NATIONAL PHYSICAL RESEARCH LABORATORY

Environmental Research Projects

INTERNAL REPORT
FIS NO 204

Report on

A) The distribution of trace metals in the Wilderness Lakes and Algoa Bay areas

B) The monitoring of Knysna Lagoon for trace elements

C) Trace metal monitoring of the south-eastern Cape

D) A study of the chemical speciation of toxic metals in the environment and their determination

Being the Annual Report to the National Committee for Environmental Sciences for the period
1 January to 31 December 1979

by

R J Watling, H R Watling and L R P Butler

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A. THE DISTRIBUTION OF TRACE METALS IN THE WILDERNESS LAKES AND ALGOA BAY AREAS

SUMMARY

This section outlines the work carried out at the National Physical Research Laboratory, CSIR, during the period January to December 1979 on the distribution of trace metals in the Wilderness Lakes and Algoa Bay areas. The project is supported by the Department of Environmental Planning and Energy through the National Committee for Environmental Sciences.

Surface sediments, sediment cores and water samples were collected along the beach from Woody Cape to the Great Fish River and from Cape Recife to Cape St Francis. In addition the Krom, Kowie, Gamtoos, Bushmans, Kariega and Great Fish Rivers were also sampled. Biological samples were collected where available. Copper, lead, zinc, iron, manganese, cobalt, nickel, cadmium, mercury, sodium, potassium, calcium, magnesium, strontium, aluminium and chromium were determined in all the sediment samples; fewer elements were determined in the water and biological samples.

All results have been computed and interpreted and base line reports are at present in preparation.

A.1 Introduction

Reports on the trace metal status of the Wilderness Lakes(1) and Swartkops River(2) have already been produced. Current work has centred around the surveys of the Kowie, Bushmans, Sundays, Kariega, Gamtoos, Krom and Great Fish Rivers.

A.2 Kowie River

The Kowie River enters the sea at Port Alfred. Seven water samples, four surface sediments and three sediment cores were taken. Sample preparation and analysis techniques have previously been described(1 and 2). All sediment and biological samples were analysed for copper, lead, zinc, iron, manganese, cobalt, nickel, cadmium, sodium, potassium, calcium, magnesium, strontium, aluminium, chromium and mercury, and all water samples for copper, lead, zinc, iron, manganese, cobalt, nickel, cadmium and mercury.

A.3 Bushmans River

The Bushmans River enters the sea to the south-west of Kenton-on-Sea some twenty kilometres to the south-west of Port Alfred. Four samples of each of water, sediment and core material were taken between the river mouth and salinity 4 parts per thousand. All samples were analysed as described in section A.2.

A.4 Kariega River

The Kariega River enters the sea some two kilometres north-east of the Bushmans River. Four samples of each of water, sediment and core material were taken between the river mouth and salinity 4 parts per thousand. All samples were analysed as described in section A.2.

A.5 Great Fish River

The Great Fish River represents the extreme north-easterly limit of the survey area and enters the sea some 25 kilometres north-east of Port Alfred. Five samples of each of water, sediment and core material were taken between the river mouth and salinity 4 parts per thousand. All samples were analysed as described in section A.2.

A.6 Gamtoos River

The Gamtoos River enters the sea in St Francis Bay some 50 kilometres west of Port Elizabeth. Seven samples of each of water, sediment and core material were taken between the river mouth and salinity 4 parts per thousand. All samples were analysed as described in section A.2.

A.7 Krom River

The Krom River enters the sea in the south-west corner of St Francis Bay. Seven samples of each of water, sediment and core material were taken between the river mouth and salinity 4 parts per thousand. All samples were analysed as described in section A.2.

A.8 Cape St Francis to Cape Recife Survey

Seventeen beach samples were collected between Cape Recife and Cape St Francis. Surf water samples and biological samples (where available) were also collected at each site. All samples were analysed for trace metals as described in section A.2.

A.9 Woody Cape to the Great Fish River Survey

Eight beach samples were collected between Woody Cape and the Great

Fish River. Surf water samples and biological samples (where available) were also collected at each site. All samples were analysed for trace metals as described in section A.2.

A.10 Data Handling

All data has been computerised and is at present being interpreted.

A.11 Programme for 1980

All data collected during 1979 must be interpreted, anomalies investigated and reports written for each river system and coastal area.

B. THE MONITORING OF KNYSNA LAGOON FOR TRACE ELEMENTS

SUMMARY

This project was not funded for the 1979/80 financial year. However, a report of the total survey(3) was completed during this period.

B.1 Introduction

The project was designed to establish levels of metals in Knysna Lagoon. The lagoon itself has been suggested as an area for further development, notably a marina complex, but it is also the site of South Africa's most important shellfishery.

B.2 Metal surveys in South African estuaries. II Knysna Estuary

A report with the above title has been prepared and is available on request.

C. TRACE METAL MONITORING OF THE SOUTH-EAST CAPE

SUMMARY

The South African Marine Pollution Monitoring Programme has identified eight sites in Algoa Bay, seven sites in the Krom River, five in the Swartkops River, seven in the Sundays River and six in the Great Fish River which are to be sampled twice annually, (February and August). These sites are detailed in the South African Marine Pollution Monitoring Programme report(4).

C.1 Introduction

The trace metal monitoring programme for the south-eastern Cape is designed to monitor changes in the status of the Algoa Bay and St Francis Bay areas. The sites were established after a detailed survey conducted earlier in the year.

C.2 Krom River

Water, sediment and core samples were collected in August from seven sites in the Krom River. All samples were analysed by the methods described in the Manual of Methods for use in the South African Marine Pollution Monitoring Programme(5). In addition, all core samples were analysed using a nitric/perchloric acid leach and results thus obtained are being compared to obtain continuity of data between the survey and the monitoring phases of the programme.

C.3 Swartkops River

Water, sediment and core samples were collected in August from five sites in the Swartkops River. All samples were analysed using the techniques described for the Krom River, section C.2.

C.4 Sundays River

Water, sediment and core samples were collected in August from seven sites in the Sundays River. All samples were analysed using the techniques described for the Krom River, section C.2.

C.5 Great Fish River

Water, sediment and core samples were collected in August from six sites in the Great Fish River. All samples were analysed using the techniques described for the Krom River, section C.2.

C.6 Algoa Bay

Water, sediment, sediment cores and biological material were collected from eight sites in Algoa Bay. Metal contents in all samples were determined using the methods described in section C.2.

C.7 Results

As yet only the first monitoring cycle of the South-East Cape area has been undertaken and until the February sampling has been completed, no conclusions can be drawn from the raw data. A report will be submitted during 1980 on the total programme for the first year.

D. A STUDY OF THE CHEMICAL SPECIATION OF TOXIC METALS IN THE ENVIRONMENT AND THEIR DISTRIBUTION

SUMMARY

This section outlines the work carried out in the National Physical Research Laboratory, CSIR, during the period April, 1979 to December, 1979, on the study of the chemical speciation of toxic metals in the environment and their distribution.

A method for differential thermal release of mercury compounds was investigated and a qualitative separation achieved.

A selective leaching technique was investigated and preliminary results indicated that separation into chemical 'forms' of metals, at least qualitatively, is possible.

A computer program was developed to normalize data to geochemically derived metals. Results are reported for the Swartkops River.

The extraction technique for selenium, arsenic and antimony from fresh and sea water was extended to include biological samples and the method has been submitted for publication.

D.1 Introduction

The form in which the chemical elements occur is of paramount importance as this will affect not only toxicity, but uptake rates, residence times in the environment and pathways through both ecological and biochemical cycles.

D.2 Mercury differential thermal release

Initial experiments to design an apparatus which was capable of controlled thermal release of mercury from its compounds, were somewhat difficult, due to problems associated with uneven sample heating and unburnt organic vapour entering the optical path. These problems were particularly noticeable at temperatures below 200°C. The final apparatus (to date) is shown in Figure 1. This consists of a silica combustion tube containing the sample (10 g) in a ceramic boat. The tube is heated by a resistance heater and the temperature of the sample is measured directly, using a thermoprobe buried in the sample. Air, at the rate of 850 ml min^{-1}, is passed over the sample and the entrained evolved volatile material passed through a cracking cell at 750°C. The cracking cell is necessary to avoid evolved organic vapour passing unburnt into the optical path. In addition this cell serves to break down organo-mercury compounds, although this is not absolutely necessary as the quartz tube in the optical path is heated by an argon (entrained air)-hydrogen flame.

From the thermal cracking cell the heated vapour passes into the quartz tube, which is aligned in the optical path of the spectrometer, where atomic absorption by the mercury atom takes place. Simultaneous background correction is used throughout and results are recorded as peaks on a chart recorder.

Composite thermal release peaks for the initial experiments are shown in Figure 2. The mercury in uncontaminated samples from Knysna Lagoon (Fig. 2A) have a release peak at approximately 150°C. Samples taken in the drainage area of the town (Fig. 2B) however, have a more complicated pattern of release, with peaks at approximately 70°C, 150°C and 610°C. Sediment samples taken in the area of Swartkops (Port Elizabeth) (Fig. 2C)

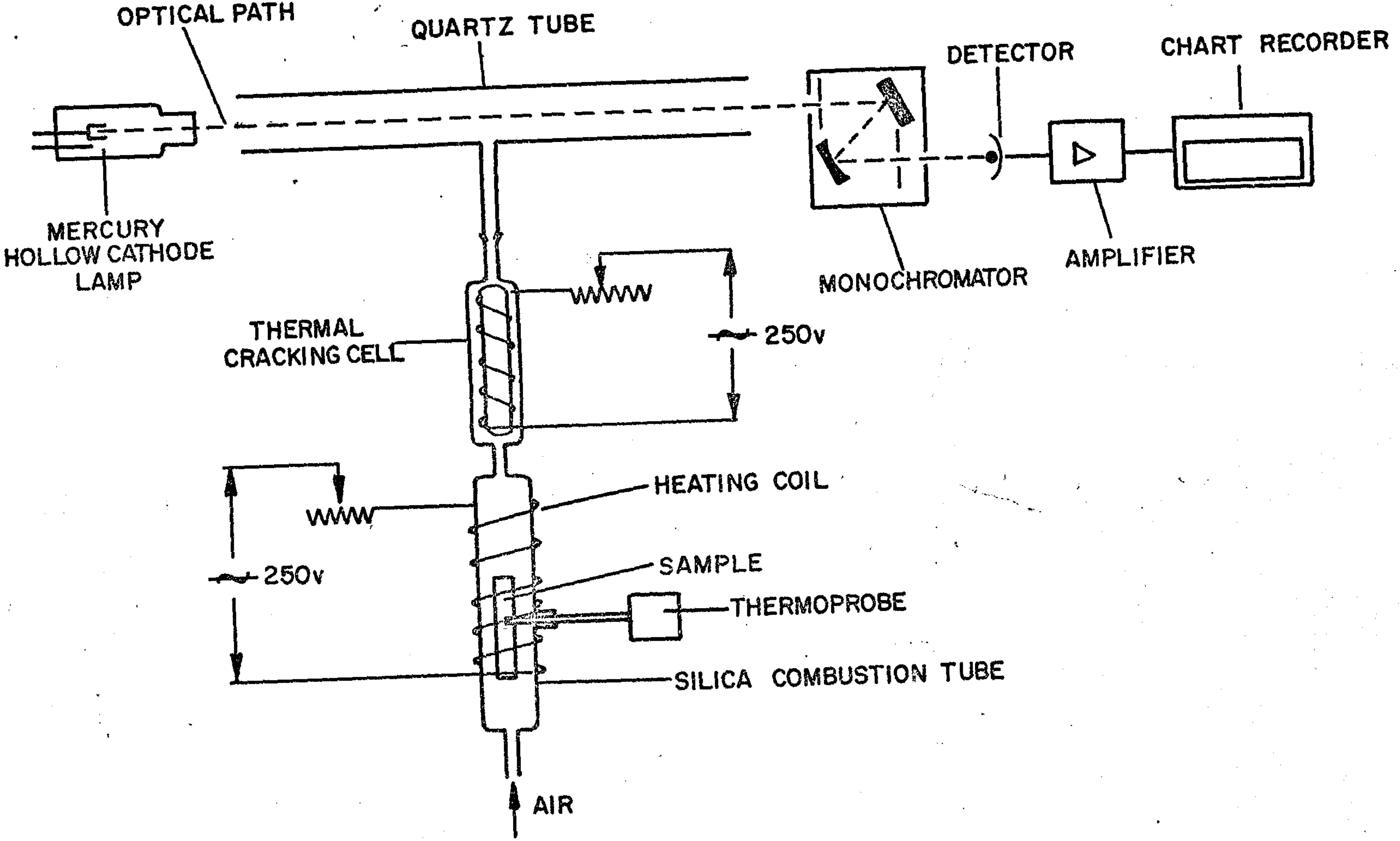

FIG.1 DIAGRAM OF APPARATUS FOR MERCURY THERMAL RELEASE

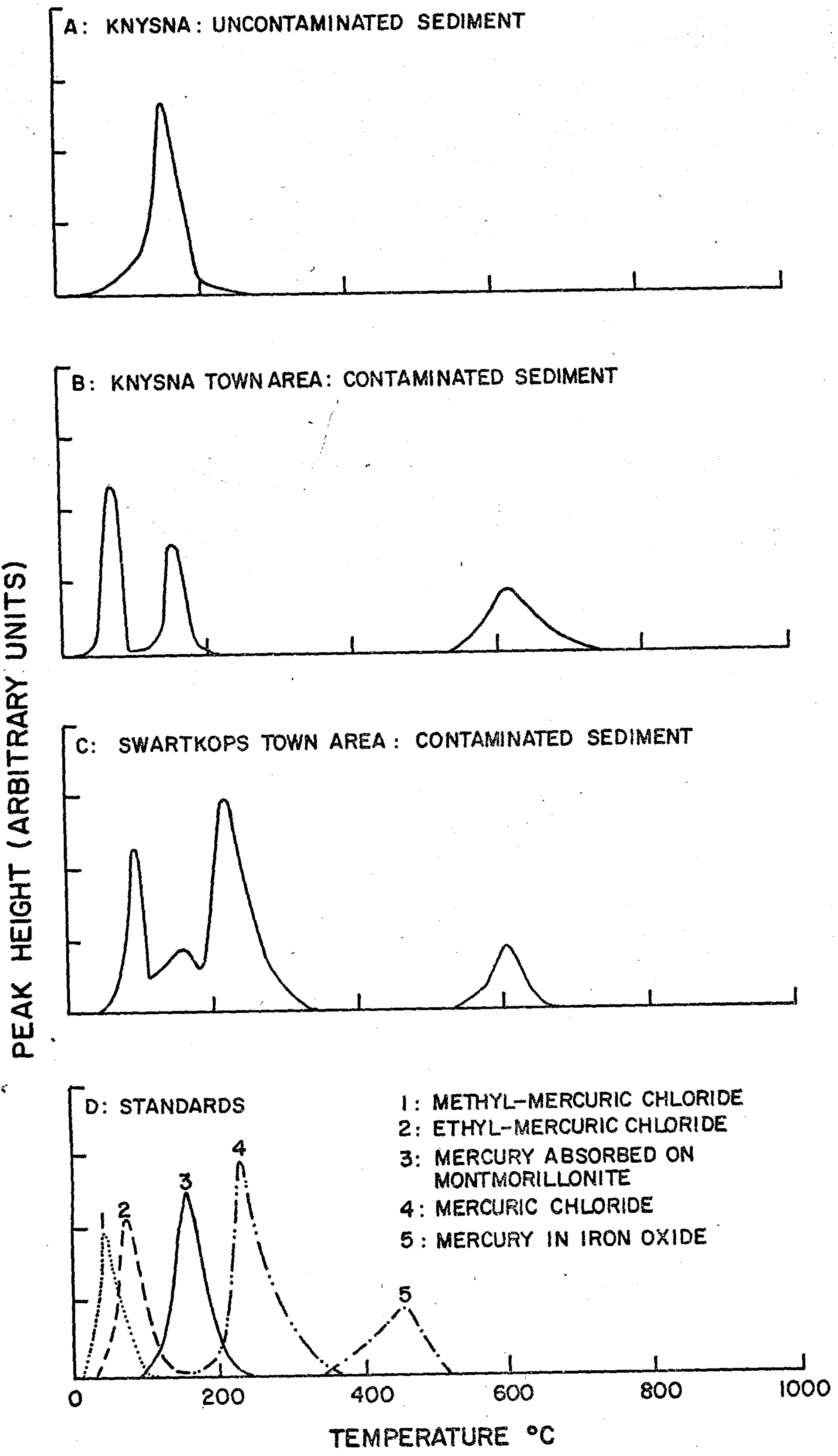

FIG. 2 COMPOSITE THERMAL RELEASE PEAKS FOR MERCURY FROM SEDIMENT SAMPLES

have even more complex patterns with peaks at approximately 100°C, 160°C, 220°C and 600°C.

A series of standards has been produced in a mixture of sand (< 50 µm), kaolin and calcium carbonate, containing methyl-mercuric chloride, ethyl-mercuric chloride and mercuric chloride. Thermal release peaks for these are shown in Figure 2D. In addition, iron oxide containing lattice held mercury and mercury adsorbed onto montmorillonite have also been mixed with the bulk diluting matrix to produce two further standards .

From the thermal release graphs of these standards there appears to be a coincidence of certain peaks. Both Knysna and Swartkops town sediments have mercury release peaks which occur in the same temperature range as those from the ethyl-mercuric chloride standard and the adsorbed mercury standard. Swartkops town sediments also have a peak in the same position as the mercuric chloride standard. A peak which occurs in samples from all three areas is also coincident with that of the adsorbed mercury release peak.

At this stage it is far too early to suggest that any of the release peaks are from specific mercury compounds and a great deal more work is necessary before this can be achieved. However, it can be said that the sediments from the contaminated areas of Knysna town and Swartkops town contain more than one mercury compound and that these compounds are different from those found in uncontaminated areas.

The high temperature peak (Fig. 2B and C) is as yet unresolved. However from its shape, it is probably lattice-held mercury in a discrete mineral phase and is likely to be of primary geochemical significance.

D.3 Selective leaching of sediments

An attempt has been made to provide a differential leaching technique for sediments in an effort to establish the 'form' of the metal in the sediment. The leaching scheme is detailed below.

A) 10 cm lengths of core material are cut from the extruded core(5) and sectioned longitudinally in half. One half is weighed and placed in a beaker containing 500 ml of previously analysed sea water. The mixture is stirred on a magnetic stirrer for 30 min, allowed to settle and 250 ml of water removed. This sample is filtered through a 0,45 µm membrane and extracted using NaDDC/$CHCl_3$(6). The metal content is determined using flame atomic absorption and related back to the original sample. The second half of the sample is weighed and dried to establish water content.

The following leach stages (B-F) are carried out using the same 5 g sample.

B) The 5 g sample is placed in a 100 ml beaker and 25 ml 1 M magnesium chloride solution (pH 7) added. The mixture is stirred for 15 min using a magnetic stirrer and then allowed to settle. A portion of the supernatant liquid is removed and filtered through a 0,45 µm prewashed membrane filter. The filtrate is stored to await analysis. The residue is transferred to a Whatman 541 filter paper and washed three times with distilled water to remove all traces of the leach solution. The sample is then dried prior to the next leach.

C) The sample is placed in a 100 ml beaker and 25 ml 1 M acetic acid added. The mixture is stirred for 15 min using a magnetic stirrer and then allowed to settle. A portion of the supernatant liquid is removed and filtered through a 0,45 μm prewashed membrane filter (this can be the same filter as for (B)). The filtrate is stored to await analysis. The residue is treated in exactly the same manner as for (B).

D) The sample is placed in a 100 ml beaker and 25 ml 0,04 M hydroxylammonium chloride made up in 20% v/v acetic acid added. The mixture is stirred on a heating magnetic stirrer at 90°C for 1 hour and then allowed to settle. A portion of the cold supernatant liquid is removed and filtered through a 0,45 μm prewashed membrane filter (this can be the same filter as for (B)). The filtrate is stored to await analysis. The residue is treated in exactly the same manner as for (B).

E) The sample is placed in a 100 ml beaker and 25 ml 4:1 nitric:perchloric acid added. The mixture is evaporated dry at approximately 130°C and when dry, 10 ml 10% v/v nitric acid are added and the residue resuspended. The mixture is allowed to settle and the supernatant liquid drawn off the top using a pipette. This solution is transferred to a separate container to await analysis. The residue is treated in exactly the same manner as for (B).

F) The sample is placed in a 100 ml teflon beaker or 50 ml platinum dish and 25 ml 5:4:1 hydrofluoric:nitric:perchloric acid added. This mixture is taken to dryness at approximately 130°C and when cold, 10 ml 10% v/v nitric acid are added to leach the residue. The mixture is then allowed to settle and the supernatant liquid drawn off the top using a pipette. This solution is transferred to a separate container to await analysis.

G) 20 ml concentrated hydrochloric acid are added to a fresh 5 g sample of sediment contained in a 100 ml teflon beaker. When the effervescence has stopped, 25 ml 5:4:1 hydrofluoric:nitric:hydrochloric acid are added and the mixture evaporated to dryness at 130°C. When dry, a further 10 ml hydrofluoric acid and 20 ml perchloric acid are added and the mixture again evaporated dry. When cold 10 ml 10% v/v nitric acid are added to dissolve the residue and the resulting solution reserved for analysis.

This leach scheme is far from ideal, However, it is proposed that it will selectively leach the metal 'forms' shown in Table 1.

TABLE : 1 METAL 'FORMS' REMOVED BY SUCCESSIVE LEACHES

Leach	
A	Metal in interstitial water
B	Extractable metal
C	Metal in the carbonate fraction
D	Metal in the iron and manganese hydroxide fraction
E	Metals bound to clay minerals, in clay lattices and in organic material
F	Total residual metal either in the oxide or another mineral form or included in quartz or silicate materials
G	Total metal

One feasibility study has been undertaken using samples from the Swartkops River, Figure 3. Only preliminary results have been obtained and a method of presentation has not yet been finalised. However, Table 2 gives an indication of the kind of data a leach scheme such as that detailed here will produce.

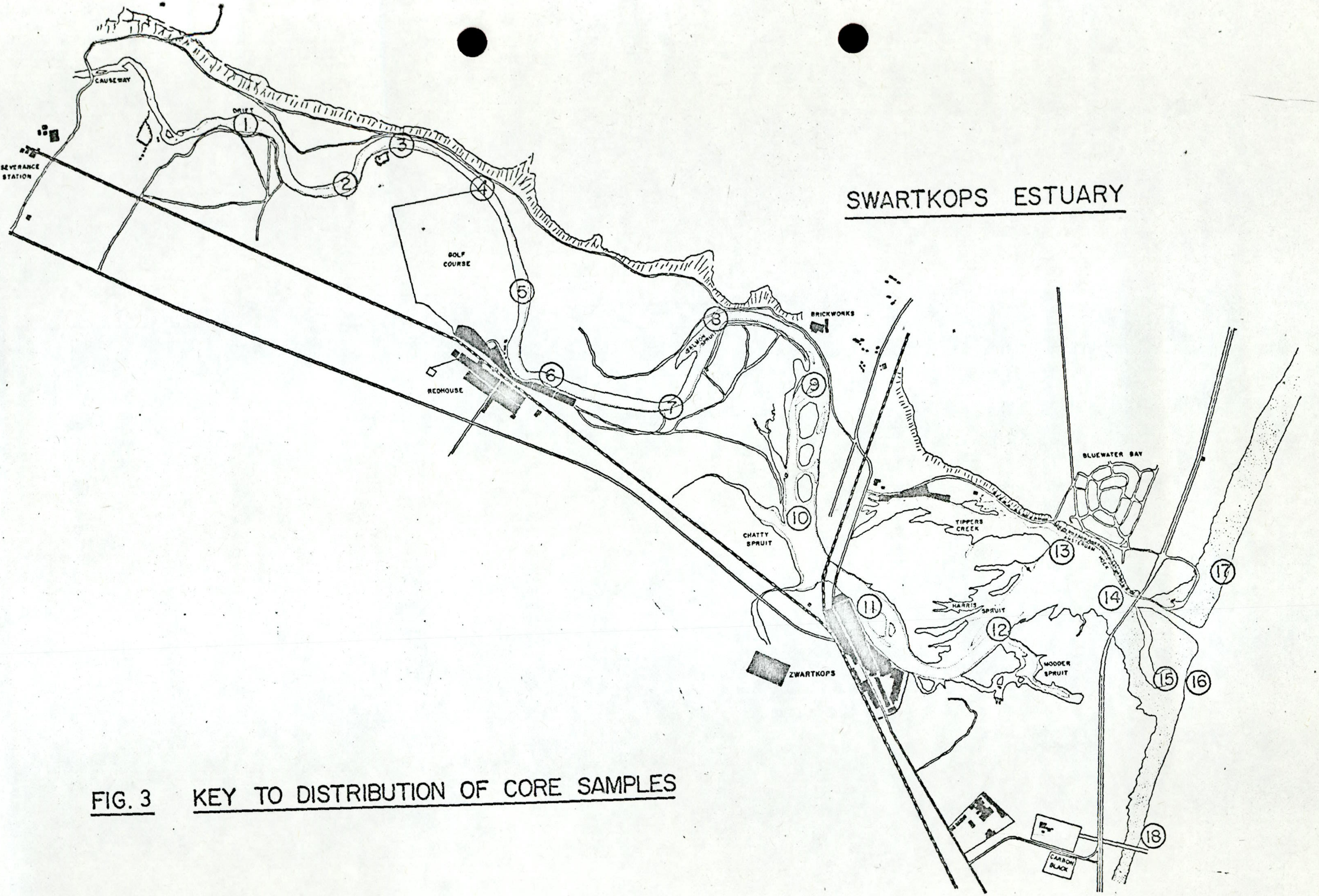

FIG. 3 KEY TO DISTRIBUTION OF CORE SAMPLES

TABLE : 2 CHEMICAL 'FORMS' OF METALS FROM THE SWARTKOPS ESTUARY

SITE No.	Cu	Pb	Zn	Co	Ni	Cd	Cr
8	E	E	E	E	E	E	E
9	E	E	E	E	E	E	E
10	AE	AE	AE	AE	AE	AE	AE
11	AE	F	AE	E	E	AE	E
13	A	AF	AF	AEF	AE	AE	AE
14	A	AF	A	AF	AEF	AE	AE

Letters refer to leach method see Table 1.

Although it is possible to produce a qualitative indication of 'chemical form' of metals in sediments, a considerable amount of work needs to be undertaken before this or a similar scheme will produce quantitative and reproducible results.

D.4 Normalization of sediment data to Fe/Al, Al/Fe, Co/Ni, Ni/Co, Ni, Co, Fe and Al

A computer program was written to normalize all sediment data to Fe/Al, Al/Fe, Co/Ni and Ni/Co ratios and to Ni, Co, Fe and Al. All river and estuarine samples (2261) and all coastal samples (1490) collected between Mossel Bay and the Great Fish river were normalized by this technique. It has been established that when results are normalized to Fe/Al and Co/Ni, it is possible to determine sites of anomalous metal input and metal accumulation in the sediment, even though these sites may not have significantly elevated total metal levels. Background normalized metal values have been established for both the entire coastal region and each river, but owing to the large volume of data, only preliminary results for Cu, Pb, and Zn are available. These are shown in Table 3.

TABLE : 3 NORMALIZED VALUES FOR COPPER, LEAD AND ZINC IN SEDIMENTS FROM THE SOUTH EAST CAPE

Area and Element	Normalization Fe/Al	 Co/Ni
A - Coastal Sites		
Cu	1,5 1,0 - 1,5	4,0 + 2,0 - 4,0
Pb	3,0 + 1,5 - 3,0	9,0 + 5,0 - 9,0
Zn	1,5 + 2,0 - 1,5	2,0 + 1,5 - 2,0
B - River and Estuarine Sites		
Cu	2,0 + 1,5 - 2,0	4,0 + 3,0 - 4,0
Pb	3,0 + 2,0 - 3,0	10,0 + 8,0 - 10,0
Zn	7,0 + 5,0 - 7,0	20,0 + 10,0 - 20,0

The wide standard deviation of results is due to the fact that the survey covers about 600 kilometres of beach with varying sedimentary regimes. This is also true for the river and estuarine survey as fourteen rivers are included. If individual river systems are investigated in isolation, the standard deviation decreases and it is possible to obtain more detailed information. Figure 4 shows the results for the Fe/Al normalization of copper, lead and zinc in the Swartkops River (Fig. 3). From this it can be seen that there is a general increase in the normalized values for all these elements with a peak at site 9, downstream from the brickworks. Further downstream, at site 10, values begin to drop, while opposite Swartkops village, site 11, values increase again.

Equivalent results are obtained using Ni/Co as the normalizing ratio. These two techniques identify sites 7, 8, 9, 11 and 13 as being anomalous.

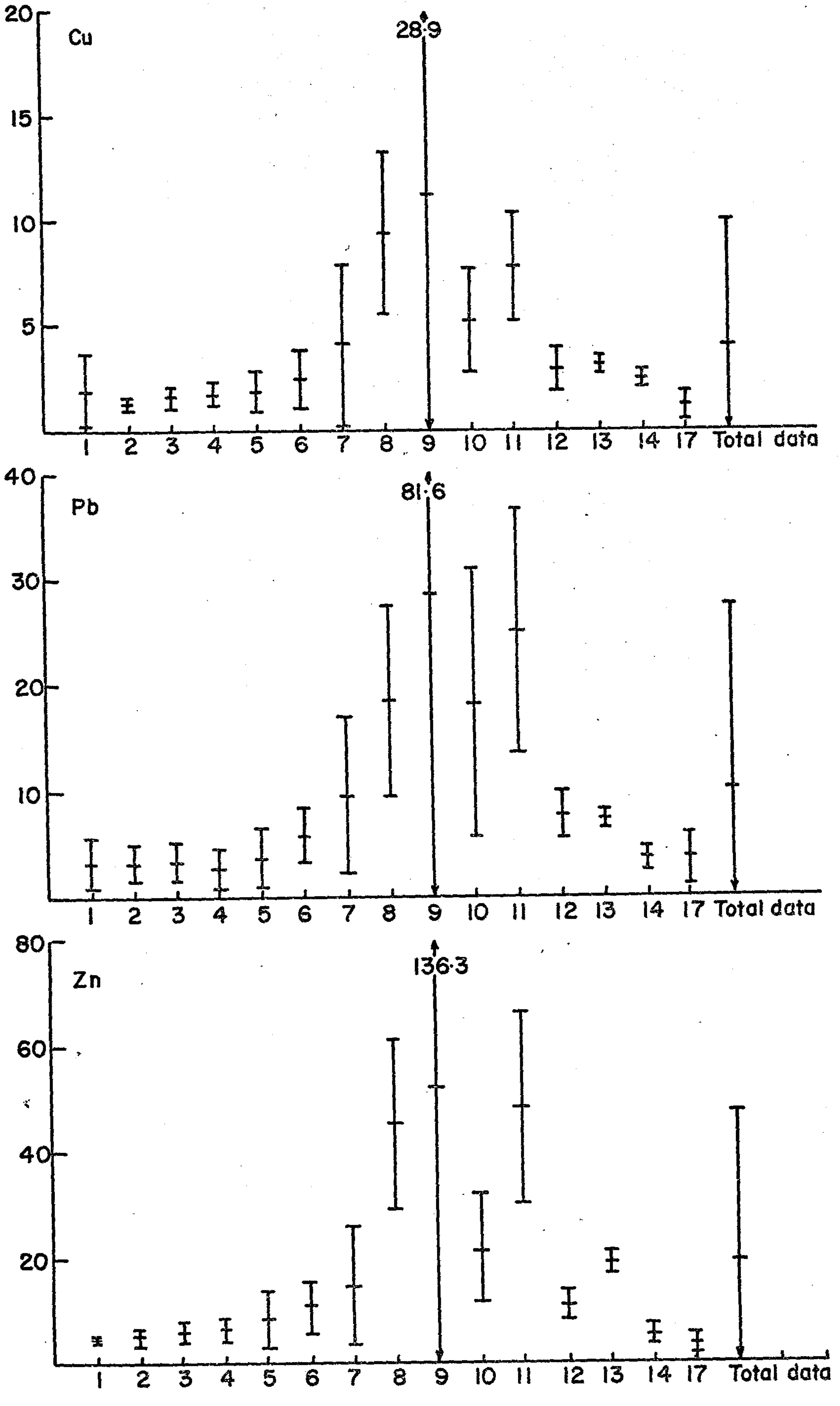

FIG.4 TRACE METAL CONCENTRATIONS IN SEDIMENTS FROM THE SWARTKOPS RIVER NORMALIZED TO Fe/Al

These sites are the same as those previously identified using a matrix webbing technique(2).

In the previous survey(2), the Redhouse area was also identified as being anomalous. However, this was established on the basis of water chemistry alone and not sediment chemistry and this is the reason for the normalized sediment values not being anomalous.

D.5 The determination of As, Sb and Se

A paper describing the preconcentration and analysis of arsenic, antimony and selenium was presented at the XXI CSI and 8th ICAS meeting in Cambridge in July, 1979. This paper has also been submitted for publication.

D.6 The oxidation of biological material

A paper entitled "The oxidation of biological material prior to the AAS analysis of As, Sb, Se and Hg" was presented at the Management and Control of Heavy Metals in the Environment Conference, London, in September 1979(7).

D.7 Manual of Analytical Methods(5)

A manual of methods to be used by participants in the South African Marine Pollution Monitoring Programme has been prepared and will be circulated to all participants in the near future.

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