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### SOMMAIRE

Les composants dissouts et particuliers des précipitations dans les alentours du Firth of Forth ont été analysés pour leur teneur en Pb, Cu, Zn et Fe. Les résultats sont considérés relativement aux travaux précédents (Davies, 1976) et on met l'accent sur le matériau particulaire et la contribution qu'il apporte à la déposition atmosphérique de ces métaux dans le Firth of Forth.

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## FURTHER OBSERVATIONS OF THE ATMOSPHERIC DEPOSITION OF SOME HEAVY METALS AROUND THE FIRTH OF FORTH

by

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### Summary

The dissolved and particulate components of rainfall around the Firth of Forth have been analysed for Pb, Cu, Zn and Fe. The results are discussed with reference to previous work (Davies, 1976), and emphasis is given to the particulate material, and its contribution to the atmospheric input of these metals to the Firth of Forth.

### Introduction

The preliminary results of an investigation of the atmospheric input of certain heavy metals to the Firth of Forth, E. Scotland, were reported last year (Davies, 1976). The general conclusion reached was that the inputs of lead, copper, zinc, and mercury were less important in the Forth than had previously been shown to be the case in the Clyde Sea (Topping, 1974) and the North Sea (Cambray *et al.*, 1975). The results presented were confined to the dissolved portion collected between February and December 1975. In this paper similar results for most of 1976 are discussed, together with analyses of particulate material filtered from the rain-water collected.

### Sampling and analysis

The positions (Fig. 1) and descriptions of the six sampling sites around the Firth of Forth are given in Davies (1976). In addition, sites have been operated in exposed coastal positions at Loch Ewe, Ross-shire (Grid ref. NG 823884) and Rattray Head, Aberdeenshire (NK 093583). The sampling apparatus, and analytical procedure for the dissolved component have been fully described (Davies, 1976). Particulate material was analysed for lead, copper, zinc, and iron by conventional flame atomic absorption after digestion in concentrated nitric acid. The estimated precisions are respectively  $\pm 15\%$ ,  $15\%$ ,  $2\%$ ,  $2\%$ .

### Results

#### a. Dissolved component

The monthly deposition of copper, lead, zinc and mercury in 1976 largely confirmed the findings of 1975. The quantities deposited were very variable, and the tendency for the copper, lead, and zinc deposition to increase with rainfall was confirmed. Again, the concentration of mercury was negatively correlated with rainfall, as had previously been noted.



Neither the concentration of dissolved iron in the rainwater nor the quantity collected per month showed any relationship to the rainfall, or to the other elements determined. Iron differs from copper, lead and zinc in that it is predominantly found in particulate form in rainwater (Cambray *et al.*, 1975). Only about 25% of the total iron is in the dissolved state, whilst usually 75-95% of the copper, lead, and zinc are dissolved (Cawse, 1974; Topping, 1974). At 'clean' rural sites iron is usually found associated with elements such as aluminium and scandium, and is probably derived from soil particles (Cawse, 1974). However, certain contaminated areas can receive a considerable anthropogenic input of iron (Pattenden, 1974).

Examination of the seasonal mean copper concentrations (Table 1) shows that there is no consistent seasonal pattern for the two years of sampling, although the overall means for January - March, and April - June for the two years are similar. The results for lead, zinc, and iron also showed no consistent seasonal pattern.

The two year mean concentrations did show significant regional variation (Table 2). The Firth of Forth sites, with the exception of Cullaloe, all give similar mean concentrations for each of the four elements. Cullaloe has the highest mean for each element, the effect being most marked in the lead and iron results. The two sites distant from the Forth show markedly lower mean concentrations (with the exception of the Loch Ewe zinc result).

#### b. Particulate component

The quantity of particulate deposition of copper, lead, zinc and iron varied considerably from site to site (Table 3). It was highest for all elements at Cullaloe and Leven, whilst the other four Firth of Forth sites experienced lower, and broadly similar depositions. The 'background' Loch Ewe site had markedly less input of all four elements. Cawse (1974) found similar differences between semi-rural and urban sites. It is known that more atmospheric dust is found in urban than rural areas. Cawse (1974) has tabulated various values and shown that population and industry can cause concentrations to rise by factors of 10-40.

There is some indication of seasonal variation of particulate deposition. Deposition was high in the winter months December 1975 to March 1976. At Carnbee it decreased from February to June 1975, and was high in October and November 1976 (Fig 2). There is therefore a tendency for higher particulate deposition in the winter months. In contrast, the rainfall is highest in the summer (Davies, 1976). The increased input must therefore be related to seasonal changes in the dry deposition rate, or the availability of insoluble particulate matter in the atmosphere. Cawse (1974) reported a tendency towards higher levels of atmospheric particulate material in winter than in summer, the two being related by a factor of about 1.7. He attributed this to reduced atmospheric dispersion under conditions of persistent low inversion layers, and the increased combustion of fuels during winter. Similar effects have been reported for atmospheric lead (Chow and Earl, 1970), smoke (Stocks *et al.*, 1961), and some other metals (Kneip *et al.*, 1970). Cawse (1974) also illustrates the similarity in monthly patterns of the concentration in air of iron, zinc and lead.

In addition to real variations in quantity of particulate input, compositional differences are also found. The ratios (Table 4) Fe/Pb, Fe/Zn and Fe/Cu increase in progression from Loch Ewe to Cullaloe. Similar changes in ratio can be seen between the Plynlimon and Styrrup sites (Cawse, 1974), although the absolute values of the ratios differ. It is not clear whether these changes in the Forth area reflect increased input of terrestrial material, or of 'pollutant' iron.

The monthly deposition of particulate copper, lead, zinc and iron did not show any close correlation with the corresponding monthly deposition of dissolved metals. However, these four elements show considerable similarities in the pattern of monthly deposition at 'clean' (eg Carnbee, Fig. 2) and more polluted sites (eg Cullaloe, Fig. 3).

The relative significance of the particulate and dissolved components also varies between sites (Table 5). Cambray *et al.* (1975) found that at all their coastal sites lead, copper and zinc were predominantly in the dissolved state, ie the ratio of the particulate to dissolved metal was 0.3-0.1, whilst the majority of the iron was particulate (Cawse, 1974) (ratio = 2-8). The deposition at Loch Ewe is of similar character to that at Lerwick and the east coast stations, with perhaps a lesser influence of particulate material. In the Forth area, the particulate component, especially for lead, zinc and iron is of greater importance than at the sites operated by AERE (Cawse, 1974; Cambray *et al.*, 1975). It is most evident at Leven, where similar amounts of lead and copper are found in the particulate phase and in solution; and about 96% of the iron is particulate. It would seem therefore that, accompanying the enhanced input of dissolved material in the west of the Forth area (Table 6) there is much greater increase in the particulate input.

In Davies (1975) details were given of a method of calculating the atmospheric input of metals to the Firth of Forth. This method has been applied to the data on soluble and particulate inputs for the periods February 1975 to October 1976 (soluble) and February 1975 to December 1976 (particulate) to obtain annual mean deposition rates for certain metals, and an estimate of their annual mean inputs to the sea (Table 6).

The inputs to the Firth of Forth of lead and zinc are very similar to those calculated for the North Sea and Clyde sea area (Cambray *et al.*, 1975), and are similarly distributed between the dissolved and particulate phases. The input of copper to the Firth of Forth is significantly lower than to the other sea areas, the main reduction being in the dissolved component. The mean for iron deposition is strongly influenced by the Cullaloe site and is 2-4 times greater than that observed by Cambray *et al.* (1975), the main increase being in particulate iron. If the Cullaloe result is omitted, the mean input becomes similar to that to the Clyde Sea.

An assessment has been made (Davies, 1976) of the possible significance of atmospheric input to the metal budget of the Firth of Forth. It was concluded that this input was not of major importance to the area as a whole because of the dominance of sewage and other discharges (W. Halcrow, pers. comm.). In general terms, the additional information presented here does not materially alter this conclusion. However, it may well be that atmospheric input is of more importance in areas distance from major sources of metals, or in westerly parts of the Firth, where the deposition can be considerably higher than the mean for the whole area.

#### Acknowledgements

I wish to acknowledge the invaluable co-operation of the controllers of the sampling sites throughout the project. Scientists of the then Forth and Lothians River Purification Boards, who assisted with the initial organisation of the project, and various members of the Marine Laboratory, who undertook sampling and analysis, contributed significantly to the work.

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Table 1

Seasonal mean copper concentrations ( $\mu\text{g l}^{-1}$ )

	Carnbee	Leven	Cullaloe	Newliston	Craigielaw	Tantallon	Overall
1975							
Feb-March	4.5	2.2	6.2	4.7	4.7	4.5	4.5
April-June	5.2	5.9	4.3	4.8	3.9	3.1	4.5
July-Sept	6.9	5.9	8.4	3.7	3.9	6.1	5.8
Oct-Dec	4.6	6.0	10.4	4.1	12.2	9.3	7.8
1976							
Jan-Mar	3.3	3.9	7.2	2.3	2.6	8.1	4.6
April-June	6.7	6.3	6.4	3.2	3.3	4.2	5.0
July-Sept	2.8	3.5	3.5	4.0	3.1	1.6	3.1

Table 2

Mean dissolved metal concentrations for the period 1975-6 ( $\mu\text{g l}^{-1}$ )

	Pb	Cu	Zn	Fe
Carnbee	15.4	5.0	135	118
Leven	12.7	5.0	174	75
Cullaloe	42.5	6.6	210	549
Newliston	16.6	3.8	131	60
Craigielaw	23.4	4.8	187	79
Tantallon	22.9	5.4	176	131
Loch Ewe	6.2	3.2	144	29
*Rattray Head	2.8	1.8	84	32

\* Jan-June 1976 only

Table 3

Total collections of selected metals in particulate  
material Feb 1975 - Dec 1976

	Pb	Cu	Zn	Fe $\mu\text{g}$
Carnbee	59.9	14.0	59.8	6100
Leven	165.0	40.7	144.4	10310
Cullaloe	235.5	60.8	175.6	47260
Newliston	84.7	11.3	51.7	5340
Craigielaw	104.6	19.6	92.6	9560
Tantallon	102.6	17.7	74.0	6420
Loch Ewe	18.8	3.9	9.0	580

Table 4

Inter-element ratios in particulate material

	Fe/Pb	Fe/Cu	Fe/Zn
Carnbee	102	436	102
Leven	62.5	253	71.4
Cullaloe	201	777	165
Newliston	63.0	473	103
Craigielaw	91.4	488	103
Tantallon	62.6	362	86.8
*Plynlimon	19.1	17.6	18.6
*Styrrup	57.4	90.5	49.5
Loch Ewe	10.9	149	64.4

\* Cawse (1974)

Table 5

Ratios of particulate to soluble deposition for Feb 1975 - Oct 1976

	Pb	Cu	Zn	Fe
Carnbee	0.38	0.22	0.06	9.8
Leven	2.86	1.17	0.09	26.9
Cullaloe	1.49	1.89	0.16	24.8
Newliston	0.60	0.23	0.06	16.2
Craigielaw	0.72	0.32	0.07	16.5
Tantallon	0.48	0.25	0.04	8.1
Loch Ewe	0.21	0.05	0.01	1.0
*East Coast	0.1-0.3	0.1-0.7	0.03-0.25	2-8
*Lerwick	0.2	0.3	0.05	6

\* Cambray et al., (1975).



Table 6

Annual mean deposition  $\mu\text{g cm}^{-2} \text{yr}^{-1}$ 

	Lead			Copper			Zinc			Iron		
	Total	D <sup>1</sup>	P <sup>2</sup>	Total	D	P	Total	D	P	Total	D	P
Carnbee	1.06	0.70	0.36	0.36	0.27	0.09	9.00	8.64	0.36	40.9	3.9	37
Leven	1.66	0.82	0.84	0.44	0.23	0.21	10.46	9.73	0.73	54.6	2.6	52
Cullaloe	4.29	2.85	1.44	0.70	0.33	0.37	12.06	10.99	1.07	310	21.0	289
Newliston	1.55	1.08	0.47	0.26	0.20	0.06	6.11	5.82	0.29	32.8	2.8	30
Craigielaw	1.23	0.68	0.55	0.27	0.17	0.10	6.47	5.99	0.48	52.1	2.1	50
Tantallon	1.64	1.10	0.54	0.33	0.24	0.09	5.97	5.58	0.39	38.6	4.6	34
Loch Ewe	0.42	0.32	0.10	0.26	0.24	0.02	9.27	9.22	0.05	5.5	2.5	3
<sup>3</sup> Mean	1.91	1.20	0.70	0.39	0.24	0.15	8.35	7.79	0.56	88.2	6.2	82

Annual mean <sup>4</sup> input to sea areas  $\mu\text{g cm}^{-2} \text{yr}^{-1}$ 

Firth of Forth	1.72	1.08	0.64	0.35	0.22	0.13	7.52	7.01	0.51	79.4	5.6	73.8
<sup>5</sup> North Sea	1.55	1.35	0.20	1.30	1.05	0.25	7.1	6.5	0.6	16.5	4.0	12.5
<sup>5</sup> Clyde Sea	1.95	1.55	0.40	1.70	1.25	0.45	8.1	7.6	0.5	34	4.9	29.9

1. D: Dissolved.

2. P: Particulate.

3. Mean for the Firth of Forth sites.

4. Calculated from mean deposition at the six sites, and a correction factor of 0.9 for the decreased rainfall at sea (Davies, 1976).

5. Cambrey et al., 1975

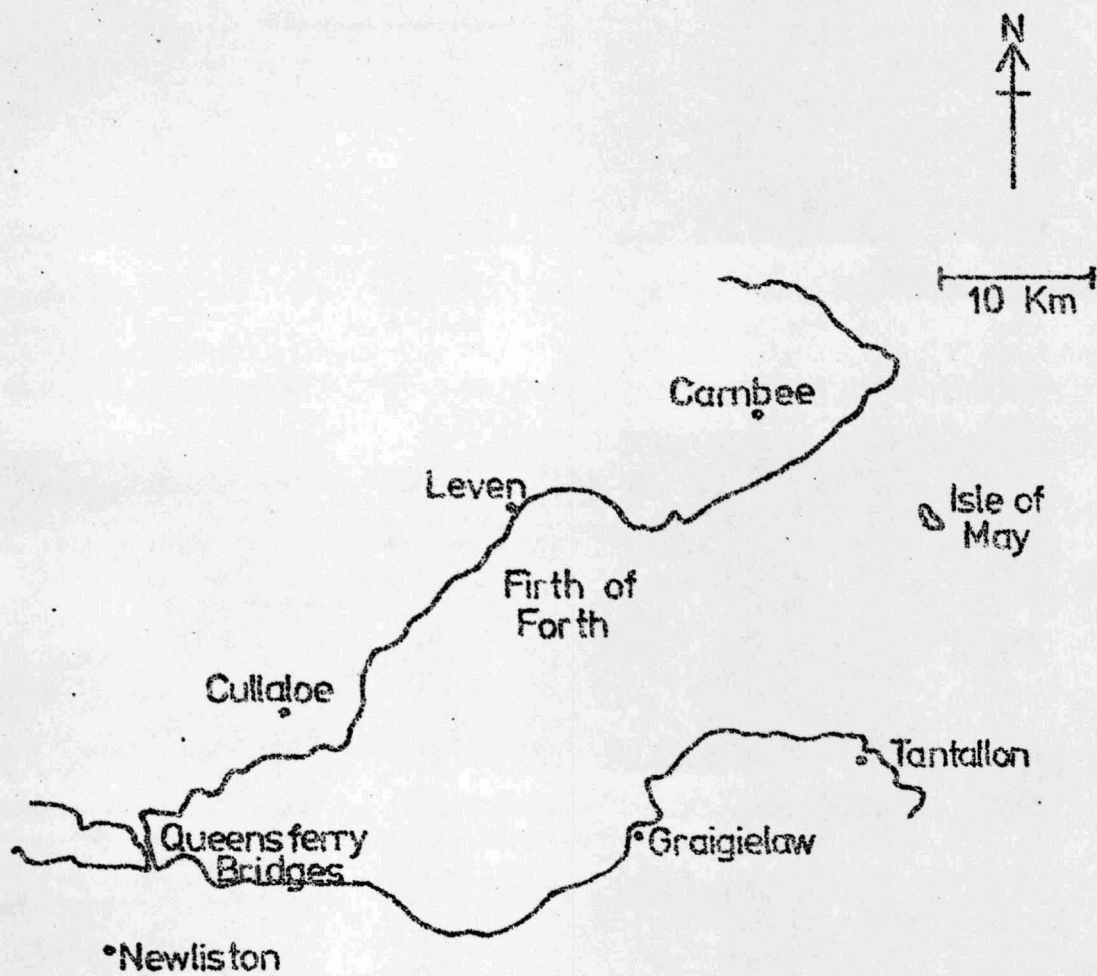


Figure 1. Location of atmospheric sampling sites around the Firth of Forth.

Figure 2. Monthly collections of metals in particulate material at Carnbee. September and October 1976 collections were combined.

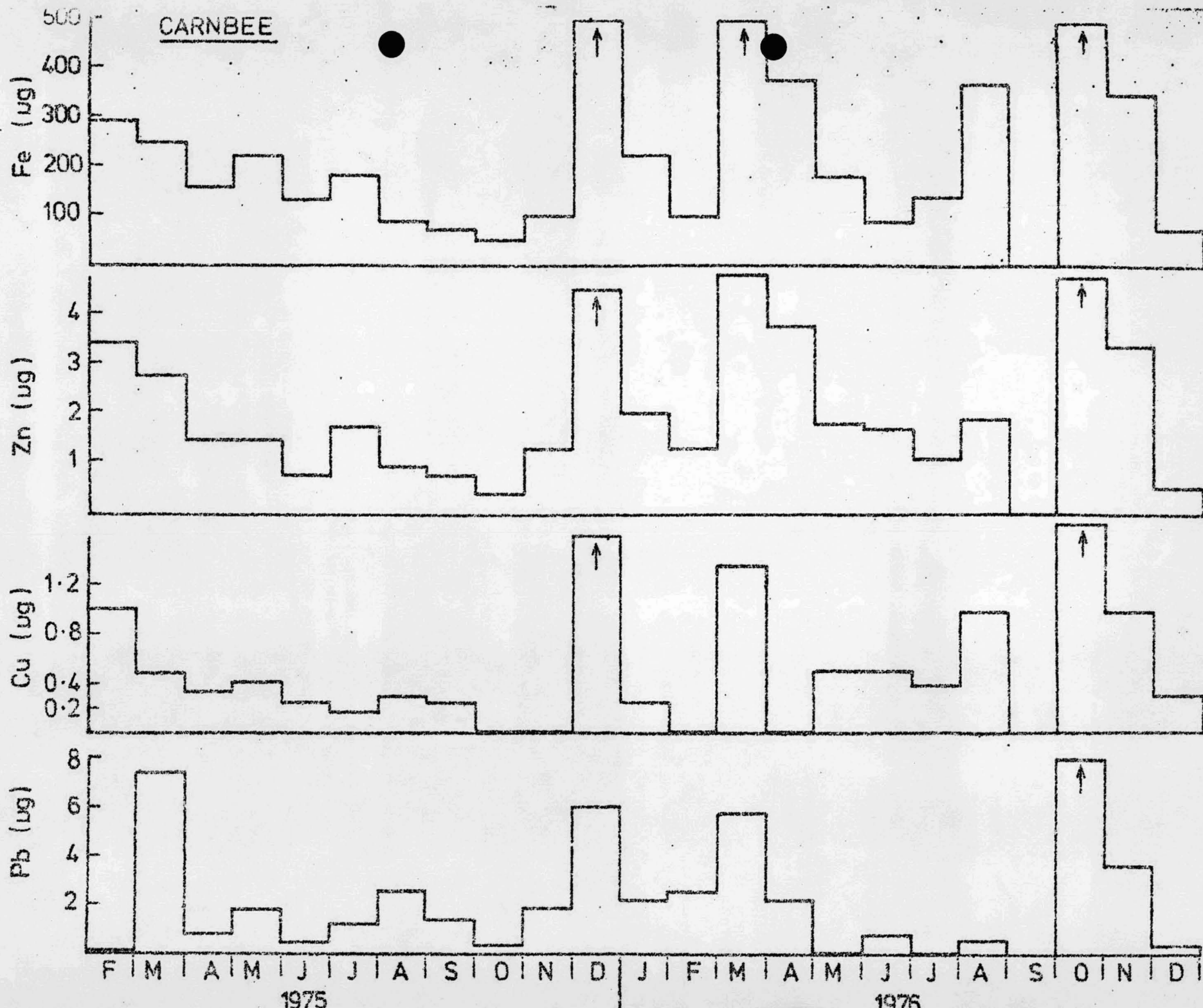




Figure 3. Monthly collections of metals in particulate material at Cullaloe. September and October 1976 collections were combined. No collections were made in September 1975 and May 1976.

