THE STATE OF COBALT IN SEA WATER AND ITS
UPTAKE BY MARINE ORGANISMS AND SEDIMENTS

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Weiss and Shipman (1956, 1957) reported the occurrence of ^{60}Co in the clam, *Tridacna gigas*, at the U. S. Pacific Proving Ground. Lowman et al. (1957) reported the presence of ^{57}Co , ^{58}Co and ^{60}Co in samples of marine algae, plankton, sponges, coconut crabs, hermit crabs, tridacnids, bonito, flying fish, tuna, mullet, herring and terns collected at Bikini and Eniwetok Atolls. Since then, radionuclides of cobalt have been found in marine samples collected throughout the world.

Most of the ^{57}Co , ^{58}Co and ^{60}Co now present in the marine environment has been produced by weapons tests. In the future, however, part of the marine inventory of ^{58}Co and ^{60}Co will be produced as a result of the operation of power reactors cooled by river or sea water. The radionuclides of cobalt are produced by neutron activation of metals in and near the reactor cores and are released, mainly, in ionic form. The similarity of distribution patterns of the natural cobalt and the introduced radionuclides in the marine environment and the biota are dependent upon the similarities or differences in their chemical and physical forms. Stable dissolved cobalt is assumed to occur in sea water in the ionic form (Goldberg et al., 1971); however, investigations by the authors show that, in the estuarine waters of Puerto Rico, approximately half of the dissolved stable cobalt occurs as complexes which are not ionic. The present studies were done to determine the effects of the chemical-physical state of cobalt in sea water upon their chemistry and biological distribution in the sea.

MATERIALS AND METHODS

Capsules of Vitamin B 12 tagged with ^{57}Co were dissolved in 85 ml of distilled water and passed through a column (4 mm x 25 mm) of Chelex-100. Ionic cobalt in the Vitamin B 12 solution was chelated onto the column and the B 12 cobalt passed in the eluate. The solution of tagged vitamin was standardized for gamma activity and kept in a refrigerator until used in the experiments. The total gamma activity in the solution was 3.06 μC of ^{57}Co (7.9×10^4 d/m/ml). The solution contained 8.5 μg of stable cobalt (0.1 μg of complexed Co/ml) and 3.1 μg of cyanocobalamin (MW 1355).

Aliquots of carrier-free ^{58}Co were passed through a column (4 mm x 25 mm) of Chelex-100. Ninety-one percent of the activity was retained on the columns. The cobalt was eluted from the columns with 6 N HCl, taken almost to dryness on a hot plate and redissolved in distilled water. The solutions of ionic cobalt were standardized for gamma activity and were stored in

a refrigerator until used in the experiments. Stable cobalt could not be detected in the solutions by atomic absorption spectrophotometry. Neither the organically-bound cobalt solutions nor the ionic cobalt solutions changed chemical form, under refrigeration, during an interval of six months.

For analysis of stable cobalt in sea water, the metal is usually preconcentrated from the water by coprecipitation, liquid-liquid extraction or by adsorption onto chromatographic columns. Relative preconcentration of ionic cobalt and cyanocobalamin cobalt from sea water was tested by coprecipitation with ferric hydroxide, manganese dioxide, saturated sodium carbonate, hydrogen sulfide and α -nitroso- β -naphthol precipitates. Relative adsorption of the two forms of cobalt onto columns of Chelex-100 and activated charcoal was also measured as well as the degree of extraction into dithizone, APDC + MIBK and α -nitroso- β -naphthol in chloroform. Standard methods for preconcentration were used (Joyner et al., 1966).

One hundred liters of sea water collected near Puerto Rico, but removed from the outflow of rivers, were placed in a polyethylene container which had previously been treated with silicone. Twenty-six clams (*Donax denticulatus*) were suspended in the aquarium in baskets and allowed to equilibrate for three days before radionuclide tracers were added. At the time of addition of 452,000 c/m of ^{57}Co cobalamin and 400,800 c/m ionic ^{58}Co all of the clams were actively pumping. No clams died during the experiment, which lasted for 17 days. Ten of the clams were removed from the aquarium daily, placed in a beaker of non-radioactive sea water and counted by gamma spectrometry. They were returned to the aquarium after each counting. On the sixth day the clams were removed to a 20 liter aquarium containing non-radioactive sea water and counted daily by gamma spectrometry for a period of seven days.

On the third day, six of the remaining clams were separated into soft parts and shells and the two parts counted separately. The soft parts were analyzed for stable cobalt and the shells were used for experiments to determine the site of deposition of the radionuclides of ^{57}Co and ^{58}Co in the shells.

Eight other clams were removed, one each, on the fourth, fifth, seventh, tenth, fifteenth and seventeenth days, counted entire, dissected, and the soft parts and shells counted separately.

In addition to the living clams, shells were removed from 21 other clams. Sets of shells were subjected to 1 N HCl, antibiotic, 1% EDTA, 10% formalin, or no treatment. After treatment

they were rinsed in distilled water and placed in the aquarium. Each shell was counted by gamma spectrometry three times during a four-day interval.

Individual juvenile lobsters (Panulirus argus), two to five grams wet weight, were placed in 20 liter aquaria and allowed to equilibrate. The lobsters were removed daily, placed in beakers of non-radioactive sea water, counted for ^{57}Co and ^{58}Co activity, fed and returned to the tagged aquaria. They were in non-radioactive water less than 20 minutes per day.

Uptake experiments on marine phytoplankton, zooplankton, crab larvae and marine pelagic crustacea were done at sea. Two experiments for phytoplankton were done. In each, 10 liters of sea water, rich in phytoplankton, were inoculated with ^{57}Co cobalamin and ionic ^{58}Co . One liter aliquots were sampled by filtering through membrane filters at intervals. The filters were counted by gamma spectrometry.

Zooplankton and ^{57}Co cobalamin and ionic ^{58}Co were placed in 10 liters of water containing phytoplankton. One liter aliquots were filtered at 1-1/2 and 14 hours and counted.

Pelagic macrurid crustacea were placed in two 10 liter aquaria. In one aquarium only sea water, containing ^{57}Co cobalamin and ionic ^{58}Co , was present at a ratio $^{57}\text{Co}/^{58}\text{Co}$ of 1. The other aquarium contained a mixture of phytoplankton and zooplankton which had previously concentrated ^{57}Co cobalamin 14/1 over ionic ^{58}Co .

Marine periphyton was raised on glass plates in a 200 liter polyethylene aquarium. ^{57}Co cobalamin and ionic ^{58}Co were added and the periphyton was scraped from the glass plates at intervals. The periphyton was concentrated on membrane filters for gamma spectrometry.

Estuarine marine water with suspended sediments was collected and inoculated with the two forms of radioactive cobalt. The water was filtered through membrane filters and the filters were analyzed by gamma spectrometry.

Ten liters of fresh water, containing fresh water phytoplankton, from Gatun Lock in the Panama Canal were inoculated with the two chemical forms of cobalt tracer. One liter aliquots of the water were filtered through membrane filters at 1 and 3-1/2 hours. The filter papers were analyzed by gamma spectrometry.

PRECONCENTRATION OF COBALT FROM SEA WATER

Relatively large amounts of cobalt occur in the estuarine waters of Puerto Rico. The ionic form normally constitutes 50% to 65% of the total cobalt content and is present at levels of 2 to 5 μg per liter of sea water. The remaining 35% to 50% of the cobalt is in complexed forms. Precipitates of ferric hydroxide, manganese dioxide (at pH 9) and sea water calcium precipitated with saturated sodium carbonate coprecipitated less than 1.5% of ^{57}Co cobalamin tags from sea water, but scavenged 83% to 100% of the carrier-free ionic ^{58}Co tags (Table I). Similarly, the chelating resin Chelex-100 retained only 0.6% of the organically complexed cobalt and 91% of the ionic form. Extraction of cobalt into dithizone, APDC and α -nitroso- β -naphthol in organic solvents removed only 0.5% to 1.8% of the ^{57}Co cobalamin from sea water, but extracted 75% to 97% of the ionic ^{58}Co .

In contrast, the sulfide precipitate (tin carrier), formed by the thioacetamide, coprecipitated 81% of the organically bound cobalt and α -nitroso- β -naphthol extracted 48% of the organic form of cobalt from sea water. Activated charcoal removed 100% of the ^{57}Co cobalamin from sea water.

The precipitate of manganese dioxide, formed by heating sea water containing potassium permanganate and ethyl alcohol, appeared to coprecipitate about 51% of the ^{57}Co cobalamin and all of the ionic ^{58}Co . However, most of the coprecipitated ^{57}Co was in the ionic form and was released by oxidation of cyanocobalamin by the permanganate.

The coprecipitation of ionic and cobalamin-cobalt by manganese dioxide, formed by adding manganous sulfate and potassium permanganate to sea water, was pH dependent (Fig. 1). At pH values less than 9, 8% to 10% of the cobalamin ^{57}Co was coprecipitated. At pH 9 only 1.2% of the cyanocobalamin was coprecipitated. The coprecipitation of ionic ^{58}Co varied almost linearly from 3.3% coprecipitation at pH 5 to 100% coprecipitation at pH 9 (Fig. 1).

The coprecipitation of ionic and cobalamin-cobalt by thioacetamide-sulfide precipitation was also pH dependent (Fig. 2). A pH of 1.5 was optimum for the coprecipitation of ^{57}Co cobalamin which was coprecipitated, 81%. Coprecipitation of ionic cobalt increased with decrease in pH. At the optimum pH for coprecipitation of the cobalamin (pH 1.5), 1% of the ionic cobalt was coprecipitated.

Combinations of the above methods in series may be used to preconcentrate normally occurring ionic cobalt in one

Table I

TESTS ON PRECONCENTRATION METHODS FOR ISOLATING
ORGANICALLY BOUND AND IONIC COBALT FROM SEA WATER

<u>Method</u>	<u>% separated from the water</u>	
	<u>Organically Bound (^{57}Co)</u>	<u>Ionic (^{58}Co)</u>
Fe(OH)*	0.8	83.
Mn O ₂ **	51.	100.
Chelex-100	0.6	91.
Mn O ₂ (pH 9)***	1.2	100.
Saturated sodium carbonate	1.1	100.
Dithizone extraction****	1.3	97.
APDC + MIBK extraction+	0.5	88.
α -nitroso- β -naphthol extraction++	1.8	75.
Thioacetamide sulfide ppt.+++	81.	1.
α -nitroso- β -naphthol ppt.	48.	89.
Activated charcoal	100.	67.

* Two precipitations

** Potassium permanganate + ethyl alcohol + heat

*** Potassium permanganate + manganous sulfate

**** Three extractions

+ Two extractions

++ Into chloroform

+++ pH 1.5, tin carrier

Fig. 1

The effect of pH on the coprecipitation of ionic cobalt and cobalamin-complexed cobalt by manganese dioxide in sea water

Fig. 2

The effect of pH on the coprecipitation of ionic cobalt and cobalamin-complexed cobalt by tin sulfide precipitation in sea water

fraction and organically bound cobalt in another. Several combinations of methods have been successfully used by the authors including: (1) adsorption of ionic cobalt onto chelating resin followed by adsorption of the organically complexed cobalt onto activated charcoal and (2) extraction of ionic cobalt by dithizone in carbon tetrachloride followed by sulfide coprecipitation of the organically complexed cobalt. Carrier-free ionic ^{58}Co and high specific activity ^{57}Co cobalamin were added to the sea water before treatment to provide estimates of chemical yield.

TURNOVER OF ^{57}Co COBALAMIN AND IONIC ^{58}Co BY THE CLAM DONAX DENTICULATUS, LINNE

Donax denticulatus is a select deposit feeder which lives in the surf zone of sandy beaches near the outflows of rivers. The clams vary from 2.5 to 3 cm in length and weigh 2.5 to 3 grams. The weight ratio of shell/soft parts is about 2:3. The average stable cobalt content of the soft parts of six of the clams used in the present experiment was 1.39 μg cobalt/gram wet weight and the total stable cobalt in all of the soft parts of clams used in the experiments was 38.3 μg .

The aquarium for the experiment contained 100 liters of sea water with 3 μg of stable complexed cobalt and 4300 c/m ^{57}Co cobalamin per kilogram of water. Stable ionic cobalt was present at 4.3 μg and ionic ^{58}Co at 4900 c/m per kilogram of water. During the experiments, the clams and clam shells accumulated 3% of the total ^{57}Co and 7% of the total ^{58}Co in the water. The ratio of total clams/water was 0.0092; soft parts/water, 0.0028; and shells/water, 0.0064.

The rates of accumulation and loss, with time, of ionic ^{58}Co and ^{57}Co cobalamin in the shells and soft parts of Donax denticulatus are shown in Figs. 3 and 4. The rates per gram of soft parts or shell are shown in Fig. 5.

On a total clam basis the accumulation of ionic ^{58}Co was about double that of ^{57}Co cobalamin (Figs. 2 and 3). However, on a weight basis the uptake rate of ionic ^{58}Co was only about 1.1 times the uptake rate of ^{57}Co cobalamin (Fig. 5). During the first five days of the experiment the uptake rates which were measured for ^{57}Co and ^{58}Co represented an uptake of stable ionic cobalt by the shell of 0.049 $\mu\text{g}/\text{day}$ and of stable complexed cobalt in the soft parts, 0.044 $\mu\text{g}/\text{day}$. Thus, the uptake rates per gram of organ for both the radionuclide tags and the two forms of stable cobalt were about the same.

Fig. 3

Diagram of uptake and loss of ionic ^{58}Co in the shell and ^{57}Co cobalamin in the soft parts of the clam *Donax denticulatus*. The water contained .003 μg of complexed cobalt, 4.3 c/m ^{57}Co cobalamin, .0043 μg of ionic cobalt and 4.9 c/m ionic ^{58}Co per ml

Fig. 4

Diagram of uptake and loss of ionic ^{58}Co in the soft parts and ^{57}Co cobalamin in the shell of the clam Donax denticulatus

Fig. 5

Diagram of uptake and loss per gram wet weight of ionic ^{58}Co and ^{57}Co cobalamin in the shell and soft parts of the clam Donax denticulatus. The water contained .003 μg of stable complexed cobalt, 4.3 c/m ^{57}Co cobalamin, .0043 μg of ionic cobalt and 4.9 c/m ionic ^{58}Co per ml

Most of the ^{57}Co cobalamin was accumulated in the soft parts and the ionic ^{58}Co in the shell. At 3, 8 and 17 days 89%, 92% and 94%, respectively, of the total ^{57}Co cobalamin accumulated by the clams were in the soft parts. At the same times, 92%, 91% and 90%, respectively, of the total ionic ^{58}Co became associated with the shells.

In both the shell and soft parts of the clams, the rate of loss of the ^{58}Co was less than that of the ^{57}Co . Thus, in the shells, 5.3% of the ^{57}Co and 1.9% of the ^{58}Co was lost per day. In the soft parts 3.2% of the ^{57}Co and 0.8% of the ^{58}Co were lost per day. Because of this, the ratio $^{57}\text{Co}/^{58}\text{Co}$ in the clams decreased with increased time of exposure in the tagged water. At day 1 the $^{57}\text{Co}/^{58}\text{Co}$ ratio in the soft parts was 8 and decreased to a steady ratio of 4 by the 7th day, and through the 17th day. At day 1 the $^{57}\text{Co}/^{58}\text{Co}$ ratio in the shells was 0.084 and decreased to a steady ratio of about 0.03 by the 7th day and through the 17th day.

The clams which were removed from the tagged water on the 6th day and placed in clean sea water also exhibited a continuing decline, with time, in the ratio $^{57}\text{Co}/^{58}\text{Co}$ in the shells and in the soft parts. The ratio of $^{57}\text{Co}/^{58}\text{Co}$ in the soft parts declined from a value of 4 the first day in the clean water to a value of 3.2 on the 11th day. Similarly, in the shells the $^{57}\text{Co}/^{58}\text{Co}$ ratios were 0.04 and 0.02 on the 1st and 11th days, respectively.

Because the amount of stable cobalt (1.39 μg) per gram of clam soft parts and the rates of loss of ^{57}Co and ^{58}Co were known and the amounts of ^{57}Co cobalamin, ionic ^{58}Co , stable complexed cobalt and stable ionic cobalt per gram of sea water had been measured*, the theoretical curves for uptake rates of complexed ^{57}Co and ionic ^{58}Co could be compared with the measured uptake rates. The diagrams are shown in Fig. 6. The theoretical curves (dashed lines) coincide with the measured uptake rates (solid lines). The final apparent concentration factors would be about 460 based on complexed cobalt in sea water and about 320 for ionic cobalt. However, at 180 days the cobalt in the soft parts of the clam would be 99.7% at equilibrium with the complexed cobalt in sea water, but only 75.7% at equilibrium with the ionic cobalt in sea water.

The calcium carbonate shells of pelecypods are deposited by biological activity of the clams. It would be logical to

* For ^{57}Co ; 0.003 μg of complexed cobalt and 4.3 c/m ^{57}Co cobalamin per gram of sea water; 1.39 μg of cobalt/gram of clam soft parts with 3.2% exchange with water per day (63.75 c/m ^{57}Co and 0.044 μg of complexed cobalt per day). For ^{58}Co ; 0.0043 μg of ionic cobalt and 4.0 c/m of ionic ^{58}Co per gram of sea water; 1.39 μg of cobalt/gram of clam soft parts with 0.76% exchange with water per day (12 c/m ^{58}Co and 0.01 μg of ionic cobalt per day).

Fig. 6

Diagram of the uptake of ^{57}Co cobalamin and ionic ^{58}Co measured in the soft parts of 10 clams, Donax denticulatus, (solid line) and the projected uptake curves based on the amounts of stable elements and radionuclides in the water, the measured turnover rates in the soft parts and the total stable cobalt pool in the soft parts of the clam

expect that the accumulation of cobalt in the shell would also result from biological activity of the animals. If cobalt were deposited by the mantle of Donax the radionuclides should occur on the insides of the shells.

Four clams which had been in the tagged water for four days were separated into soft parts and shells. The shells from two of the clams were painted with epoxy laquer on the inside and the shells from the other two, on the outside. The shells were etched with 1 N HCl and counted by gamma spectrometry. The shells from which the inner surfaces had been removed by acid had an average of 8.5 c/m ^{57}Co and 310 c/m ^{58}Co . Those from which the outer surfaces were etched had an average of 3 c/m ^{57}Co and 4.5 c/m ^{58}Co . Thus, the cobalt had been deposited on the outside of the shell.

Shells from 9 clams which had been kept in non-radioactive water were removed from the soft parts and treated with antibiotics, acid etching (1 N HCl) and no treatment. The results are shown in Fig. 7. The shells treated with 1 N HCl did not subsequently accumulate either ^{57}Co cobalamin or ionic ^{58}Co . The shells treated with antibiotics accumulated both ^{57}Co and ^{58}Co at approximately the same rate and at a rate equal to that of shells of living clams. The results showed that the soft parts of the clams were not necessary for the normal accumulation of ^{57}Co cobalamin and ionic ^{58}Co by the shells and that the periphyton, normally present on the outside of the shells, did not contribute significantly to the uptake patterns of the two forms of cobalt.

The shells were removed from 9 other clams and treated with EDTA, formalin and no treatment. The uptake of ^{57}Co cobalamin and ionic ^{58}Co was similar in all three treatment groups, indicating that neither EDTA nor formalin had altered the surface of the shells sufficiently to change the uptake of the radionuclides from that which occurred in untreated shells.

The average rates of uptake and loss for ^{57}Co cobalamin and ionic ^{58}Co in the spiny lobster, Panulirus argus, are shown in Fig. 9. The equilibration rates for both radionuclides were much higher (i.e., equilibration occurred more rapidly) in the lobsters than in the clam, Donax, but the concentration factors at equilibrium were lower. The concentration factor for ionic ^{58}Co at equilibrium was about 100 and for ^{57}Co cobalamin, about 36. The lobsters equilibrated with the ^{57}Co in the water at about 50 hours, but had not arrived at equilibrium with ^{58}Co , even at 180 hours. The difference in equilibrium times was reflected in the continued increase, with time, in $^{58}\text{Co}/^{57}\text{Co}$ ratio

Fig. 7

Diagram of the influence of pretreatment of clam shells from living animals upon the accumulation of ^{57}Co cobalamin and ionic ^{58}Co from sea water

Fig. 8

Diagram of the influence of pretreatment of clam shells from living animals upon the accumulation of ^{57}Co cobalamin and ionic ^{58}Co from sea water

Fig. 9

Diagram of the uptake of ^{57}Co cobalamin and ionic ^{58}Co by juvenile spiny lobsters (Panulirus argus). The loss of ^{58}Co and the change in ratio $^{58}\text{Co}/^{57}\text{Co}$ are also shown

in the animals. The lobsters were not large enough to dissect for analysis of distribution patterns of the ^{57}Co and ^{58}Co in the organs or for stable element analysis. Estimates of the distribution patterns could be made, however, by analyzing animals which molted. In six lobsters which molted during the experiment the newly molted lobsters discriminated 4.1/1 in favor of uptake of ionic ^{58}Co over ^{57}Co cobalamin, compared with the amounts in the water. The molts discriminated 2/1 in favor of uptake of ionic ^{58}Co . One lobster and its molt were counted over a period of seven days with the following results:

Time After Molting In Days	Discrimination in Favor of ^{58}Co	
	Lobster	Molt
1	2.2	1.1
2	3.1	1.6
3	3.3	1.9
7	4.4	2.4

The intact animal discriminated in favor of ionic ^{58}Co at about twice the discrimination rate which occurred in the molt. On the basis of these data it appears that discrimination in favor of the uptake of ionic ^{58}Co is more pronounced in the internal organs of the lobster than in the exoskeleton.

Two uptake experiments with phytoplankton were only partially successful because the organisms could not be kept alive aboard ship for more than four days and, on the basis of uptake ratios ^{57}Co cobalamin/ionic ^{58}Co , the cultures started deteriorating at about 24 hours. In both experiments the maximum discrimination in favor of ^{57}Co cobalamin was about 15 times with respect to the amounts of the radionuclides ^{57}Co and ^{58}Co in the water. In contrast, fresh water phytoplankton discriminated 5:1 in favor of ionic cobalt. Mixed zooplankton and the brine shrimp, *Artemia*, discriminated 15/1 in favor of the uptake of ^{57}Co cobalamin over ionic cobalt in comparison with the amounts of the radionuclides in the water.

One zooplankter, a macruran crustacean, was sampled in large numbers off the west coast of Costa Rica. Specimens placed in water containing ^{57}Co cobalamin and ionic ^{58}Co at a ratio 1:1 exhibited a $^{57}\text{Co}/^{58}\text{Co}$ ratio of 1 for two hours after introduction into the tagged water. After two hours the crustacea discriminated steadily in favor of ionic ^{58}Co . At 20 hours the $^{58}\text{Co}/^{57}\text{Co}$ ratio in the animals was 4:1 (Fig. 10). Other specimens of this macruran crustacean were placed in clean sea water containing mixed plankton with a $^{57}\text{Co}/^{58}\text{Co}$ ratio of 14. At seven hours the $^{57}\text{Co}/^{58}\text{Co}$ ratio in the crustacea was 4.7; at 13 hours, 3.2; and at 27 hours, 1.28. In both cases,

Fig. 10

Diagram of the change in the ratio of uptake of ^{57}Co cobalamin and ionic ^{58}Co in pelagic macruran crustaceans placed in sea water with a $^{57}\text{Co}/^{58}\text{Co}$ ratio of 1 and in non-radioactive sea water containing mixed plankton with an initial $^{57}\text{Co}/^{58}\text{Co}$ ratio of 14

uptake from sea water and uptake from food, the macruran crustaceans discriminated in favor of the uptake of ionic ^{58}Co .

Marine periphyton, grown on glass plates, discriminated 4/1 in favor of the uptake of ^{57}Co cobalamin over that of ionic ^{58}Co .

Estuarine sediments discriminated 2:1 in favor of the uptake of ionic ^{58}Co over ^{57}Co cobalamin. The major reservoir for most trace elements released to the estuarine environment is the sediments. Duursma and Gross (1971) reported distribution coefficients 6×10^3 for ^{60}Co in oxygenated sediments and 1.4×10^4 in anoxic sediments. Thus, with the relatively great mass of the sediments and their marked ability to adsorb radionuclides of cobalt and many other trace elements, the estuarine sediments usually constitute the determining factor in the availability of many radionuclides in the near-shore marine areas.

The present studies have shown that there is a marked difference between organisms in their response to the element cobalt in the complexed form or in ionic form in sea water. These differences are summarized in Table II.

DISCUSSION

Most of the radionuclides of cobalt from weapons tests, reactor operation or as by-products of nuclear technology are released into the marine environment in particulate or ionic form. The concentrations of soluble radionuclides in sea water are usually determined by preconcentration methods followed by gamma spectroscopy. Because most of the preconcentration methods are not efficient for collecting complexed cobalt, large errors may be introduced if stable cobalt analysis is done on total sea water or sea salt and the radionuclide analysis on coprecipitates, organic liquid chelates, or solid chelates. Analyses done this way may produce erroneous data in which marine organisms apparently have higher specific activities (μC of radionuclide/ μg of stable element) than the water in which they are collected. For the heavier elements, including radionuclides of cobalt, this is, of course, impossible.

Concentration factors for trace elements in marine organisms are usually derived by determining the amount of trace elements per gram of living organism and sea water. If the analysis for the trace element in sea water accounts only for the ionic form (which may constitute only 50% of the total element), then the derived concentration factor would be high by a factor of 2.

Table II

DISCRIMINATION FACTORS FOR MARINE ORGANISMS AND
SEDIMENTS AND FRESH WATER PHYTOPLANKTON FOR ORGANIC
AND IONIC COBALT IN WATER

<u>Sample Type</u>	<u>Uptake Ratio Organic Co/Ionic Co</u>
Marine phytoplankton	15
Marine zooplankton	15
<u>Artemia</u>	15
Crab larvae	5
<u>Donax</u> soft parts	4
Marine periphyton	4
Pelagic macruran crustacea	0.9
Estuarine sediments	0.5
Spiny lobster molt	0.5
Spiny lobster (whole)	0.4
Fresh water phytoplankton	0.2
<u>Donax</u> shell	0.03

Concentration factors, derived from stable element analyses, are sometimes used for predicting transfer of radionuclides through food webs to man. If the concentration factors are in error due to the above described factors and if the organisms discriminate strongly in favor of a form of the element different from that on which the concentration factors are based, significant errors in prediction may result.

REFERENCES

- (1) WEISS, H. V., SHIPMAN, W. H., The biological concentration of cobalt-60 by "killer" clams as derived from fallout, U. S. Naval Radiological Defense Laboratory Report USNRDL-TR-90 (1956).
- (2) WEISS, H. V., SHIPMAN, W. H., Biological concentration by killer clams of cobalt-60 from radioactive fallout, Science 125 (1957) 695.
- (3) LOWMAN, F. G., PALUMBO, R. F., SOUTH, D. J., The occurrence and distribution of radioactive non-fission products in plants and animals of the Pacific Proving Ground, USAEC Rep. UWFL-51 (1957).
- (4) GOLDBERG, E. D., BROECKER, W. S., GROSS, M. G., TUREKIAN, K. K., "Marine chemistry", Ch. 5, Radioactivity in the Marine Environment, Nat. Acad. of Sciences, U.S.A. (1971).
- (5) JOYNER, T., HEALY, M. L., CHAKRAVARTI, D., KOYANAGS, T., Preconcentration for trace analysis of sea waters, Symp. on Trace Characterization - Chemical and Physical, Nat. Bur. of Standards, U.S.A. (1967).
- (6) DUURSMA, E. K., GROSS, M. G., "Marine sediments and radioactivity", Ch. 6, Radioactivity in the Marine Environment, Nat. Acad. of Sciences, U.S.A. (1971).

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