

Much of our knowledge of the behaviour of Co in the marine biosphere comes as a result of studies with ^{57}Co , ^{58}Co and ^{60}Co , all of which are present in fallout and in discharges from nuclear facilities. These radionuclides have been detected in a variety of marine species, with reported concentration factors (CF) for phytoplankton, crustaceans, and fish of about 1500, 700, and 250, respectively (GOMEZ *et al.*, 1991), in agreement with values reported for stable Co by PENTREATH (1977). In contrast, CFs obtained from laboratory radiotracer studies tend to lie between 10 and 50 (HARRISON, 1986). Upon consideration of the work by LOWMAN & TING (1973) on the preferential uptake of Co-cobalamine over cobalt in marine organisms, we questioned whether the speciation of the metal could be responsible for the observed differences in CFs. Instances abound where the physicochemical speciation of substances are known to affect their bioavailability, e.g. in food *vs* water (Co, Ru, Cs, Sr; SUZUKI *et al.*, 1979) and organic *vs* inorganic (Co; UEDA *et al.*, 1981) experiments.

In seawater, the metal is present primarily as the Co^{++} ion, and its chloro-, sulfato-, and carbonato-complexes. Of the soluble cobalt fraction, cationic, anionic, and neutral species have been detected, and there have been several reports of the formation of complexes with various organic ligands in natural waters and under laboratory conditions (LOWMAN & TING, 1973). Concentrations of the metal in seawater vary up to ca 0.1 $\mu\text{g l}^{-1}$, decreasing away from continental margins to 7 ng l^{-1} in oceanic surface waters (KNAUER *et al.*, 1982, COUGHTREY & THORNE, 1983). Co-cobalamine has also been detected in seawater, but at levels of the order of 0.1 ng l^{-1} (LOWMAN & TING, 1973). Thus, cobalt associated with cobalamine represents about a one thousandth part of the total soluble metal in open waters. It has not been shown whether the Co-cobalamine in seawater is utilised by biota. Here we describe the results of laboratory radiotracer studies which have examined the relative bioavailability of ionic cobalt and co-cobalamine to different marine organisms.

Experimental Results

We completed studies on the uptake and retention of both cobalt species in a simple marine food chain comprising phytoplankton (*Dunaliella tertiolecta* and *Chaetoceros pseudocurvisetum*), copepods (mainly *Centropages* sp.), and fish (*Serranus scriba*). Retention of both forms of Co from the diet was also studied for the latter two organisms.

Phytoplankton accumulated more than 60 times as much Co-cobalamine as of CoCl_2 from the water, and retained the metal for a significantly longer period (a retention half-time of 4.4 *vs* 0.6 d). Accumulation of CoCl_2 after ingestion of radiolabelled phytoplankton by copepods was not measurable, whereas retention of Co-cobalamine reached 42% of the quantities ingested. Fish accumulated Co-cobalamine 21 times more rapidly from seawater than they did CoCl_2 . They retained ingested Co-cobalamine (100%) 20 times more efficiently than ingested CoCl_2 (5%), with one third of the ingested Co-cobalamine being retained with a half-time of 8 d and the remaining two thirds with a half-time of 53 d, a value which was not significantly different from the retention half-time of CoCl_2 (47 d).

Discussion and Conclusions

The application of the measured parameters to a simple three-compartment biokinetic model (NOLAN *et al.*, 1990) showed that food is the main source of the metal in marine fish and that preferential accumulation in the food web of the Co-cobalamine complex over inorganic cobalt species could explain the cobalt concentrations measured in marine organisms. When the model parameters are modified, so that inorganic cobalt parameters are used for uptake from water, and cobalamine parameters are used for uptake from food, then a CF of 200 (80% of which is accounted for by the diet) is predicted. This value is greater than anything reported from laboratory investigations, but is similar to environmentally determined CF values, which were based on stable cobalt analysis in fish (PENTREATH, 1977).

In conclusion, we consider that there is preferential uptake and retention of cobalamine-associated cobalt by marine biota. Because of the persistence of the vitamin in the water column, and in spite of the relatively tiny fraction of the total soluble cobalt which is associated with it, this compound represents a major source of the metal in marine organisms, the importance of which is out of all proportion to its relative concentration in the water.

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Abstract

The results of instrumental neutron activation analysis of 16 elements and the determination of artificial and natural radionuclide levels in the Mediterranean tuna fish homogenate (IAEA-350 and IAEA-352, reference materials) are reported.

Introduction

Tuna fish (about 200 kg) were collected in the Western Mediterranean Sea in April 1988 in order to establish a new biological reference material. The flesh was separated from approximately half the fish and prepared as an intercomparison sample of trace metals and organochlorine compounds. A second sample, consisting of 80% fish flesh and 20% bones, was prepared for the radionuclide analyses. This paper represents our contribution to the intercomparison exercises for these two reference materials organized by the IAEA Marine Environment Laboratory in Monaco.

Experimental

For neutron activation analysis, the samples and standards (MA-A-2/TM and Soil-7) were irradiated in a VVR-S reactor at $10^{11} - 2.10^{12} \text{ n.cm}^{-2} \text{ s}^{-1}$ flux. The induced and natural gamma spectra were measured using a high resolution HPGe detector coupled to a multi-channel analyzer.

Results and Discussion

Our results for concentrations of Cr, Fe, Rb, Sb, Se, Zn and their certified values are presented in Table 1. Except for Se, our values are in very good agreement with the certified values. Concentration values for Al, As, Au, Br, Cl, Co, Cs, K, Mg and Na determined in our laboratory, but non-certified, are presented in Table 2.

Table 1. Certified values of elemental concentrations in tuna fish flesh (IAEA-350, reference material)

Element	Concentration	Confidence interval	Our values
Cr (ppm)	0.75	0.55 - 1.01	0.82 ± 0.11
Fe (ppm)	72.1	66.7 - 77.3	74.6 ± 3.7
Rb (ppm)	2.50	2.41 - 3.40	2.9 ± 0.3
Sb (ppb)	20	3 - 80	41 ± 3
Se (ppm)	5.51	4.40 - 5.95	6.9 ± 0.2
Zn (ppm)	17.4	16.6 - 18.5	16.9 ± 0.7

The ^{40}K and ^{137}Cs activities determined by direct gamma spectrometry are presented in Table 3. Concerning ^{134}Cs activity, from the eleven results submitted, eight included "less than" and one N.D. An upper limit of 2.4 Bq/kg for ^{134}Cs has been estimated in our laboratory.

Table 2. Non-certified values of elemental concentrations in tuna fish flesh (IAEA-350, reference material) determined in our laboratory

Element	Concentration
Al (ppm)	35 ± 3
As (ppm)	5.6 ± 0.3
Au (ppb)	1.0 ± 0.3
Br (ppm)	16.3 ± 0.6
Cl (ppm)	2179 ± 50
Co (ppb)	34 ± 4
Cs (ppm)	0.21 ± 0.03
K (%)	1.541 ± 0.060
Mg (ppm)	2664 ± 247
Na (ppm)	1506 ± 47

Table 3. Certified values of radionuclide activity in tuna fish flesh (IAEA-352, reference material) Reference date: 1 January 1989

Radionuclide	Activity (Bq/kg $^{-1}$)	Confidence interval	Range of accepted lab means	Our values
^{40}K	391	379 - 405	300 - 470	370 ± 8
^{137}Cs	2.7	2.5 - 2.8	1.9 - 3.5	2.8 ± 0.3

Our results in Table 3 are also in good agreement with the certified activity values for ^{40}K and ^{137}Cs .