A SURVEY OF HEAVY METALS IN SEDIMENTS AND WATERS OF THE PRESTON RIVER — JULY 1984

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A SURVEY OF HEAVY METALS IN SEDIMENTS AND WATERS OF THE PRESTON RIVER - JULY 1984

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ABSTRACT

Water and sediment samples were collected along the Preston River, near Bunbury in the southwest of Western Australia. Analyses for certain metals (cadmium, lead, mercury and copper) were performed in order to determine whether any contamination of the environment was taking place from a fertilizer plant. Other physio-chemical measurements were made in conjunction with these studies. It is concluded that there was no obvious metal accumulation in the Preston River or environs. At the time of sampling, no measurable change in water quality was detected downstream of the fertilizer plant drain outlet.

INTRODUCTION

The association is well known between fertilizer production and heavy metal contamination of the nearby environment. In Western Australia, cadmium (Cd) and mercury (Hg), in particular, have been linked with the fertilizer factory outfalls at Cockburn Sound (Chegwidden, 1979). More recently, the superphosphate factory at Albany has come under scrutiny where elevated metal concentrations, especially those for lead (Pb) (Talbot, 1983) and Hg (Jackson et al., 1984), have been reported in discharges and nearby sediments.

The aim of the present project was to determine whether or not Pb and Hg concentrations are significantly different upstream and downstream from the fertilizer factory at Picton Junction (adjacent to sampling site D1, Fig. 1), located on the banks of the Preston River which enters Vittoria Bay (part of Leschenault Inlet) near Bunbury.

DESCRIPTION OF THE STUDY AREA

The Preston River rises on the southern edge of the Darling Range, approximately 60 km southeast of Bunbury. Most of the upper catchment area is jarrah forest whilst the lower part has been cleared for agriculture. The river flows in a northwesterly direction for approximately 80 km, and has its outlet in the Leschenault Inlet at Vittoria Bay (Plate 1).

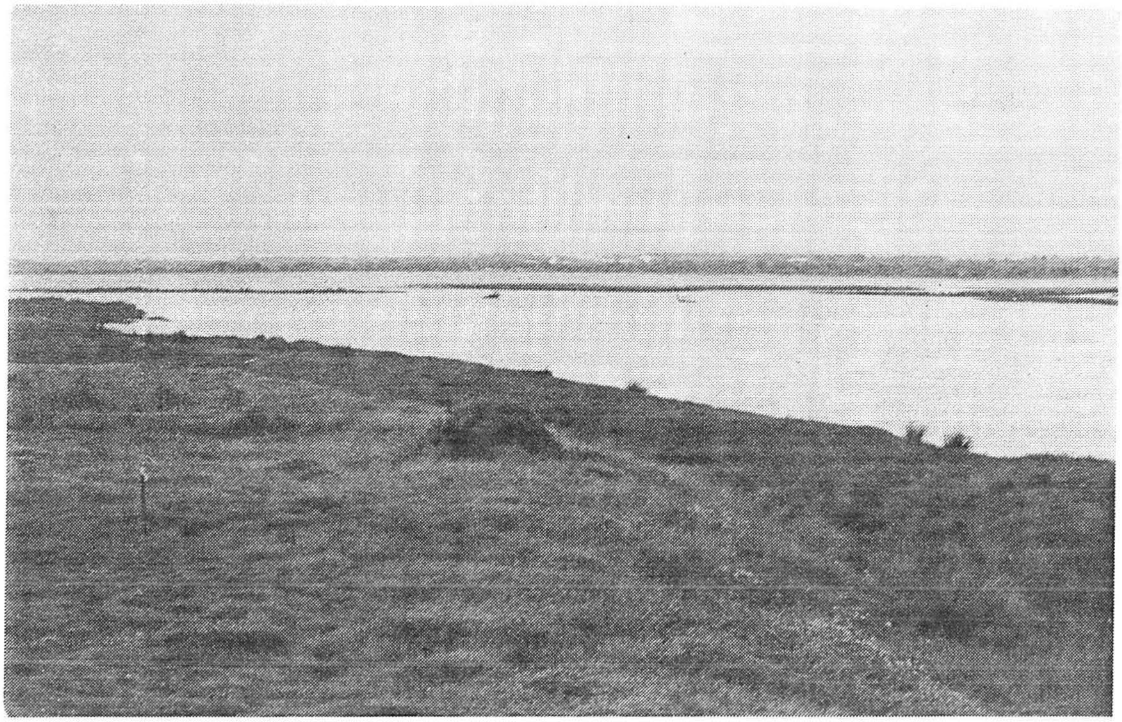


Plate 1: The mouth of the Preston River (Leschenault Inlet).

The Ferguson River is a small tributary to the Preston which it joins about 6 km from the mouth (Plate 2). It comprised, at the time of sampling, approximately one tenth of the combined flow at their junction.

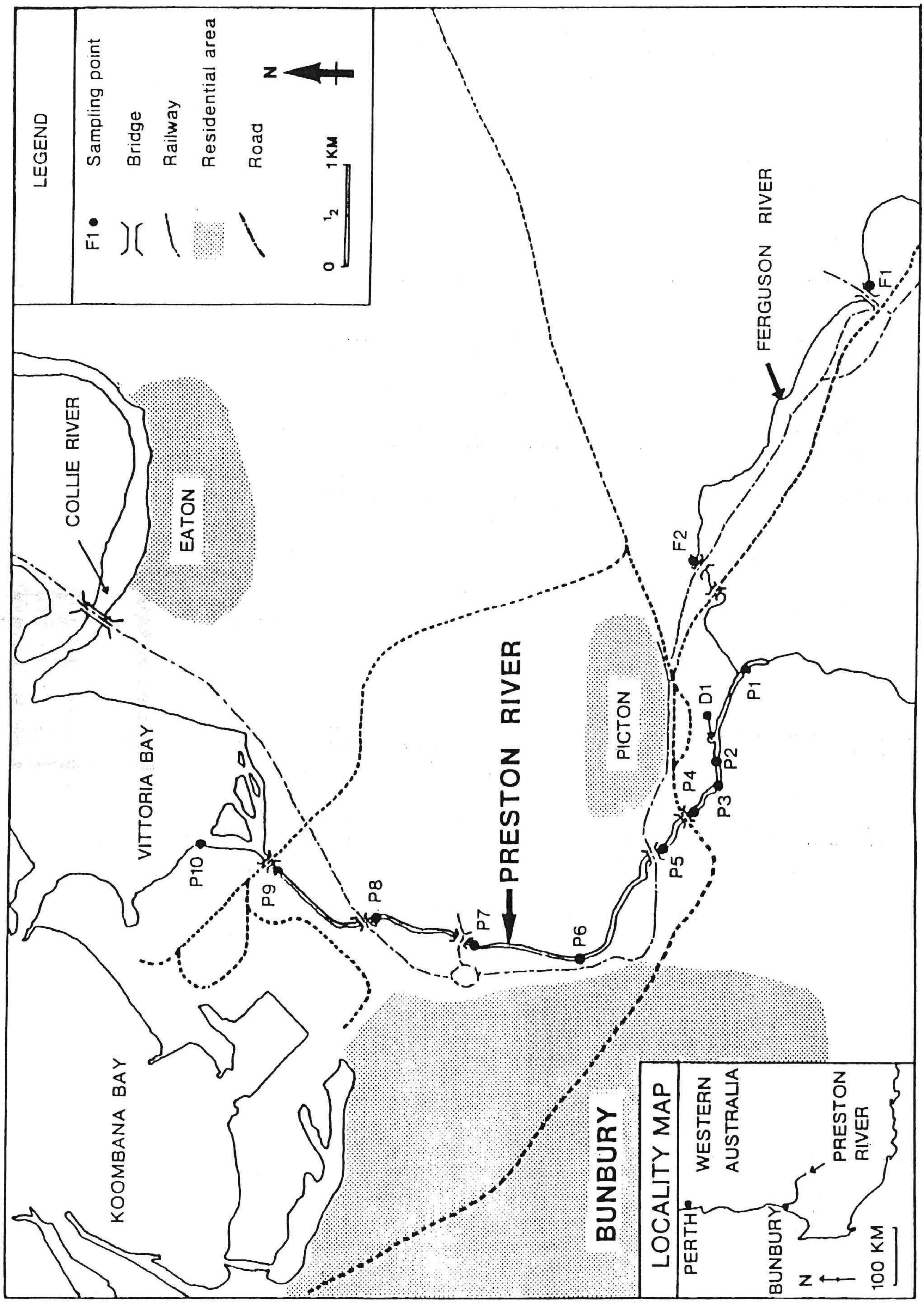


Figure 1: Sampling points in the Bunbury area.

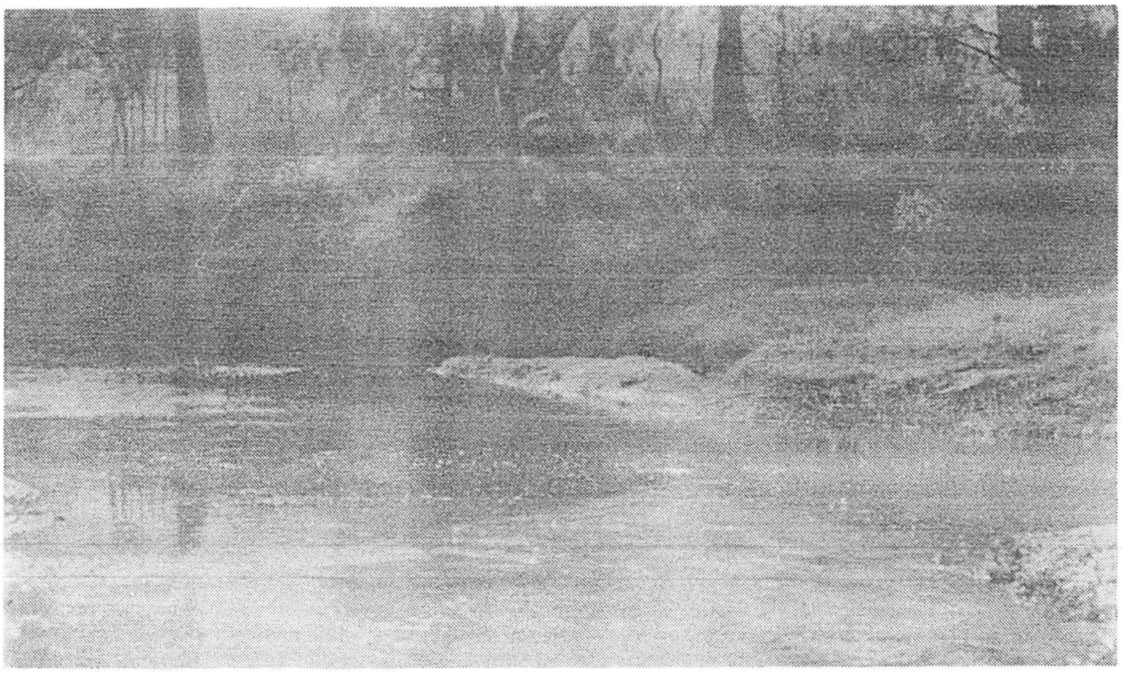


Plate 2: The confluence of the Ferguson and Preston Rivers.

The Preston River is tidal for about 4 km from the mouth (sample sites P5 to P10 inclusive); width at this section is about 30 m, and the river is bordered on both sides by levees. Above this section the river narrows and its banks have been eroded to varying degrees. A drain and pipe from a fertilizer factory discharge into a small recess of the river (sampling site D1)just above the remains of a derelict bridge where the flow was estimated to be about 1 m/sec. (Plate 3).

From sampling sites P5 to P1 the river follows numerous channels comprising, usually, a main channel approximately 0.5 m to 2 m in depth, and several smaller channels, which have been separated from the main channel by sediment deposition. At the time of sampling (September), no rain had been recorded in the area for over seven days; the structure of the river channels change considerably after even moderate rainfall.

The Ferguson River joins the Preston just below site P1. Its width averages about 1-2 m and depth about 0.5 m. The banks at sampling point F2 were severely eroded (Plate 4).

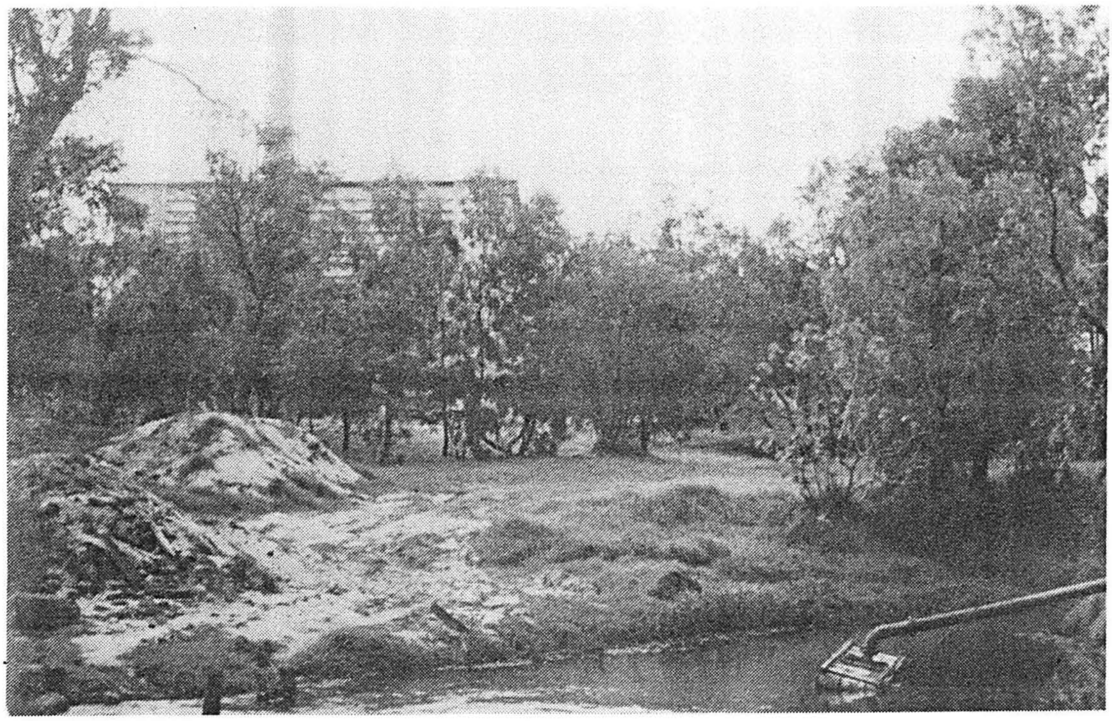


Plate 3: The drain sampling point with the fertilizer factory in the background.

Plate 4: Sampling point F2 showing severe erosion of river bank.

MATERIALS AND METHODS

Sample and storage

During September, water, sediment and decaying plant material were collected from sampling sites along the Ferguson and Preston Rivers to the Leschenault Inlet over a period of three days.

Nine sites sampled were downstream from the fertilizer factory (P2-P10), three sites were sampled upstream (F1 and F2 on the Ferguson River and P1 on the Preston River) and one at the drain site itself (D1). Access to the sampling sites F2 to P5 was by canoe, commencing at F2.

a) Water

Surface water samples (surface - 0.5 m) were collected in 500 ml polyethylene, acid washed, screw-top containers. Samples were filtered, under suction, (0.45 µm, Millipore 90 mm, HAWP) in a perspex filtration apparatus and acidified with 5 ml of concd. nitric acid (BDH, Aristar grade). De-ionized water was similarly treated in a separate container and served as a check for contamination. Also, at each site, a duplicate water sample was collected and left untreated. All water samples were stored for 72 hours prior to analysis for trace metals.

b) Sediment

Three sediment samples, (≈100 g) were collected, in acid rinsed containers, from the top 30 mm of the river bed, at each site to represent a transect across the river. A fourth sample, composed of decaying organic material, was also collected for comparative purposes, from the top 30 mm of the sides of the river bed.

These samples were freeze dried (Dynavac, FD2) for four days, and then stored at ambient temperature (about 20°C), for a maximum of three weeks prior to analysis.

Analytical procedures

a) Water

The filtered, acidified water sample underwent no further pre-treatment before being analyzed directly for Hg, by the cold vapour generation technique (Hatch and Ott, 1968). Filtered and unfiltered water was analyzed for trace metals by anodic stripping voltammetry (ASV) using a CSIRO designed portable digital voltammeter (Mann and Lintern, 1984).

Unfiltered water samples were analysed for bicarbonate ions using a dilute sulphuric acid titration procedure (Brown et al., 1970). Measurements for pH were determined using a Radiometer PHM71 MK2 Acid-Base Analyzer. Total dissolved solid concentrations were estimated from a recording of conductivity in µmhos, using a CSIRO designed conductivity meter. Anions were determined by ion chromatography using a Dionex system. Major cations were determined by atomic absorption spectrophotometry (Varian, 875 AAS).

b) Sediment

Sediments were passed through a coarse mesh screen to remove larger pieces of material (>3 mm). Loss on ignition (at 1050°C) and XRD data were obtained on fractions of these samples. For the latter, samples were alcohol smear mounted on glass,and were scanned at 1° per minute using CuKα radiation.

Hg concentrations in sediments and plant material were analyzed according to the method used by the Western Australian Government Chemical Laboratories which is a modification of that of Deitz et al. (1973). The method was as follows: approximately 5.0 g of freeze dried sample and

20 ml of digest mixture (0.25% ammonium metavanadate in 2+1 concd. sulphuric/nitric acid) was mixed at room temperature in a 100 ml Kjeldahl flask for approximately 4 h. After digestion, the cooled acid was diluted to 100 ml and filtered (Whatman 541). Cold vapour AAS (Hatch and Ott, 1968) was used to determine the Hg concentration of 20 ml of the final solution.

Pb, copper (Cu) and Cd concentrations in sediments were determined following partial acid digestion. About 2.0 g of freeze dried sample were weighed and mixed with 20 ml of 1M hydrochloric acid and heated in a boiling water bath for 1 h in a 40 ml polyethylene centrifuge tube. After cooling, a 5 ml aliquot was added to 45 ml of ascorbate (0.2M)/sodium chloride (2M) electrolyte buffer and then analysed by ASV.

All chemicals used in the acid digestions were of analytical grade (BDH, Analar).

Quality control

Repeat analyses were performed on selected sediment samples to obtain statistical information on the variability of metal concentrations within each sample. The results of this are shown in Table 1.

Table 1: Statistical analysis of separate digestions of sediment material from three sampling areas. (All values in mg/kg)

SAMPLE LOCATION	METAL	SAMPLE SIZE	MEAN	STANDARD DEVIATION	% RELATIVE STAND. DEV.	RANGE (LOW - HIGH)
D1(M)	Pb	11	24.9	2.9	11.8	20.0-30.5
	Cu	11	7.6	0.8	10.2	6.4-9.3
	Hg	15	0.0043	0.0024	54.9	<0.005-0.010
P9(L)	Hg	7	0.0130	0.0046	35.4	0.010-0.023
D1(L)	Pb	11	203	19.7	9.7	180-249
	Cu	11	35.2	5.5	15.5	29.7-49.0

Generally, the higher the concentration of metal present, the less the variation between duplicate samples; where sub-microgram amounts of Hg are reported, the relative standard deviation is as much as 54.5% (for D1(M)). "Spiking" sediment with known concentrations of metals indicated that there was good recovery (>90%) on subsequent analysis.

RESULTS

Metal concentrations in water

Metal concentrations in water samples are shown in Table 2. Detection limits varied depending on the water sample being analyzed. This was due to the method of standards addition being used, i.e. spiking the analytical samples with a known amount of metal which produced different increases in peak heights. The larger the increment in peak height, the more sensitive the analytical sample was toward that metal and thus a lower detection limit could be calculated.

Table 2: Metal concentrations in waters (μg/L) both for unfiltered (A) and filtered (B) samples.

A) Unfiltered water samples

SAMPLE LOCATION	Pb	Cu	Hg	Cd
F1	0.6	1.0	<0.2	<0.2
F2	0.4	0.9	<0.2	<0.2
P1	<0.2	0.6	<0.2	<0.2
D1	6.5	6.8	<0.2	0.7
P5	22	6.7	<0.2	1.7
P9	<0.2	<0.5	<0.2	<0.2

B) Filtered water samples

SAMPLE LOCATION	Pb	Cu	Hg	Cd
F1	1.3	13.2	<0.2	<1.0
F2	0.9	2.9	<0.2	<0.8
P1	0.7	3.6	<0.2	<1.0
D1	4.3	4.4	<0.2	<0.8
P5	0.8	0.7	<0.2	<0.5
P9	1.0	1.2	<0.2	<0.7

Pb concentrations in the unfiltered water samples were all below 2µg/L save for those collected at site D1 (the discharge pipe) and site P5 (1 km downstream of the pipe) which had values of 6.5 µg/L and 22 µg/L respectively. These Pb values were considerably higher than those recorded for the corresponding filtered samples and probably reflect matrix bound metals or metal adsorption onto particulate matter which is subsequently released in the low pH analytical medium. The Cu concentrations recorded were variable with no clear trend emerging. The highest Cd concentration (1.7 µg/L at site P5) coincides with the highest Pb value obtained (22 µg/L). Most Cd and all Hg values were below the operating range for the technique used.

Metal concentrations in sediments and decaying organic material.

Metal concentrations in the sediments and organically biased sediment samples are shown in Table 3. Values for Pb and Cu samples taken adjacent

Table 3: Concentrations (in mg/kg) of metals in the sediment samples. L, R and M signify the left hand, right hand and middle parts of the river respectively, facing downstream. N.C. signifies that no sample was collected.

SAMPLE LOCATION	L			R			M			ORGANICALLY BIASED		
	Pb	Cu	Hg	Pb	Cu	Hg	Pb	Cu	Hg	Pb	Cu	Hg
F1	5.7	7.1	<0.005	5.1	15.2	<0.005	5.0	3.1	<0.005	9.4	14.8	0.006
F2	3.0	2.7	<0.005	3.8	3.8	0.006	4.3	3.3	<0.005	19.8	10.9	0.008
1	5.9	2.2	<0.005	1.7	0.7	<0.005	2.3	<0.1	<0.005	4.3	4.0	0.018
D1	203.0	35.2	<0.005	3.9	1.5	<0.005	24.9	7.6	<0.005	42.0	17.9	0.006
P2	5.7	4.5	<0.005	6.4	0.8	<0.005	6.0	0.6	<0.005	7.3	5.9	0.043
P3	6.8	4.3	0.006	3.6	0.5	<0.005	3.5	0.7	<0.005	10.8	5.7	<0.005
P4	6.3	1.2	0.008	2.0	0.1	<0.005	1.9	0.5	<0.005	6.8	3.8	0.006
P5	1.6	0.4	0.006	5.9	1.2	0.006	7.3	0.1	<0.005	12.3	8.7	0.014
P6	17.1	4.8	0.019	2.1	1.3	<0.005	–	N.C.	–	16.9	11.1	0.059
P7	0.3	0.3	<0.005	1.8	0.5	0.006	1.2	0.3	0.012	8.6	9.8	<0.005
P8	14.0	2.7	<0.005	7.1	7.1	0.006	–	N.C.	–	13.5	9.3	0.010
P9	14.3	4.6	0.013	5.2	1.7	0.010	–	N.C.	–	13.9	7.4	0.010
P10	2.6	2.9	0.006	–	N.C.	–	–	N.C.	–	–	N.C.	–

to the drain (site D1) were generally higher than concentrations in samples at other sampling sites. The highest Pb and Cu concentrations were obtained from the left bank of the discharge area (203 and 35.2 mg/kg, respectively). By contrast, concentrations of Hg were greatest in the organically biased samples, downstream of the drain. The highest Hg value was obtained at site P6 (0.059 mg/kg) situated 2 km downstream from site D1. At each sampling site, values of Hg were generally higher in the organically biased sample suggesting a close association of Hg with organic matter. Cd concentrations were below the detection limit (2 mg/kg).

Loss on ignition

Loss on ignition data are presented in Table 4. Values range from 0.2%, in three quartz-dominated stream samples, to 46.2% in an organically biased sample from site P2. The loss on ignition values in general verified the use of visual criteria in the selection of "organically biased" samples.

Table 4: Percentage loss on ignition for sediment and decaying organic material samples.
N.C. signifies no sample was collected.

SAMPLE LOCATION	LEFT BANK %	RIGHT BANK %	MIDDLE %	ORGANICALLY BIASED %
F1	5.5	9.4	1.2	9.4
F2	1.5	8.5	2.5	8.4
P1	1.4	0.5	0.2	18.4
D1	9.4	1.5	6.0	8.4
P2	8.4	0.2	0.5	46.2
P3	4.3	0.6	0.4	12.4
P4	0.9	0.8	0.4	13.1
P5	0.7	2.4	0.2	13.5
P6	8.2	0.6	N.C.	16.2
P7	0.3	0.5	0.2	10.0
P8	1.1	10.0	N.C.	28.4
P9	4.6	5.7	N.C.	22.0
P10	6.3	N.C.	N.C.	N.C.

Water quality

Other measurements were taken on water samples and recorded in Table 5.

Table 5: Major cation and anion concentrations (in mg/L) for unfiltered water samples. Fluoride, nitrate and phosphate concentrations were all below the detection limit (1 mg/L).

SAMPLE LOCATION	pH	T.D.S.	HCO_3^-	Cl^-	SO_4^{2-}	Si^{4+}	Mg^{2+}	Ca^{2+}	Na^+	K^+
F1	7.3	200	75	130	16	5	12	7	80	3
F2	7.2	300	55	181	21	5	17	9	105	3
P1	7.0	350	50	240	25	3	20	10	127	3
D1	3.2	500	0	303	200	11	24	48	166	15
P5	6.8	350	55	220	26	3	19	10	127	3
P9	7.1	450	60	350	41	4	26	13	179	6

Clearly, the water sample collected from the drain (site D1) has higher concentrations of certain cations and anions than those collected upstream. By comparing the upstream (site P1) and downstream (site P5) water samples however, it can be seen that there has been no detectable effect of the drain effluent on chemical characteristics of the Preston River.

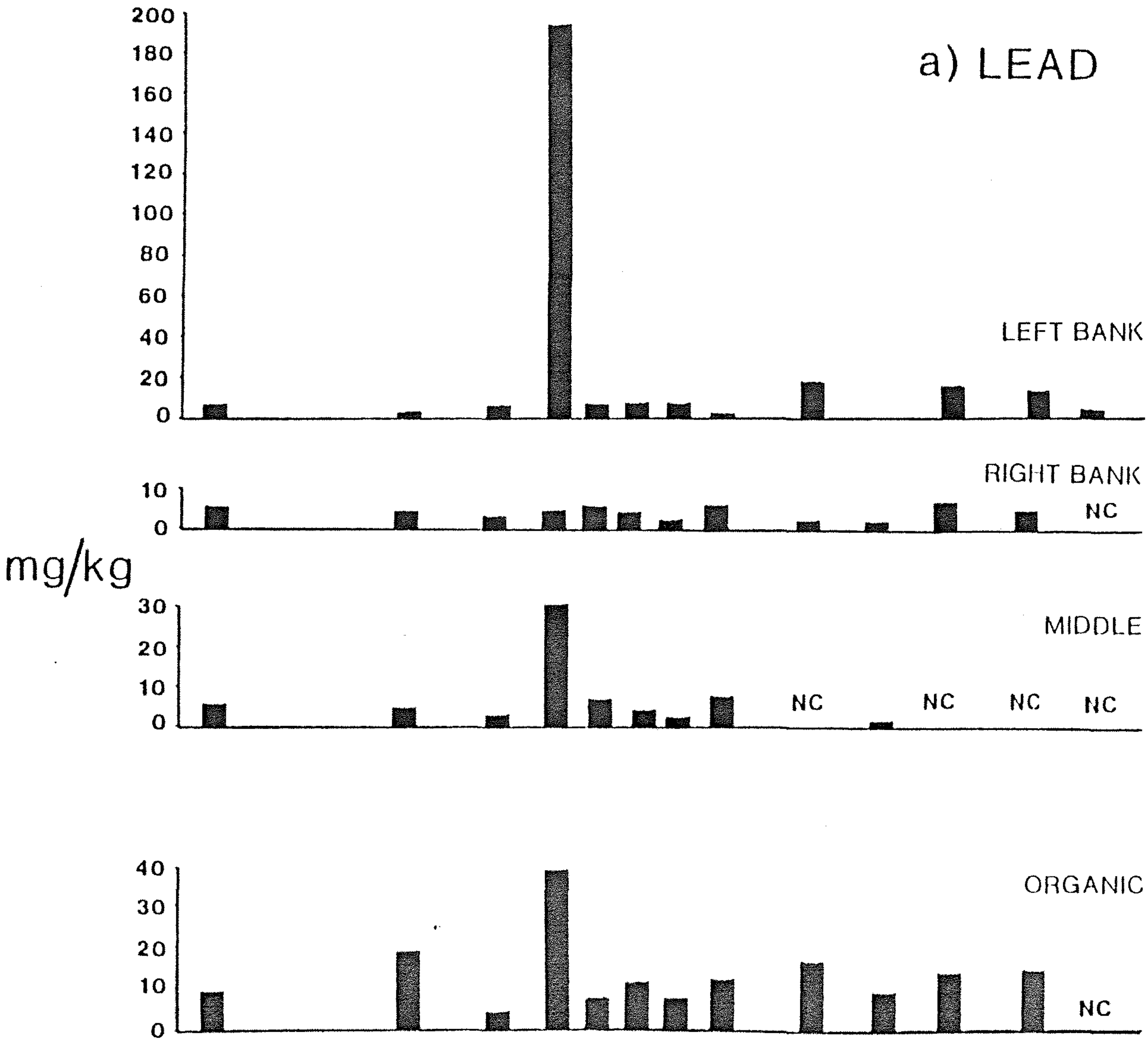
X-Ray diffraction (XRD) on sediments

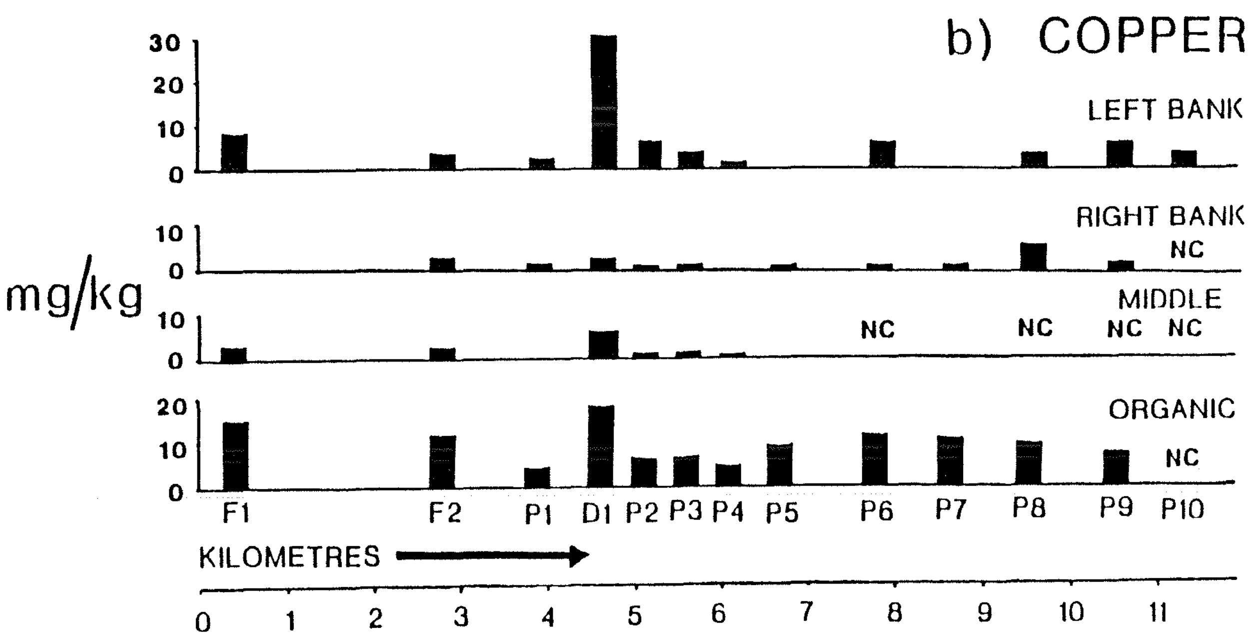
All samples analysed indicated the presence of large amounts of quartz; some samples exhibited small amounts of feldspar (as plagioclase and orthoclase). Granite outcrops are a feature of the source area of both the rivers. The components of the stream sediments were consistent with mechanical liberation from both granite and tertiary sediments of the coastal plain followed by transport to temporary deposition in favourable sites in the mature section of the river. Ilmenite, which was seen at some locations sampled, was not present in sufficient quantity to be recorded on XRD traces.

DISCUSSION

The most striking feature of the metal sediment analyses is the large but isolated concentration of Pb recorded at the left bank of the discharge area (Fig. 2), which is over ten times that recorded for upstream samples. The Cu value here is also many times higher than background. The discharge area forms a side entry to the main river flow, (Plate 3), and a build-up of contaminants might be expected. Away from the drain

Figure 2: Graphical representation of the data shown in Table 2, illustrating the metal concentration in the sediment for a) Pb (in mg/kg), b) Cu (in mg/kg) and c) Hg (in ng/g) and the distances separating the sampling points. N.C. signifies no sample was collected. The dotted line on c) represents the detection limit (5 ng/g).




b) COPPER
mg/kg
LEFT BANK
30
20
10
0
RIGHT BANK
10
0
NC
MIDDLE
10
0
NC
NC
NC
NC
ORGANIC
20
10
0
NC
F1
F2
P1
D1
P2
P3
P4
P5
P6
P7
P8
P9
P10
KILOMETRES
0
1
2
3
4
5
6
7
8
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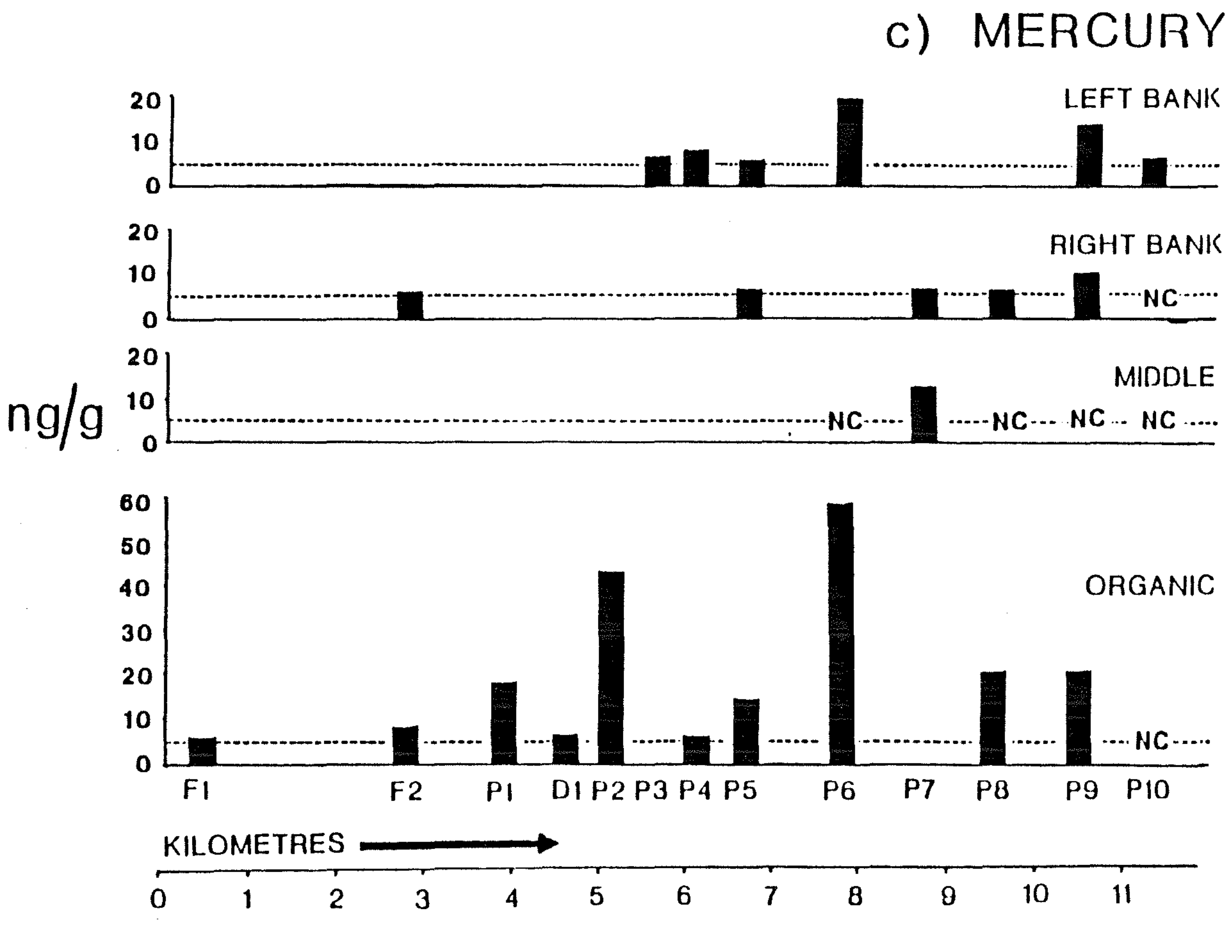
10
11


c) MERCURY
ng/g
LEFT BANK
20
10
0
RIGHT BANK
20
10
0
NC
MIDDLE
20
10
0
NC
NC
NC
NC
ORGANIC
60
50
40
30
20
10
0
NC
F1
F2
P1
D1
P2
P3
P4
P5
P6
P7
P8
P9
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KILOMETRES
0
1
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11

there is no evidence to suggest significant deposition of Pb and Cu. The contribution of sediment due to erosion seen at many parts of the river bank, undoubtedly leads to dilution of metal concentrations in sediment. Because of its association with organic matter, Hg appears to be retained in river sediments. The presence of Hg, however, cannot be associated unequivocally with any particular contaminating source especially since the Hg value for the sample near the drain is below the detection limit for the analytical method used.

The water analysis data suggest that particulate matter ($>0.45\mu m$) might play a role in the transport of Cu and Pb, away from the drain. Again, dilution, this time in the form of the greater volume of the Preston River when compared with the discharge, removes evidence for the movement of such material further than 1 km downstream of D1.

Table 6 places the heavy metal concentrations of the present study in perspective with those of other similar studies. The Preston River samples in general have heavy metal concentrations well below those recorded for sediments that are known to be contaminated. Cu values for Swan River samples for example, are three times higher than those recorded for the Preston River. The drain sample (which represents a maximum area of some 200 square metres), however, has Cu and Pb concentrations of the same order as those of other contaminated areas. Cd and Hg values are substantially lower for the Preston River and the drain discharge area than any other area recorded in the table.

The major problem in sampling the Preston River, is that the amount of transported material in the river, will influence the concentrations

Table 6: Metal concentrations (in mg/kg) for sediments found in this study and similar studies in other areas. Values shown are for the highest value recorded in each study. N.A. signifies no data are available.

Study	Cd	Cu	Hg	Pb
Drain sample (site D1) (present study)	<2	35.2	0.006	203
Preston River, W.A. (present study)	<2	15.2	0.06	17.1
Cockburn Sound, W.A. (Collett <u>et al</u>., 1981)	N.A.	N.A.	1.9	N.A.
Cockburn Sound, W.A. (Talbot and Chegwidden, 1983)	25.2	44.5	N.A.	44.8
Princess Royal Harbour, Albany, W.A. (Talbot, 1983)	7.7	122.1	N.A.	N.A.
Swan River, W.A. (Chegwidden, 1980)	4.4	327	N.A.	N.A.
Northampton Area, W.A. (Mann and Lintern, 1983)	90	850	N.A.	11,100
St. Clair River, North America (Cline <u>et al</u>., 1973)	N.A.	N.A.	1700	N.A.
River Rhine (Banat <u>et al</u>., 1972)	13	286	9	369

actually present in the water and/or sediment samples collected. The dilution effects already mentioned are enhanced at times of maximum river flow. During the present survey it was fortunate, that for the time of year, the river was at a low level. As a result, it is likely that if metal pollution of the river was taking place it would have shown up in the survey.

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