D-2.2 Uptake of Pollutants by Marine Zooplankton and their Behavior in the Marine Food-Chain

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Abstract

Zooplankton, fry and pelagic eggs were collected from the Japan Sea, the Pacific Ocean, and some polluted bays including Tokyo, Osaka and Fukuoka Bays. Thirty-seven elements were analyzed in the samples by neutron activation and ICP-AES analyses. Although the zooplankton sometimes contained somewhat high concentrations of Al, Si, Sc, Ti and Fe resulted probably from the inorganic impurities incorporated in the digestive organs, approximate concentrations of elements in the planktonic tissue were estimated by the selective HNO_3-digestion of the samples. Concentrations of several major elements (e.g. P) was approximately constant regardless of variation in body weight of zooplankton (0.002-16.0 mg), while those of heavy metals slightly increased with decreasing the weight. When the MKT-plot (plot of τ_R x CF_{sw} vs. CF_{sw}; τ_R: mean oceanic residence time of elements, CF_{sw}: concentration factors of elements from seawater to the samples) was applied to the plankton, slopes of the plots were clearly higher in the samples from the bays (av.=0.22) than those from the open-sea (av.=0.13), indicating the increased heavy metal contamination in the bay plankton. Slopes of the MKT-plots for fry samples were generally higher (0.12-0.30) than those for zooplankton. In addition, the slopes were much higher in the case of pelagic eggs (0.39). This may indicate the accumulation of heavy metals in fishes (zooplankton-eaters) through the marine food-chain.

Key Words Zooplankton, Pollution, Heavy Metals, Marine Food-Chain

1. Introduction

In the marine ecosystem, pollutants (e.g. heavy metals) resulting from human activities are incorporated into primary producers initially, and then transfered into carriers at higher trophic levels through the marine food-chain. Zooplankton is a very important intermediate carrier in the food-chain and plays a significant role in the circulation of pollutants in the marine ecosystem. In addition, the concentrations of pollutants in zooplankton might reflect the levels of pollution in specific sea areas because of their suspension characteristics. The aim of this study was to elucidate the role of zooplankton as a pollutant-carrier in the marine ecosystem and monitor the polluted levels of specific sea areas based on its elemental composition obtained by neutron activation analysis and ICP-atomic emission spectrophotometry.

2. Materials and Methods

Sample collection and pre-treatment: Zooplanktonic samples were collected with a ORI plankton net (mesh size: 0.328 mm) hauled horizontally in the upper water layer (0 - 150 m) of the Japan Sea, the Pacific Ocean, and some polluted bays (i.e. Tokyo, Osaka, and Fukuoka Bays). The sampling was carried out in summer between 1986 and 1994. Additional sampling was also carried out in Tokyo Bay on Dec., Jan. and Feb. in 1991-1992. Just after sampling, the zooplankton was transfered to a XX13 net (0.095 mm), freed from macrocontaminants, and then washed with 0.5M $HCOONH_4$ containing 0.01M NaN_3 for sterilization. The samples thus obtained were brought back to the laboratory at -4 C and washed again with 0.5M $HCOONH_4$ thoroughly by centrifugation or sieving, and finally lyophilized (multi-species zooplankton).

Separation of planktonic species: Some samples collected in 1989-1994 were divided into individual species using a dissecting microscope. The species obtained were *Calanus* sp., *Euphausia* sp., *Undinula* sp., *Euchaeta marina, Oncaea venusta, Temora discaudata,* *Labidocera* sp., *Iasia zonaria, Thalia democratica, Abylopsis* sp., *Sagitta enflata, Sagitta crassa, Vellela lata, Creseis acicula, Themisto* sp., *Siphonophorae* sp., *Decapoda* sp., *Portunus trituberculatus, Lucifer reynaudii, Pseudodiaptomus marinus, Acartia omorii, Centropages abdominalis, Idotea metallica*, Gammaridea, and larvae of Alima, Erichthus, Zoea and Megalopa. Fry and pelagic eggs trapped casually in the net were also collected. The fry included *Mugil cephalus, Cololabis saira, Stephanolepis cirrhifer, Pictiblennius yatabei, Cantherhines pardalis, Syngnathus schlegeli, Goniistius zonatus, Microcanthus strigatus, Apogon lineatus, Trachinocephalus myops, Gonorynchus abbreviatus, Etrumeus teres, Diaphus watasei, Hyporhamphus sajori* and *Sebastes* sp. Although seven samples were obtained, pelagic eggs could not be identified except for those of *Engraulis japonicus*. These samples were also washed in a similar manner as that for multi-species zooplankton, and finally lyophilized.

Acid-digestion for ICP-AES analysis: Acid-digestion of the dried samples was performed by using a stainless steel high-pressure bomb equipped with teflon double vessels1). Several-20 mg of the samples were taken in an inner vessel (7 ml Tuf-Tainer vial) and acid {HNO_3 (1 ml) or HNO_3 + HF (1 ml + 0.5 ml)} was added in an outer vessel. The digestion was performed at 140 C for 6 h. After dissolving the digested residue with 3 ml of water, the supernatant was subjected to ICP-AES analysis. Some operation including weighing and dissolution was carried out in a clean-room (class: 1000) or a clean-box (Yamato CYH-2) to avoid contamination.

Elemental analysis: Thirty-seven elements in total were determined by neutron activation2), 3) and ICP-AES4) analyses. The elements analyzed include B, Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Mo, Ag, Cd, Sb, Cs, Ba, La, Ce, Sm, Tb, Lu, Ta, Pb, Th and U.

3. Results and Discussion

The samples, especially multi-species zooplankton, sometimes contained sosmewhat high concentrations of Al, Si, Sc, Ti and Fe, resulted probably from the inorganic impurities. Since the impurities were not removed by thorough washing, they must have been incorporated in the digestive organs of the plankton. Two varieties of acids, i.e. HNO_3 and HNO_3 + HF, were successfully used to digest planktonic tissue alone and that plus inorganic impurities, respectively. Therefore, even though the multi-species samples have been contaminated with considerable amount of inorganic impurities, the samples digested only with HNO_3 were available for evaluating the approximate concentrations of elements in the planktonic tissue. In addition, the difference in concentration between the samples digested with two acids serves to characterize the impurities. Based on this empirical technique, some impurities were found to have similar elemental compositions to those of sludge, which has been a dominant waste dumped in the sea near Japan.

Table 1 shows a selected part of the data obtained in this study, i.e. elemental composition analyzed by ICP-AES coupled with HNO_3-digestion in 24 different species of zooplankton, fry and pelagic eggs. Since information on elemental composition of marine organisms, especially of phyto- and zooplanktons, has been extremely limited, these data may be original.

From the analysis of the specific plankton whose population was known, the elemental content per individual as well as that per weight was also calculated. As a result, concentrations of several major essential elements (e.g. P) were approximately constant regardless of variation in body weight of the zooplankton (0.002-16.0 mg), while those of heavy metals slightly increased with decreasing the weight (Fig. 1).

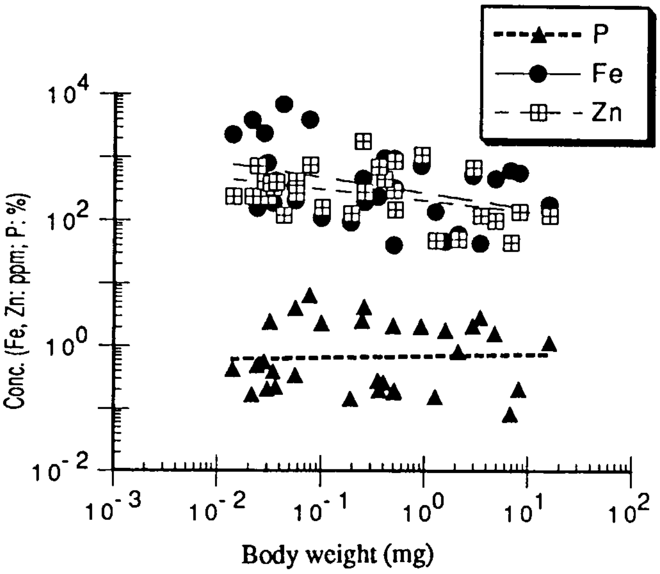

Fig. 1 Relationship between elemental concentrations and body weight of the zooplankton

Table 1 Elemental composition of zooplankton, fry and pelagic eggs collected from the sea near Japan (by ICP-AES)

Sample	Sampling		Ca	Mg	Na	P	Al	As	B	Ba	Cd	Cr	Cu	Fe	K	Mn	Mo	Ni	Pb	Se	Si	Sr	Ti	V	Zn
Species	Site	Period		%											ppm										
(Zooplankton)																									
Sagitta crassa	Tokyo B.	91,12	0.021	0.030	0.041	0.39	1665			21		34		1430	240	54		21	45		85				325
		92,2	4.395	3.350	0.148	5.25	170	21	6	26		6	24	2085	62	205		9	8		38	700	17		590
Calanus sinicus	Tokyo B.	91,12	0.032	0.005	0.053	0.42	448							1270											285
		92,2	0.053	0.008	0.062	0.37	65							295											565
Euphausia similis	Osaka B.	92,7	0.017	0.013	0.055	0.20	110	6						330	260										150
	C-3		6.390	1.800	0.540	4.20	200	12	10	130	4	4	15	200	210	15	1.5	5		7	170	2260	20		280
Euphausia sp.	A-1	93,8	2.040	1.430	0.420	2.58	220	37	14	13	16	41	74	470	300	26	4.2	35	20	65	190	260	9	5	1840
Themisto sp.	A-1	93,8	5.180	1.038	1.065	2.07	300	37	17	15	17	55	66	1105	578	34	3.3	73	12	56	53	663	13	5	1090
	A-3	93,8	3.490	1.030	0.500	2.12	100	40	18	18	53	80	81	530	160	59	3.3	74	14	77	39	450	9	8	700
Iasis zonaria	C-3	92,7	0.790	0.675	3.265	0.16	160	20		8			18	140	1090					7	86	91	7		49
Lapidocera sp.	D-7	92,7	0.020	0.005	0.024	0.29	120						41	240	130			21	66		54				710
Criseis acicula	E-6	92,7	27.80	0.059	0.330	0.15	82	19		4				95		3		6		20	82	400	6		130
Decapoda (large)	D-4	92,7	2.860	0.808	2.075	1.83	12	5	5	31	1	2	11	88	1073	7	0.3	5	1		10	538	3	1	168
Decapoda (small)	D-4	92,7	3.460	0.560	0.750	2.13	19	10	2	120		3	8	41	300	13		8		4	12	690	2	2	300
Velella sp.	D-7	92,7	0.018	0.007	0.021	0.27	130							1000											450
	B-8	93,8	0.240	0.250	1.110	0.21	110	12	3	2	2	22	10	580	500	7	1.4	28	5	16	94	76	120	3	140
Siphonophorae	C-5	92,7	0.170	0.520	2.700	0.03	110	65	19	42				6990	570	39				30	130	35			120
	B-8	93,8	0.058	0.048	0.260	0.17	1910	130	26	13	19	216	76	3950	990	53	51.0	150	220	260	430	8	140	58	240
Stomatopoda	C-8	92,7	5.710	0.820	0.300	2.88	25	6	2	67		4	8	44	76	9		8		4	18	990	4		120
Calanoida	B-8	93,8	0.024	0.010	0.046	0.19	610		29	2	9	74	43	970	73	12	15.0	140	53	200	240		11	26	880
Pterosoma planum	D-7	92,7	0.340	1.100	5.740	0.08	170	10	4	6		74		640	1940	12	2.6	34			120	71	9		45
Zoea larva	Tokyo B.	92,1	21.56	7.690	8.410	15.62	360	34	50	103		25	78	580	6580	332		39		40	180	4220	22		2380
	Osaka B.	92,7	0.190	0.056	0.250	0.35	410							350	250						51				270
	E-1		4.500	0.900	0.210	2.34	38	13	2	72		4	5	110		31		8			21	1340	7		160
Alima larva	Osaka B	92,7	0.098	0.110	0.010	0.20	9	4	2	2			4	11	1	18		1	3	7	5	13			11
	Osaka B.		0.250	0.470	0.016	0.84	38	20	9	6			18	62		74					22	34			51
Portunidae	Osaka B.	92,7	15.10	1.050	0.390	1.61	340	17	11	37		1	63	470	87	78		18	16	4	29	1740	17		100
	B-2	93,8	9.260	0.940	0.860	1.17	84	43	17	20	6	20	15	180	1010	33	1.5	25	7	53	590	1970	9	6	120
(Fishes)																									
Mugil cephalus	A-1	93,8	5.520	0.530	0.170	3.87	15	17	17	8	2	5	10	120	980	12	1	11	0.1	29	11	220	2.7	2	260
Cololabis saira	A-3	93,8	6.840	0.290	0.088	4.23	51	15	14	26	6	10	450	290	170	29		24		17	63	370	5.1	2.3	410
Stephanolepis cirrhifer	B-2	93,8	5.060	0.330	0.630	3.32	20	18	23	24	1	3	7	95	4100	22	1	5	0.4	17	260	270	3.4	1.5	140
Unknown species	E-6	92,7	3.780	0.100	0.072	0.83	75	14		16		2	5	88		7		7			72	280			260
(Pelagic eggs)																									
Engraulis japonicus	Tokyo B.	93,8	0.036	0.029	0.090	0.52	120	14	3	4	1	120	21	650	24	6	3	70	8	19	35	8	6	3	690
	Tokyo B.	93,8	0.020	0.012	0.030	0.51	83	1	1	1	1	13	16	260		7	4	25	7	19	34	1	2	1	1890
Unknown species	C-3	92,7	0.010	0.010	0.040	0.19							0	15					7						160
	C-5	92,7	0.017	0.058	0.250	0.19	1	7	1				19	9				5		3	4	3			500
	C-8	92,7	0.002	0.002	0.005	0.19	9						21	24					6		6				180
	B-2	93,8	0.011	0.025	0.120	0.17	28	9	2		1	23	23	180	47	3	3	39	9	14	1	2	2	5	540
	B-8	93,8	0.035	0.007	0.016	0.23	22	14	5		3	15	15	100		2	5	43	16	36		2	1	2	310

Values are based on the dried materials. Sampling site: the Pacific Ocean (B, C, D), the Japan Sea (A, E).

Fig. 2 shows the relationship between the mean oceanic residence time of elements (τ_R) calculated from the mean dissolved riverine input and average concentration factors (CF_{sw}) of elements for 6 multi-species samples collected from the open sea in 1990, in which CF_{sw} was defined as C_{pl}/C_{sw} (C_{pl} and C_{sw}: elemental concentrations in zooplankton and seawater, respectively)5). Although the plots showed a scatter within about two orders of magnitude, log-log linearity with a slope of ca. -1 was observed. Although the mechanism is not clear, this suggests a significant role of zooplankton in scavenging of elements from the ocean, as has been pointed out by several authors5), 6). In Fig. 3a, the products of τ_R and CF_{sw} were plotted against CF_{sw} (MKT-plot)5), and were nearly constant over 7 orders of variation of CF_{sw}. Since τ_R x CF_{sw} is given by 36,000 x CF_{rw} (concentration factors of elements for zooplankton with respect to mean dissolved reiver-water concentration), CF_{rw} is also nearly constant within a factor of ca. 10. This constancy may be available for evaluating the contamination of samples with heavy metals. In Fig. 3b, s similar log-log relationship was shown for multi-species samples collected from Tokyo Bay. In contrast to the open-sea samples (Fig. 3a), plots for the bay sample showed a positive slope of 0.135 and indicated possible contamination with heavy metals. Since the elemental concentrations analyzed by neutron activation were used for the plots in these figures, the heavy metals incorporated in the planktonic tissue cannot be distinguished from those in the digestive organs. However, when more selective analysis by HNO_3-digestion/ICP-AES was used, both individual species and multi-species samples also showed higher positive slopes in the bays (av.= 0.22, n=11) than the open-sea (av.= 0.13, n=11). This suggested the contamination of planktonic tissue with heavy metals.

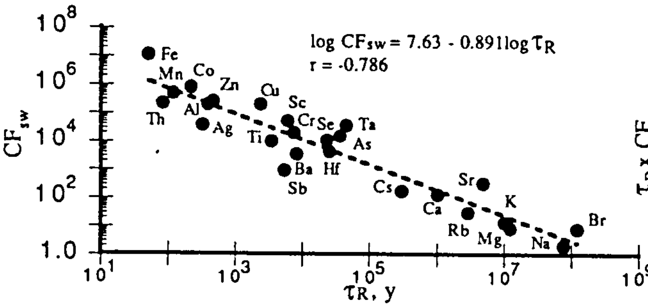

Fig. 2 Relationship between τ_R and CF_{sw} for multi-species samples collected from the open sea

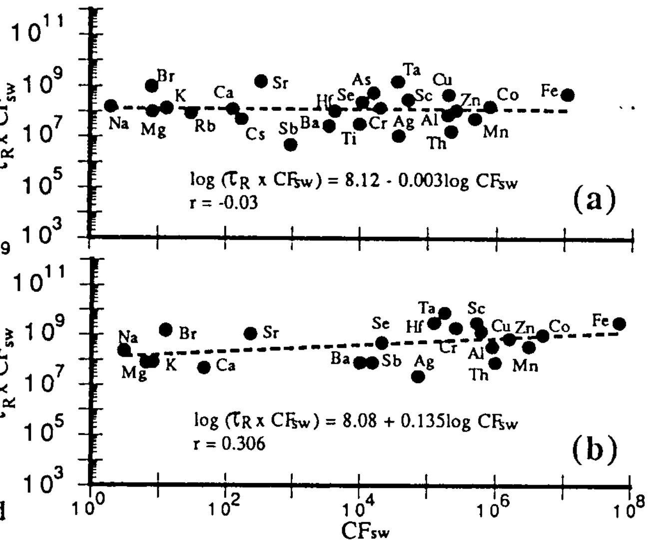

Fig. 3 The MKT-plot for multi-species samples collected from the open sea (a) and Tokyo Bay (b)

When the MKT-plot was applied to several fry samples, slopes of the plots (0.12-0.30) were generally higher than those for zooplankton (Fig. 4). In addition, the slopes were much higher in the case of pelagic eggs (av.= 0.39) (Fig. 5). This may indicate the accumulation of heavy metals in fishes (zooplankton-eaters) through the marine food-chain.

From the above results, the MKT-plot appeared to be an useful approach to evaluate the contamination of zooplankton with heavy metals and to study their transfer mechanism through the marine food-chain.

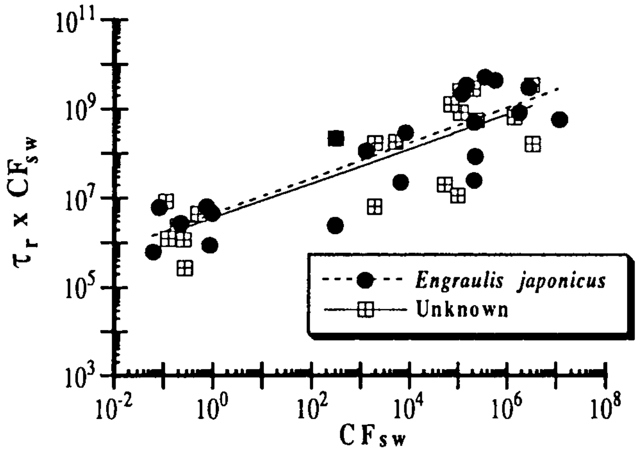

Fig. 5 The MKT-plot for pelagic eggs
E. japonicus: log(τ_R x CF_{sw})=6.61+0.397logCF_{sw}
Unknown: log(τ_R x CF_{sw})=6.57+0.3851logCF_{sw}

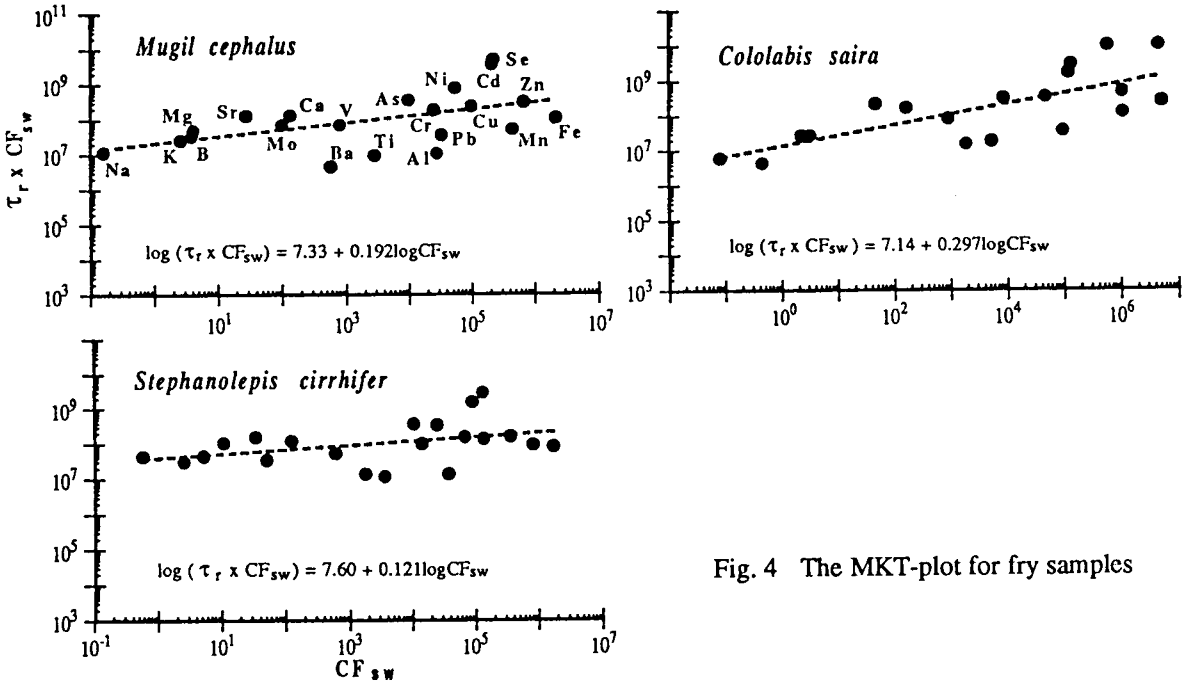

Fig. 4 The MKT-plot for fry samples

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