The Distribution of Trace Metals in the Wilderness Lakes

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Abstract

Water, sediment and sediment core samples were taken in the Wilderness Lakes area and the concentrations of up to seventeen elements were determined. Results have enabled the construction of a comprehensive three-dimensional picture of the trace and major metal distribution in the area. With the exception of Island Lake and Sedgefield Lagoon opposite Sedgefield town, no areas show marked evidence of metal contamination by man.

Introduction

The accumulation of metals in the sediments and waters of rivers, lakes, dams and estuaries has long been a cause for concern amongst environmental chemists. The subject is, however, receiving considerable attention both in South Africa (Wittmann and Förstner, 1975; Wittmann and Förstner, 1976; and Willis et al., 1977) and abroad (Wisseman and Cook, 1977; Taylor, 1976; Halcrow et al., 1973; Thornton et al., 1975; and Jaffe and Walters, 1976). Although important, it is nevertheless incomplete to simply establish metal distribution in surface sediments; metal concentrations in sediment cores should also be investigated. It is only by so doing that the historical impact of heavy metals, if any, can be assessed and baseline levels, before metal build-up, established.

The aim of this study is to provide information on the present trace metal status of the Wilderness Lakes area and, by using sediment cores, to establish trends in metal build up.

Location and general geomorphology

The Wilderness Lakes region is situated on the Southern Cape coast between the cities of Cape Town and Port Elizabeth (Figure 1). The lakes occupy east-west valleys approximately parallel to the coast and generally at right angles to the main drainage direction, being defined by parallel ridges of Pleisto-

cene dune rock (Morton, 1962 and Hill, 1975). The history of the development of the Lakes is somewhat unclear, but the main theories seem to suggest their origin as early coastal lagoons impounded behind offshore bars, flooded interdunal depressions, or as original river valleys diverted by dune formation to seaward.

In general, the catchment areas of the individual lakes are small in relation to their surface area (Table 1) and this would be expected in the case of their formation through coast-line drowning. Swartvlei, however, does receive water from three reasonably large rivers, the Diep, the Hoogenkraal and the Karatara, and it is also tidal, being separated from the sea by a bar. There is also a bar at the western end of the lakes at Wilderness Lagoon. The exception to this system is Groenvlei, which is separated from Swartvlei by a wide strip of alluvium and from Ruigtevlei and the sea by dune formation rising to a maximum elevation of 180 m above sea level. In addition, at its eastern end it is separated from the adjacent Goukamma river by dune sand. The lakes can therefore all be considered as predominantly fresh water, with the exception of their immediate entrances to the sea at Sedgefield and Wilderness.

SURFACE	AREA	AND	CATCHMENT	OF	THE
	WII	DERN	IESS LAKES		

Lake	Surface Area km²	Catchment Area km ²				
Swartvlei	10,73	397,6				
Groenvlei	2,46	9,45				
Langvlei	2,14	20,79				
Island Lake	1,48	11.16				
Rondevlei	1,41	4,76				
Ruigtevlei	1,18	15,10				

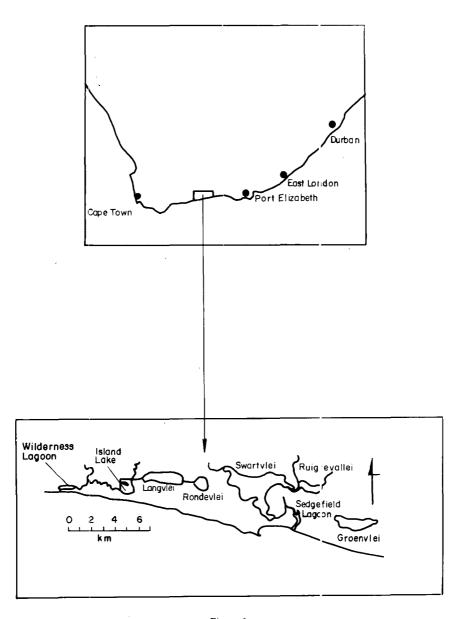


Figure 1
Location and map of the Wilderness Lakes

The geology of the area has been extensively investigated (Schwartz, 1905 and Potgieter, 1950). The igneous and metamorphic Pre-Cape rocks in the west and the Table Mountain Sandstone in the east form a peneplain, levelled during the Tertiary, into which rivers have cut deep meanders. Sea attack on this raised plain has produced an impressive cliffed coastline especially in the west near Wilderness Lagoon.

Sample collection and analysis

All samples were collected during April 1977.

Water

Surface water samples were taken 0,5 m below the actual lake surface using an NIO sampling bottle suspended on a nylon

coated steering cable. In addition to surface samples, profiles were also taken in Swartvlei. This lake is by far the largest of the Wilderness Lakes with a surface area of 10,73 km² and a maximum depth of 12,5 m, although this varies somewhat with respect to the height of the bar at Sedgefield. The bathymetry of Swartvlei and positions of the profile sites are given in Figure 2. At each site a depth, salinity and temperature profile was carried out at 0,5 m intervals and it was established that although a thermocline was not present, there was a very significant halocline at a depth of approximately 6 m. Water samples were collected at each depth and returned to the surface for extraction. Immediately after collection, one litre of sample was transferred to a stripped 2,3 l high density polyethylene bottle. A separate 500 ml sample was collected for mercury determination.

The pH of the 1l sample was adjusted to neutral, 10 ml of a buffered solution of sodium diethyldithiocarbamate added and the mixture shaken for 5 min (Watling and Watling, 1976).

Samples were stored in this form until the end of each day when they were returned to the laboratory and the chelate extracted into chloroform. After evaporation of the chloroform with 2 ml of concentrated nitric acid, the residue was dissolved in 10 ml of 10% nitric acid. The concentrations of copper, lead, zinc, cobalt, nickel, iron, manganese and cadmium in the sample were determined using flame atomic absorption spectrometry.

The mercury sample was mixed with 10 ml of 5% potassium permanganate solution and 2 ml of concentrated sulphuric acid. The bottle was stoppered and the mixture left for 24 h to oxidise the organic mercury compounds to ionic mercury. Subsequently the excess permanganate was reduced using 10% hydroxylammonium chloride and the elemental mercury evolved using stannous chloride. Mercury determination was

carried out using a microwave-induced argon plasma emission system (Watling, 1975).

The distribution of water samples is shown in Figure 3.

Surface sediment

Surface sediment samples were taken using an aluminium drag which was trawled across the bottom of the lake on the end of a nylon rope. The drag was towed slowly behind the boat for approximately 50 m in each of three sweeps and the composite sample obtained, mixed and subsampled to provide approximately 500 g of sediment. Each sample was stored in a plastic bag during sampling and finally air-dried between filter paper

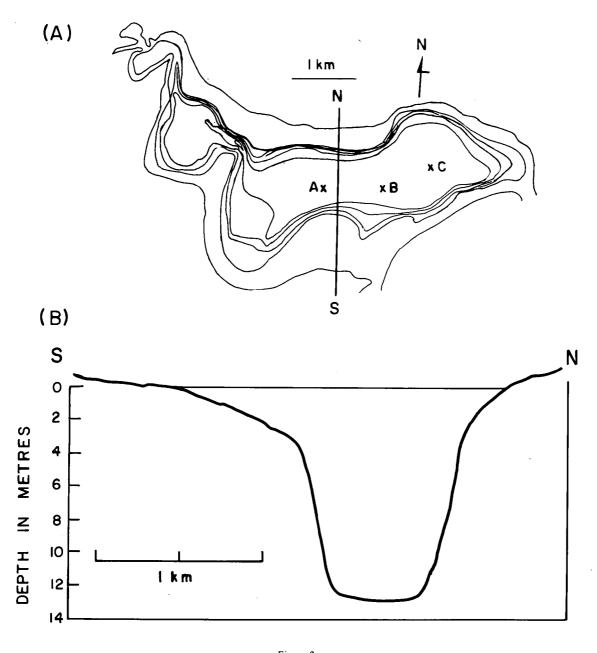


Figure 2

A) Bathymetric map of Swartvlei with transect line and position of profile samples (contour interval 3 m)

B) Cross section along transect line

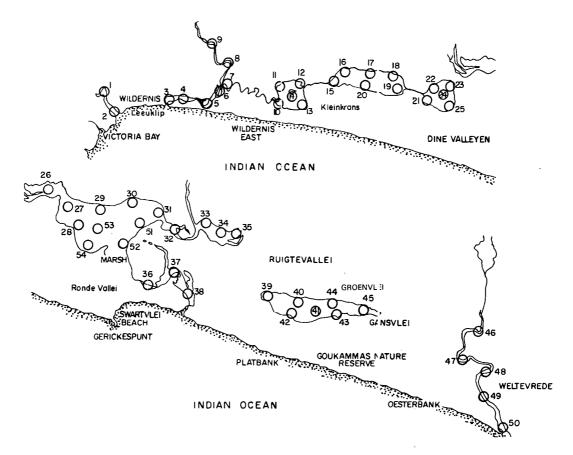


Figure 3
Distribution of water samples

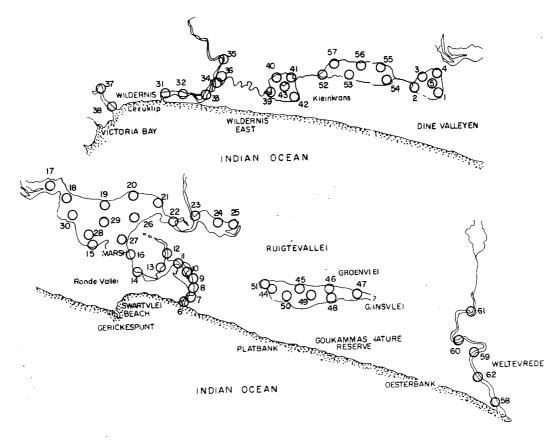


Figure 4
Distribution of sediment samples

sheets. The whole sample was disaggregated using a porcelain pestle and mortar, taking care not to grind the sample and the fraction passing through a 210 μ m sieve screen was reserved for analysis.

Subsamples (5 g) of the original sample were subsequently transferred to 100 ml conical flasks and 20 ml of concentrated redistilled nitric acid added. The mixture was taken to dryness at 120°C and 25 ml of a mixture of 4:1 nitric/perchloric acids added. The mixture was again taken to dryness and when cold, 10 ml of 10% nitric acid added to dissolve the soluble component of the residue. The concentrations of copper, lead, zinc, cobalt, nickel, iron, manganese, sodium, potassium, calcium, magnesium, strontium, aluminium and chromium were determined using flame atomic absorption spectrometry, absorbance values being compared to artificial standards.

The preparation and analysis procedure for mercury was, however, somewhat different (Watling, 1978). Sediment (2 g) was transferred to a ceramic boat and placed in a combustion tube inside a tube furnace pre-set to 700°C. A flow of 700 ml/min of oxygen was directed over the sample during its slow combustion inside the furnace. The exhaust gases were passed through acidified potassium permanganate to absorb the evolved mercury. The sample was heated for seven minutes after

which time the acidified permanganate was reduced using hydroxylammonium chloride and the mercury determined using a modified cold vapour technique (Watling, 1975). The distribution of surface sediment samples is shown in Figure 4.

Core samples

Core samples of 50 mm width and up to 600 mm in length were taken in each of the Lakes 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 core liner, containing the sample, removed. The core liner was then sealed using cork stoppers covered with polyethylene and the whole sample frozen to -20° C.

Cores were stored frozen for about eight weeks before sampling, but no deterioration was observed. Each core was cut longitudinally using a band-saw and both halves scraped clean with a stainless steel knife. One half was reserved to act as a reference sample, resealed in polyethylene and refrozen. The other half was measured and catalogued sedimentologically before sampling. Samples of unsieved core material weighing approximately 4 g were taken at 2 cm intervals and also on ob-

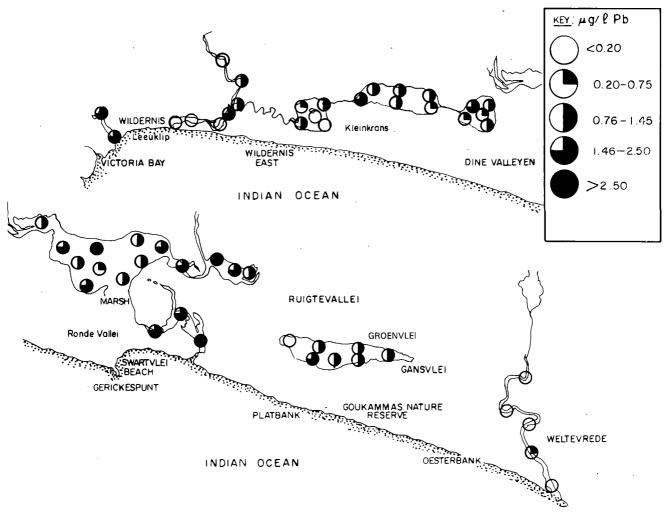


Figure 5
Concentrations of lead in water from the Wilderness Lakes

TABLE 2 TRACE METAL CONCENTRATIONS IN WATERS FROM THE WILDERNESS LAKES ($\mu g/l$)

ample No.	Cu	P b	Zn	Fe	Mn	Co	Ni	Cd	Hg
1	1,7	1,7	1 , 5	456	20,2	0,3	0,4	0,6	<0,01
2	1,4	2,0	2,3	461	25,3	0,3	0,6	1,3	(0,01
3	0,5	<0 , 1	1,9	41	4,4	<0,1	<0,1	1,8	0,09
4	0,5	<0,1	1,4	1 00	11,7	<0,1	<0,1	<0,1	0,0)
5	0,5	0,1	1,7	325	25,3	₹0,1	0,2	3,2	0,20
6	0,7	2,2	1,5	405	31,0	0,3	1,1	0,2	0,20
7	0,6	1,4	2,3	431	24,6	<0,1	<0,1	1,1	<0,01
8	1,0	1,2	2,4	475	33,5	<0,1	<0,1	2,9	0,08
9	1,0	<0,1	1,6	534	38,1	⟨0,1	<0,1	0,1	0,37
10	0,5	1,1	0,8	76	49,2	₹0,1	0,1	0,1	0,52
11	0,7	0,6	1,6	62	49,6	<0,1	0,1	0,8	0,01
12	0,5	1,0	0,6	5 2	50,3	<0,1	0,1		
13	0,2	0,1	1,4	61 .	54 , 0	<0,1	<0,1	<0,1	0,11
14	0,5	0,1	0,8	62	50,0	<0,1	(0,1	0,2	
15	0,2	1,7	0,8	47	36 , 5		<0,1	<0,1	1 00
16	0,5	1,1	0,7	25	10.5	0,1	<0,1	0,1	1,00
17	<0,1				19,5	<0,1	<0,1	0,4	2.26
18		1,3	0,6	29	22,7	0,3	0,1	0,1	0,06
19	1,4	1,3	1,3	124	32,4	0,3	0,1	0,3	
	0,2	0,6	0,5	66	26,0	0,1	0,1	0,1	0,62
20	0,2	1,2	0,7	41	28,4	0,1	<0,1	0,4	
21	0,4	0,5	1,0	17	11,0	0,1	0,2	0,6	0,51
22	1,6	1,7	2,0	27	10,0	0,1	0,3	0,7	0,17
23	0,4	1,1	0,9	31	12,0	0,1	0,3	0,4	0,39
24	0,2	0,5	1,2	21	16,0	<0,1	0,3	0,3	0,53
25	0,4	1,1	1,5	13	10,0	0,1	0,1	1,1	0,11
26	0,2	1,1	0,7	260	215,0	<0,1	<0,1	0,3	0,11
27	0,2	1,7	0,5	82	137,0	<0,1	<0,1	0,2	<0,01
28	0,2	1,1	0,8	59	137,0	<0,1	0,2	0,3	
29	0,2	2,8	1,4	68	158,0	<0,1	<0,1	0,3	
30	0,4	1,1	0,6	102	181,0	0,1	0,1	0,3	
31	0,2	1,7	0,5	225	146,0	0,1	0,2	0,3	
32	9,8	1,7	0,6	478	143,0	0,1	0,2	0,3	0,05
33	0,4	2,8	1,2	977	24,0	<0,1	0,1	0,7	•,•,
34	0,4	2,2	1,5	1086	36,0	0,1	0,2	1,2	0,42
35	1,9	1,7	1,2	1025	26,0	0,2	0,1	1,2	0,12
36	0,4	1,7	0,7	42	18,0	<0,1	<0,1	0,3	
37	0,2	1,7	0,8	37	8,0	<0,1	0,1	0,3	0,11
38	0,4	2,8	0,6	26	2,0	<0,1	0,2	0,3	0,
39	0,5	<0,1	1,9	15	4,1	<0,1	<0,1	0,5	0,430
40	0,9	1,0	1,2	19	1,8	<0,1	<0,1	0,1	0,15
41	2,2	1,4	2,4	25	4,8	0,1	<0,1	0,4	
42	0,5	1,6	1,6	20	0,5	0,1	⟨0,1	0,7	0,03
43	3,4	1,0	2,4	20	0,5	` <0,1	<0,1	1,3	0,05
14	0,7	1,0	1,7	12	0,7	<0,1	<0,1	0,4	
4 5	0,5	1,2	1,8	21	2,3	0,2	0,1	0,5	0,05
16	0,5	0,1	1,4	572	33,3	<0,1	0,1	0,1	<0,01
17	0,5	0,1	1,0	308	22,1	<0,1	0,1	0,1	0,590
18	0,9	0,1	1,1	397	21,6	0,1	0,1		0,77
19	0,2	0,5	1,1	259	16,8	<0,1		0,1	
50	0,7	<0,1	0,8	23 3 75	7,6	ZO, 1	0,1	0,4	ZO 017
51	0,2	1,1	0,8	114	186,0	<0,1	<0,1	0,1	<0,010
52	0,2	1,1	0,6	93		<0,1	0,1	0,3	
53	0,8	0,6	0,6	2 7 3	98 , 0 ∤268 , 0	<0,1	<0,1	0,5	0.40
54	0,8	1,7	4,2 0,7	213 68		<0,1	0,2	0,3	0,190
· r	٠,٤	٠,٠	σ , ϵ	00	153,0	<0,1	0,1	0,2	

vious sedimentary boundaries, and oven-dried at 90°C. Accurate masses before and after drying were recorded. Samples were then leached using the method already described and their metal contents determined by means of atomic absorption spectrometry. Mercury was determined in air-dried subsamples in the same way as described for surface sediments.

Results and Discussion

The concentrations of nine trace metals in surface water are given in Table 2.

In general, there is very little overall variation in values for copper, lead, zinc, nickel, cobalt and cadmium throughout the surface waters of the Lakes, although local anomalies do occur. Relatively high levels of lead are found towards the northern and eastern ends of Swartvlei and near Sedgefield, this latter being a possible result of urban pollution (Figure 5). As can also be seen from this figure the seaward end of Wilderness Lagoon is low in lead while values in the upper reaches, near road workings and a holiday camp, increase markedly by comparison; this again is probably the result of pollution. The concentrations of metals in water and sediment on text diagrams are expressed as contour points. The intervals of the contours are defined by evaluating sub-populations for the area on the basis of frequency diagrams and are not merely arbitrary. The reason for identifying the distribution of metals like this is that actual samples may never be repeated and consequently finite concentrations do not have as great a significance in identifying anomalous areas as the establishment of a general trend.

Because iron is derived from catchment rocks by leaching and as each lake has a distinct catchment area, it would be expected that the distribution of iron in the Lakes waters would be quite specific. Extremely high levels occur in Ruigtevlei, being greater than $1\ 000\ \mu g/l$; this is because of the general euxinic nature of the lake. Swartvlei also has high levels, primarily be-

cause the streams from the catchment bring large quantities of iron into the lake. The rest of the Lakes have very low levels, the values for Groenvlei and Rondevlei being conspicuously lower than those for any others. The importance of iron in water is that it is usually unstable and when oxidised, the hydrated ferric oxides can co-precipitate metals, thereby increasing the level of certain transition elements in the bottom sediments.

The distribution of manganese in the Lakes water is similar to that of iron with one notable exception. Ruigtevlei has the highest iron values, but very little manganese. Swartvlei has nigh levels of manganese in its surface water, as do Langvlei and Island Lake. However, the manganese levels in the water of these last two lakes are relatively higher than the corresponding iron values. Both iron and manganese occur in relatively low levels in Groenvlei. This is probably because the majority of this lake's water comes from percolation through the surrounding dune sands and replacement of these metals by leaching from these sands is extremely small.

The variation in concentrations of iron and manganese through the Swartvlei halocline is of special interest. However, with the exception of these two elements, the other metals investigated in this study show little change in concentration across the halocline, although lead does appear to increase slightly at the base of the water column (Table 3).

Iron and manganese show considerable change (Figure 6), as would be expected, as the haloclinal boundary is also an Eh/pH boundary (Howard-Williams, 1978). Below the halocline the concentration of hydrogen sulphide in the water increases markedly and the consequent change in pH enables both iron and manganese to remain in solution. The concentration of manganese increases sharply just above, and that of iron just below, the halocline. Towards the bottom, concentrations appear to decrease slightly, but this is probably due to colloidal precipitation of iron and manganese sulphides as there is an abundance of hydrogen sulphide in the water at this depth. Swartvlei appears to be the only lake deep enough to support a

TABLE 3 VARIATION IN TRACE ELEMENT CONCENTRATION ACROSS THE SWARTVLEI HALOCLINE												
Site*	Depth m	Salinity %	Cd	Zn	Cu	Pb (μg/ <i>l</i>)	Со	Ni	Fe	Mı		
A	1	8,1	1,0	6,2	1,2	0.1	<0.1	0,1	57	148		
	4	8,1	0,2	1,9	0,2	0,1	<0,1	0,5	45	152		
	6	12,8	0,4	1,6	0,5	<0,1	<0,1	0,5	37	1750		
	8	15,7	0,3	1,8	1,0	0,3	0.1	0,3	304	1425		
	10,5	17,1	1,3	2,0	0,5	0,2	<0,1	0,2	161	120		
В	1	8,2	<0,1	0,6	<0,1	<0,1	< 0,1	<0,1	41	14		
	4	8,1	0,5	1,2	0,7	<0,1	<0,1	<0,1	66	14		
	6	12,5	0,5	1,6	0,5	<0,1	<0,1	0,1	51	150		
	8	15,6	0,5	2,0	0,7	0,3	< 0,1	Q, 1	333	160		
	10	16,6	0,1	1,4	0,7	0,2	< 0,1	0,1	172	1250		
С	1	8,3	0,7	1,1	0,7	<0,1	<0,1	0,1	51	16		
	4	8,3	0,1	1,0	0,2	<0,1	<0,1	<0,1	43	155		
	6	12,8	1,0	1,5	0,5	<0,1	<0,1	<0,1	44	1324		
	8	15,6	0,1	1,6	0,2	<0,1	< 0,1	0,1	352	175		
	10	16,6	1,1	1,5	0,2	0,4	<0,1	<0,1	112	1264		
			* R.	efer to posit	ions on Figu	re 9A						

TABLE 4
TRACE METAL CONCENTRATIONS IN SEDIMENTS FROM THE WILDERNESS LAKES

Sample No.	Cu µg/g	Pb µg/g	Zn µg/g	Fe µg/g	Mn µg/g	Co µg/g	Ni μ g/g	Cd μ g/g	Na. %	К % ———	Са. % 	Mg %	Sr µg/g	Al μg/g	Cr µg/
1	2,0	0,8	5,4	840	41	<0,2	1,2	0,4	0,10	0,:)4	4,20	0,06	38	1180	ο,
2	8,0	4,4	12,4	4640	11	1,4	2,8	<0,2	0,53	0, 15	>30,0	0,37	1060	5080	1,
3	2,0	1,0	5,0	940	49	<0,2	0,4	0,4	0,09	0,04	4,38	0,06	50	1440	o,
4	6,0	4,0	9,6	3220	52	<0,2	2,4	<0,2	0,43	0, 0	>30,0	0,31	680	2240	1,
5	4,0	4,2	9,6	3720	80	0,8	2,4	0,2	0,38	0, 2	>30,0	0,28	516	4440	1,
6	4,0	3,2	12,6	4420	31	0,6	1,6	0,2	0,18	0, 0	>30,0	0,44	886	2120	1,
7	4,0	3,4	14,6	5200	35	0,2	2,0	0,4	0,18	0, 5	>30,0	0,48	878	2500	1,
8	6,0	3,2	19,6	5600	45	0,8	5,6	<0,2	0,28	0,::3	>30,0	0,47	856	4540	2,
9	8,0	6,2	23,4	6120	45	1,0	7,8	0,4	0,39	0,28	>30,0	0,46	572	5540	2,
10	6,0	4,2	16,6	5560	40	0,2	6,0	0,4	0,37	0,::6	>30,0	0,36	224	5240	2,
11	4,0	3,0	10,2	4080	28	0,2	2,8	<0,2	0,23	0, 3	>30,0	0,23	270	3420	1,
12	4,0	1,8	10,8	4060	26	0,6	2,8	0,2	0,22	0, 2	17,8	0,20	108	3480	1,
13	4,0	3,2	11,2	4080	33	<0,2	1,4	0,4	0,14	0, 0	4,20	0,27	490	2880	1,
14	4,0	4,0	13,4	5550	23	<0,2	2,2	0,2	0,15	0, 2	17,2	0,34	642	3300	2,
15	2,0	1,2	6,4	2500	27	0,2	2,8	<0,2	0,03	0,05	1,99	0,08	18 248	3100 4740	1,
16	4,0	4,2	15,2	5900 20800	45 170	1,0 2,2	3,0	<0,2	0,11	0, 4	>30,0	0,26	36	10800	2,
17	6,0	16,4	29,8 22,0	5680	270	3,0	7,8 6,0	<0,2 <0,2	0,46 0,45	0,10 0,19	2,12 1,28	0,49 0,39	32	10200	3, 2,
18 19	6,0 10,0	12,6 24,6	48,0	51800	790	12,0	12,0	0,2	1,32	0,1.9	3,48	0,82	68	10800	4,
20	10,0	22,6	52,0	30800	510	11,4	13,2	0,4	2,04	0,86	3,08	0,88	60	11800	4,
21	12,0	24,8	56,0	30200	520	10,2	13,4	0,2	1,66	1,02	3,28	0,86	64	11600	4,
22	8,0	13,6	37,4	776 0	72	3,0	7,0	0,4	0,43	0, 29	2,34	0,52	56	9200	2,
23	8,0	16,0	29,9	7740	75	3,8	8,0	<0,2	0,35	0,12	1,66	0,39	38	9400	2,
24	6,0	8,8	21,4	6880	67	2,6	4,4	0,4	0,33	0,435	2,04	0,30	36	7780	1,
25	10,0	16,8	48,0	282CO	66	6,8	10,0	<0,2	0,41	0,42	3,54	0,70	68	10800	3,
26	12,0	26,4	54,0	34400	590	11,8	13,2	0,2	2,18	2,12	2,16	0,90	50	12000	5,
27	2,0	3,6	14,8	5560	340	2,2	3,6	0,4	0,05	0,15	4,42	0,18	34	4480	1,
28	<2,0	2,6	17,6	4860	170	1,8	2,8	<0,2	0,04	0,11	2,02	0,18	16	3880	1,
29	10,0	26,2	56,0	37800	910	11,4	14,0	0,2	1,34	0,68	2,64	0,90	52	13000	6,
30	8,0	24,6	46,0	29600	430	8,4	11,6	0,2	1,32	0,51	3,52	0,76	54	12400	4,
31	2,4	1,6	13,0	5800	29	1,8	3,4	0,1	0,10	0,10	10,9	0,39	960	1874	15,
32	2,0	5,0	11,0	6200	66	1,4	3,6	0,2	0,07	0,11	7,12	0,23	542	3840	16,
33 ,	1,8	5,4	10,8	3800	27	1,0	2,6	0,1	0,08	0,(8	3,02	0,16	322	5080	8,
34	6,8	76,4	44,2	21400	125	3,6	7,6	0,2	0,30	0,29	3,04	0,55	318	27200	34,
35	9,6	42,4	48,8	27800	81	5,2	12,4	0,1	0,23	0,16	0,37	0,62	64	37400	36,
36 27	3,2	28,0	19,8	9000	53	1,8	4,8	0,2	0,26	0,14	3,42	0,28	342	9220	16,
3 7	6,0	10,4	28,8	17400 5800	81 31	2,8	8,6	0,1	0,28	0,24	0,24	0,45 0,41	3 940	12320 4160	19, 14,
38 39	2,6 3,0	2,6 6,4	13,0 17,8	10800	108	1,6 2,6	3,4 4,8	0,2 0,2	0,16 0,20	0,12 0,17	9,98 0,42	0,23	46	14380	19,
40	6,2	17,4	29,6	25800	142	5,4	10,2	0,1	0,25	0,33	0,19	0,45	34	43800	41,
41	2,2	5,4	13,0	8600	113	1,8	3,4	0,1	0,13	0,10	0,12	0,16	18	11200	13,
42	9,8	23,2	42,4	28800	209	6,0	13,2	0,1	0,58	0,42	1,62	0,66	154	55800	50,
43	4,2	10,2	19,6	16200	94	2,6	6,6	0,2	0,24	0,21	0,14	0,29	24	28200	26,
44	5,2	0,8	7,8	1660	47	0,2	1,8	0,4	0,28	0,(3	>0,0€	0,76	54	1100	4,
45	5,0	2,2	7,8	2260	64	1,2	1,6	0,1	0,28	0,05	>0,0€	1,26	416	2080	7,
46	5,0	2,4	9,2	1980	49	1,0	3,0	0,2	0,27	0,(5	21,7	1,38	2680 -	1980	6,
47	1,2	0,4	4,2	1160	18	0,4	2,0	0,2	0,06	0,04	3,50	0,28	5600	1700	4,
48	2,0	1,2	7,4	2920	48	0,2	1,6	0,2	0,15	0,07	6,32	0,39	1220	2740	6,
19	4,4	2,6	7,2	2780	79`	0,6	1,0	0,4	0,32	0,07	30,0	1,06	2940	2880	8,
57	4,8	2,8	8,0	2820	62	1,0	0,8	0,2	0,32	0,07	27,3	1,22	2940	3140	9,
	1,2	1,0	4,4	2120	16	0,4	0,6	0,4	0,04	0,04	1,86	0,11	224	2240	7,
	1,0	0,8	4,2	1320	20	0,2	0,2	0,2	0,06	0,02	0,21	0,04	34	1840	4,
53	1,2	2,8	4,6	2380	40	0,2	1,2	0,2	0,13	0,04	1,08	0,07	18	4290	7,
54	12,6	17,2	32,4	23400	131	4,2	9,2	0,4	0,68	0,36	0,29	0,55	52	42200	41,
55	8,2	15,4	19,4	11400	69	2,6	5,8	0,2	0,76	0,23	0,33	0,42	56	26400	25,
56	4,2	12,6	12,6	5400	43	0,2	1,8	0,2	0,56	0,08	0,42	0,18	72	8100	12,
57	0,8	1,6	3,8	1020	9 19	0,2	0,4	0,2	0,05	0,01	0,09	0,33	14	1580	4,
58	3,8	3,4	11,4	6400 17600	49 38	0,8	2,4	0,2	0,21	0,13	19,7	0,42	1460	4100 24600	19,
59 60	6,4	12,4	28,6		38 25	2,4	6,6 5.0	0,4	0,84	0,23 0,10	1,36	0,46	142 136	8660	19, 10,
60 61	4,4	6,4 5,4	16,8	8400 6200	21	0,8 0,6	5,0 2,2	0,2 0,1	0,36 0,17	0,10	1,10 3,98	0,25 0,22	350	6100	11,
61 62	3,2	5,4 5,4	14,6 18.0		32			0,1	0,17				400	10200	17,
62	4,6	5,4	18,0	9000	32	0,8	4,4	0,2	0,27	0,15	4,84	0,19	400	10200	1

halocline, although this is sometimes lost when inversion occurs, a situation which can be aggravated by mechanical opening of the mouth at Sedgefield. There is little evidence of the existence of a thermocline in Swartvlei.

Results for metal concentrations in the sediments of the Wilderness Lakes are given in Table 4.

In general, the level of copper in the sediments is low, although occasional isolated anomalies do occur such as that at the eastern end of Langvlei, which probably represents man-

made pollution from adjacent road workings. In this area there is considerable activity involving road machinery, water pipes and pumping apparatus, together with a road-workers camp, all of which could contribute metals to the area. The most consistently high levels of copper occur in Swartvlei, although, at the stagnant east end of Ruigtevlei, values again rise. Swartvlei, however, represents a coherently high area associated with the deepest part of the lake (Figure 7) and this is probably due to increases in levels of copper sulphide precipitating and remaining

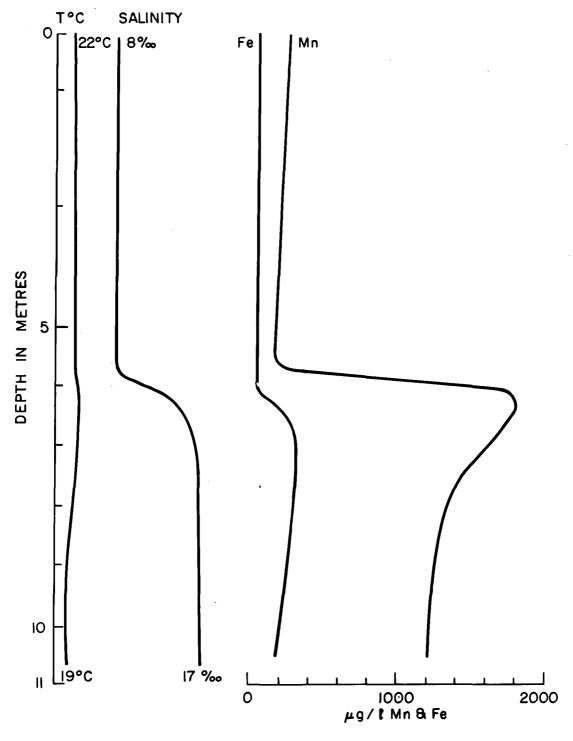


Figure 6
Variation in iron and manganese through the Swartvlei halocline

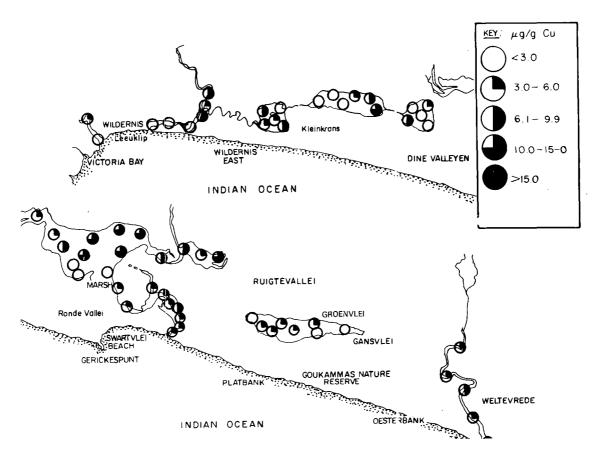


Figure 7
Concentrations of copper in sediments from the Wilderness Lakes

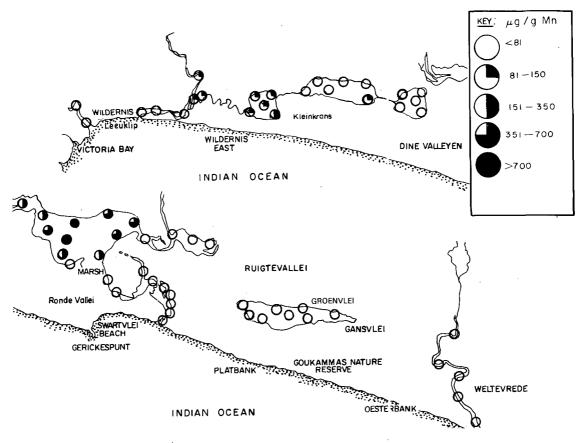


Figure 8
Concentrations of manganese in sediments from the Wilderness Lakes

unreactive in the reducing muds of the area, the copper initially being derived from weathering and probably not from manmade sources. The most likely copper minerals to be found would be covellite (CuS) and chalcopyrite (CuFeS₂), although as copper concentrations are less than $15\,\mu\mathrm{g/g}$ their existence can be postulated on physico-chemical grounds only.

The distribution of lead and zinc appears quite uniform although elevated levels are associated with the roadworks in the upper reaches of Wilderness Lagoon. The same area of Swartvlei which has elevated copper levels also has elevated levels of lead and zinc. Because of the highly reducing, sulphide rich nature of the water and bottom sediments, these metals could be present as syngenetic galena (PbS) and sphalerite or wurtzite (ZnS), having been originally precipitated from the water column. The yacht club sample (42) and holiday camp sample (40) in Island Lake also have elevated lead and zinc values. In this instance, however, metals introduced into the lake by man were probably co-precipitated with hydrated manganese and iron oxides and incorporated into the sediment. Groenvlei has the most coherently low levels of zinc and lead in the Lakes.

The distribution of iron can in general be correlated with input from catchment leaching. There may, however, be some exceptions. The Island Lake area, for example, may derive a considerable percentage of its iron from contamination by man via the recreational facilities. The concentrations in the upper reaches of Wilderness Lagoon and downstream from Sedgefield may also result from contamination. The Swartvlei-Ruigtevlei anomalous area is probably entirely natural and its relationship to the halocline has already been discussed.

The sediments in Ruigtevlei have relatively low concen-

trations of manganese. There are, however, consistently elevated levels of manganese in the bottom sediments of Swartvlei (Figure 8). This is expected in view of the relative concentrations of manganese in the waters of the two lakes.

Island Lake has high levels of cobalt. It is interesting to note that as the drainage direction is from Rondevlei through Langvlei to Island Lake, the levels of cobalt at the western end of Langvlei indicate quite clearly that the cobalt in Island Lake does not come from there. Nickel is far more ubiquitous in the area than cobalt. However, there is good correlation between the distribution of these two elements. Again the yacht club sample (42) is anomalous together with samples adjacent to Sedgefield and these probably represent man-made contamination. Swartvlei again has the highest levels in the sediments of the deeper area below the halocline and, although these may represent a natural accumulation, the sample adjacent to the Swartvlei holiday camp (30) may represent contamination.

The distribution of chromium in the Lakes can, in many cases, be correlated with man-made contamination. Island Lake has the highest chromium levels of all, with the highest concentration being adjacent to the yacht club $(50\mu g/g)$ and the second highest concentration adjacent to the holiday camp on its northern shore $(41\mu g/g)$. In Wilderness Lagoon, the samples near the holiday camp area and roadworks are also anomalous. One area of special interest is Groenvlei, which can be regarded as the most unpolluted lake in the area. Here chromium values are generally elevated, probably representing a natural subpopulation dependent upon lake bottom facies.

Cadmium levels are generally uniform and no distinct populations could be established.

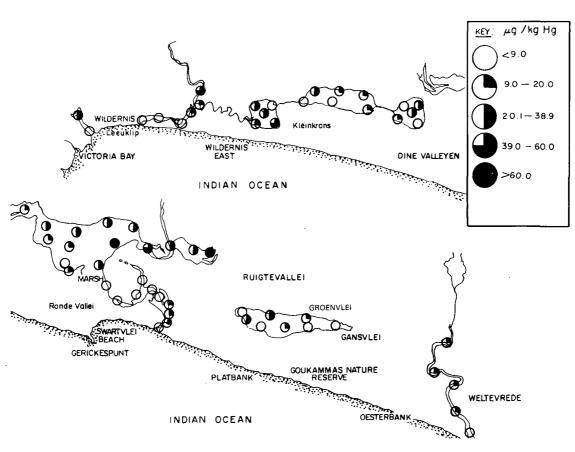


Figure 9
Concentrations of mercury in sediments from the Wilderness Lakes

TABLE 5
SEDGEFIELD TOWN CORE

Dark Grey medium-fine sand with some silt fraction 81

80

79

78

77

76

75

74

Grey medium sand with Black mottling. Mollusc shells

58

				TF	LACE	METAL	IN COL	RE 3 (μ	g/g)						
Sample	Cu	Pb	Zn	Fe	Mn	Co	Ni	Cd	Na	K	Ca	Mg	Sr	Al	Cr
83 82 81 80 79 78 77 76	1,6 1,3 1,8 1,6 1,1 0,8 0,9	17,6 11,0 9,4 14,4 5,1 3,8 2,1 1,6	7,38,8 9,6,5 5,5 4,6 4,0	3160 3470 5400 3680 2750 2020 2360 2210	13 7 16 9 11 8 11	0,4 0,6 0,4 0,3 0,3	1,6 1,6 2,5 1,9 1,8 1,3 1,3	8,01 9,01 9,01 9,01 9,01 9,01 9,01	3380 4470 7260 4130 3750 2760 3060 2620	860 1070 1000 1000 690 500 570 470	37100 35100 28300 33500 31800 33400 37600 36400	1580 1840 2470 1630 1620 1240 1380 1310	250 230 230 210 190 200 200 180	2900 3400 4540 3000 2750 2190 2210 1830	6,8 5,6 10,4 8,2 7,2 5,8 6,2 5,3
75 74 73 72 71 70 69 68 67	0,9 0,7 0,7 0,7 0,7 0,7	1,9 2,7 2,4 2,8 1,5 1,6 2,6	4,53,76,91,52 4,53,691,52	1880 2150 2270 1820 1230 1210 1210 1300 1140	10 11 8 7 5 4 4 6 5	0,2	1,2 1,3 1,2 1,1 0,8 0,9 1,0 0,9 0,8	0,01 0,02 0,01 0,02 0,01 0,02 0,03 0,06 0,02	3020 3030 2700 2210 2470 2410 2410 2230 2110	560 590 520 470 400 420 440 400 410	45900 47500 49500 47300 49300 49000 50000 51800 55200	1420 1480 1420 1370 1310 1250 1240 1270 1260	250 290 280 280 310 300 290 320 340	2150 2090 2220 2110 1570 1450 1420 1370 1350	5,8 5,8 5,1 3,8 4,8 3,5
66 65 64 63 62 61 60 59 58	0,8 1,0 0,8 0,8 0,7 0,4 0,7 0,6 0,7	8,4 3,8 4,5 2,1 1,9 3,7 2,0 1,0 2,1 3,4	3,9 4,1 3,3 1,9 3,2 2,7 4,6 9	1820 1990 1740 1210 990 530 970 840 1020 920	8687435354	0,2 0,3 0,2 0,2 0,1 0,1 0,3 0,3	1,0 1,1 1,0 0,7 0,6 0,3 0,7 0,9 0,7	0,03 0,03 0,01 0,01 0,01 0,01 0,02 0,04	2410 2710 2550 2400 2330 1170 2180 1990 2230 1880	480 520 510 380 420 180 450 320 330	52100 51100 55300 56000 58100 34800 53400 47200 55900 51700	1400 1490 1450 1360 1370 830 1300 1120 1440 1190	310 320 350 380 360 240 350 350 400 360	1560 1130 1600 1120 1120 560 1320 1090 1370 1210	4,10 4,7,6 8,2 1,4 2,4 4,4

CORRELATION MATRIX FOR LAKES CORES (CORE 3) Mg Al Co Ni Ca Na. Sr Cr Mn Cu 0,813 0,949 0,918 0,758 0,889 -0,197 0,879 0,927 -0,588 0,848 -0,449 0,868 0,842 Рb 0,738 0,696 0,483 0,598 0,621 -0,186 0,562 0,787 -0,514 0,538 -0,356 0,653 0,581 0,936 Zn 0,787 0,897 0,913 -0,239 0,941 0,913 -0,605 0,922 -0,457 0,858 0,946 Fе 0,895 -0,614 0,960 0,854 0,861 0,965 -0,287 0,946 0,925 -0,702 0,935 -0,619 0,738 -0,626 0.821 Mn 0,719 0,851 -0,276 0,784 0,708 0,910 Co 0,864 -0,125 0,868 0,788 -0,637 0,821 -0,473 0,834 0,769 Ni -0,260 0,919 -0,714 -0,655 0,896 0,849 0,949 0,947 -0,288 Cd 0,267 0,347 -0,224 0,314 -0,263 -0,273 Na 0,866 -0,609 0,956 -0.470 0,928 0,870 K 0,614 0,829 -0,539 0,916 0,843 -0,641 Ca -0,405 0,910 -0,598 Mg -0,267 0,875 0,809 Sr -0,613 -0,649 Al 0,907 Cr -

Although it is possible to establish sub-populations for mercury in the Lakes (Figure 9), the metal is probably all of natural derivation and none of the levels constitute real anomalies. One is tempted to attribute the slightly elevated levels around Sedgefield, Island Lake and Wilderness Lagoon to manmade causes, but this cannot really be justified in the light of the Groenvlei values. The high levels in Swartvlei and Ruigtevlei probably arise either as a result of co-precipitation of mercury with ferric hydroxides or by direct precipitation of cinnabar or metacinnabar.

The distribution of the remaining elements, sodium, potassium, calcium, magnesium and strontium, are all related to facies. Sodium, aluminium and potassium may be considered as indicators of clay minerals, although organic debris may be responsible for a large percentage of the sodium present in some sediments. The analytical method, however, does not completely break down any of these alumino-silicates and although higher concentrations were obtained with a complete digestion, no differences in the relative concentrations were apparent. In general, there appear to be few clay minerals in Rondevlei, Groenvlei, Sedgefield Lagoon and at the entrances of the three rivers entering the sea, although shell debris is found in abundance in these areas. Clay minerals are however found to predominate in the other Lakes.

Concentrations of each of the study elements in the sixteen Lakes cores were analysed statistically to obtain interelement relationships (Watling, 1977). As well as confirming the results already obtained for the surface sediment, these cores provided evidence concerning man-made effects in the area. In addition, there is a tendency for lead to increase markedly in the top few centimetres of certain cores and this could suggest pollution from motor fuels, outboard motors or paint. The town of Sedgefield also shows evidence of trace metal contamination (Table 5). Similar tables have been prepared for all sixteen cores (Watling, 1977) but have not been included in this paper. Table 5 is presented as an example of the information which can be obtained from detailed investigations of individual cores when trying to assess the impact of man in an area. In this table the correlation matrix is given for all elements and the correlation coefficients underlined represent significant interrelationships. As can be seen the relationship to aluminium and potassium is much greater than to the carbonate facies elements, calcium and strontium, although the latter correlation is in accordance with the presence of calcareous material. Only three cores, Sedgefield town, Island Lake Yacht Club and Island Lake Holiday Camp, show any evidence of contamination by man.

Conclusions

On the basis of trace element concentrations the Lakes area appears to be unpolluted and, with the exception of Island Lake, few areas show marked evidence of trace metal contamination by man. The halocline in Swartvlei is quite marked. However, the only metal concentrations which appear to be affected significantly by the Eh/pH boundary are iron and manganese. Trace metal levels in the water are generally low with the exception of iron in Ruigtevlei and Swartvlei and manganese in Swart-

vlei. Correlation frequency diagrams indicate that the area is generally unpolluted with respect to metals.

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