Transport of heavy metals into and out of the Seto Inland Sea, Japan

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Total and dissolved concentrations of heavy metals—V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd and Pb—in the Seto Inland Sea and in surface water from the adjacent seas of Japan have been determined. The water samples were collected with a specially designed clean sampler, and particulates were separated by filtration and/or centrifugation in a clean bench on board ship or in a clean room on land. The heavy metals were preconcentrated with a chelating resin column and detected by GFAAS in a clean laboratory on land. All the elements analyzed were divided into three groups in accordance with the ratio of dissolved to total concentrations for the Seto Inland Sea. Fe, Mn and Pb were mostly particulate forms, while Cu, Zn and Co were divided fifty-fifty between dissolved and particulate forms. Cd, Ni, Mo and V were almost dissolved forms. Two different methods for separating particles were compared to determine the characteristics of particulates.

The flux of heavy metals from the Inland Sea to the open ocean was estimated, assuming that only the dissolved forms of the metals are transported outward.

INTRODUCTION

A large amount of both natural and anthropogenic heavy metals are supplied to estuaries from the land through rivers. An estuary is a junction point for the transport of heavy metals to the ocean. In an estuary, river water mixes with saline water, and physical and chemical conditions change drastically. Organic matter concentrations are very high and heavy metals behave according to their physicochemical characteristics and biological roles. Heavy metals are removed in particulate form from sea water by coagulation following the increases of salinity (Li *et al.*, 1984; Ackroyd *et al.*, 1986), and by coagulation and adsorption with particulate organic matter or various minerals (Boyle *et al.*, 1977; Sholkovitz, 1978; Sholkovitz and Copland, 1981; Gibbs, 1986). Many factors

affect the distribution and behavior of heavy metals in the estuary. To clarify each factor, various studies have been performed, i.e., surface microlayer sampling (Hardy *et al.*, 1985), removal of particulates by the filtration method (Windom *et al.*, 1983; Danielsson *et al.*, 1983; Mart and Nurnberg, 1986), study of the particulate composition of heavy metals (Feely *et al.*, 1986; Akagi *et al.*, 1988) and estimate of dissolved chemical species (Batley and Garoner, 1978; Hart and Davies, 1981).

However, there is still no satisfactory explanation of factors and mechanisms which govern the distribution and behavior of heavy metals in estuaries. One reason is that the determination of individual chemical species is quite difficult. Moreover, before the last decade, the analytical results for the concentration of heavy metals in estuaries may be unreliable. The nature of the

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estuarine zone is dependent on the topography, water quality of the river draining into, the distance from the river mouth to the shelf edge and so on. This is another factor which complicates the study of the estuary. The study on the behavior of heavy metals in the estuary, therefore, should be based on sampling from various types of estuaries, separation of dissolved and particulate forms for each metal, comparison of heavy metals having different characteristics and the introduction of clean techniques.

Most estuarine processes proceed rapidly along the Japan coast, because of its steep topography, short rivers and narrow estuaries. It is rather difficult to investigate the behavior and the fate of materials which are carried to estuaries through rivers, because they are rapidly transported to the ocean. The Seto Inland Sea was, therefore, selected as our experimental field. The Inland Sea is joined to the open ocean by four narrow channels, and consists of several basins and bays which are connected to each other through narrow straights. The area of the Inland Sea is 17.1×10^3 km², the average depth being 31 m. Among the bays, Osaka and Hiroshima bays are semi-closed and have rather large rivers draining. The inner parts of these two bays are considered to be good places to investigate rapid estuarine processes. In contrast, at the offshore, or central part, of the Inland Sea, salinity ranges from 31.5 to 34‰, and physical and chemical processes proceed slowly. The heavy metals carried by rivers encounter drastic removal processes followed by their transport offshore into the Inland Sea. There, the metals have rather slow reactions and are gradually transported to the open ocean. Most of the water in the Inland Sea is exchanged by the tidal current through two of the four channels. The residual current is quite small and directed eastward. The mean residence time of water in the Inland Sea was estimated as 1.2y (Takeoka, 1984; Fujiwara, 1985).

A preliminary study (Akagi *et al.*, 1986) on the total heavy metal concentrations in and out of the Inland Sea is the only acceptable work on

the heavy metals in the water of the Inland Sea, because a clean technique was applied to this study. They reported that the concentrations of heavy metals decreased with increasing salinity in the offshore area of the Inland Sea. They also pointed out that the chemical and physical features of suspended particles including biological substances should be examined to understand further the behavior and distribution of trace metals in the coastal areas.

Thus, the purpose of this study is to elucidate the distributions of dissolved and particulate forms of heavy metals in an estuary, and to reveal the processes of their removal and supply in the estuary and their transport to the ocean. In this study, ten heavy metals—V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd and Pb—having different characteristics are chosen as indicators. Clean techniques for all steps of the experiments—such as sampling, separation of particulates, and analytical treatment—are introduced in this study. Total and dissolved heavy metal concentrations in the Inland Sea are determined and the transport of heavy metals from the Inland Sea to the open ocean is discussed.

SAMPLING AND ANALYTICAL PROCEDURES

The sampling stations are shown in Fig. 1. Surface, subsurface and bottom seawater samples were collected in the area from Hiroshima Bay to Iyo Nada and from Osaka Bay to Kii Channel, and in the central area of the Seto Inland Sea from Aki Nada to Harima Nada. The R/V Toyoshio Maru of the Faculty of Applied Biological Science, Hiroshima University, was utilized for these sampling cruises. Surface seawater was sampled with a self-made sampler, consisting of a 6 L polyethylene bottle at the head of the ship running at 2 knots to avoid contamination from the ship. Subsurface and bottom seawater samples were collected by a specially designed contamination-free sampler (Tsubota, 1985).

To remove particles, the samples were immediately filtered through a nitric acid-cleaned 0.4 μ m Nuclepore filter using a nitrogen-pressurized

Fig. 1. Sampling stations in the Seto Inland Sea. (○) Jun. 1983 cruise; (●) Nov. 1983 cruise; (△) Nov. 1984 cruise.

Teflon in-line filtration apparatus in clean-bench on board, or centrifugalized for 1 hour at 6000 rpm (5000 G) in Class-100 clean room in the laboratory on land within 6 hours after sampling. The samples for total and dissolved heavy metal determination were stored in a cleaned polyethylene bottle and acidified to pH lower than 2 with sub-boiled nitric acid. They were kept for about 2 months in order to dissociate organically bound metals completely.

To the acidified 1 L sample, 1 mL acetic acid was added and a pH was adjusted to 5.3–5.5 with aqueous ammonia. The solution was passed through a Chelex-100 column (16φ × 160 mm). The column was washed with 200 mL 1 M ammonium acetate solution (pH 5.5) to remove major elements, followed by 50 mL of sub-boiled water. The heavy metals adsorbed on the column were eluted with 2 M nitric acid. The eluate was dried on a hot plate in a nitrogen-flow-clean-box and then the residue was dissolved and diluted with 2 M nitric acid to 10 mL. Thus, 100-fold preconcentration was achieved. Ten heavy

metals in this solution were determined by graphite furnace atomic absorption spectrophotometer (Perkin-Elmer Model 5000 with HGA-500 and AS-40). Analytical precisions in percent for V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd and Pb were 3, 2, 4, 2, 2, 2, 5, 6, 2 and 2%, respectively. The preconcentration process was performed in the clean room and all reagents and water used in this process were purified by sub-boiling distillation.

RESULTS AND DISCUSSION

Distribution and behavior of heavy metals

The results of heavy metal analyses for three cruises are presented in Tables 1 to 3. The centrifugal method was employed to determine the dissolved heavy metal concentrations for the June 1983 cruise, and the filtration method was employed for the other two cruises. In the results of this study, total heavy metal concentrations offshore in the Seto Inland Sea agree with those reported by Akagi *et al.* (1986).

Table 1. Heavy Metal Concentrations and salinity for Jun. 1983 cruise

Stn.	Depth (m)	Cu (ng/l)	Zn (μg/l)	Fe (μg/l)	Pb (ng/l)	Mn (μg/l)	Ni (ng/l)	Cd (ng/l)	Co (ng/l)	Mo (μg/l)	V (μg/l)	S (‰)
A-1	0-T	320	0.340	0.844	17	1.31	330	24	12	10.9	1.34	33.46
	20-T	165	0.201	0.338	61	0.637	374	28	8.0	11.7	1.17	33.40
	20-C	129	0.115	0.0956	9.0	0.515	167	15	6.1	11.3	1.49	
A-2	0-T	262	0.229	4.35	77	1.17	348	25	15	10.4	1.46	33.31
	20-T	257	0.257	8.76	68	1.48	415	29	16	10.9	1.41	33.28
	20-C	115	0.134	1.17	6.4	1.55	194	18	4.4	11.3	1.73	
A-3	0-T	533	0.463	41.0	100	3.30	375	27	38	10.7	1.67	33.10
	0-C	202	0.156	1.69	6.3	0.934	192	16	12	10.4	1.46	
	20-T	434	1.04	83.3	170	7.10	476	29	86	11.7	1.64	33.32
A-4	0-T	182	0.313	6.75	11	0.952	231	21	13	11.7	1.64	
	0-T	461	0.606	19.1	47	4.59	293	17	24	12.2	1.84	33.06
	0-C	201	0.32	1.25	23	1.07	242	19	11	11.1	1.41	
A-5	20-T	438	2.11	66.4	130	12.7	425	17	59	13.1	1.96	33.11
	20-C	220	0.934	4.53	14	1.14	331	22	11	10.7	1.47	
	0-T	582	0.885	3.87	39	6.25	320	17	17	9.34	1.48	32.70
A-6	0-C	313	0.592	0.586	2.8	0.297	276	21	8.3	10.7	1.23	
	0-T	626	4.20	45.9	230	25.4	558	23	60	10.3	1.83	31.58
	0-C	556	1.36	1.56	15	1.61	418	20	19	9.97	1.24	
A-7	17-T	463	1.42	48.8	78	26.2	355	17	39	12.4	1.70	32.63
	17-C	220	0.721	7.04	14	1.49	312	23	10	11.5	1.68	
	0-T	1190	5.01	28.8	94	22.5	497	57	46	12.1	1.75	30.79
A-8	0-C	737	2.18	1.78	8.4	1.45	398	44	16	10.6	1.26	
	0-T	961	5.52	57.9	180	35.1	686	35	75	12.7	1.84	31.34
	0-C	620	3.23	2.07	20	9.55	604	36	44	9.98	1.21	
A-9	8-T	423	1.94	16.1	35	11.3	361	16	25	11.4	1.68	32.47
	8-C	430	1.41	4.95	10	1.02	349	25	11	10.8	1.30	
	0-T	1880	7.39	61.5	230	64.8	824	44	70	12.4	1.80	29.31
A-10	0-C	834	5.56	4.18	43	9.47	736	41	50	8.98	1.19	
	0-T	1700	7.01	95.4	540	124	566	37	180	8.55	1.87	29.40
	0-C	933	4.34	—	78	4.03	461	38	92	7.20	1.01	

T: Total Metal; C: Dissolved Metal (centrifugal method).

The chief water movement in the Seto Inland Sea is a tidal current, while river discharges are rather small there. The behavior of elements flowing into the bay from the rivers is dominated not only by the dispersion of fresh water but also by bio-uptake and flocculate precipitation during the alternate tidal motions, even though these elements are dissolved in the river water. Consequently, the distribution of the elements—especially particulate-forming and bio-essential—is very complicated in each bay. Therefore, we will ignore the differences between each bay or basin and discuss only the region offshore in the Inland Sea joining the two bays, Osaka Bay and Hiroshima Bay, to make up for the deficiency of low salinity regions. Hayami and Unoki (1970) separated the whole Inland Sea into 36

boxes and calculated the yearly-average chlorinity in each box. They pointed out that chlorinity increases from Harima Nada to Bungo and Kii Channel. Salinities in this study were in the same range and distribution as their results. This means that our samples were representative of the offshore Inland Sea from the viewpoint of salinity.

For Fe, Mn and Pb, dissolved concentrations were very low, ranging from a low salinity region (inner parts of Hiroshima Bay and Osaka Bay) to a high salinity region (Iyo Nada and Kii Channel). These metals were mostly in particulate form in the Seto Inland Sea. Danielsson *et al.* (1983) reported that Fe and Pb were mainly associated with particulate in the Göta River Estuary. Correlations of total and dissolved Fe

Table 2. Heavy Metal Concentrations and salinity for Nov. 1983 cruise

Stn.	Depth (m)	Cu (ng/l)	Zn (μ g/l)	Fe (μ g/l)	Pb (ng/l)	Mn (μ g/l)	Ni (ng/l)	Cd (ng/l)	Co (ng/l)	Mo (μ g/l)	V (μ g/l)	S (‰)
B-1	0-T	613	0.633	6.96	46	43.1	544	22	49	11.1	2.11	32.333
	0-F	372	0.932	0.641	69	53.7	499	20	43	10.8	1.98	
	20-T	563	0.729	57.4	110	20.9	430	22	63	12.5	2.44	32.532
	20-F	478	1.09	0.868	97	29.5	360	23	28	10.6	2.03	
B-2	0-T	589	2.40	16.5	120	29.0	588	26	49	12.5	2.18	32.633
	0-F	518	2.62	0.818	—	15.9	521	23	39	10.3	1.73	
	18-T	629	0.852	53.5	150	26.4	492	23	60	13.0	2.29	32.622
	18-F	377	—	0.519	110	—	414	26	30	11.0	1.95	
B-3	0-T	461	0.661	20.3	87	28.3	378	32	38	12.5	2.22	32.602
	0-F	372	—	0.834	—	20.1	342	35	25	10.7	1.84	
	20-T	618	1.19	75.3	160	32.0	438	33	82	13.4	2.39	32.595
	20-F	329	1.55	4.07	110	19.7	321	29	29	11.4	2.12	
B-4	0-T	593	0.937	32.5	93	19.9	405	21	45	12.6	2.23	32.729
	22-T	594	1.15	40.1	91	19.6	427	20	43	12.6	2.11	32.782
B-5	0-T	421	0.583	8.01	34	3.30	317	20	14	10.3	1.91	32.887
B-6	0-T	650	0.500	12.6	—	1.96	—	9.0	—	—	—	33.012
	0-F	370	0.360	6.30	—	0.620	—	7.0	—	—	—	
	47-T	470	0.790	21.2	—	2.03	—	8.0	—	—	—	33.045
	47-F	460	0.510	—	—	0.86	—	6.0	—	—	—	
B-7	0-T	399	0.359	27.3	110	5.27	438	18	21	9.39	1.89	32.979
B-8	0-T	350	1.44	31.7	—	11.1	—	11	—	—	—	31.809
	8-T	450	1.44	55.5	—	13.9	—	12	—	—	—	31.839
B-9	0-T	320	1.01	7.00	—	6.0	—	14	—	—	—	—
	15-T	290	0.730	40.4	—	11.9	—	11	—	—	—	32.353
B-10	0-T	220	1.78	16.4	—	5.12	—	7.0	—	—	—	32.723
	32-T	620	2.34	24.5	—	5.28	—	9.0	—	—	—	32.731
B-11	0-T	210	2.15	16.3	—	3.12	—	8.0	—	—	—	33.003
	27-T	360	0.530	27.5	—	4.22	—	12	—	—	—	32.984
B-12	0-T	200	0.310	17.4	—	2.69	—	9.0	—	—	—	33.052
	53-T	220	1.73	23.1	—	3.12	—	10	—	—	—	33.084

T: Total Metal; F: Dissolved Metal (filtration method).

concentrations to salinity are given in Fig. 2. Total Fe concentrations show negative but weak correlation versus salinity. Their concentrations are distinctly higher in bottom waters than in surface waters for both total and dissolved Fe even in the central part of the Inland Sea. At these stations, Fe may be supplied from sediment by re-suspension and re-dissolution. Except for some points encircled, which are mostly in the inner part of Hiroshima Bay in June '83, dissolved Fe shows a good linearity with salinity. Similar characteristics were obtained for Mn and Pb. It is suggested that these heavy metals were removed rapidly as particles in the Inland Sea.

Dissolved concentrations of Cu, Zn and Co were about one half of the total concentrations in the Inland Sea. Correlations of total and

dissolved Cu concentrations with respect to salinity are given in Fig. 3. Both total and dissolved Cu concentrations show a good linearity and behave conservatively, except for points in some basins such as Fe (Fig. 2). No difference between surface and bottom water was found for both total and dissolved Cu. A similar behavior was found for Zn. The distribution of Co was considered to be grouped with Fe, but the observed distribution for Co shows a pattern similar to Cu and Zn. This is probably caused by the solubility of the hydrated oxide and the low abundance of Co. This physio-chemical behavior for some heavy metals will be discussed elsewhere.

No distinct differences between total and dissolved concentrations were found for Cd, Ni, Mo and V. These metals were mostly in the

Table 3. Heavy Metal Concentrations and salinity for Nov. 1984 cruise

Stn.	Depth (m)	Cu (ng/l)	Zn (µg/l)	Fe (µg/l)	Pb (ng/l)	Mn (µg/l)	Ni (ng/l)	Cd (ng/l)	Co (ng/l)	Mo (µg/l)	V (µg/l)	S (‰)
C-1	0-T	850	1.47	36.2	130	7.98	633	38	36	10.3	2.20	32.946
	7-T	797	1.41	35.0	150	13.0	711	44	35	9.52	2.17	32.933
C-2	0-T	418	1.16	40.6	130	7.38	596	42	31	11.7	2.32	33.145
	0-F	396	0.507	0.544	42	8.00	423	32	18	11.7	1.73	
	21-T	963	2.16	84.2	250	15.5	710	39	79	12.0	2.47	33.172
	21-F	518	0.391	0.425	24	3.48	407	27	17	11.5	1.84	
C-3	0-T	617	0.530	27.6	150	12.6	563	32	35	10.7	2.17	32.970
C-4	0-T	910	1.90	66.4	190	10.2	614	41	53	13.1	2.65	32.800
	0-F	609	0.943	0.485	21	0.328	448	42	6.4	12.0	1.86	
	16-T	660	0.926	76.6	170	21.3	622	29	76	11.0	2.51	32.790
C-5	16-F	517	1.13	0.321	20	0.611	448	43	6.7	10.3	1.67	
	0-T	400	0.714	16.7	66	7.00	392	18	21	10.8	2.14	32.979
	0-F	325	0.593	0.262	27	1.45	372	15	11	11.1	1.74	
	25-T	401	0.307	18.5	73	6.14	390	15	24	12.3	2.19	33.065
C-6	25-F	297	0.295	0.168	33	1.10	373	20	8.9	11.0	1.80	
	0-T	424	0.453	28.4	82	8.97	423	16	26	11.9	2.13	33.027
	0-F	320	1.62	1.18	39	0.491	384	12	11	9.69	1.81	
	30-T	427	0.438	31.6	96	13.3	446	16	28	11.7	2.09	33.029
	30-F	368	0.611	0.220	44	1.47	405	12	10	11.4	1.90	
	40-T	389	0.381	30.2	94	12.1	439	13	27	11.5	1.94	33.031
C-7	40-F	330	0.441	0.324	47	1.54	383	12	9.0	10.4	1.75	
	0-T	485	0.913	33.1	120	9.78	483	19	35	11.7	2.16	32.800
C-8	0-T	940	6.29	62.8	190	75.9	3750	19	18	9.22	1.98	30.440
C-9	0-T	707	4.32	32.3	140	12.1	2950	15	91	8.55	1.69	31.127
	0-F	490	3.21	2.21	32	—	2520	13	72	7.73	1.36	
	12-T	633	2.29	73.5	240	27.6	1160	13	92	12.4	2.27	32.610
C-10	12-F	363	1.23	0.716	31	7.39	1010	11	34	10.8	1.65	
	0-T	426	1.67	0.351	61	15.5	1520	14	49	9.57	1.59	32.213
	0-F	375	1.61	1.07	35	22.4	1390	15	49	11.3	1.53	
	16-T	393	0.946	30.0	120	26.0	893	14	42	9.86	1.96	33.006
	16-F	301	0.746	0.537	23	3.85	764	9.5	23	10.23	1.57	
C-11	0-T	401	1.56	0.775	110	18.4	1130	15	37	8.68	1.65	32.648
C-12	0-T	360	0.553	21.2	74	6.84	509	13	22	9.80	1.91	33.223
	0-F	253	0.492	0.336	15	0.506	517	12	10	9.31	1.61	
	30-T	408	0.513	25.8	89	5.35	595	13	26	9.79	1.84	33.213
C-13	30-F	294	0.565	2.81	30	0.596	609	14	12	11.0	1.71	
	0-T	208	0.206	14.4	66	15.5	309	7.6	17	11.7	1.90	34.038
C-14	0-T	30.1	0.006	0.415	15	0.275	149	1.4	1.1	12.6	1.81	34.549
	0-F	—	—	—	—	0.080	141	—	—	13.3	1.54	
	50-T	28.1	0.00	0.505	11	0.182	155	2.2	1.1	13.6	1.68	34.448
	50-F	—	—	0.557	—	0.055	148	—	—	12.8	1.60	

T: Total Metal; F: Dissolved Metal (filtration method).

dissolved form in the Inland Sea. Danielsson *et al.* (1983) also reported that Ni was mostly in the dissolved form in the Göta River Estuary. Figure 4 shows the correlation of total and dissolved Cd concentrations with respect to salinity. Total and dissolved Cd concentrations decrease with increasing salinity and show negative correlation, with some exceptions such as Fe. No difference between surface and bottom water was found

both total and dissolved Cd. A similar behavior was obtained for Ni and V. Mo showed positive correlation with salinity. It is considered that Cd, Ni, Mo and V are conservative and exist in seawater as a chloro-complex, chloro- and sulfate-complexes, molybdate anion and vanadate anion, respectively.

Comparison between centrifugal and filtration

Fig. 2. Total and dissolved Fe concentrations vs. salinity. (○) surface water; (●) subsurface or bottom water. Points categorized with a line are for the inner part of Hiroshima Bay in June '83, see text.

Fig. 3. Total and dissolved Cu concentrations vs. salinity. (○) surface water; (●) subsurface or bottom water.

methods

To separate the particles, centrifugal and filtration methods were employed on a cruise-by-cruise basis. The analytical results showed some differences. By comparing these two methods, it may be possible to obtain good information on the characteristics of the heavy metal particulates. Generally, particles are removed by specific gravity with a centrifuge and by particulate size with filtration. The centrifugal method was employed only for the cruise near the vessel base, where we could use a centrifuge. Then, another cruise confirmed the difference be-

tween the two method in Nov. 1985. The results of the comparison for Fe and Pb are given in Fig. 5, as an example. ST-1, 2, 3 and 4 in the figure are near stations A-1, -4, -6 and -8 in the June 1983 cruise, respectively (cf. Fig. 1). The filtration method removed more particles than the centrifugal method for Fe. In contrast, in the case of Pb, the centrifugal method removed more particles than the filtration method, except for ST-1. The reason for this exception is not clear yet, although the centrifugal separation of the samples from ST-1 was delayed by about 20 hrs. These results suggest that particulate Fe may

Fig. 4. Total and dissolved Cd concentrations vs. salinity. (○) surface water; (●) subsurface or bottom water.

consist of relatively large-size and a light particles, such as gelatinous hydrated oxide or particulate organic matter, while Pb may contain small but heavy particles. Mn, Cu, Zn and Co had the same tendency as Fe.

Transport of heavy metals from rivers to the ocean through the Seto Inland Sea

The ten heavy metals analyzed were divided into three groups in accordance with the ratio of dissolved to total concentrations for the Seto Inland Sea. The transport of heavy metals from rivers to the ocean through the Inland Sea is schematically shown in Fig. 6. In this figure, downward arrows show the removal from seawater as particles, and upward arrows show the return into seawater as the dissolved form.

A large part of Fe, Mn and Pb carried from land is removed rapidly at the river mouth as particles, while a small part is transported to the ocean through the offshore area of the Inland Sea. Feely *et al.* (1986) pointed out that particulate Fe, Mn and Pb were rapidly scavenged as hydrated oxide. Kasemsupaya *et al.* (1989) reported that ^{210}Pb was largely removed offshore in the early stage of mixing between the Kuroshio and the coastal waters. In these processes, a small amount returns again from the sediment. Cu, Zn and Co are gradually removed as particulates. The ratios of their particulate form

are reduced during the transport to the ocean by mixing with oceanic water. Cu may precipitate with humic acids and iron hydrated oxides as reported by Sholkovitz and Copland (1981). Cd, Ni, Mo and V are mostly in the dissolved form and hardly removed as particles at the river mouth. They are transported to the ocean mostly in the dissolved form by mixing with oceanic water. Mo concentrations in oceanic water are higher than those in estuarine water, so that Mo is transported from the ocean to the Inland Sea by mixing with oceanic water.

Sometimes, Pb shows a character intermediate between the first and the second groups, while Ni between the second and third groups.

Flux of heavy metals from the Seto Inland Sea to the open ocean

Estimates of the flux of heavy metals from the Seto Inland Sea to the open ocean are based on two assumptions as follows.

1. Particulate heavy metals are removed to sediment in the Inland Sea.
2. Only the dissolved form of heavy metals is transported out to the open ocean by mixing with oceanic water from the Inland Sea.

These assumptions have some difficulties. One is the neglect of the re-dissolution process. As shown in Fig. 2, a high concentration of dissolved Fe is sometimes observed, particularly at the

Fig. 5. Comparison between the centrifugal method and the filtration method. Concentrations of Fe and Pb for the Nov. 1985 cruise.

red tide period, but it is accompanied by a high concentration of organic substances. This may be a temporal and local phenomenon observed only at the innermost part of the bay. The second assumption follows from the fact that the ratios of the particulate form for Cu in the Inland Sea are almost constant and decrease in the open ocean.

The fluxes of heavy metals are calculated by the equation:

$$\text{Flux} \approx V_o(C_i - C_o)/\tau_w$$

where V_o is the seawater volume in the Inland Sea (530 km^3), and τ_w is residence time of seawater of the Inland Sea (1.2y, Takeoka, 1984; Fujiwara, 1985). C_i is the average concentration of the dissolved heavy metal in the Inland Sea, and C_o is the concentration of the dissolved heavy metal in the surface layer of the open ocean. The C_o value for each metal is that of surface water collected at $29^\circ 05' \text{N}$, $142^\circ 51' \text{E}$, by the same authors.

The parameters and results of the calculation are given in Table 4. High concentrations of Fe,

Fig. 6. The schematic diagram for transport of heavy metals from rivers to the ocean through the Seto Inland Sea.

Table 4. The flux of heavy metals from the Seto Inland Sea to the ocean

	Fe	Mn	Pb	Cu	Zn	Co	Cd	Ni	Mo	V
Flux (ton/year)	270	400	19	160 (240)	300 (750)	4	13	97	-440	180
C_i ($\mu\text{g/l}$)	0.7	1	0.05	0.4	0.7	0.02	0.03	0.35	10	2
C_o ($\mu\text{g/l}$)	0.1	0.09	0.007	0.04	0.02	0.01	0	0.13	11	1.6

The values in parenthesis are reported by Hoshika *et al.* (1988).

Mn and Pb are supplied to the Inland Sea through rivers. However, a large part of these metals is removed in the Inland Sea and their fluxes are small. The flux of Mo is negative. This shows that Mo is supplied from the ocean to the

Inland Sea. Hoshika *et al.* (1988) reported the flux of Cu and Zn from the Inland Sea to the ocean. These values, cited in parenthesis in the table, are higher than those calculated in this study. They estimated these values by using the

sedimentation rates and heavy metal contents of the core sediments, and also different values for τ_w and C_o . The difference suggests, if their estimation is shown to be better than the present study, that some of the particulate Cu and Zn may be transported out to the ocean contrary to our assumption that only dissolved forms are transported.

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REFERENCES

- Ackroyd, D. R., A. J. Bale, R. J. M. Howland, S. Knox, G. E. Millward and A. W. Morris, (1986) Distributions and behavior of dissolved Cu, Zn and Mn in the Tamar Estuary. *Est. Coast. and Shelf Sci.* **28**, 327–338.
- Akagi, T., H. Haraguchi and H. Tsubota, (1988) A study on mineral composition of suspended particles in coastal estuarine water using X-ray diffraction. *Chem. Lett.* **1988**, 331–334.
- Akagi, T., T. Kodama, H. Haraguchi, K. Fuwa and H. Tsubota, (1986) Distribution of heavy metals in seawater around the Shikoku Island. *Geochem. J.* **20**, 127–135.
- Batley, G. E. and Garoner, (1978) A study of copper, lead and cadmium speciation in some estuarine and coastal marine waters. *Est. Coast. Mar. Sci.* **7**, 59–70.
- Boyle, E. A., J. M. Edmond and E. R. Sholkovitz, (1977) The mechanism of iron removal in estuaries. *Geochim. Cosmochim. Acta* **41**, 1313–1324.
- Danielsson, L. G., B. Magnusson, S. Westerlund and K. Zhang, (1983) Trace metals in the Göta River Estuary. *Est. Coast. Shelf Sci.* **17**, 73–85.
- Feely, R. A., G. J. Massoth, E. T. Baker, J. F. Gen-dron, A. J. Palson and E. A. Crecelius, (1986) Seasonal and vertical variations in the elemental composition of suspended and settling particulate matter in Puget Sound, Washington. *Est. Coast. Shelf Sci.* **22**, 215–239.
- Fujiwara, T. (1985) Flux and Balance of Mass in the Seto Inland Sea. Ph. D. thesis, Tokyo University.
- Gibbs, R. J., (1986) Segregation of metals by coagulation in estuaries. *Mar. Chem.* **18**, 149–159.
- Hardy, J. T., C. W. Apts, E. A. Crecelios and N. S. Bloom, (1985) Sea-surface microlayer metals enrichments in Urban and Rural Bay. *Est. Coast. Shelf Sci.* **20**, 299–312.
- Hart, B. T. and S. H. R. Davies, (1981) Trace metal speciation in the freshwater and estuarine regions of the Yarra River, Victoria. *Est. Coast. Shelf Sci.* **12**, 353–371.
- Hayami, S. and S. Unoki, (1970) Water exchange and material dispersion in the Seto Inland Sea. *Proceedings of the 17th Conference on Coastal Engineering*. Japan Society of Civil Engineers. 358–393.
- Hoshika, A., T. Shiozawa and Y. Kitano, (1988) Mass balance of heavy metals in the Seto Inland Sea, Japan. *Mar. Chem.* **24**, 327–335.
- Kasemsupaya, V., M. Yashima, H. Tsubota and Y. Nozaki, (1989) Comparative behavior of ^{210}Pb and Ra isotopes in the waters of Tokyo Bay and Osaka Bay mixing zones. *Geochem. J.* **23**, 129–138.
- Li, Y. H., L. Burkhardt and H. Teraoka, (1984) Desorption and coagulation of trace elements during estuarine mixing. *Geochim. Cosmochim. Acta* **48**, 1879–1884.
- Mart, L. and H. W. Nurnberg, (1986) Cd, Pb, Cu, Ni and Co distribution in the German Bight. *Mar. Chem.* **18**, 197–213.
- Sholkovitz, E. R. (1978) The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. *Earth Planet. Sci. Lett.* **41**, 77–86.
- Sholkovitz, E. R. and Copland D., (1981) The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochim. Cosmochim. Acta* **45**, 181–187.
- Takeoka, H., (1984) Exchange and transport time scales in the Seto Inland Sea. *Continental Shelf Res.* **3**, 327–341.
- Tsubota, H. (1985) The distribution and behavior of heavy metals in the ocean. *Ocean Characteristics and their changes* chapter 4, 225–236, ed. K. Ka-jiura, Koseisha Koseikaku, Tokyo (in Japanese).
- Windom, H., G. Wallace, R. Smith, N. Dudek, M. Maeda, R. Dulmage and F. Stori, (1983) Behavior of copper in southeastern United States estuaries. *Mar. Chem.* **12**, 183–193.