日本産海洋生物のコバルト,セシウム,亜鉛濃度

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Levels of Cobalt, Cesium and Zinc in Some Marine Organisms in Japan

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Skin, muscle, viscera and bone of various species of marine fishes were analysed by the neutron activation method to determine cobalt, cesium and zinc concentrations. Muscle contains much less cobalt and zinc than do the other tissues, whereas cesium is distributed rather uniformly in all of these tissues. The soft part of the short-necked clam showed much higher concentrations of the three elements than did fish muscle. Cobalt and zinc levels in shrimp (soft part and carapace), sea urchin (ovary) and sea cucumber (whole body) are higher than those in fish muscle, but the cesium level in these animals is somewhat lower than in any fish tissues. The concentration factors of cobalt, cesium and zinc were calculated for various tissues of animals by using the average concentrarion of the elements in sea water. Values of concentration factors for the animals analysed are in the range of 10 for cesium, 10^2 for cobalt and 10^3 for zinc with some exceptions.

Marine organisms are generally able to concentrate various metallic elements to levels far in excess of the concentration in environmental water through direct absorption and food chain. This phenomenon has received considerable attention in recent years in relation with the contamination of fishery products by industrial wastes containing heavy metals and by radioactive nuclides released from nuclear power plants.

As the concentration factor of radionuclides can be assessed by using the levels of their stable isotopes in marine organisms and in sea water, one of the present authors reported many years ago the concentration factors of some radionuclides in marine organisms which were calculated by this method.[1] At that time, however, information on the content of stable elements in marine organism was extremely limited especially for cesium. Since that time, a number of reports on trace elements content in marine organisms were published by foreign investigators whereas these information on Japanese species are still very limited. In view of this, concentration of stable cobalt, cesium and zinc was determined by neutron-activation analysis for many Japanese species of marine fishes and some edible invertebrates in the present investigation because the radioactive isotopes of these three elements are most significant nuclides found in radioactive wastes from nuclear energy industry as the contributors of radiation dose to man through marine food chain. Some species of fishes caught by Japanese fishing ships in the sea along the South American countries were also used for this purpose.

Materials and Methods

Sample preparation: Fishes were usually dissected into four portions, *i.e.*, skin,

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muscle, viscera and bone. Some specific organs such as ovary and liver were sampled from large fishes. In case of marine invertebrates, edible parts were used for samples to be analysed. Tissue samples were dissected on a plastic plate by using forceps coated with teflon and plastic knives in order to avoid metallic contamination of the samples. Difficulty of dissection with a plastic knife was overcome by heating fresh bodies in an electronic range in advance. These samples were then dried and ashed at 450°C in a muffle furnace.

Irradiation: The ashed sample (about 0.1 g) was packed in a polyethylene bag and heat-sealed. A 100 μl aliquot of Co, Zn or Cs was placed on a 4×4 cm polyethylene sheet and dried carefully under an infrared lamp as a standard sample. The five samples and two standards were packed together in a polyethylene bag. The irradiation was carried out for 5 hours in the Triga Mark II reactor with a thermal neutron flux of about 4×10^{12} n/sec. cm^2 at the Musashi Institute of Technology.

Radiochemical procedure: Chemical separation of the activated elements was carried out as described below[2]. The irradiated sample was transferred into a crucible with 100 μg of Co, Zn and Cs carrier. Then, about 1 g of sodium hydroxide and sodium peroxide were added and the mixture was fused in a muffle furnace at 450°C for 5 hours. The resulting fusion cake was dissolved in about 1 N hydrochloric acid and filtered. Diluted ammonia water was added to the filtrate until to raise the precipitate of hydroxide using methyl red as an indicator. After filtering it, the filtrate was evaporated to dryness by heating the beaker on a sand-bath.

Separation of zinc: The residue was dissolved with dilute hydrochloric acid and the pH was adjusted to about 5 with diluted ammonia water. Then 1% sodium diethyldithiocarbamate solution was added till precipitation is complete. Zinc was extracted with acetone-chloroform (2: 5) mixture by shaking for a minute. Zinc was back-extracted with two 5 ml portion of 1 N hydrochloric acid and then purified by anion exchange method to remove cadmium if any. Zinc containing solution was transferred to counting vial for ^{65}Zn γ-ray spectrometry.

Separation of cobalt: After back-extract of zinc, the organic phase was scrubbed with two 5 ml portion of 10% potassium cyanide solution. The remaining organic phase was evaporated to dryness on a sand-bath. The residue was dissolved in 5 ml of nitric acid and transferred to counting vial for γ-ray spectrometry on ^{60}Co.

Separation of cesium: After extract of zinc and cobalt, the remaining aqueous phase was evaporated on a sand-bath, and the residue was dissolved with about 30 ml of 1 N hydrochloric acid solution. Then ^{134}Cs was adsorbed on the copper-ferrocyanide-anion exchange resin[3] and the resin was transferred to counting vial for γ-ray spectrometry on ^{134}Cs.

Activity measurement: A Hitachi/RAH-400 channel pulse height analyser with

Table 1. Concentration of cobalt, cesium and zinc in various tissues of marine organisms

Sample name	Sampling place & date	Tissues	Co μg/kg fresh weight	Cs μg/kg fresh weight	Zn μg/g fresh weight
flounder	Tateyama	skin	12	13	9.3
Limanda	Apr. 1969	muscle	2.7	13	1.5
herzensteini		viscera	48	10	3.8
		bone	5.4	12	13
		skin	29	12	20
flounder	—	muscle	11	12	0.7
		viscera	96	7	2.1
		bone	7.1	11	6
		skin	89	7.4	18
flounder	—	muscle	4.3	13	1.4
		viscera	47	8.6	12
		bone	14	11	4.2
		skin	13	7.6	3.9
flounder	—	muscle	6	14	0.6
		viscera	54	11	12
		bone	18	8.8	24
dolphin	Kamakura	skin	20	48	4.3
Corphaena	June 1969	muscle	1.8	3.7	0.8
hippura		ovary	5.2	26	5.7
		liver	0.3	40	0.4
		bone	0.3	20	—
surf perch	Aburatsubo	skin	10	50	7.6
Ditrema	June 1969	muscle	18	24	0.9
temmincki		viscera	107	42	2.1
		bone	12	74	7.9
flying fish	Kamakura	skin	38	12	95
Prognichthys	June 1969	muscle	1.8	17	2.4
agoo		viscera	34	15	31
		bone	6.7	25	20
flying fish	—	viscera	37	13	34
		bone	18	15	26
file fish	—	skin	—	37	105
Stephanolepis		muscle	4	4.1	1.6
cirrhifer		viscera	24	2.8	16
		bone	9	15	—
porgy	—	skin	33	48	48
Chrysophrys		muscle	5.8	12	4
major		viscera	24	17	20
		bone	25	—	5
porgy	—	skin	21	5.9	24
		muscle	2.7	—	2.5
		viscera	16	4.7	7.1
		bone	23	21	21
shad	—	skin	22	4.1	92
Harengula		muscle	11	6.4	4.6
zunasi		viscera	24	—	29
		bone	57	11	—
sting fish	—	skin	13	6.6	18
Sebastes		muscle	3.7	18	3.8
inermis		viscera	13	5.6	13
		bone	9.5	5.5	15

Table 1. (continue)

Sample name	Sampling place & date	Tissues	Co μg/kg fresh weight	Cs μg/kg fresh weight	Zn μg/g fresh weight
sting fish	Kamakura June 1969	skin	7.5	11	28
		muscle	3.9	14	3.9
		viscera	18	6.7	16
		bone	9.8	4	18
grunt *Parapristipoma trilineatum*	—	skin	64	5.2	66
		muscle	6.4	6.6	2.5
		viscera	28	4	30
		bone	40	6.5	19
grunt	—	skin	34	1.5	60
		muscle	5.6	9.5	2.9
		viscera	22	8.2	18
		bone	32	5.1	16
yellow porgy *Dentex macrocanus*	South America Apr. 1967	skin	4.4	3.6	37
		muscle	3.4	14	4.3
		viscera	59	20	196
		bone	6.3	1	5.8
yellow porgy	—	skin	13	20	71
		muscle	2.8	11	4.3
		viscera	17	20	19
		bone	0.3	—	—
false-whiting *Sciaena deliciosa*	Peru Apr. 1967	skin	36	9.5	44
		muscle	4.1	15	3.8
		ovary	44	8.4	110
		viscera	284	66	78
		bone	9.3	13	17
hake *Merluccius gayi*	South America Apr. 1967	skin	21	20	51
		muscle	2.6	34	3.5
		viscera	35	11	15
		bone	5.6	20	23
ghost shark *Callorhinchus Callorhinchus*	Chile Apr. 1067	skin	28	12	24
		muscle	1.5	—	3.2
yellow tail *seriola quinqueradiata*	Kamakura June 1969	muscle	5.5	7.2	5.4
		viscera	15	6.8	20
		bone	8.4	10	6.6
horse mackerel *trachurus japonicus*	—	skin	131	12	93
		muscle	9.7	13	5.2
		viscera	33	9.5	45
		bone	15	17	20
horse mackerel	—	skin	72	6.7	55
		muscle	—	14	5.5
		viscera	26	8.3	22
		bone	11	16	15
sand smelt *Sillago sihama*	—	skin	17	7.6	22
		muscle	4.2	6.2	2.7
		viscera	54	1.4	25
		bone	5.2	9.2	17
sand smelt	—	skin	24	1.5	25
		muscle	2.2	2.7	1.4
		viscera	202	4.5	34
		bone	22	12	34

Table 1. (continue)

Sample name	Sampling place & date	Tissues	Co μg/kg fresh weight	Cs μg/kg fresh weight	Zn μg/g fresh weight
white croaker	Kamakura	skin	20	5.6	27
Argyrosomus	June 1969	muscle	2.5	7.2	3.9
argentatus		viscera	24	5.4	33
		bone	8.7	6.7	15
white croaker	—	skin	48	10	47
		muscle	8.1	11	6.7
		viscera	32	8.9	13
		bone	37	5.5	28
big-eye sardine	Odawara	skin	13	26	107
Etrumeus	Nov. 1969	muscle	2.6	15	11
micropus		viscera	19	15	27
big-eye sardine	—	skin	14	9.4	71
		muscle	4.8	28	5.1
		viscera	13	19	23
		bone	12	26	44
mackerel	—	skin	10	5.5	145
Scomber		muscle	9.9	15	7.4
japonicus		viscera	9.4	6.9	18
		bone	9	13	26
		liver	51	13	27
mackerel	—	skin	4.2	1.8	55
		muscle	2.5	7.9	—
		liver	71	2.6	29
file fish	Odawara	skin	28	1.5	198
Navodon	Dec. 1969	muscle	2.7	6.2	9.7
modestus		viscera	22	—	27
		bone	13	4.7	35
file fish	—	skin	66	3.1	117
		muscle	3.6	6.2	5
		bone	19	5.7	51
short-necked	Chiba	soft part	220	49	24
clam	Apr. 1969	soft part	140	42	15
Tapes		soft part	110	86	17
philippinarum		soft part	120	63	18
		foot, mantle	110	83	21
		gill, viscera	180	113	19
		foot, mantle	540	84	20
		gill, viscera	96	104	—
shrimp	market	soft part	20	5.1	13
Penaeus	1970	carapace	30	3.5	25
orientalis					
shrimp	—	soft part	14	4.9	12
		carapace	36	5.8	32
sea urchin	market	ovary	76	7.6	31
Strongylocentrotus	1970	ovary	72	6.5	41
pulcherrimus		ovary	77	4.8	50
		ovary	71	4.4	40
		ovary	84	4.2	42
sea cucumber	—	whole body	8.2	2.5	16
		whole body	19	6.1	17

a 1-3/4×2-inch well type NaI crystal and Ge(Li) solid state detector (25 cc) were used for the quantitative measurement of photopeaks of ^{65}Zn at 1.11 MeV, ^{60}Co at 1.17, 1.33 MeV and ^{134}Cs at 0.604 MeV. The sample and standard were counted alternately and the results were calculated by comparison of the data observed.

Results and Discussion

The analytical data on the concentration of the three elements in tissues of individual fishes and invertebrates are shown in Table 1 and the average value for each tissue in Table 2.

Cobalt content in fish tissues varies considerably among different tissues showing the highest level in viscera and the lowest in muscle which has several times less content than other tissues. Soft part of clam shows much higher cobalt content than fishes and other invertebrates. Edible parts of shrimp, sea urchin and sea cucumber have the level between fish muscle and clam.

On the contrary, cesium level in fish tissues is almost the same among the four tissues analysed. Invertebrates showed somewhat less cesium content than fish tissues except clams which have several times higher value than fishes.

Zinc level in marine organisms exceeds that of cobalt and cesium by a factor of one thousand. Difference of zinc content among animal species or tissues is not conspicuous except that in fish muscle which is one order of magnitude below other samples.

Concentration factors (C.F.) of the three elements for different animal tissues over sea water can be obtained by the following formula.

$$\text{C.F.} = \frac{\text{element concentration in tissue}}{\text{element concentration in sea water}}$$

Using the rounded value 10^{-1} μg Co/l, 5×10^{-1} μg Cs/l and 10^{-2} mg Zn/l for average concentration in sea water[4], the concentration factors were calculated as shown in Table 2. As a general feature, C.F. values for cesium, cobalt and zinc are in the order of 10^1, 10^2 and 10^3 respectively with some exceptions. It is noted that there is a strong relation between cobalt and zinc levels in these samples except clam.

Although the information on the concentration of the three elements in different tissues of fishes and in sea urchin and sea cucumber is not available in the past reports, some of the past data on fish muscle, viscera and clam can be compared with the results of present investigation.

Cobalt content in fish muscle of various Japanese species determined by TSUTIYA[5] is in the range of 4 to 25 (av. 13) μg/kg(wet)*. ROBERTSON[6] reported 1.2 to 19 (av. 6.7) μgCo/kg(wet) for muscle and 6.2 to 37 (av. 19) μgCo/kg (wet) for visceral organ of

* As the original data is expressed in terms of dry weight, these figures were obtained by calculation.

Table 2. Average values of Co, Cs and Zn in marine organisms and concentration factors of these elements

Marine Organisms	Tissues	Co			Cs			Zn		
		μg/kg wet w.	(no. sample)	C.F.	μg/kg wet w.	(no. sample)	C.F.	μg/g wet w.	(no. sample)	C.F.
Fishes	skin	31	(31)	3×10^2	13	(32)	3×10	49	(30)	5×10^3
	muscle	5	(32)	5×10	12	(31)	2×10	3.9	(30)	4×10^2
	viscera	48	(30)	5×10^2	13	(28)	3×10	28	(29)	3×10^3
	bone	15	(31)	2×10^2	14	(29)	3×10	18	(25)	2×10^3
Clam	soft part	190	(8)	2×10^3	78	(8)	2×10^2	19	(7)	2×10^3
Shrimp	soft part	17	(2)	2×10^2	5	(2)	10	13	(2)	10^3
	carapace	33	(2)	3×10^2	4.7	(2)	10	29	(2)	3×10^3
Sea urchin	ovary	76	(5)	8×10^2	5.5	(5)	10	41	(5)	4×10^3
Sea cucumber	whole body	14	(2)	10^2	4.3	(2)	10	17	(2)	2×10^3

marine fishes caught off Oregon, U.S.A. SEGAR *et al.*[7] found 100 to 2400 μg/kg (wet) for cobalt content in various bivalves in Irish sea, and Japanese short-necked clam was analysed by Shimizu[8] with result of 27 to 154 μg Co/kg (wet). These reported data on cobalt content are not very different with our results.

Cesium content in marine fishes on wet weight basis was reported as 11 to 18 μg/kg (Black sea and Barents sea)[9], 12 to 14 μg/kg (Black sea and Barents sea)[10] and 4 to 25 μg/kg (off Oregon)[6] for muscle and viscera. Recent data on the the muscle of Japanese coastal fishes are in the range of 17 to 26 μg/kg[11]. BUROVINA *et al.*[9] reported 2.5 to 12 μg/kg (wet) for cesium content in soft part of marine shells of Black sea and Barents sea. These data on cesium content in fishes coincide well with ours, but that in our clam exceeds significantly BUROVINA's data. More information on cesium content in other species is necessary.

More information is available on zinc content in marine organism than on the other two elements. Zinc contents in muscle and viscera of fishes caught off Oregon were 2 to 19 (av. 8) μg/g and 11 to 75 (av. 26) μg/g (wet) respectively.[6] For Japanese fishes, 2 to 31 (av. 7) μg/g (wet) were obtained as zinc content in muscle.[12] SEGAR *et al.*[7] reported 10 to 133 μg/g (wet) as zinc content in soft part of Irish sea bivalves, whereas PENTREATH[13] determined zinc content in various tissues of mussel with the results of 10 to 23 μg/g (wet). Zinc levels found in our samples are in accord with these informations. Species difference is rather significant in zinc level of various bivalves[7] and our clams seem to correspond to those of low zinc concentration.

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