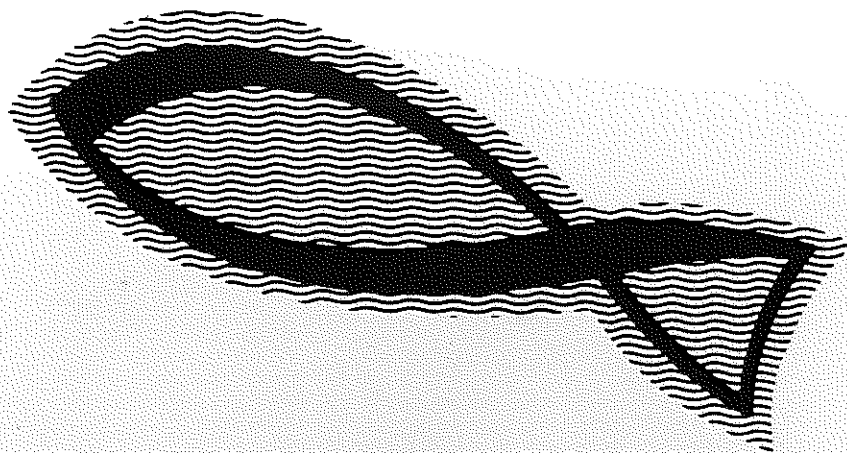




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**Heavy Metals in Mussels and
Sea-Water from the Irish Coast**



by

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Heavy metals in mussels and sea-water

from the Irish coast

by

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SUMMARY

Samples of mussels and sea-waters from various locations (Fig 1) around the Irish coast were analysed for certain heavy metals using Atomic Absorption (AA) Spectroscopy. The results are presented and discussed below.

SAMPLING

Mussel and water samples were taken within thirty minutes of low water. The water was invariably taken from a pier or jetty by means of a cleaned plastic bucket. One litre of the sample (measured by graduated cylinder) was treated with 4 mls of concentrated Nitric Acid (Analar) and transferred to a clean plastic container where it was stored at ambient temperature until analysis (1). All samples were taken by the same operator. The mussels were taken from a point as near as possible to where the water samples had been taken. Samples consisted of 10 healthy adult mussels between 50 and 60 mm long (2-3 years old). The mussels were stored in deep freeze before analysis.

EXPERIMENTAL

(i) Sea-waters

In the analysis of sea-waters for trace metals by AA Spectroscopy it is

necessary to solvent extract the samples both to eliminate interferences from the gross presence of NaCl and other alkali salts, and to concentrate the metals of interest which are usually present in very small concentrations. The usual method of extraction is to use Ammonium Pyrollidine Dithiocarbamate (APDC) and Methyl Iso Butyl Ketone (MIBK), with appropriate pH control (2, 3). It was found that using this system alone neither Cr nor Mn were satisfactorily extracted. If, however, the chelating agent Sodium Diethyl Dithio Carbamate (SDDC) (4) is used in conjunction with APDC at pH 4.2, Mn is extracted in a satisfactory manner. In the analysis 100 mls of seawater at the correct pH were treated with 5 mls. of a purified solution which was 1% in both APDC and SDDC, and extracted with purified MIBK.

Standards were similarly extracted. The extracts were analysed by flameless AA Spectroscopy, except for Zinc which was analysed in a conventional Air/Acetylene flame using a Boiling Three-Slot Burner. Even using both chelating agents Cr failed to be extracted, so after experimentation it was decided to use the method of Ediger, Peterson and Kerber (5) wherein a solution of NH_4NO_3 is added to the unextracted sample in the graphite tube. The efficacy of this approach hinges on the fact that the NH_4NO_3 reacts with the NaCl in the seawater to form relatively volatile products which can be thermally removed before the Cr becomes vaporised, hence the interference is effectively removed. The analysis for Hg is, of course, different from that of other metals, in that it is sufficiently volatile to measure its vapour at room temperature. In the case of Hg the cold flameless technique of Hatch and Ott (6) was used.

(ii) Mussels

Consideration was given to several methods of preparation of the mussel samples, including dry ashing, traditional wet ashing in strong acid and the relatively new technique of solubilising with Tetramethyl Ammonium Hydroxide (TMAH) (7, 8, 9, 10). At an early stage it was decided to eliminate wet ashing because published studies (11, 12) as well as unpublished investigations in this laboratory indicate that there is no significant difference in the recovery of

many elements - even for the more volatile ones such as Pb and Cd - between the two techniques. Consequently, since wet ashing is a time consuming and tedious process we set it aside. Since the laboratory has had no previous experience of the TMAH solubilising technique a brief preliminary comparison between it and dry ashing was performed which indicated that there is no significant difference in recovery between the two preparation techniques. Therefore, since the TMAH procedure is more convenient in practice it was decided to use it for all samples.

TMAH method of dissolving samples:-

The flesh of the mussels was removed from the shells, quickly rinsed in distilled water, dried on filter paper and approx. 30g (i.e. 4 - 6 mussels) accurately weighed and introduced into a flask. A 25% aqueous solution of TMAH (Pfaltz and Bauer) was added in the ratio two of solvent and one of sample, and the mixture was placed in a waterbath at 70° for two hours with occasional shaking. Most samples were completely dissolved within an hour to yield a transparent (clear) dark brown solution, but were allowed to digest for 2 hours to ensure complete dissolution. Prolonged heating in TMAH was avoided since it has been found (10) that this can cause loss of some metals.

When digestion was complete, the solutions were made up to various volumes in de-ionised water, depending on the concentration of the metal of interest.

The digested samples were analysed using the HGA 72 Graphite Tube Furnace, or Air/Acetylene flame with the appropriate lamp and conditions as laid down in the manufacturers instructions (13). Dilutions were made of the samples as appropriate. Blanks of TMAH which had been carried through the same digestion sequence, without sample, were also analysed and their peak heights subtracted from those of the sample. (In most cases they were insignificant compared to the sample signal).

INSTRUMENTAL

A Perkin-Elmer 303 Atomic Absorption Spectrophotometer, fitted with a Deuterium Background Corrector, and a HGA 72 Graphite Cell was used. The samples were introduced into the cell by means of a Finn Pipette with disposable plastic tips. A vol. of 10 ml was used. In the actual analysis the HGA was programmed for the cycle: drying, ashing, atomisation. A temp. of 105°C was used for drying in all cases. The ashing and atomisation temps. are given in Table 1. For the Mercury analysis a Perkin-Elmer Mercury Analysis System (Part No. 303 - 0830) was employed.

The signal was monitored with a Perkin-Elmer 56 recorded in conjunction with a Recorder Readout Accessory. Single Element Perkin-Elmer Intensitron Hollow Cathode Lamps were used for the majority of determinations. In the case of Cadmium, however, an Electrodeless Discharge Lamp (EDL) was used, while for Mercury a Discharge Lamp was employed. Lamp currents and slit-widths were as laid down in the manufacturers hand-book (13). Analytical wavelengths, together with furnace temperatures are summarised in Table 1, below.

TABLE I

Element	Analytical Wavelength	Ashing Temperature	Atomisation Temperature
Cu	324.7 nm	900°C	2600°C
Pb	283.3 nm	550°C	2040°C
Zn ^(a)	213.9 nm	--	--
Cd	228.8 nm	350°C	1800°C
Mn	279.5 nm	1100°C	2600°C
Cr	357.9 nm	1350°C	2660°C
Hg ^(b)	253.6 nm	--	--

NOTES

(a) Flame AA was used for this element.

(b) Cold flameless AA was used for Mercury.

RESULTS AND DISCUSSION

It should be pointed out initially that mussels were selected because of their ubiquitous nature and their well known ability to concentrate heavy metals, as well as their significance to the Irish fishing industry.

The results are presented in Tables II and III.

An examination of the results in Table II and a comparison of them with similar previously published surveys (14, 15, 16, 17, 18) indicates that, with a single exception, there is no evidence of pollution by the metals concerned. This anomaly is in the chromium content of mussels from Dungarvan, and to a lesser extent a few other locations on the East coast.

The results shown in Table III are less easy to correlate with the existing literature because values given for trace metals in seawater (cf, e.g., 19) generally refer to the open ocean and not to samples taken at the shore line, as in this case. It is significant, however, that the elevated chromium level found in the Dungarvan mussels is reflected in the seawater analysis as Table IV illustrates.

Table IV

Comparison of chromium concentrations in Dungarvan with those for the rest of the country.

Water		Mussels	
Mean Value for Country	Value for Dungarvan	Mean Value for Country	Value for Dungarvan
0.04 p.p.m.	0.130 p.p.m.	0.61 p.p.m.	6.40 p.p.m.

We have not been able to discover a similar relationship between water and mussel chromium levels for the other instances (i.e. Carlingford, Mornington, Malahide and Wexford) where relatively high levels were found in the shell fish. It is, of course, possible that there is intermittent elevation of the water

chromium levels in these locations which failed to be noticed in the survey. The fact that the reported "Enrichment Factor" in mussels is highest for chromium (20) lends credence to this notion.

In any event, it is clear that there is, in the case of the Dungarvan area at least, an instance of chromium pollution both with regard to seawater and mussels. This is probably exacerbated by the high enrichment factor that operates in this particular system. Otherwise there is no evidence of pollution of mussels by the other metals examined.

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REFERENCES

- (1) R D Ediger, A. A. Newsletter, 1973, 12, 151.
- (2) R R Brooks, B J Presley, and I.R. Kaplan, Talanta, 1967, 14 809.
- (3) P E Paus, S. Anal. Chem., 1973, 264, 118.
- (4) J D Kinrade and J C Van Loon, Anal. Chem., 1974, 46, 1894
- (5) R D Ediger, G E Peterson, and J D Kerber, A.A. Newsletter, 1974, 13, 61.
- (6) W R Hatch and E L Ott, Anal. Chem., 1968, 40, 2085
- (7) A J Jackson, M Michael and H J Schumacher, Anal. Chem., 1972, 44 1064.
- (8) P D Kaplan, M. Blackstone, and N Richdale, Arch. Environ, Health, 1973, 27, 387
- (9) L Murthy, E E Menden, P M Eller, and H G Petering, Anal. Biochem., 1973, 53, 365
- (10) S B Gross and E S Parkinson, A.A. Newsletter, 1974, 13, 107
- (11) J Anderson, A.A. Newsletter, 1972, 11, 88.
- (12) H C Giron, A.A. Newsletter, 1973, 12, 28.
- (13) Analytical Methods for Atomic Absorption Spectroscopy, 1973 Ed., Perkin-Elmer.

- (14) J Navrot, A J Amiel, and J Kronfield, *Environ. Pollut.*, 1974, 7, 303.
- (15) G J Horvath, R C Harriss, and H C Matthaw, *Marine Pollution Bulletin*, 1972, 3, 182.
- (16) G Nickless, R. Stenner, and N Terrille, *ibid*, 1972, 3, 190.
- (17) K V K Nair and A T Andersen, ICES, C.M. 1972/E:20.
- (18) G Topping, *ibid*, C.M. 1972/E:21.
- (19) J P Riley in "Chemical Oceanography", Vol 2, Eds J P Filey and G Skirrow, Academic Press, London, 1965, p 343 et seq.
- (20) M Merlini in "Impingment of Man on the Oceans", Ed by D W Wood, Wiley-Interscience, New York, 1971, p 470.

TABLE II: Concentrations of Cu, Pb, Zn, Cd, Mn, Cr, in *Mytilus edulis*
p.p.m. (wet weight).

Location	Cu	Pb	Zn	Cd	Mn	Cr
Carlingford Lough	1.07	0.35	6.75	0.97	1.33	1.60
Dundalk	0.08	3.12	8.80	0.60	0.87	0.17
Mornington	0.35	0.41	23.00	-	3.27	2.10
Malahide	0.55	0.47	22.00	-	1.92	2.10
Arklow	-	-	-	-	-	-
Wexford	1.38	0.01	29.00	-	3.35	2.21
Waterford	4.00	2.30	10.80	-	2.33	0.32
Dungarvan	0.83	1.20	29.00	-	2.70	6.40
Youghal	0.52	N.D	9.90	0.28	1.30	N.D
Cork	0.35	N.D	23.30	0.23	1.40	N.D
Oysterhaven	0.43	N.D	7.56	0.03	0.54	0.02
Kinsale	0.34	0.02	1.22	-	-	0.41
Courtmacsherry	1.25	N.D	8.33	0.31	0.89	N.D
Clonakilty	1.10	N.D	10.40	0.31	0.98	0.26
Rosscarberry	0.66	N.D	8.60	0.28	1.80	N.D
Glandore	0.75	0.08	8.20	0.23	1.00	N.D
Roaringwater Bay	0.90	0.11	5.20	0.96	2.40	0.04
Bantry Bay	0.14	N.D	9.60	0.34	0.65	N.D
Castletownbere	0.34	0.07	10.40	0.08	2.00	N.D
Dingle	-	-	-	-	-	-
Shannon Estuary	0.60	N.D	7.70	0.20	2.10	N.D
Clarecastle	-	-	-	-	-	-
Ballyvaughan	0.09	0.30	15.60	0.20	1.03	0.02
Galway	0.80	0.14	10.04	0.29	1.60	0.13
Killary	1.00	0.09	5.30	0.07	1.40	N.D
Killala	0.65	0.01	7.00	0.23	1.20	N.D
Sligo	0.60	0.08	12.00	0.45	1.20	N.D
Donegal	0.13	0.03	10.01	0.24	1.60	0.11
Killybegs	0.24	0.01	19.00	0.20	1.20	0.08
Mean	0.75	0.34	12.26	0.31	1.60	0.61

"-" = Not examined.

"N.D." = Not detected.

TABLE III: Heavy metals concentrations in Irish coastal waters.

Parts per million

Location	Cd	Mn	Cr	Hg
Carlingford Lough	0.003	0.005	0.010	0.001
Dundalk	0.001	0.008	0.010	0.001
Drogheda	0.002	0.002	0.010	0.001
Skerries	0.008	0.002	0.001	0.001
Malahide	0.002	0.003	0.010	0.001
Arklow	0.001	0.020	0.010	0.001
Wexford	0.001	0.006	0.010	0.002
Waterford	0.002	0.040	0.006	0.001
Dungarvan	0.005	0.008	0.130	0.002
Youghal	0.001	0.011	0.012	0.002
Cork	0.002	0.020	0.006	0.001
Kinsale	0.002	0.020	0.006	0.003
Courtmacsherry	0.001	0.009	0.003	0.001
Clonakilty	0.003	0.002	0.010	0.003
Rosscarbery	0.001	0.001	0.012	0.002
Glandore	0.002	0.006	0.028	0.004
Roaringwater Bay	0.002	0.080	0.012	0.001
Bantry Bay	0.001	0.013	0.012	0.001
Castletownbere	0.003	0.001	0.028	0.004
Dingle	0.001	0.005	0.012	0.001
Shannon Estuary	0.002	0.008	0.018	0.001
Clarecastle	0.001	0.028	0.029	0.001
Ballyvaughan	0.001	0.001	0.008	0.001
Galway	0.001	0.012	0.006	0.001
Killary	0.001	0.005	0.008	0.001
Killala	0.001	0.008	0.005	0.001
Sligo	0.001	0.007	0.005	0.001
Donegal	0.001	0.015	0.001	0.001
Killybegs	0.001	0.006	0.010	0.001
Mean	0.002	0.012	0.014	0.001

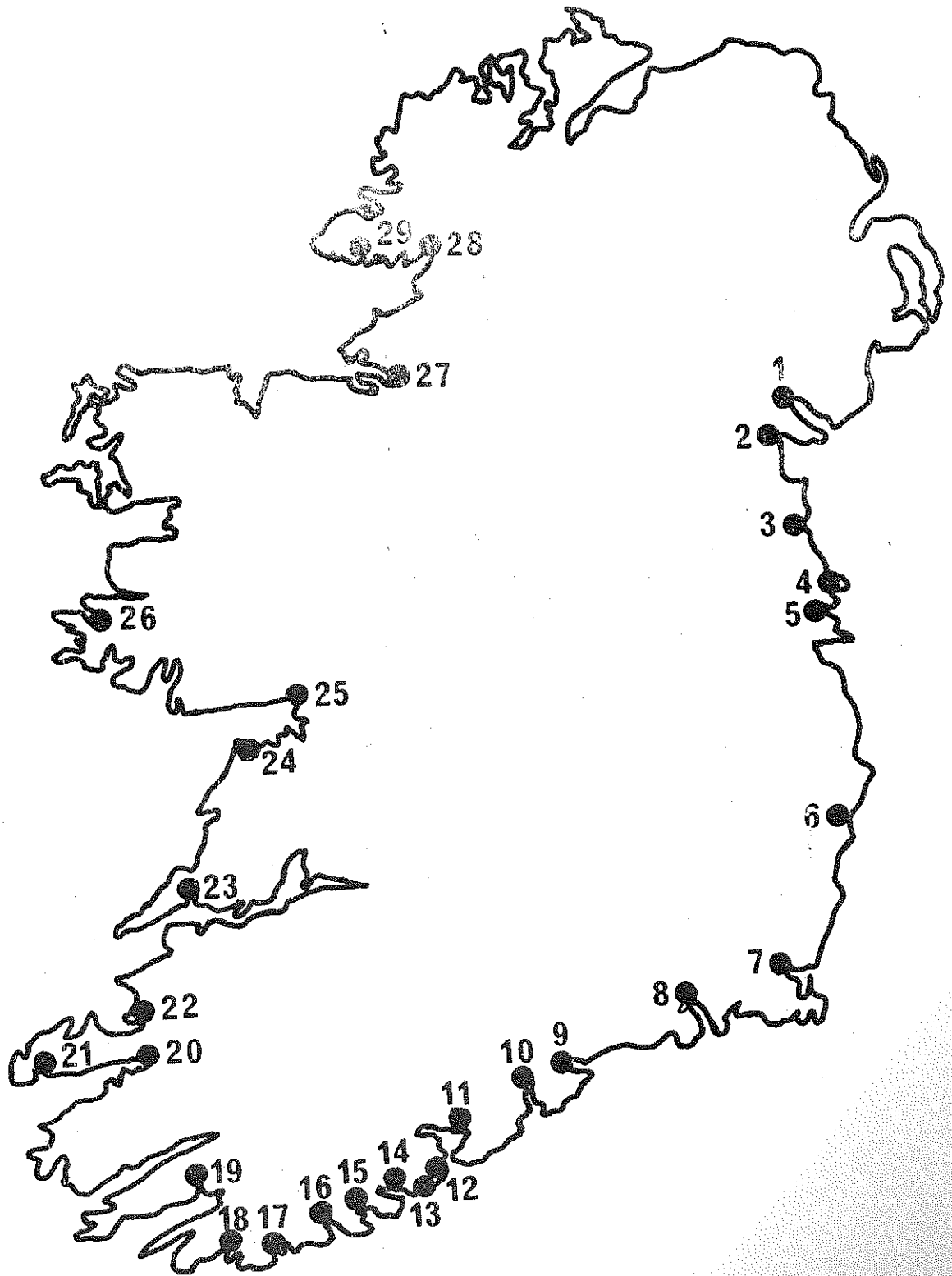


Fig. 1. Map of Ireland showing sampling stations.