International Council for the Exploration of the Sea
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THE ATMOSPHERIC INPUT OF SOME HEAVY METALS TO THE FIRTH OF CLYDE AND ITS RELATION TO OTHER INPUTS

by

G Topping
Marine Laboratory, Aberdeen, Scotland.

Summary

This report describes the analytical and sampling procedure used in this investigation together with a summary of the results for the metals copper, cadmium, lead and zinc. An attempt is also made to assess the impact of this input on the heavy metal concentrations in sea water. The results suggest that the atmospheric input of heavy metals to the Firth of Clyde is a significant fraction of the total input and that it could significantly affect the level of metals in surface waters.

Introduction

The introduction of trace metals to the marine environment may occur through a number of pathways (i) rivers (ii) direct injection from outfalls or dumpings and (iii) atmospheric fallout. Recent studies (Anon, 1972) have suggested that the atmospheric fallout might well represent a significant portion of the total input and comparisons have been made for river and atmospheric transport (Anon 1971). The data in Table 1 taken from this latter publication compares mining production of heavy metals with an assessment of river transport and atmospheric washout. Chow and Patterson (1966) have in fact claimed that the lead values of surface ocean waters have dramatically increased as a result of the "rainout" of man introduced lead from the atmosphere, primarily derived from petroleum products.

Although considerable work has been done on the measurement of airborne particulate and the associated heavy metals (review recently by Rice et al, 1973) few field studies have been set up to study the actual transfer of this material to the sea surface. In view of the importance of this pathway as a possible source of heavy metals the Marine Laboratory, Aberdeen, has included measurements of this type in its heavy metal studies in the Firth of Clyde. In conjunction with AERE, Harwell an atmospheric sampling station was erected on the Isle of Arran to assess monthly input to this area. This station formed part of a network of 7 stations which were established to examine the concentration and deposition of 30 trace elements in the UK. This report describes the basic equipment used in this study together with a summary of selected heavy metals (zinc, copper, cadmium and lead). An attempt is also made to assess the impact of this input on the heavy metal concentrations in sea water and comparison is made with other inputs of heavy metals.

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Sampling and Analyses

The sampling station was located on the southern tip of Arran near the coastguard station at Kildonan (Fig. 1). The equipment used in this type of programme together with subsequent analytical procedure has been described in detail elsewhere (Cawse and Pearson, 1972). The overall procedure was briefly as follows:

Samples of dry and wet deposition (rain water) together with airborne particulate were collected at monthly intervals during the period June 1972 - May 1973. The equipment used in this work consisted of

(a) a pump that draws air ($50m^3$/week) through a filter paper (Whatman 40, 6 cm diameter) in order to collect airborne dust near ground level. The inlet faces downwards to avoid intake of rain and is capable of collecting particles of $\leq 150\,\mu m$.

(b) a polythene bottle, enclosed in a black plastic bag to inhibit the growth of algae, and funnel to collect rain water. The funnel was protected by a terylene mesh to prevent insects from entering the collection bottle.

(c) a pad of filter paper, mounted horizontally under a shelter, to collect dry deposition.

These samples were forwarded monthly to AERE, Harwell, England where they were examined for some 30 trace elements principally by the method of instrumental neutron activation analysis. Atomic absorption and x-ray fluorescence techniques were also used. By combining these results with details of rainfall and 'washout' factors it was possible to produce monthly profiles of airborne particulate levels and wet and dry deposition for these elements.

Results

Limited space prevents full tabulation of all the results obtained in this exercise. The disucussion will be confined to the four heavy metals previously mentioned. It is hoped that a more detailed tabulation and discussion of these results together with those from the other 6 stations in the UK network will be published shortly (Cambrey, Jefferies and Topping, in preparation).

The monthly deposition data ($\mu g/cm^2$) for these four metals together with rainfall data (mm) are presented in Table 2. The following general observations may be made on these data,

1. monthly deposition rates vary by at least one order of magnitude for all four metals.

2. although highest deposition rates for all metals are found in the periods of heavy rainfall (Dec. 72 - Feb 73) there appears little correlation between input and the amount of rainfall/month.

3. the soluble fraction of the deposition represents the major fraction of this deposition.

Using the data in Table 1 it is possible to estimate the annual amount of metal deposited at the sea surface, provided one corrects for the lower rainfall observed over the sea surface. On average the rainfall over the sea is considered to be 55% of the rainfall observed on the adjacent land.

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(R S Cambrey, personal communication). On this basis the daily and annual inputs ($\mu g/cm^2$) of these metals to the sea surface have been calculated and are presented in Table 3, where comparison has been made to the amount of metal in varying columns (0.01m, 1m, 10m and 55m) of 1 cm^2 cross section, the latter depth corresponds to the mean depth of the Clyde Sea. The assumption made in this comparison that there is no metal gradient in the water column is not strictly true but for the purposes of this calculation the metal concentratation has been assumed to be uniform over the entire water column. The data in Table 3 would suggest that the atmosphere input to the upper 10m of the sea surface could significantly affect the level of metal in this water column and that in the short term (<1 week) the level of metal observed in the upper layers of the sea might well reflect the fluctuating atmospheric input. More detailed information on the distribution of metals in the upper layers of the sea is required before we can measure the real effects of this input on trace metal levels.

Comparison of inputs of Metals

To the best of our knowledge the main inputs of heavy metals to the Clyde Sea are (i) Brackish water outflow from the main shipping channel (ii) Sewage sludge deposits at Garrochhead (iii) Run off from the Ayrshire coast (iv) Input from the Irish Sea via- the estuarine compensating flow and (v) Atmospheric input.

The amounts of heavy metals associated with (i) and (iii) have recently been the subject of investigation by workers at the Clyde River Purification Board. According to this source (T Leatherland, personal communication) there are substantial amounts of some heavy metals discharged annuallly from these sources; the annual amounts of copper, zinc, lead and cadmium are shown in Table 4.

The annual input of metals from sewage sludge dumping, currently running at 1×10^6 tons, can be assessed from some recent sewage sludge analyses (McKay and Topping, 1970). These data are also presented in Table 4.

The compensating estuarine inflow for the Clyde Sea is thought to consist partly of water from the Irish Sea and enters this area along the eastern part of the Firth (Steele et al, 1973). Previous surveys concerned with the distribution of selected metals in sea water (Preston et al, 1972) have shown that the metal levels in sea water from the Irish Sea, in particular from the eastern coastline, are higher than levels found in the main body of West Coast waters. The retention time of the inflow water may be sufficiently long enough to allow this water to give up this excess metal load to the Clyde before leaving this area in the southerly surface outflow. In this case this inflow would represent a net inflow of metals and should be considered in any comparison of inputs. The volume of this inflow water is presently the subject of some debate and should be resolved quite soon. Most workers agree on the range of values for this inflow and for the sake of this comparison the minimum and maximum (60×10^6 and 366×10^6 m^3/day respectively) have been used. The excess metal load has been computed by taking these flow rates and multiplying by the difference between the mean sea water values for the Irish Sea and the Western Approaches. Preston et al (1972) refers to these areas as Area 3 and 4 respectively. These data are presented in Table 4.

Assuming that the fallout data on the Isle of Arran can be applied to the whole of the sea area surrounding it (see Fig. 1) it is possible to calculate the annual input of metals from the atmosphere to the relevant sea surface. The data presented in Table 4 is based on an area of 2.59×10^3 km^2 plus an annual rainfall of 55% of that observed at Arran.

The results of this study indicate that although much more information is needed on all inputs of heavy metals to the Clyde the atmospheric input appears to be of major importance.

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The results of this study indicate that although much more information is needed on all inputs of heavy metals to the Clyde the atmospheric input appears to be of major importance.

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Table 1

World Heavy Metal Production and Potential Ocean Input*

Element	Mining production	Transport by rivers to oceans	Atmospheric washout
		(millions tons/yr)	
Pb	3	0.1	0.3
Cu	6	0.25	0.2
Cd	0.01	0.0005	0.01
Zn	5	0.7	-
Hg	0.009	0.003	0.08

* Anon (1971)

Table 2

Atmospheric Deposition of Copper, Lead, Zinc and Cadmium at Kildonan, Isle of Arran.

	Metal Input* ($\mu g/cm^2$/month)				
Month	Copper	Lead	Zinc	Cadmium	Rainfall (mm)
June	0.078/0.073	0.322/0.279	0.469/0.449	-	133
July	0.076/0.072	0.101/0.094	0.279/0.257	0.007	58
Aug.	0.175/0.150	0.195/0.187	0.395/0.392	<0.001	55
Sept.	0.035/0.030	0.062/0.045	0.429/0.413	<0.001	11
Oct.	0.188/0.091	0.448/0.335	1.974/1.891	-	86
Nov.	0.033/0.020	0.023/0.011	0.123/0.109	0.009	20
Dec.	0.292/0.192	0.436/0.299	5.06/5.00	-	167
Jan.	0.558/0.340	0.319/0.269	2.15/1.93	0.003	166
Feb.	0.416/0.248	0.251/0.205	1.00/0.934	0.007	134
Mar.	0.782/0.760	0.623/0.546	0.661/0.511	0.038	87
Apr.	0.188/0.150	0.228/0.166	0.602/0.559	0.004	92
May	0.185/0.180	0.443/0.399	1.50/1.44	-	118

* Total Metal Deposited/Soluble Component of this deposition

Table 3

Effect of Atmospheric Input on Metal Levels in Seawater

Metal	Surface Seawater Range of Values (μg/1) (Mean)	Atmospheric Input μg/cm^2		Amount of Metal (μg) in Water Column (1 cm^2 x H)			
		Daily	Annually	H=0.01m	1m	10m	55m
Zinc	2.7 - 6.5 (4.6)	0.022	8.1	0.0046	0.46	4.6	25.3
Copper	0.2 - 2.9 (1.1)	0.0046	1.68	0.0011	0.11	1.1	6.1
Lead	0.1 - 1.3 (0.5)	0.0043	1.56	0.0005	0.05	0.5	2.75
Cadmium	0.1 - 0.5 (0.2)	0.00013	0.05	0.0002	0.02	0.2	1.1

Table 4

Comparison of Inputs of Metals to the Clyde Sea

INPUT SOURCE	ANNUAL INPUT (Kg)			
	ZINC	COPPER	LEAD	CADMIUM
Outflow from upper estuary* (shipping channel)	45 000	10 000	20 000	400
Run off from Ayrshire coast*	50 000	10 000	35 000	600
Sewage sludge deposits	60 000	25 000	25 000	250
Input from the Irish Sea (a)	44 000	7 000	1 300	660
(b)	267 000	43 000	8 000	4 000
Atmospheric input	209 000	43 000	40 000	1 300

* T Leatherland, personal communication

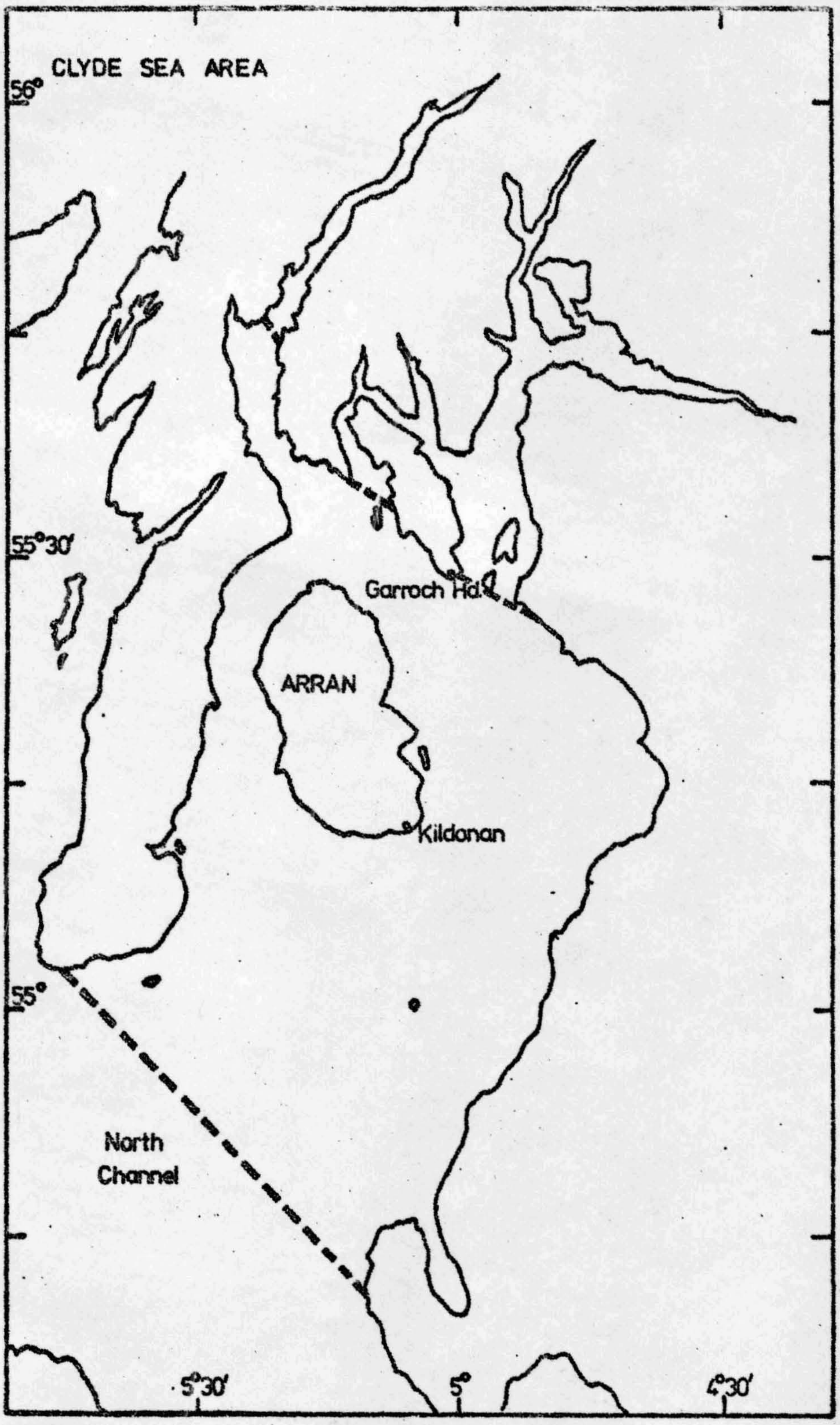

FIG. 1 ----- BOUNDARY LINES USED IN THE CALCULATION OF THE ATMOSPHERIC INPUT OF TRACE METALS TO THE SEA SURFACE.