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Environmental health aspects of lead

Die gesundheitlichen Aspekte der Umweltverschmutzung durch Blei

Les problèmes sanitaires posés par le plomb présent dans l'environnement

THE OCCURENCE OF LEAD IN NATURAL WATERS

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Summary.

The distribution of dissolved and particulate lead in the coastal waters of the eastern Irish Sea, and in rivers flowing into part of this region, is considered. Possible causes of accumulation of lead in these sea areas are discussed, and the regions of industrial and 'natural' pollution defined.

The analytical procedures used in these surveys are briefly described.

THE OCCURRENCE OF LEAD IN NATURAL WATERS.

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In the past, the distribution of trace metals in natural waters has been studied principally because of its geochemical interest. In recent years, however, the awareness of the dangers of pollution of the aquatic environment has given new impetus to the study of these metals, and in particular to those such as lead, known to have a toxic effect on aquatic life.

This toxicity can be caused directly by the dissolved and particulate compounds of lead, but a more dangerous and insidious hazard arises by the concentration of this toxic element up the various stages of the food chain[2]. It is vital, therefore, to be able to determine accurately the levels of lead in the habitat of these organisms, in order to be able to forecast possible long-term effects on activities such as the fishing industry.

The average concentration of lead in deep sea water is usually considered to be ca. 0.03 µg/l[4], but this figure is considerably lower than the range found by the authors in their study of coastal waters of the Irish Sea, where levels from 0.3 to >5 µg Pb/l were found.

Methods of analysis.

On account of its speed and reasonable sensitivity, atomic absorption spectrophotometry is the most commonly used method for the determination of lead in natural waters. A preconcentration step is usually necessary for the determination of dissolved lead, and this may involve solvent extraction of the chelates of the metal[3] or utilise ion-exchange resins [1,5].

Even greater sensitivity has been made available by the sophistication of established electrochemical methods of analysis such as polarography. The pulse polarograph, for example, permits the determination of reversibly reducible ions down to about 10^{-8} M, and a method has been developed using this instrument, which combines the required sensitivity with the speed necessary for routine analysis.[1]

This method was used to determine the lead distribution in the areas subsequently to be discussed. After a ten litre sample of water had been filtered through a washed 0.45 µ Oxoid membrane, it was passed through a column of Chelex - 100 chelating resin in its calcium form, which removed certain heavy metals, including lead, from the water. The metals were eluted from the column with 2N nitric acid, and the eluant was exposed to ultra-violet radiation to remove organic materials. After conversion to the chloride form by repeated addition of hydrochloric acid and bringing to dryness on the water bath, the eluant was made up to 25 ml with 0.2 N hydrochloric acid, and the derivative polarogram was measured.

The calcium chloride present due to elution of calcium from the column acts as the base electrolyte, but to ensure that no errors could arise from sample-to-sample variations of this matrix, the determinations in each sample were calibrated using a standard addition technique. The lower limit of sensitivity for lead in the concentrated sample is 0.05 µg/ml, compared with 0.5 to 1 µg/ml by atomic absorption.

The lead in the suspended matter was determined by treating the membrane filters with warm 2N nitric acid. The residue was separated by centrifugation, and the acid-extract brought to dryness. It was then redissolved and made up to a suitable volume with 0.2 N hydrochloric acid to prevent precipitation of any of the metals in solution. Determination was by atomic absorption as the levels of lead in the extracts were usually well above the sensitivity limit.

Sources of the lead introduced into the sea.

These can be divided into the following categories :

(i) A small contribution is released by weathering of sedimentary and igneous rocks.

(ii) A much larger percentage of the total load found in sea water comes from the weathering of lead mineral deposits, and of the lead minerals associated with deposits of other metals. This is greatly increased in areas where the deposits have been exposed by mining activities.

(iii)Variable amounts of lead in coastal waters arise from human activity in adjacent land areas.

Lead from these three sources is ultimately removed to the deep ocean by circulatory processes.

Work done on this subject[20] has shown that the rate at which lead is being introduced into the ocean has increased twenty-seven fold since the Pleistocene period. Some of this has arisen from agricultural activity causing denudation of the land, but the dramatic increase in the last sixty years has resulted from industrial activity, in particular as a result of the use of lead tetra-ethyl as an additive to petrol. It has also been suggested that the lead washed to the sea each year from smeltery and incinerator wastes and from petrol used by automobiles may amount to 1 % of the total annual world lead production. Much of this industrial contribution comes directly from the atmosphere, and this is reflected in the fact that the mixed surface layer of the ocean contains ca. 0.2 µg Pb/l compared with the deep water content of 0.03 µg Pb/l.

The main species of lead in solution are probably Pb^{2+}, $PbOH^{+}$ and $PbCl^{+}$[19].

Lead in river water.

Figure I shows the rivers examined for their heavy metal content from October 1970 to October 1971. This region is rich in mineral deposits, and extensive mining activity has taken place since Roman times, reaching its peak in the nineteenth century. No mines are being worked at the present time, but surveys are being made with a view to future mining of the deeper lodes. Piles of spoil are in evidence near old lead workings, and it is not difficult to find pieces of galena among this material. The major ore deposits of the region[21] are marked on Figure I.

It is reasonable to assume that rivers flowing through the areas of mineral deposits, and particularly those with tributaries flowing through old workings, will be enriched with the metals present in the lodes. This is indeed the case, as can be seen from Table I.

The mean dissolved lead content of water from a station on the River Glaslyn, a typical example of a river unaffected by lead deposits, has a mean annual value of 0.92 µg/l with a range of from 0.4 to 2.1 µg Pb/l. The River Ystwyth on the other hand, a stream flowing through a mineralised zone particularly rich in lead, has a mean annual dissolved lead content in its upper reaches of 8.5 µg/l with a range varying from 0.8 to 30 µg Pb/l. The River Twymyn, a tributary of the River Dovey, flows through former lead workings soon after its source. Samples collected about three miles downstream from these workings have a mean annual dissolved lead content of 25.5 µg/l with variations from 6.6 to 58.9 µg Pb/l.

Both the dissolved and the suspended lead in all the rivers listed in Table I show month to month variations similar in magnitude to the examples quoted above. The principal factor involved in this variation appears to be the amount of run-off at the time of sampling. The highest levels of both dissolved and suspended lead are found in the streams after a heavy deluge because of elution of lead from partially weathered material.

If the mean values over the year are considered, a good correlation is found between the dissolved lead content and the concentration of lead in the suspended matter, indicating that the same overall ratio between dissolved and suspended species occurs in each lake and river sampled, regardless of its absolute content of lead.

Work done earlier this century (4, 6, 7, 10, 11, 13) showed that the levels of lead in the Rivers Ystwyth and Rheidol were so high that there was total mortality of the fish population. Since mining activities in the area ceased, further studies have shown a partial recovery of the fauna[12]. Indeed, a comparison of the figures quoted in the present paper for these rivers (less than 10 µg Pb/l) and those in some earlier papers (5, 17) showing lead levels from 0.5 p.p.m. upwards, demonstrates that there has been a great improvement in water quality.

There is some evidence to show that the toxicity of lead is reduced as the hardness of the water increases[9]. If this is so, any lead present in the water of the Rivers Rheidol and Ystwyth is likely to have maximum toxic effects on the fauna, since the calcium levels are very low.

Effect of run-off on coastal waters.

The major factor controlling the distribution of lead and other heavy metals in coastal waters is the nature and quantity of run-off from the adjacent land mass. Other contributory factors include circulatory processes, exchange with the open sea, and biological activity. An example of the last category is the phytoplankton phaeocystis, which is known to remove some soluble trace metals from sea water and combine these into its cellular tissue. During a bloom of phaeocystis the amount of these metals in the material filtered from the water is found to be much higher than usual[15].

Figure II shows the distribution of dissolved lead in Liverpool Bay (March 1971), Cardigan Bay (March 1970) and the Bristol Channel (April 1971). Figure III shows the distribution in the same areas for the concentration of lead in the suspended material from the water.

(i) Cardigan Bay.

The high levels of dissolved lead are caused by the input of river water from the mineralised zones of Wales. The pattern of distribution shows unusual features which can only be explained by a study of the circulation in the Bay. This was described by Lee[14], who suggested that the tidal flood and residual currents are in the form of a cyclonic eddy, which implies that there is limited exchange between the water mass of central Cardigan Bay and open sea water. The bulk of the lead carried into the Bay from the North Cardiganshire mineralised zone will be added to this water mass and will consequently cause a build up of lead in this region.

The suggested existence of a cyclonic eddy also implies that Tremadoc Bay, the northernmost part of Cardigan Bay, will be reasonably well isolated. The low levels here are probably a result of the small amounts of dissolved lead in the rivers draining into this region.

Suspended lead in Cardigan Bay shows some unexpected features. The isolation of Tremadoc Bay is clearly seen, but the levels of lead farther to the south are very low, approaching open sea levels. The correlation between dissolved and suspended lead is negative, the complete opposite of the situation found in river water.

(ii) Liverpool Bay.

The lead content of this region arises primarily from the large amounts of industrial and domestic waste discharged. On the whole, the levels of dissolved lead are quite low, apart from four zones, two of which are associated with discharge from the Rivers Mersey and Ribble, and which can be attributed to industrial waste. A third zone off the North Wales coast may be due to run-off from the mineralised area of Flintshire where there are known lead deposits, and similarly the high levels to the north-west of the Bay are likely to originate from run-off from the mineralised areas of the Isle of Man.

In contrast to the distribution of suspended matter in Cardigan Bay, that of this region shows a marked correlation with the distribution of dissolved lead, high levels being found off the North Wales coast and outside the estuaries of the Rivers Mersey and Ribble.

It can be seen that the same orders of magnitude are found for both dissolved and suspended lead, in areas of industrial and 'natural' pollution.

(iii) Bristol Channel.

Apart from a small patch off the South Wales coast near Cardiff, the levels of dissolved lead in the eastern part of the Channel are very low. It is likely that the zone of high concentration in the middle of the Channel is caused by a combination of industrial effluent from the South Wales coast and run-off from the mineralised areas of North Devonshire. A build-up in this area probably arises from the restriction of outflow from the Channel into the open sea, resulting from eddy circulation in the outer part of the Channel.

The 1-2 µg/l area extends farther to the west than is indicated on Figure II, in fact to at least the boundary of the sampling area, 10 miles to the west of Lundy Island.

The most striking feature of the distribution of suspended lead is the region of very high concentrations found to the extreme west of the sampling area. This is almost completely separated from the rest of the Channel by a band of water, the suspended matter of which contains less than 100 p.p.m. of lead. One possible explanation of this could be the accumulation of lead into a planktonic bloom.

Farther to the east a patch of high concentration occurs off the Devonshire coast which may arise from run-off from areas of lead-bearing mineral deposits. Otherwise the suspended lead of this region is homogeneously distributed.

Conclusions.

By considering three isolated coastal sea areas this study has shown evidence of lead pollution caused by industrial activity and by run-off from land areas containing lead deposits. This run-off has also been studied and shown to have a major effect on the distribution of the lead in the coastal waters.

The results show that the three areas may each have limited exchange with open sea water because of their geographical boundaries and because of tidal and residual current effects. It is apparent that restricted circulation can cause very rapid accumulation of toxic material from a relatively minor source.

TABLE I

Mean fresh water lead concentrations

from October, 1970 to October, 1971.

Column A is the concentration of lead in µg/l water passing through a 0.45 µ membrane filter.

Column B is the total weight of suspended lead in µg per litre of water filtered.

Column C is the concentration of lead in p.p.m. in the filtered material.

	A	B	C
Llyn Padarn (lake)	1.78	0.44	218
R. Saint	1.35	0.61	441
Llyn Cwellyn (lake)	0.88	0.47	193
Llyn Gwynant (lake)	0.95	0.57	345
Llyn Dinas (lake)	0.93	2.06	522
R. Glaslyn (middle)	0.92	0.41	554
R. Glaslyn (downstream)	1.06	0.40	418
R. Dwyryd	1.29	1.45	378
R. Mawddach (upstream)	1.19	0.75	699
R. Mawddach (above R. Wnion)	1.09	0.30	545
R. Wnion	2.12	0.40	523
R. Mawddach (above estuary)	0.98	3.26	142
Tal-y-Llyn (lake)	0.71	0.34	442
R. Dysinni	1.24	0.74	296
R. Dovey (upstream)	1.77	0.80	336
R. Rhiw	1.20	0.48	220
R. Iaen	1.15	0.97	178
R. Twymyn (upstream)	25.54	23.06	7968
R. Twymyn (above R. Iaen)	5.74	24.54	5076
R. Twymyn (above R. Dovey)	3.40	8.84	2021
R. Dovey (below R. Twymyn)	1.31	3.56	858
R. Dulas South	1.66	1.13	498
R. Dulas North	1.46	0.44	392
R. Dovey (below R. Dulas North)	1.26	1.75	568
R. Dovey (downstream)	1.15	3.02	708
R. Leri	1.61	3.18	1119
R. Rheidol (upstream)	2.19	3.36	1194
R. Rheidol (middle)	2.23	4.81	2054
R. Rheidol (downstream)	2.63	8.19	1883
R. Ystwyth (upstream)	8.46	3.35	6056
R. Ystwyth (downstream)	2.53	12.46	2146

TITLES FOR FIGURES.

Fig. I Major rivers and lakes of North and Mid-Wales.

Fig. II Distribution of dissolved lead in the eastern coastal areas of the Irish Sea.

Fig. III Distribution of suspended lead in the eastern coastal areas of the Irish Sea.

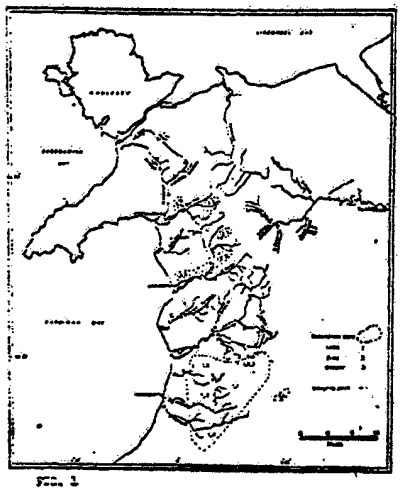
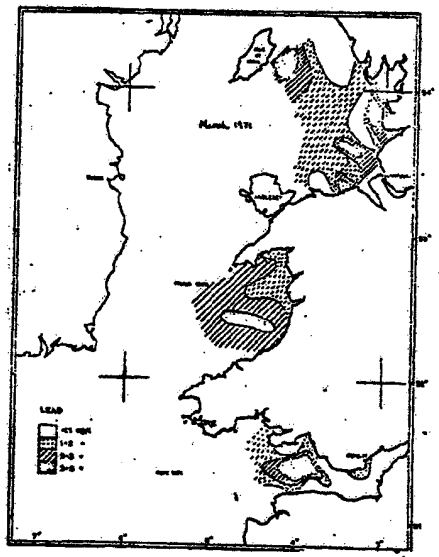


FIG. 1



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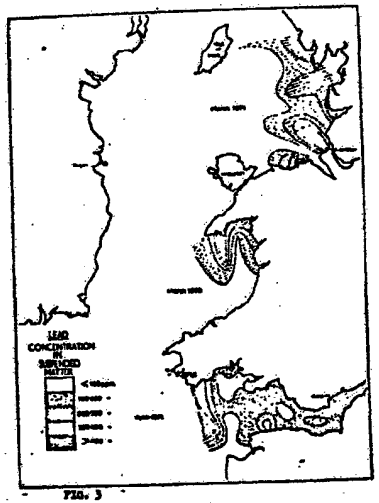

FIG. 3