050	2 690	3	20 200	23,4	0,161
5	1,8	3,2	7,3	16 500	300	2,1	4,6	0,02	4 130	1 960	1 790	250	3	15 900	2,4	0,037
LITTLE BRAK RIVER																
6	1,8	10,0	2,9	1 350	18	0,3	0,7	0,02	1 960	400	89 200	240	31	1 240	2,6	0,001
7	1,9	6,8	9,3	5 580	33	1,3	2,8	0,07	2 870	1 050	5 320	1 080	2	4 730	3,7	0,005
8	7,1	16,5	22,5	13 100	150	5,0	9,4	0,03	6 200	2 250	10 900	2 910	50	16 000	20,3	0,009
9	5,2	9,4	14,7	9 190	180	3,5	3,7	0,04	5 330	2 030	9 790	2 790	91	15 300	15,6	0,006
GREAT BRAK RIVER																
10	0,9	1,9	2,4	1 690	7	0,1	0,6	0,02	1 490	260	70 100	2 040	28	990	2,4	0,003
11	1,2	4,2	6,5	4 050	25	0,5	1,1	0,02	1 500	350	95 500	2 670	830	1 610	6,1	0,002
12	1,5	8,8	6,2	4 250	25	0,5	1,1	0,04	1 580	430	85 500	2 580	560	2 180	6,6	0,003
13	1,5	4,5	6,6	3 360	22	0,8	1,3	0,02	2 920	600	58 200	1 940	514	330	12,0	0,017
14	6,0	9,4	14,0	11 900	103	3,7	6,0	0,02	7 210	2 100	1 820	2 010	21	1 850	19,2	0,006
15	5,9	8,6	13,1	10 400	58	2,2	4,6	0,01	8 860	1 660	1 350	280	21	1 480	14,8	0,034
16	6,3	9,4	17,1	10 900	64	2,6	4,3	0,02	9 400	1 890	1 400	250	20	1 540	16,2	0,010
17	1,7	4,2	6,5	13 600	240	1,2	2,4	0,01	10 600	2 100	1 350	270	20	1 650	8,4	0,007
18	1,8	2,1	4,6	15 400	360	0,6	0,9	0,01	15 400	2 400	960	170	3	2 140	5,9	0,006

TABLE 3  
GEOMETRIC MEANS OF METAL CONCENTRATIONS ( $\mu\text{g/g}$ ) IN SEDIMENT CORES

Site	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr	Hg
HARTENBOS RIVER																
1	2	9	6	1 845	32	0,7	1,5	0,03	1 984	702	81 709	2 100	26	2 079	3	0,002
3	3	9	11	9 933	52	1,7	4,2	0,01	3 638	2 121	3 077	2 269	3	11 517	8	0,020
4	7	21	20	11 399	187	5,1	11,4	0,03	1 808	3 564	1 307	2 629	45	22 005	19	0,065
LITTLE BRAK RIVER																
6	2	9	3	1 415	22	0,2	0,7	0,03	1 951	380	89 717	2 507	100	1 079	3	0,002
7	3	11	12	7 326	50	1,9	4,7	0,03	2 772	1 436	3 921	1 904	1	7 719	10	0,013
8	3	10	11	7 520	78	2,2	4,1	0,02	2 810	1 212	28 543	1 880	18	7 691	11	0,065
9	3	6	9	6 709	85	2,0	3,0	0,02	3 009	1 207	15 940	1 870	124	7 960	11	0,020
GREAT BRAK RIVER																
10	1	2	3	2 057	11	0,3	0,8	0,01	1 862	259	77 180	2 393	40	1 263	3	0,001
11	1	2	6	3 933	23	0,5	1,1	0,02	1 904	392	89 820	2 603	702	1 895	6	0,005
12	1	3	6	3 706	22	0,5	1,0	0,03	2 144	445	80 690	2 446	524	2 227	6	0,002
13	3	7	15	7 897	61	1,8	3,4	0,03	5 479	1 262	45 350	2 550	407	6 423	21	0,045
14	11	17	36	15 366	107	3,1	5,9	0,06	7 149	2 320	1 670	2 818	25	1 943	801	0,035
15	6	10	16	11 661	100	2,4	4,6	0,02	5 997	1 964	1 126	2 252	14	1 701	34	0,055

nickel and chromium are also elevated. In addition, chromium concentrations are elevated between sites 13 and 16 on the Great Brak River. Mercury concentrations in surface sediments from the Little Brak and Great Brak Rivers are at background levels for the eastern Cape. In the Hartenbos River, however, there is evidence of mercury build-up, especially at site 4 near a farm track.

### Metals in Sediment Cores

Thirteen sediment cores were collected in these three rivers and analysed for those elements already determined in the surface sediments. Sample locations are coincident with those of the water and surface sediment samples as shown in Figure 1 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 a few 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.

Sediment cores were collected at sites 1, 3 and 4 in the Hartenbos River, sites 6 to 9 in the Little Brak River and sites 10 to 15 in the Great Brak River (Fig. 1). Metal concentrations in every core sample, together with a scale drawing and sedimentological description of the core and an inter-element correlation matrix have been detailed elsewhere (Watling and Watling, 1980a).

The geometric means for the concentrations of each element in these cores have been calculated and are listed in Table 3. While this is not an ideal way to display core data, it does serve as an easy method for identifying anomalous areas.

Site 4 in the Hartenbos River (Table 3) is an extremely marshy area adjacent to a farm track. Mean levels of lead, cobalt and nickel are the highest for any of the cores collected in this river. Examination of the core data (Table 4) shows that the higher metal levels are found in the top half of the core. These high levels coincide with an increase in the clay content of the sediment. However, while this is expected to give rise to a general increase in metal levels it does not account entirely for the increase which is observed. The area is probably acting as a trap for metals which may have entered this environment intermittently over a prolonged period.

Some metal accumulation in the sediment column has also occurred at site 3, lead, zinc, cobalt, nickel, and chromium being about twice the expected background levels. Although the area has a disused causeway associated with it, this is unlikely to be the source of metals. Instead, elevated levels are probably due to a seepage anomaly or to redistribution of metals from further upstream.

The Little Brak River is also contaminated by metals, two possible sources being the road and the railway. For example, there is a distinct enrichment of copper, lead, zinc, cobalt, nickel, cadmium and chromium in the top 140 mm of the sediment core from site 9, suggesting the relatively recent introduction of these elements into the surface sediments. Although conditions are not inhospitable to marine life, any severe flooding could remobilize a considerable quantity of metals from the sediment.

The Great Brak River has been contaminated extensively by metals which have been introduced by man. In many areas core profiles show shells at depth in what was originally a coarse, well-oxygenated sand. These shells are almost absent in the upper layers, indicating that the onset of inhospitable conditions in this river took place rapidly.

TABLE 4  
METAL CONCENTRATIONS ( $\mu\text{g/g}$ ) IN HARTENBOS SEDIMENT CORE, SITE 4

Sample	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr	Hg
HARTENBOS RIVER																
1	15.0	88.5	28.8	24 000	557	11.5	13.5	0.144	5 960	3 850	7 110	1 460	3 23 100	34.6		
2	9.2	41.2	20.6	20 600	412	7.3	11.8	0.066	3 090	3 310	7 260	1 940	3 18 400	25.7	0.116	
3	7.5	17.9	20.3	16 000	240	7.1	12.7	0.047	1 700	4 010	3 500	2 640	<1 23 600	22.6		
4	3.6	13.8	19.0	7 210	106	3.4	5.6	0.028	910	1 820	596	940	<1 10 000	10.6	0.120	
5	7.3	26.0	24.5	12 700	206	5.9	13.2	0.053	1 620	4 660	1 790	3 480	7 26 000	23.5		
6	7.5	18.4	21.9	10 300	180	6.4	13.3	0.038	1 590	4 290	459	3 130	<1 29 200	21.0	0.096	
7	7.1	16.8	18.8	9 960	138	5.7	13.0	0.015	1 420	3 950	314	2 570	<1 26 800	23.4		
8	8.0	23.6	24.5	9 440	159	6.4	15.0	0.025	1 670	5 320	386	3 130	<1 30 900	22.7	0.088	
9	9.8	25.4	32.4	8 200	215	7.0	18.3	0.027	2 260	7 460	539	4 300	<1 41 000	21.1		
10	7.8	21.5	26.6	9 550	184	5.8	16.4	0.027	1 810	5 530	392	3 340	<1 34 100	25.6	0.084	
11	10.1	23.9	27.9	13 300	226	6.6	24.8	0.092	2 170	6 240	531	3 720	<1 37 200	28.3		
12	9.2	16.9	29.0	12 900	192	3.9	14.1	0.019	1 720	4 230	169	3 020	<1 30 400	25.9	0.071	
13	8.1	16.5	26.9	11 300	222	4.5	15.2	0.013	2 040	5 040	217	4 090	12 33 000	20.4		
14	7.6	14.8	17.4	13 500	182	4.0	11.0	0.016	1 610	2 460	352	2 170	14 19 900	22.0	0.091	
15	2.5	7.3	11.4	8 960	106	3.3	6.2	0.002	1 090	1 280	255	1 170	92 8 970	11.4		
16	2.6	7.2	12.7	10 600	109	3.8	5.5	0.003	1 200	1 610	322	1 450	161 8 560	11.6	0.047	
17	2.3	5.9	10.1	8 140	62	2.2	3.6	0.005	1 070	1 290	197	1 130	194 6 180	9.3		
18	1.2	3.4	5.6	5 940	29	1.1	1.6	0.003	719	875	231	112	162 5 650	5.0	0.023	
19	0.9	4.0	4.0	3 760	21	0.9	1.4	0.002	649	511	199	118	185 4 140	3.2		

TABLE 5  
METAL CONCENTRATIONS ( $\mu\text{g/g}$ ) IN GREAT BRAK RIVER SEDIMENT CORE, SITE 14

Sample	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr	Hg
1	0,5	1,6	2,2	1 990	14	0,3	0,7	0,005	859	277	1 610	349	18	277	4	
2	1,5	6,3	5,3	3 790	40	0,6	1,4	0,002	2 780	732	4 040	881	48	464	8	0,067
3	10,0	13,8	20,5	18 100	138	5,7	10,5	0,023	13 800	3 430	1 290	3 860	14	3 120	27	
4	9,3	13,1	21,6	16 500	165	6,3	8,5	0,038	10 600	3 220	1 190	2 670	13	2 610	30	0,083
5	8,7	12,4	20,4	19 300	160	5,8	9,1	0,029	8 030	2 880	948	2 260	10	2 770	27	
6	12,5	18,6	38,0	27 900	255	7,3	9,7	0,069	10 900	4 860	1 210	3 240	13	3 420	41	0,054
7	5,8	14,4	27,2	13 200	181	2,0	4,5	0,024	9 050	1 730	1 230	2 260	17	1 610	45	
8	4,2	12,6	22,0	10 000	150	1,5	4,0	0,020	8 000	1 500	1 200	2 200	17	1 500	44	0,026
9	3,4	9,0	11,8	7 090	102	1,1	3,0	0,003	4 290	1 300	945	1 360	16	1 070	25	
10	3,2	8,5	10,9	7 000	100	1,0	3,0	0,003	4 000	1 300	900	1 300	15	1 000	25	0,039
11	4,4	10,9	15,6	8 100	71	1,5	3,7	0,012	3 740	1 530	872	1 440	11	1 320	56	
12	7,1	12,7	25,4	15 200	91	3,4	6,6	0,050	6 500	2 690	1 520	2 690	18	2 260	47	0,023
13	7,8	17,9	21,2	15 600	84	3,1	7,3	0,016	7 320	2 900	1 900	3 240	22	2 660	56	
14	9,4	17,6	23,3	17 600	82	3,0	6,9	0,037	7 550	2 950	1 760	3 460	21	2 550	138	0,030
15	11,4	17,9	31,7	21 500	108	3,9	7,2	0,072	6 890	3 230	1 560	3 530	18	2 710	137	
16	9,7	29,7	33,5	14 600	97	3,0	7,0	0,075	5 780	3 350	1 350	3 300	17	2 720	540	0,060
17	12,3	34,7	52,9	15 500	85	3,9	6,4	0,133	5 130	2 410	1 280	2 990	18	1 940	1 230	
18	46,4	46,7	178,6	42 800	154	6,7	10,0	0,333	17 800	3 570	4 170	7 500	101	2 830	11 310	0,027
19	45,0	40,0	170,0	40 000	150	6,0	10,0	0,330	17 000	3 000	4 000	7 000	100	2 500	1 100	
20	6,7	17,2	25,7	11 200	60	1,6	4,5	0,085	3 620	1 860	1 340	2 200	16	1 410	970	0,026
21	4,7	8,4	17,7	7 020	43	1,1	2,9	0,026	2 270	1 140	969	1 540	12	892	434	
22	20,8	27,1	49,3	13 900	83	2,5	6,9	0,027	6 520	2 500	2 360	4 170	37	2 260	2 920	0,030
23	2,9	9,3	12,2	5 280	41	0,9	2,6	0,004	1 910	996	772	1 380	11	793	211	

Core 14 (Table 5) is of particular interest. This core, approximately 550 mm long, was collected from an area of reducing sands and silts in an area of the river which was inundated by oil following the collision between the oil tankers *VENOIL* and *VENPET*. At a depth of about 400 mm the chromium concentration rises to a level above 1%, while concentrations of zinc, cadmium, copper, lead, cobalt and nickel in this sediment are the highest found for the survey of the Great Brak River. The occurrence of these high metal concentrations at depth in the sediment indicates a more recent reduction in the input of metals by local industry and may reflect a change in the manufacturing process.

Metal levels, particularly cobalt and nickel, are also elevated in the bottom half of the sediment column at site 13 and at site 15, immediately downstream of the town, where the sediment is also oily with tar balls occurring throughout the top 200 mm of the core.

## Conclusion

The results of this survey indicate that all three rivers suffer from some degree of contamination by metals. However, metal levels are generally low and do not pose a pollution threat. The obvious exception is the chromium in the Great Brak River which, were it to be remobilized during, for example, a period of flooding, could present a serious problem to the estuarine flora and fauna.

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