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THE OCCURRENCE OF CADMIUM IN SEAWATER AND IN MARINE ORGANISMS AND SEDIMENTS

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ABSTRACT

Methods have been developed for determining cadmium in seawater, marine organisms, and marine sediments. The procedure, based on the dithizone extraction method of Saltzman, is capable of detecting less than 10 μg of the element and can be used for determining cadmium in silicate rocks; only thallium interferes. To confirm the presence of cadmium and to ensure freedom from contamination, the dithizone extracts were examined spectrographically.

The average cadmium concentration found in waters of the Irish Sea and of the English Channel was 0.113 $\mu\text{g}/\text{l}$ (1.0 $\mu\text{g at}/\text{m}^3$), with values ranging from 0.024 to 0.25 $\mu\text{g}/\text{l}$ (0.21–2.2 $\mu\text{g at}/\text{m}^3$) depending upon position and season. It is probable that the variations are due to adsorption or utilization of the element by plankton outbursts or to adsorption by detritus.

The occurrence of cadmium in several marine plants and animals (dried at 110°) has been observed and the concentration varied between 0.134 (*Laminaria digitata*) and 16.4 $\mu\text{g}/\text{g}$ (*Patella vulgata*). The distribution of the element in various organs of *Pecten maximus*, *Buccinum undatum*, *Chlamys opercularis*, and *Porania pulvillus* has been investigated. Cadmium in calcareous shells is usually less than 0.02 $\mu\text{g}/\text{g}$, muscle contains about 1.5 $\mu\text{g}/\text{g}$, and high concentrations (up to 500 $\mu\text{g}/\text{g}$) are found in the digestive glands and renal organs of molluscs.

A representative selection of marine sediments has been analysed; the mean values of cadmium for diatomaceous oozes (0.39 $\mu\text{g}/\text{g}$), globigerina oozes (0.42), and radiolarian oozes (0.45) are close to the average value reported by Goldschmidt for the concentration of cadmium in the upper lithosphere. Two manganese nodules

contained 8.4 and 5.1 $\mu\text{g/g}$ of cadmium respectively; thallium (ca 2 $\mu\text{g/g}$) was also detected in each case.

INTRODUCTION

In a recent note (1) the authors have given a preliminary description of the detection of cadmium in seawater; it is the purpose of this paper to amplify this account and to describe studies of the cadmium contents in a number of marine organisms and sediments.

Neither Bardet *et al* (2) nor Noddack and Noddack (3) were able to detect cadmium spectrographically in seawater, and the latter workers consider that its concentration must be less than 0.5 $\mu\text{g/l}$. Goldschmidt (4) has reviewed the geochemistry of the elements and has quoted average figures of 80, 0.18, and 0.5 $\mu\text{g/g}$ for the abundances of zinc, cadmium and mercury respectively in the lithosphere. The concentrations of zinc (3, 5, 6) and mercury (3) in seawater are 8–20 and 0.3 mg/m^3 respectively. Buljan (7), who has compared the terrestrial abundances of elements with their concentrations in seawater by plotting their concentrations (as log gm-at/ton) against their atomic numbers, has found certain regularities among members of the same group of the periodic table. His results, when corrected for an erroneous mercury concentration, indicate that the concentration of cadmium in seawater should be ca 1.8 mg/m^3 . Ishibashi and Shigematsu (8) have predicted the abundances of most of the elements in seawater from a relationship between log (percentage of the element in the lithosphere/percentage of the element in seawater) and ionic potential of the element. They concluded that seawater contains 0.045 $\mu\text{g Cd/l}$.

The concentration of metals from seawater by organisms is well known. The first record of the occurrence of cadmium in the animal kingdom is due to Fox and Ramage (9) who detected the element spectrographically in the livers of 11 separate specimens of the lamellibranch, *Pecten maximus*. Noddack and Noddack analysed 10 sea organisms spectrographically and reported cadmium concentrations ranging from 0.03 to 11 $\mu\text{g/g}$ in the dried specimen (for the shell of an echinoid, *Brissopsis lyrifera*, and a whole jellyfish, *Cyanea capillata*, respectively). Malyuga (10) has determined cadmium polarographically in a number of sea animals and plants, finding 0.1–1 $\mu\text{g/g}$ in dried algae and 1.1 $\mu\text{g/g}$ in *Asterias rubens*; in the other sea animals examined, cadmium was just detectable.

Most of the other studies (11, 12, 13, 14, 15) of trace elements in marine organisms have been carried out on algae, but cadmium has been rarely reported, perhaps due to its concentration being normally below the limits of direct spectrographic detection.

The geochemistry of cadmium is as yet incompletely known; rarely does the element seem to be enriched in igneous rocks, in which the abundance ratio Zn : Cd is *ca* 900 : 1. Practically no data are available on the occurrence of cadmium in sedimentary rocks, but since its ionic radius in octahedral co-ordination (1.03A) is practically identical with that of calcium (1.06A) and since zinc and cadmium carbonates (Smithsonite and Otavite) are isomorphous with calcite, Goldschmidt (17) has considered that in small amounts they may replace calcium in carbonate sediments. Both of these elements occur in considerable amounts (up to 0.3% Zn and 0.01% Cd) in the marine phosphorites of organic origin of the South Sea Islands (16). Goldschmidt (17), who has discussed the fate of cadmium in marine hydrolysates such as muds and clays, has stated that it may be leached from the hydrolysate, like calcium, or be incorporated in the clay minerals by ion exchange because of its ability to form tetrahedral bonds. Owing to its large ionic radius, its ability in the latter direction is likely to be much more restricted than zinc.

Development of a Method for Determining Cadmium in Seawater.

Since the concentration of cadmium in seawater is below the limits of direct detection, a preliminary concentration of the element is necessary. The use of dithizone extraction for this purpose has been investigated from the theoretical standpoint by Koroleff (18). Cadmium can be extracted quantitatively from solutions more basic than pH 6.5 by using a solution of dithizone in chloroform. A solution of dithizone in carbon tetrachloride has been used (19) as the stationary phase on a cellulose acetate column in a partition chromatographic method for the separation of certain trace metals (including cadmium) from seawater.

A review of the literature indicated that the dithizone extraction method described by Saltzman (20) offered the greatest prospect for success. In this procedure cadmium is extracted with a chloroform solution of dithizone in the presence of hydroxylamine hydrochloride from a strongly alkaline solution (*ca* 1.6 N in NaOH) containing tartrate and cyanide to minimise the extraction of interfering elements. The cadmium is extracted from the chloroform layer by means of tartaric acid. The aqueous layer is then made strongly alkaline with sodium hydroxide, and the cadmium is re-extracted with dilute dithizone in the presence of hydroxylamine and a small concentration of cyanide. The optical density of the extract is measured at 518 m μ , the wavelength of maximum absorption of cadmium dithizonate. Quantities of cadmium as low as 5 μ g can be determined in the presence of at least 1000 times as much silver,

bismuth, copper, cobalt, iron, manganese, lead, tin and zinc and of 20 times as much mercury; thallium alone interferes. Saltzman's procedure is not directly applicable to seawater since the alkalinity used in the first dithizone extraction would lead to the precipitation of calcium carbonate and magnesium hydroxide.

Experiments were carried out to extract cadmium at a concentration of 0.5 $\mu\text{g/l}$ from both distilled water and seawater buffered to pH 8.3 or 6.5 by means of ammonium chloride and sodium hydroxide; sodium citrate was added to prevent the precipitation of the hydroxides of iron and aluminium. The determination was carried out as described on p. 108. In each case recoveries of over 97% of the added cadmium were obtained and in all further work the preliminary extraction was carried out at pH 8.3.

Effect of Foreign Ions. Since dithizone is not a specific reagent and will in fact form chloroform extractable complexes with 17 elements (21), the combined effect of these elements was examined at 25 times their maximum recorded concentrations in seawater (*viz* Hg^{2+} 10; Cu^{2+} 250; Zn^{2+} 250; Pb^{2+} 100; Mn^{2+} 125; Co^{2+} 5; Ni^{2+} 10; Bi^{2+} 10; Ag^{2+} 10 $\mu\text{g/l}$). It was found that the optical density (at 518 $\text{m}\mu$ in a 4 cm cell) of the final dithizone extract was only 0.012 greater than the reagent blank; therefore the interference of these elements at their seawater concentrations is negligible. Since the method was also applied to marine sediments, the effects of a number of these elements at higher concentrations were investigated, with the following results:

Element	Cu^{2+}	In^{3+}	Pb^{2+}	Hg^{2+}	Tl^{+}	Zn^{2+}
Concentration ($\mu\text{g/l}$)	500	10	500	100	10	500
Optical density*	0.009	0.002	0.017	0.000	0.057	0.025

* Measured at 518 $\text{m}\mu$ in a 4 cm cell, reagent blank deducted.

The only appreciable interference at low concentrations is caused by thallium, which has not yet been detected in seawater but which is concentrated to a slight extent by marine organisms (3). The concentration of the element in marine sediments is not likely to exceed 2 $\mu\text{g/g}$. Thus it is improbable that it is a source of error in the present work, but, to guard against this, all dithizone extracts were examined spectrographically, and in only two cases (both manganese nodules containing thallium) has any other dithizone-extractable element, save cadmium, been detected.

Determination of Cadmium. In order to test the modified method, varied amounts of cadmium were added to one litre samples of metal-

free water and extracted as described elsewhere. The optical densities of the final dithizone extracts (final volume 7 ml), measured at 518 μ in 4 cm cells, were:

Wt. of cadmium (μ g)	0.1	0.2	0.3	0.5	1
Optical density	0.041	0.082	0.118	0.197	$\left\{ \begin{array}{l} 0.401 \\ 0.408 \end{array} \right.$
[less reagent blank (0.033)]					

EXPERIMENTAL

Reagents. All reagents and solutions were prepared with water freshly distilled from a silica still. All chemicals used were of analytical reagent grade.

(1) Standard cadmium solution (10 mg/l). Dissolve pure cadmium (10 mg) in 3 ml of nitric acid (30% v/v). Evaporate the solution to dryness on a waterbath. Take up the residue in 0.5 ml of 60% perchloric acid and fume to dryness under a Vitreosil infra-red heater. Dissolve the product in water and dilute to 1 l. This stock cadmium solution was diluted as required for calibrating the extraction method.

(2) Ammonium chloride 1 N (53.5 g/l). Preserve in a polyethylene bottle.

(3) Potassium cyanide (2.5%). Dissolve 2.5 g of potassium cyanide in 100 ml of water. Store in a polyethylene bottle and dispense from a 10 ml tilt measure.

(4) Tartaric acid (20 g/l). Store in the refrigerator and reject if growth of mould has commenced.

(5) Sodium citrate (100 g/l).

(6) Hydroxylamine hydrochloride (2.5 g/25 ml). Prepare fresh reagent each week.

(7) Sodium hydroxide-potassium cyanide reagent. Dissolve sodium hydroxide (40g) in 70 ml of water. When cool, add a solution of 0.05 g of potassium cyanide in 5 ml of water and dilute to 100 ml. Store in a polyethylene bottle.

(8) Dithizone reagents. The dithizone was supplied by British Drug Houses. The chloroform employed conformed to the British Pharmacopeia specification; it was recovered after use, as described by Mullin and Riley (22).

(a) Extraction dithizone. Prepare a solution of dithizone in chloroform containing 120 mg/l and store in a dark glass bottle in the refrigerator.

(b) Standard dithizone. Dilute 5 ml of the extraction dithizone to 100 ml with chloroform. Store in the refrigerator. Slight variations in the strength of the reagent were of no account, but it was prepared freshly fortnightly.

(9) Nitric acid. Redistil pure concentrated nitric acid from an all-glass still.

(10) Perchloric acid (60% w/w).

(11) Hydrofluoric acid (40% w/w).

Determination of Cadmium in Seawater. The filtered (Whatman No. 2) seawater (950 ml) was placed in a one litre glass-stoppered short-stemmed separating funnel, followed by 10 ml of 1 N ammonium chloride, 25 ml of sodium citrate solution, and 10 ml of 2.5% potassium cyanide solution. The mixture was extracted by shaking for five minutes with 15 ml of extraction dithizone. The chloroform layer was run into 10 ml of 2% tartaric acid contained in a short-stemmed 50 ml separating funnel. The seawater was re-extracted with an additional 15 ml of extraction dithizone. The combined chloroform extracts were shaken vigorously with the tartaric acid for two minutes and the lower layer was then discarded. The aqueous layer was washed with 3 ml of pure chloroform; the lower layer was carefully rejected, and any drops of chloroform floating on the surface were removed with a gentle current of air.

The tartaric acid layer was treated with 0.25 ml of hydroxylamine hydrochloride solution, made alkaline with 2.5 ml of sodium hydroxide-potassium cyanide reagent; then 7.0 ml of standard dithizone were added from a pipette. The separating funnel was shaken vigorously for one minute. The lower layer was separated and then dried by passing it through a dithizone-extracted chloroform-washed plug of ashless filter paper in the stem of a 2.5 cm funnel. The optical density of the extract was measured at 518 m μ in a 4 cm cell. The reagent blank was determined by using 950 ml of water distilled from glass or quartz apparatus. A calibration curve was prepared by carrying out the determination with known amounts of cadmium in distilled water. In later work, two litre samples of seawater were analysed in order to increase the accuracy of the determination; the same quantities of reagents were employed except that the first extractions were carried out with 25 ml of extraction dithizone.

Determination of Cadmium in Biological Materials. It was found that dry ashing of biological materials, even at temperatures as low as 400°, could lead to losses of up to 50% of the cadmium present. Cadmium was therefore determined after destruction of the organic matter with nitric acid (23).

The weighed, air-dried sample (0.5–5 g) was placed in a 250 ml conical flask, and 15 ml of 30% v/v nitric acid were gradually added. The neck of the flask was closed with a loosely fitting bulb stopper in the side of which a hole had been blown to allow vapours to escape.

The flask was heated on a hot plate, from which it was removed if the reaction threatened to become violent. When all foaming had ceased, continuous heat was applied until the mixture was evaporated to dryness. A second evaporation was carried out with another 15 ml of 30% v/v nitric acid; this was followed by repeated evaporations with 15 ml volumes of concentrated nitric acid until all carbonaceous matter had been oxidized. Normally not more than three evaporations with concentrated nitric acid were necessary to give a white residue (some organisms yielded residues stained brown with iron salts). The salts were washed into an evaporating basin with a jet of water and evaporated to dryness. The residue was taken up in 5 ml of water, and 0.5 ml of 60% perchloric acid was added; the liquid was evaporated under a Vitreosil infra-red heater until no further acid fumes evolved. The residue was digested on the water bath with 200 ml of water containing 2.5 ml of concentrated hydrochloric acid. The solution was filtered through an ashless filter paper and diluted to 250 ml. A suitable aliquot of this solution was placed in a one litre separating funnel, diluted to *ca* 950 ml, and treated with 25 ml of 10% sodium citrate solution. The pH was adjusted to *ca* 9 (phenolphthalein) by addition of 2N sodium hydroxide. Cadmium was determined in the solution as in the case of seawater. Good recoveries of added cadmium (over 98%) were obtained and the method showed a standard deviation of 1.5%.

Determination of Cadmium in Sediments. The sediment (1 g) was weighed into a platinum basin which was then covered with a clock glass; 2 ml of concentrated nitric acid were gradually added. When all effervescence had ceased, the watch glass was rinsed and removed and 30 ml of 40% hydrofluoric acid were added; the mixture was evaporated to dryness on the water bath. In the case of Green Mud, further evaporation with nitric acid was necessary to decompose organic matter. The residue was then dissolved in a small quantity of distilled water, 1 ml of 60% perchloric acid was added, and the solution was evaporated under an infra-red heater until all fumes of perchloric acid had ceased. The dried product was extracted with 2.5 ml of concentrated hydrochloric acid and treated with 150 ml of distilled water; the resultant solution was filtered through an ashless filter paper. After the solution had been diluted to *ca* 950 ml and its pH adjusted to *ca* 8, by the careful addition of sodium hydroxide, cadmium was determined as described for seawater. An exactly analogous blank determination was made in the same manner, omitting the sample. The method, which shows a standard deviation of 2.5%, has approximately ten times the sensitivity of the procedure described by Sandell (24).

Determination of Cadmium in Manganese Nodules. The finely powdered nodule, dried at 110° (1.0 g), was placed in a silica basin and covered with a watch glass; 5 ml of concentrated hydrochloric acid were added. After standing overnight, the mixture was evaporated to dryness under an infra-red heater. The residue was treated with 100 ml of 2.5% hydrochloric acid, and after solution of the salts by warming, the insoluble matter was removed by filtration through an ashless filter paper. The latter was washed well and ignited in a platinum crucible in a muffle furnace at 800° C; silica was volatilised from the cold residue by addition of 5 ml of 40% hydrofluoric acid and one drop of concentrated sulphuric acid. The liquid was evaporated to dryness and the residue was heated to a dull redness. The resultant oxides were fused with 2 g of potassium bisulphate and the cold mass was dissolved in water. After filtration, this solution was added to the main bulk of the solution of the nodule and diluted to *ca* 900 ml. The solution was brought to *ca* pH 8 by the addition of sodium hydroxide, and 10 ml of 2% hydroxylamine hydrochloride were added to avoid oxidation of dithizone by ferric iron or manganese (III). Cadmium was extracted with four 15 ml portions of extraction dithizone in the presence of citrate, cyanide, and ammonium chloride, as described for seawater. The reagent blank was determined in the same manner, but omitting the manganese nodule.

Spectrographic Analysis. In order to obtain unequivocal proof of the presence of cadmium in the materials analysed, the dithizone extracts were examined spectrographically. Such examination also had the advantage of determining whether or not the extracts were free of other elements. The technique used was a modification of the method of Wark (25), who evaporated dithizone concentrates onto graphite powder prior to spectrographic analysis. We have found that the sensitivity of detection can be considerably increased by evaporating the extract on spectrographically pure calcium carbonate instead of graphite.

Detection Method. A dropping pipette was constructed by fusing a thistle funnel of *ca* 10 ml capacity to one end of a piece of 1.5 mm bore capillary tubing. The latter was drawn out at its lower end to a fine capillary of such dimensions that it had a drop time of 2–2.5 seconds when the upper bulb was filled with chloroform. "Specpure" calcium carbonate (2 mg) was placed in a one ml microcentrifuge cone and the latter was immersed to a depth of 2 cm in a water bath at 90–95°. The tip of the dropping pipette was inserted into the centrifuge tube so that it rested against the side at approximately 1.5 cm from the top of the calcium carbonate. The dithizone extract to be examined was placed in the thistle funnel and allowed to flow

onto the calcium carbonate at such a rate that there was never a greater depth than 1 mm of unevaporated chloroform in the centrifuge cone. The dry calcium carbonate carrying the dithizonate was packed into a cavity in a 6.25 mm graphite electrode and burnt in the D.C. arc at a current of *ca* 5.7 amps against a graphite cathode. The spectrum was recorded on Ilford Ordinary plates, using a medium quartz spectrograph. Falling plate studies showed that the cadmium lines had their greatest intensity in the first 10 seconds of arcing; thereafter the intensity fell off rapidly owing to loss of cadmium by volatilization. Therefore the exposure given was 10 seconds. Tests with known amounts of cadmium showed that Cd 2288.018A was quite clearly visible with 5 μg of cadmium, Cd 3261.057A was very faint with this amount of the element, and Cd 2265.017A was visible only if more than 10 μg of cadmium were present.

RESULTS

Seawater. Sea surface samples were collected at a number of stations in the Irish Sea and in the English Channel off Plymouth, using a wooden or canvas bucket. The samples, stored in five litre polyethylene bottles, were analysed as soon as possible after collection. Experiments showed that the concentration of cadmium in filtered seawater stored in polyethylene containers did not change over a period of at least five weeks. Earlier work indicated a much higher concentration of cadmium in seawater than was found subsequently; this discrepancy was traced to contamination of the water by cadmium leached from the soft glass "salinity" bottles in which samples had been stored.

The samples were analysed as described on p. 108; the results are shown in Tables I, II and III. With the later samples, analyses were carried out on volumes of two litres in order to increase the accuracy of the determination, the amounts of dithizone used in the first extraction being increased proportionately. Duplicate determinations, carried out on a number of samples, showed good agreement (*viz* Table III).

TABLE I. OCCURRENCE OF CADMIUM IN THE SURFACE WATERS OF THE IRISH SEA

Lat. (N)	Long. (W)	Date	$\mu\text{g Cd/l}$	Date	$\mu\text{g Cd/l}$	Cl ‰
53° 26'	4° 16'	27.4.54	0.034	23.11.54	0.080	18.63
53° 24'	4° 52'	27.4.54	0.081	24.11.54	0.159	17.99
54° 16'	4° 49'	10.5.54	0.050	7.12.54	0.122	18.91
53° 52'	4° 17'	16.5.54	0.060	7.12.54	0.118	18.43
54° 02'	4° 51'	12.5.54	0.060	15.12.54	0.045	18.59
53° 50'	4° 09'			15.12.54	0.080	18.67
		Mean	0.057		0.101	

TABLE II. OCCURRENCE OF CADMIUM AND COPPER IN THE SURFACE WATERS OF THE IRISH SEA

Lat. (N)	Long. (W)	Date	Cl ‰	µg Cd/l	µg Cu/l
54° 3'	4° 36'	2.5.55	18.83	0.200	11.5
53° 57'	4° 23'	2.5.55	18.86	0.083	8.7
53° 53'	4° 06'	2.5.55	18.86	0.252	17.3
53° 44'	3° 52'	3.5.55	18.50	0.198	15.6
53° 40'	3° 36'	3.5.55	18.23	0.137	14.0
53° 34'	3° 20'	3.5.55	17.91	0.127	15.0
	Mean			0.166	13.7

The mean cadmium concentration, considering all samples given in Tables I, II and III, was 0.113 µg/l (1.0 µg at/m³), a value which is in reasonable agreement with that predicted by Ishibashi and Shigematsu (0.045 µg/l) but which is considerably less than the amount suggested by Buljan (1.8 µg/l).

The data show, however, that the cadmium concentration is variable and that as much as a threefold variation may be found over quite a small area. Similar differences have been found (26) in the copper concentration at certain of these stations (*cf* Table II). These variations may well be caused by adsorption (27, 28) or by utilization

TABLE IV. OCCURRENCE OF CADMIUM IN MARINE ALGAE

Organism	Cd µg/g	Concentration factor × 10 ^{-3*}
Chlorophyceae		
<i>Codium</i> sp. (Codiaceae)	0.865	7.6
<i>Halimeda gracilis</i> (Codiaceae)†	0.312	2.7
Phaeophyceae		
<i>Ascophyllum nodosum</i> (Fucaceae)	0.349	3.1
<i>Fucus serratus</i> (Fucaceae)	0.792	7.0
<i>F. vesiculosus</i> (Fucaceae)	2.03	18.1
	2.08	
<i>Pelvetia canaliculata</i> (Fucaceae)	0.500	4.5
	0.508	
<i>Laminaria digitata</i> (Laminariaceae)	0.134	1.2
Rhodophyceae		
<i>Lithophyllum</i> sp. (Corallinaceae)‡	0.358	3.2
<i>Corallina officinalis</i> (Corallinaceae)	0.858	7.6
<i>Lithothamnion</i> sp. (Corallinaceae)	0.844	7.4

† From Gulf of Manaar (Indian Ocean).

‡ Origin unknown; sample analysed by method used for silicates.

* Concentration factor = concentration of cadmium in air dried organism/mean concentration of cadmium in seawater (0.113 µg/l).

TABLE III. OCCURRENCE OF CADMIUM IN THE SURFACE WATERS OF THE ENGLISH CHANNEL

<i>Lat. (N)</i>	<i>Long. (W)</i>	<i>St.</i>	<i>Date</i>	$\mu\text{g Cd/l}$	<i>Date</i>	$\mu\text{g Cd/l}$	<i>Date</i>	$\mu\text{g Cd/l}$	Cl ‰
50° 20'	4° 10'	L2	11.7.54	{0.076	11.10.54	0.072	16.2.55	0.241	16.64
				{0.079					
50° 18'	4° 11'	L3	11.7.54	0.058	11.10.54	0.057	16.2.55	0.189	18.45
50° 15'	4° 13'	L4	11.7.54	{0.150	11.10.54	0.072	16.2.55	0.126	19.22
				{0.163					
50° 15'	4° 18'	L5	11.7.54	0.124	11.10.54	0.072	16.2.55	0.171	19.36
50° 06'	4° 21'	L6	19.7.54	0.040	11.10.54	0.064	16.2.55	0.256	19.48
50° 02'	4° 22'	E1	19.7.54	0.024	11.10.54	0.146	16.2.55	0.094	19.54
			Mean	0.096		0.081		0.180	

of both elements by localised communities of plankton which are well known to occur in these waters. It is interesting to note that seawater containing the lowest concentration of cadmium also had the lowest copper concentration.

TABLE V. OCCURRENCE OF CADMIUM IN MARINE ANIMALS

Organism	Cd $\mu\text{g/g}$	Concentration factor $\times 10^{-3}$ *
Protozoa		
<i>Ramulina</i> sp. (Foraminifera)†	2.18 } 2.24 }	19.5
Porifera		
<i>Halichondria panicea</i>	1.85	16.4
Coelenterata		
<i>Alcyonium digitatum</i>	1.15	10.2
Crustacea		
<i>Balanus balanoides</i> (Cirripedia)	0.146 } 0.148 }	1.30
<i>Cancer pagurus</i> (Decapoda)	0.153	1.35
<i>Corystes cassivelaunus</i> (Decapoda)	0.149	1.31
<i>Eupagurus</i> sp. (Decapoda)	1.31	11.6
Mollusca		
<i>Mytilus edulis</i> (Lamellibranchia)	Shell only 0.003 Soft parts 3.21	0.03 28.4
<i>Pecten maximus</i> (Lamellibranchia)		See Table IX
<i>Chlamys opercularis</i> (Lamellibranchia)		See Table VII
<i>Littorina littoralis</i> (Gastropoda)	3.54	31.3
<i>L. littorea</i> (Gastropoda)	Shell only 0.012 Soft parts 1.84	0.1 16.3
<i>Nucella lapillus</i> (Gastropoda)	Shell only 0.082 Soft parts 37.9	0.72 335
<i>Calliostoma zizyphinum</i> (Gastropoda)	Shell only 0.049 Soft parts 3.05	0.43 27.0
<i>Gibbula umbilicalis</i> (Gastropoda)	Shell only 0.029 Soft parts 0.829	0.26 7.3
<i>Patella vulgata</i> (Gastropoda)	16.4	145
<i>Buccinum undatum</i> (Gastropoda)		See Table VIII
Echinodermata		
<i>Asterias rubens</i> (Asteroidea)	1.66	14.7
<i>Henricia sanguinolenta</i> (Asteroidea)	1.12	9.6
<i>Luidia ciliaris</i> (Asteroidea)	14.8	131
<i>Marthasterias glacialis</i> (Asteroidea)	1.46	12.9
<i>Porania pulvillus</i> (Asteroidea)		See Table VI
<i>Stichasterella rosea</i> (Asteroidea)	6.3	56.1
<i>Echinus esculentus</i> (Echinoidea)	0.325	2.8
<i>Psammechinus miliaris</i> (Echinoidea)	0.435 } 0.450 }	3.8
<i>Spatangus purpureus</i> (Echinoidea)	Whole organism less gut 0.24	2.1
	Gut & contents 0.81	7.2
<i>Ophiocomina nigra</i> (Ophiuroidea)	0.940 } 0.963 }	8.1

† From Galle, Ceylon.

* Concentration factor = concentration of cadmium in air-dried organism/mean concentration of cadmium in seawater (0.113 $\mu\text{g/l}$).

These values are calculated from the mean value in the preceding column.

TABLE VI. CADMIUM IN *Chlamys opercularis*

	Shell	Gills	Mantle + Viscera	Muscle	Gonad
Sulphated ash, %	—	19.0	21.6	6.5	10.4
Cd, $\mu\text{g/g}$	0.008	1.24	9.71, 9.53*	0.87	2.21
Conc ⁿ . factor $\times 10^{-3}$	0.007	11	85	8	20
Cd in ash, $\mu\text{g/g}$	0.008	6.5	44.5	13.4	21.2

* Duplicate determinations on different samples.

TABLE VII. CADMIUM IN *Porania pulvillus*

	Inter- radial septa	Skin from aboral surface	Ambulacral region + Tubefoot system	Oral region + Stomach	Digestive gland	Gonad
Sulphated ash, %	73.7	60.4	88.3	95.0	11.3	—
Cd, $\mu\text{g/g}$	13.1	16.3	6.8	6.7	2.23	1.47
Conc ⁿ . factor $\times 10^{-3}$	115	144	60	59	20	13
Cd in ash, $\mu\text{g/g}$	17.7	26.9	7.7	7.0	19.7	—

Marine organisms. Cadmium has been determined in a number of species of marine algae and marine animals, obtained mainly from the Irish Sea, off Port Erin and Port St. Mary. The organisms were washed thoroughly with distilled water and dried at 110° before analysis. Unless otherwise noted, the analyses were carried out on the whole organism. Duplicate analyses, carried out in a number of cases, showed excellent agreement. In addition, the distribution of cadmium in the various organs of *Porania pulvillus*, *Chlamys opercularis*, *Buccinum undatum*, and *Pecten maximus* has been studied. Specimens of *Pecten maximus* were analysed directly after removal from their habitat and also after being allowed to purge themselves in clean seawater for seven days. The results of the analyses are shown in Tables IV-IX, together with the concentration factors [concentration of cadmium in dried organism (in $\mu\text{g/kg}$)/mean concentrations of cadmium in seawater (0.113 $\mu\text{g/l}$)].

The cadmium concentrations of the various whole organisms lie in the range 0.13 (*Laminaria digitata*) to 16.4 $\mu\text{g/g}$ (*Patella vulgata*) and show that the element is strongly extracted from seawater by marine organisms. The values found for *Fucus serratus*, *Ascophyllum nodosum*, and *Asterias rubens* accord well with those found polarographically in these organisms by Mal'uga (0.34, 0.29, and 1.1 $\mu\text{g/g}$ respectively). The extremely low cadmium content of the calcareous shells suggests that the mechanism by which the calcium of seawater is converted into calcium carbonate in the shell is extremely selective

TABLE VIII. CADMIUM IN *Buccinum undatum*

	<i>Whole animal*</i>	<i>Shell</i>	<i>Mantle</i>	<i>Foot</i>	<i>Heart</i>	<i>Digestive gland</i>	<i>Digestive tract</i>	<i>Mucous gland</i>	<i>Renal organ</i>
Sulphated ash, %	8.8	—	5.0	4.1	5.4	4.1	5.7	20.4	10.0
Cd, $\mu\text{g/g}$	31.8	0.018	0.96	0.29	2.32	68.0	3.14	1.31	17.7
Conc ⁿ . factor $\times 10^{-3}$	281	0.16	8.5	2.6	21	602	28	12	157
Cd in ash, $\mu\text{g/g}$	361	0.018	19	7	43	1659	55	6	177
	<i>Male ducts</i>	<i>Female ducts</i>	<i>Male gonads</i>	<i>Female gonads</i>	<i>Operculum</i>	<i>Osphradium</i>	<i>Ctenidium</i>		
Sulphated ash, %	5.9	3.3	—	2.1	3.7	4.0	10.9		
Cd, $\mu\text{g/g}$	0.72	0.60	24.3	11.4	1.0	15.4	11.2		
Conc ⁿ . factor $\times 10^{-3}$	6.4	5.3	215	101	8.8	136	99		
Cd in ash, $\mu\text{g/g}$	12	18	—	542	27	385	102		

* Less shell.

TABLE IX. CADMIUM IN *Pecten maximus*

<i>Unpurged</i>							
	<i>Shell</i>	<i>Gills</i>	<i>Full gonad</i>	<i>Spent gonad</i>	<i>Striped muscle</i>	<i>Unstriped muscle</i>	<i>Foot</i>
Sulphated ash, %	—	25.1	10.7	3.2	6.0	4.7	51.9
Cd, $\mu\text{g/g}$	0.001	8.5	0.79	9.3	1.95	1.86	6.3
Conc ⁿ . factor $\times 10^{-3}$	0.01	75	7	82	17	16	56
Cd in ash, $\mu\text{g/g}$	0.001	34	7.3	291	33	40	12
	<i>Mantle + Gut + Digestive gland</i>			<i>Mantle</i>	<i>Gut</i>	<i>Digestive gland</i>	<i>Renal organ</i>
Sulphated ash, %	13.9			13.3	12.6	7.2	27.2
Cd, $\mu\text{g/g}$	39.5			5.8	6.2	532	152
Conc ⁿ . factor $\times 10^{-3}$	350			49	55	4707	1348
Cd in ash, $\mu\text{g/g}$	284			44	49	7400	559
<i>Purged</i>							
	<i>Gills</i>	<i>Male gonad</i>	<i>Female gonad</i>	<i>Striped muscle</i>	<i>Foot</i>	<i>Gut + Gonad + Digestive gland</i>	<i>Renal organ</i>
Sulphated ash, %	25.0	3.0	10.2	12.7	9.3	10.9	36.7
Cd, $\mu\text{g/g}$	12.5	0.55	0.11	1.58	16.5	111	127
Conc ⁿ . factor $\times 10^{-3}$	111	45	1	14	146	983	1124
Cd in ash, $\mu\text{g/g}$	50	18	11	12	177	1018	346

TABLE X. CADMIUM IN MARINE SEDIMENTS

<i>Sample</i>	<i>Sea or Ocean</i>	<i>Lat.</i>	<i>Long.</i>	<i>Depth (m)</i>	$\mu\text{g Cd/g}$	<i>Concentration factor</i> $\times 10^{-3}$
Barbados earth ¹	—	—	—	—	0.023	0.20
Diatomaceous ooze	S. Atlantic	53° 35' S	108° 35' E	3566	0.857	7.6
Diatomaceous ooze ²	—do—	66° 40.5' S	71° 01' W	531	0.281	2.5
Diatomaceous ooze ³	—do—	54° 03' S	38° 35' W	184	0.174	1.5
Diatomaceous ooze ⁴	—do—	62° 56' S	59° 50' W	949	0.311	2.8
Diatomaceous ooze ⁵	—do—	55° 52' S	56° 53' W	4344	0.311	2.7
Globigerina ooze ⁶	—do—	25° 30' S	5° 53' E	892	0.459	4.1
Globigerina ooze	N. Atlantic	38° 55.6' N	31° 35.0' W	1295	0.275	2.4
Globigerina ooze ⁷	Atlantic	26° 07.7' S	14° 36.3' W	2260	0.516	4.6
Radiolarian ooze ⁸	S. Pacific	11° 14' S	97° 57' E	5032	0.448	4.0
Radiolarian ooze ⁸	N. Pacific	12° 42' N	152° 01' W	5300	0.251	2.2
Radiolarian ooze ⁹	S. Atlantic	46° 35' S	24° 15.5' W	4402	0.129	1.1
Radiolarian ooze ¹⁰	—do—	50° 26' S	30° 27' W	5000	0.977	8.6
Red clay ¹¹	Pacific	19° 10.2' N	177° 24.1' E	3566	0.563	5.0
Green mud	N. Atlantic	44° 37.6' N	55° 47.1' W	1049	0.268	2.3
Calcareous ooze ¹²	—do—	22° 00.5' N	76° 59.5' W	914	0.574	5.1
Drewite ¹³	Caribbean	24° 10' N	78° 00' W	—	0.124	1.1
Volcanic glass ¹⁴	S. Atlantic	62° 59' S	60° 28' W	525	0.210	1.9
Nulipore gravel ¹⁵	Atlantic	—	—	40	0.106	0.9
Manganese nodule ¹⁶	N. Pacific	37° 41' N	177° 04' W	5303	8.40	74.3
Manganese nodule ¹⁷	S. Pacific	13° 28' S	149° 30' W	4300	5.06	44.8
Organic mud ¹⁸	Irish	54° 10' N	4° 58' W	66	{ 0.075*	0.7
					{ 0.417†	3.7
Organic mud ¹⁹	Irish	54° 24' N	3° 34' W	18	{ 0.096*	0.8
					{ 0.363†	3.2

* Nitric acid soluble Cd.

† Total Cd.

for calcium (see p. 120). In general, the cadmium contents of algae and Asteroidea were higher than those of Crustacea although generally lower than those of Mollusca. It is not obvious why the cadmium concentrations of *Patella* and *Nucella* are so much greater than those of other molluscs; *Patella* is a browsing form which feeds upon the microscopic algal film covering rocks; *Nucella*, on the other hand, is carnivorous, its diet consisting mainly of *Balanus*, an organism with a low cadmium content; the related shallow water form, *Buccinum*, also has a high cadmium content (Table VIII). The cadmium content of the various organs differs widely, particularly low concentrations being found in muscle and gonads. The element is much concentrated in the digestive glands and renal organs of those molluscs whose individual organs have been examined, contents of up to 0.5% in the ash being recorded. In the case of *Pecten maximus* it was thought that the cadmium in the digestive gland might be associated with the detritus on which the animal feeds; this did not prove to be the case, since animals which had been allowed to purge themselves in filtered seawater until the gut was empty were still rich in cadmium in these organs (Table IX). Copper is much more uniformly distributed throughout the organs of *Buccinum* (26) than is cadmium; excluding the shell and foot, the Cu content ranges from 26 to 87 $\mu\text{g/g}$.

NOTES TO TABLE X

- ¹ Neritic fossil deposit, mainly Radiolarian, from Bisset Hill.
- ² "Discovery" St. W.S. 514. 11/2/30.
- ³ "Discovery" St. W.S. 52. Organic debris with siliceous skeletons.
- ⁴ "Discovery" St. No. 203. 5/4/27, Bransfield Strait, S. Shetlands.
- ⁵ "Discovery" St. W.S. 468. 9/11/29.
- ⁶ Chalky deposit.
- ⁷ Globigerina and sponge spicules.
- ⁸ Debris and sponge spicules.
- ⁹ "Discovery" St. No. 10. 13/2/26.
- ¹⁰ "Discovery" St. No. 11. 16/2/26.
- ¹¹ Mainly volcanic debris and some sponge spicules.
- ¹² British Museum sample B.M. 1955, 24.
- ¹³ From Miler Creek, South Bight, Andros Islands, Bahamas. Aragonite mud with a few drifted shells.
- ¹⁴ "Discovery" St. No. 172. 26/2/27. Off Deception Island, S. Shetlands.
- ¹⁵ From West Hebrides.
- ¹⁶ British Museum sample No. M 313. Contained 20.3% SiO_2 .
- ¹⁷ Contained 16.5% SiO_2 .
- ¹⁸ Contained 1.2% organic carbon.
- ¹⁹ Contained 1.3% organic carbon.

Marine sediments. A number of representative marine sediments have been analysed (see Table X). The cadmium contents of all the deep sea sediments, except manganese nodules, lie between 0.2 and 1 $\mu\text{g/g}$. Furthermore, there is no significant difference between the cadmium contents of diatomaceous ooze, globigerina ooze and radiolarian ooze (means 0.39, 0.42, 0.45 $\mu\text{g/g}$ respectively). The mean concentration found is similar to that quoted by Goldschmidt (4) for the upper lithosphere (0.5 $\mu\text{g/g}$).

Goldberg (29), who has found that a number of elements are concentrated in manganese nodules, has attributed this to the scavenging action of the electrically charged colloidal ferric and manganese oxides, which adsorb oppositely charged ions from seawater before they coalesce to form the nodules. Evidently this is the explanation of the comparatively high cadmium content of the nodules examined. In passing it might be added that both nodules contained appreciable amounts of thallium (*ca* 2 $\mu\text{g/g}$), an element which, as stated on p. 106, has not been detected previously in seawater.

The low cadmium contents of carbonate shells and of Barbados earth are noteworthy, since, as mentioned on p. 105, Goldschmidt considered that both cadmium and zinc should be concentrated in carbonate sediments. The chemically precipitated drevite, on the other hand, contains considerable amounts of cadmium, and in laboratory experiments we have found that aragonite, which has been precipitated by passing a current of carbon dioxide-free air through seawater saturated with calcium carbonate, contains up to 1 $\mu\text{g/g}$ of cadmium. It is apparent, therefore, that considerable amounts of cadmium are coprecipitated with chemically precipitated calcium carbonate, whereas when the latter is formed biologically the mechanism of shell formation is much more specific for calcium, with only small amounts of cadmium being incorporated in the shells.

The mud samples examined are of interest since they indicate that part of their cadmium is associated with the organic detritus which is derived from dead organisms. Assuming that the concentration of undecayed organisms in the mud was approximately twice the organic carbon content found, then the concentration of cadmium in the original organism was *ca* 4 $\mu\text{g/g}$, which is of the same order as that actually found in marine organisms.

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