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RADIONUCLIDES AND SELECTED TRACE ELEMENTS IN MARINE PROTEIN CONCENTRATES

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Abstract—The concentrations of various trace elements and radionuclides have been measured in marine protein concentrates prepared from surface feeding fishes.

As with concentrates prepared from benthic fishes, the ^{210}Pb–^{210}Po pair are the most significant radionuclides present. Concentrations of stable Pb, Co and Ag in certain concentrates are sufficiently high to contribute substantially to estimated current intakes of these elements.

INTRODUCTION

In 1967, the United States began an ambitious food-from-the-sea program to investigate methods of increasing the world's protein supply. An integral part of that effort has been the development of a commercially viable fish protein concentrate (FPC) which could be used as a protein supplement in the diet of humans. In an effort to minimize production costs, whole marine organisms are processed to produce a protein rich product (~80% protein) having the consistency of flour.

The major use of a successful FPC program would most probably be directed to alleviating the protein deficiency which is now present in the diets of some 1.5 billion persons living principally in tropical and subtropical areas.[1] However, a recent study conducted by Cornell University for the National Center for Fish Protein Concentrates indicated a potential market for several billion pounds of FPC as additives in the U.S. food industry.[2] FPC could be used to enrich commodities such as beverages, breakfast foods, canned meats and baked goods. Today, there are vigorous research programs dealing with FPC production in Sweden, Canada, France, Brazil, Germany, Morocco, Pakistan and Peru†, and it seems probable that such products will ultimately play a role in alleviating protein deficiency in human diets.

In a recent article,[3] data were presented on the concentrations of natural and artificial radionuclides in selected seafoods and FPC. We reasoned that the concentrates would be particularly interesting, since the industrial concentration of fish to concentrate (6.6 lb of wet fish produce 1 lb FPC[2]) might enhance the concentrations of radionuclides if they were not removed in processing. Indeed, the concentrations of naturally occurring ^{210}Pb ($T_{1/2} = 21.4y$) were sufficiently high to constitute a significant source of intake to humans. However, the majority of these concentrates were produced from benthic fishes (hake, sole, flounder) and we considered it of interest to compare the radionuclide concentrations of those products with others prepared using surface feeding fishes as starting materials. In addition, we have measured certain stable elements in these products as a further indication of the enrichment processes which occur in the chain: water–organism–concentrate.

METHODS

The samples analyzed were supplied by the National Center for Fish Protein Concentrate,

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† A detailed description of both the basic FPC program and the associated research effort to date is beyond the scope of the present article. There are, however, two sources where such information can be obtained: The Annual Report of the President to the Congress on Marine Resources and Engineering Development (U.S. Government Printing Office: 1970) and Fish Protein Concentrate, A Comprehensive Bibliography (Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Va.).

College Park, Maryland. Gamma-ray emitting radionuclides were analyzed as received by counting 100-g aliquots of the concentrate (in duplicate) using NaI (Tl) detection systems. Iron-55 was determined by chemically isolating the iron in the sample[4] and then measuring the 5.9 keV X-ray which results from the de-excitation of its daughter, ^{55}Mn. Polonium-210 and ^{210}Pb were determined as previously described.[3] Polonium-208 and ^{212}Pb were used as yield monitors to account for any losses which occurred during chemical processing steps. Measurement of the alpha radioactivity was done using alpha spectrometry with surface barrier diodes.

Trace element analyses for all elements except iron were performed by atomic absorption spectrometry. Iron was determined colorimetrically,[5] using O-phenanthrolein as the color-forming agent. Duplicate 20-g samples of concentrate were wet ashed in redistilled, reagent grade concentrated nitric and perchloric acids or dry ashed in a muffle furnace at 460 C, depending upon the volatility of the element of interest. For the trace elements Co, Cu, Zn, Fe, Ag and Mn, dry ashing techniques were employed. For Cd and Pb, wet ashing with concentrated acids is preferred. Elemental concentrations were determined by the method of standard additions (Pb, Mn, Zn) or by comparing sample absorbances with those prepared from standard solutions (Ag, Cd, Co, Cu).

All radiometric data have been decay corrected to collection dates and the errors associated with these measurements are the standard errors (1σ) derived from a statistical analysis of the sample and background counting rates. The errors associated with the stable element analyses approach $\pm 5\%$ (based on agreements between duplicate samples and on samples to which known amounts of trace elements have been added).

RADIOACTIVITY MEASUREMENTS

The results of our radioactivity measurements are presented in Table 1. There are significant differences between the radionuclide content of these protein concentrates and those reported earlier.[3] In general, ^{137}Cs values for concentrates prepared from surface feeding fishes are not appreciably different from those prepared from inshore benthic fishes. Manganese-54 values are lower (possibly due to physical decay) while ^{55}Fe values are generally higher. The ^{90}Sr concentration of all the concentrates was <0.05 dis/min/g dry weight. Lead-210 and ^{210}Po values are comparable to those reported earlier, with the notable exception of the anchovy taken off the Southern California coast. The value of 57.7 ± 0.5 dis/min/g dry weight anchovy concentrate was confirmed by the analysis of an aliquot of this sample by C. W. Sill of the National Reactor Testing Station. This unusually high value was at first surprising, and we therefore analyzed various organs (pooled and individual) of fresh anchovy (*Engraulis mordax*) and saury (*Cololabis saira*) to determine the distribution of the ^{210}Po, ^{210}Pb and stable Pb in these fishes. Both species represent pelagic fishes whose diet consists mainly of planktonic crustacea.[6,7]

Table 2 clearly shows that in these fishes the majority of the ^{210}Po and ^{210}Pb activity, as well as stable lead, is found in the internal organs, principally the liver, bone, stomach contents and viscera (heart, intestine, spleen, kidney, stomach and gonad). The number in parenthesis indicates the number of specimens analyzed. The values of ^{210}Po observed makes the ^{210}Po content of the anchovy concentrate less surprising. Moreover, the stable lead content of the anchovy bone and liver substantiates the high stable lead value found in the anchovy concentrate. The lead specific activities (dis./min ^{210}Pb/μg Pb) of anchovy tissue range from 0.08 to 0.3, with the lead specific activity of the anchovy concentrate being 0.09. These values, and those of the saury and other concentrates analyzed here, approximate the range of lead specific activities found by Ter Haar *et al.*,[8] in their measurements of rain waters collected in the mid-western United States.

Shannon *et al.*[9,10] have recently summarized their measurements of alpha radioactivity in marine organisms and water collected in South Africa. Although Shannon did not determine the partitioning of either ^{210}Pb or ^{210}Po into the various organs of the pelagic fishes analyzed, he did observe a mean ^{210}Po/^{210}Pb activity ratio of 157 for whole fishes. Our ^{210}Po/^{210}Pb activity ratios for the internal organs of anchovy and saury reported in Table 3

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Table 1. *Radionuclide concentrations in fish protein concentrates*

Sample	Location	Catch date	Radionuclide concentrations (dis/min/g dry weight) ^{40}K	^{54}Mn	^{137}Cs	^{55}Fe	^{210}Pb	^{210}Po
Menhaden (*Brevoortia tyrannus*)	Chesapeake Bay	June, 69	10.7 ± 0.6	n.d.	0.05 ± 0.05	0.3 ± 0.2	0.18 ± 0.02	2.2 ± 0.2
Menhaden (*Brevoortia tyrannus*)	Chespeake Bay	June, 69	9.5 ± 0.6	0.07 ± 0.05	0.25 ± 0.05	0.4 ± 0.2	0.25 ± 0.02	1.0 ± 0.2
Menhaden (*Brevoortia tyrannus*	Chespeake Bay	June, 69	10.4 ± 0.6	n.d.	0.09 ± 0.05	n.d.	0.19 ± 0.05	1.3 ± 0.2
Menhaden (*Brevoortia tyrannus*	Chesapeake Bay	June, 69	10.0 ± 1.2	n.d.	0.19 ± 0.09	1.1 ± 0.6	0.23 ± 0.02	4.6 ± 0.2
Ocean Pout (*Macrozoarces americanus*)	Mass. Coast	Jan., 69	9.1 ± 0.5	n.d.	0.16 ± 0.04	1.3 ± 0.5	0.17 ± 0.03	1.5 ± 0.02
Alewife (*Alosa pseudo harengus*)	Lake Michigan	April, 69	12.4 ± 0.5	0.06 ± 0.04	0.06 ± 0.04	10.7 ± 0.3	0.16 ± 0.04	3.2 ± 0.07
Gulf Menhaden (*Brevoortia patronus*)	Miss. Coast	May, 69	10.4 ± 0.5	0.06 ± 0.04	0.06 ± 0.04	0.9 ± 0.4	1.4 ± 0.3	3.7 ± 0.2
Anchovy (*Engraulis mordax*)	South California Coast	Jan., 69	8.0 ± 0.4	0.15 ± 0.05	n.d.	6.7 ± 0.6	0.74 ± 0.08	57.7 ± 0.5
Atlantic herring (*Clupea harengus harengus*)	Mass. Coast	Nov., 68	11.9 ± 0.5	n.d.	n.d.	11.2 ± 0.8	0.07 ± 0.02	0.2 ± 0.06

n.d. not detectable.

Table 2. *Polonium*-210, *Lead*-210 *and stable lead in pelagic fishes*

Sample	Location	Collection date	Tissue	Radionuclide Concentration (dis/min/g dry weight) ^{210}Po	^{210}Pb	Stable Lead (μg/g dry weight)
Anchovy (*Engraulis mordax*)	Oregon Coast (46°30′) (124°14′)	27 May 1969	Muscle (13)	1.6 ± 0.1	<0.1	0.2
			Bone (13)	2.0 ± 0.3	2.0 ± 0.3	26.6
			Liver (10)	255.2 ± 19.2	1.8 ± 0.4	10.1
			Viscera (10)	158.9 ± 8.3	1.5 ± 0.08	<0.1
			Stomach contents (10)	29.1 ± 3.4	2.5 ± 1.0	<0.1
			Eviscerated whole fish (31)	6.7 ± 0.8	0.12 ± 0.05	0.4
Saury (*Cololabis saira*)	California Coast (36°10′) (122°23′)	16 Sept. 1969	Muscle (19)	4.3 ± 0.3	<0.1	0.2
			Bone (19)	0.9 ± 0.2	0.9 ± 0.2	5.0
			Liver (19)	53.1 ± 3.0	0.5 ± 0.2	3.9
			Viscera (19)	114.1 ± 7.9	1.1 ± 0.1	<0.1
			Stomach contents (13)	95.0 ± 6.2	1.2 ± 0.3	3.5

Table 3. Trace element concentrations in fish protein concentrates

Sample	Location	Catch date	Trace element concentrations (μg/g dry wt. ppm)							
			Pb	Ag	Cd	Cu	Co	Fe	Zn	Mn
Menhaden (*Brevoortia tyrannus*)	Chesapeake Bay	June, 69	0.8	1.3	1.0	5.4	1.6	346	124	41
Menhaden (*Brevoortia tyrannus*)	Chesapeake Bay	June, 69	1.0	1.3	1.0	6.6	1.6	492	128	53
Menhaden (*Brevoortia tyrannus*)	Chesapeake Bay	June, 69	1.0	1.0	0.8	5.6	1.1	614	131	64
Menhaden (*Brevoortia tyrannus*)	Chesapeake Bay	June, 69	1.0	1.1	0.8	7.5	1.5	403	126	53
Ocean Pout (*Macrozoarces americanus*)	Mass. Coast	Jan., 69	0.3	1.9	1.1	6.5	6.3	254	93	9
Alewife (*Alosa pseudo harengus*)	Lake Michigan	April, 69	0.7	1.0	1.0	6.6	1.7	123	170	21
Gulf Menhaden (*Brevoortia patronus*)	Miss. Coast	May, 69	2.3	1.5	1.0	5.3	1.6	860	142	64
Anchovy (*Engraulis mordax*)	South California Coast	Jan., 69	8.2	1.5	2.3	11.7	1.1	373	143	12
Atlantic herring (*Clupea harengus harengus*)	Mass. Coast	Nov., 68	0.5	0.9	0.6	8.4	1.2	110	110	10

are in fair agreement with this ratio. Shannon has also measured the $^{210}Po/^{210}Pb$ activity ratios in zooplankton, and reports a mean value of 12. The pooled stomach contents of our anchovy specimens had a mean $^{210}Po/^{210}Pb$ activity ratio of approximately 12, again in good agreement with Shannon's findings, if we assume the stomach contents of the anchovy represent zooplankton residues.

The same high $^{210}Po/^{210}Pb$ ratio was observed for the internal organs of the saury. The stomach contents, however, showed a marked increase in this ratio, as a result of higher ^{210}Po concentrations. Unfortunately, identification of their stomach contents was not possible and we therefore cannot assign this higher ratio to a particular marine entity.

The data in Table 2 suggests that, at least in the case of Pb, ^{210}Pb and ^{210}Po, evisceration of the fish prior to processing would aid in reducing the concentrations of these entities in the final product. It is not possible to assign an absolute value for the anticipated reduction, for the weight fraction which each organ contributes to the total fish weight is only poorly known for different fish species.[11]

TRACE ELEMENT CONCENTRATIONS

Table 3 lists the concentrations of trace elements which were measured in these FPC products. The number of trace elements which are included is not exhaustive, and clearly there are important elements missing. For example, Se and As concentrations would have been informative, as would the concentrations of Mo, Ti, Si, B and Ni. We chose the trace elements shown in Table 3 because several are considered toxic in moderate amounts (Pb, Ag, Cd, Cu) while others, in small amounts, are essential to good nutrition (Co, Fe, Zn, Mn).[12]

The high concentration of Pb in the anchovy FPC is consistent with the findings shown in

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ıs (μg/g dry wt. ppm)			
Co	Fe	Zn	Mn
.6	346	124	41
1.6	492	128	53
1.1	614	131	64
1.5	403	126	53
3.3	254	93	9
1.7	123	170	21
1.6	860	142	64
1.1	373	143	12
1.2	110	110	10

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Table 2 in which the bone and liver of the fresh anchovy contained unusual concentrations of this element. It should be noted that stable lead profiles (concentration versus depth) of near-shore Southern California waters[13,14] and waters off the Oregon Coast[15] show higher lead concentrations at the surface than do similar profiles taken in Atlantic waters off Bermuda. These high surface concentrations of Pb are attributed to automotive exhaust emissions which are currently a subject of increasing concern.[16] It is probable that the lead observed in all the FPC products analyzed here comes principally from this source.

The concentrations of the remaining elements in the concentrates are not unusual considering the amounts of these elements in sea water[17] and their accumulation by marine organisms.[18,19] However, the uniformity of concentration for Ag, Cd, Co and Cu is puzzling. Addition of trace amounts of these elements during analysis is unlikely since all processing was done in pyrex glassware, and reagent blanks for all analyses were low. Contamination during production is a possibility since stainless steel vessels are used for containment and milling of the final product to a flour-like consistency does place the FPC in contact with metals. Consequently, some caution should be exercised in concluding that the concentrations of Ag, Co, Cd and Cu are derived solely from ecological concentration processes.

CONCLUSIONS AND IMPLICATIONS

In assessing the effect which FPC might have in enhancing "normal" dietary intakes of both radionuclides and trace elements, it is necessary to make some estimate of daily FPC intake. KETCHUM[1] estimates that 10–20g of animal protein would be sufficient to alleviate the deleterious effects of protein deficiency in much of the world's population. Moreover, experimental feeding programs conducted in different countries in which bakery products containing 10–20% FPC by weight have found wide acceptance, suggests that an assumed 10 g/day intake of FPC would be reasonable.[20–24]

Of the radionuclides measured in these concentrates the ^{210}Pb–^{210}Po pair are the most significant. Ingestion of moderate amounts of these products would substantially enhance "normal" dietary intakes of these radionuclides. As argued earlier[3], HOLTZMAN[25] and, more recently, MAGNO *et al.*[26] estimate the daily dietary intake of ^{210}Pb at 4 dis/min. In addition, Holtzman estimates an intake of another 4 dis/min/day by inhalation. These concentrations, over a lifetime, produce skeletal body burdens of ^{210}Pb–^{210}Po which account for some 50% of the skeletal radiation dose received from radionuclides deposited in that organ[24]. Ingestion of 10 g/day of either the anchovy FPC or the gulf menhaden FPC would add 7 and 14 dis/min, respectively, to a current dietary and inhalation intake of 8 dis/min, the effect being a near doubling and tripling of the total ^{210}Pb intake, respectively. Smaller but still significant contributions would be made from ingestion of all but the Atlantic herring FPC.

A similar assessment concerning ^{210}Po is difficult, since time lapses between processing and ingestion does afford a means of significantly reducing ^{210}Po concentrations by radioactive decay ($T_{1/2} = 138$ d). However, ^{210}Po concentrations approaching those of the anchovy FPC are important; a 10 g/day intake of fresh product would add approximately 600 dis/min to an average daily intake of 2–20 dis/min (HILL[27]). A 1 yr delay between processing and intake would reduce the anchovy FPC ^{210}Po activity to 10 dis/min/g dry weight, but would still add 100 dis/min of ^{210}Po daily to the diet at that time.

Table 4 shows a tabulation of the estimated daily intake of the various trace elements of interest to this study. Included for several of the elements are the levels which are considered as toxic. The most striking addition of any trace element to the diet, regardless of its source, would appear to be cobalt. Ingestion of 10 g/day of any of the concentrates would increase cobalt intake by greater than an order of magnitude, and in the case of the ocean pout FPC, by greater than two orders of magnitude. The anchovy FPC would contribute substantially to Pb intake (~80 μg), and all concentrates would increase Ag intake by 10–30%. The other elements would all appear to be of lesser importance in altering current intakes.

Neither the radionuclide or the trace element concentrations measured in these products approach levels that are considered toxic, although the radioactive and trace element

Table 4. Daily intake of trace elements in adult human diets (after Bowen, Ref. 8)

Element	Daily intake (μg/day)	Amount considered toxic (μg/day)
Pb	300–400	—
Ag	60–80	60,000
Cd	600	3000
Cu	2000–5000	250,000–500,000
Co	0.2	500,000
Fe	12,000–15,000	—
Zn	10,000–15,000	—
Mn	3000–9000	—

measurements of the anchovy FPC should be viewed with some concern. Moreover concentrations of both radioactivity and trace elements might be expected to vary in any given species with both time and location. It would seem prudent, nevertheless, to continue such measurements as a means of determining the suitability of any given marine organism for starting material in FPC production. Persistent and undesirable concentrations of these entities might then require process modifications for their removal.

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