# DISTRIBUTION OF HEAVY METALS IN ANTARCTIC MARINE ECOSYSTEM

### Katsuhisa Honda, Yoshiyuki YAMAMOTO and Ryo TATSUKAWA

Department of Environment Conservation, Faculty of Agriculture, Ehime University, 5–7, Tarumi 3-chome, Matsuyama 790

Abstract: Heavy metal concentrations in Antarctic surface seawaters and some marine organisms were determined, and their distributions and bioaccumulations were discussed in comparison with other marine ecosystems. Locational difference of the heavy metal concentrations in Antarctic seawater was negligible, and their concentrations were in the order of  $Zn \cdot Fe > Mn > Cu > Pb \cdot Ni > Cd > Hg$ . When compared to the western North Pacific, Japan Sea and Bering Sea, the concentrations of Fe, Zn, and Hg in Antarctic seawater were relatively low, which provides evidence that atmospheric transport of these metals from continents, either from natural or anthropogenic sources to the Antarctic water is much less. The Cd level was relatively high compared with those in the western North Pacific and Japan Sea waters, which might be due to the upwelling of Cd-enriched deep waters to the surface. In general, the heavy metal concentrations in Antarctic marine organisms were affected by the metal concentrations in the seawater. Also, it was found that bioaccumulations of metals in Antarctic marine ecosystem were characterized by a high accumulation of Cd and low accumulation of Hg, based on the short food chain with krill as key species, and also by a low accumulation of Fe in fishes as an adaptation to the cold water condition.

### 1. Introduction

Some literature concerning heavy metals in the snow, ice, seawater, atmosphere, soil and rock in the Antarctic region (LANDY and PEEL, 1981; YOSHIDA and MUROZUMI, 1977; IWASHIMA *et al.*, 1977; SANO *et al.*, 1977; NRIAGU, 1979; WATANUKI *et al.*, 1977), and animals like zooplankton, fish, penguin, whale and seal (MISHIMA *et al.*, 1977; YOSHIYAMA *et al.*, 1979; DENTON *et al.*, 1980; SOSZKA *et al.*, 1981; STOEPPLER and BRANDT, 1979; WAGEMANN and MUIR, 1984; NAGAKURA, 1974) has been published. However, analytical data on the Antarctic marine ecosystem including the seawater and biological materials for understanding the detailed distribution and bioaccumulation processes of heavy metals are rather scarce (HONDA *et al.*, 1983, 1986; YAMAMOTO *et al.*, 1987a).

The Antarctic marine ecosystem, especially beyond south of the Antarctic Convergence, is stable and old and has a higher percentage of inherent species: thus it is simple in comparison with other ecosystems. Also, since the atmospheric mixing between north and south of the Antarctic Convergence is very slow, the Antarctic area is a comparatively closed environment (KNOX, 1970). These natural barriers prevent the effects of global pollution here. But, when polluted from the inner area, e.g., from research stations such as Syowa Station, the pollution cannot be dispersed

easily and so the pollutants become localized and are concentrated in resident organisms. When highly polluted, any closed such simple ecosystems will be easily damaged.

In this report, we describe the concentration levels of heavy metals in Antarctic seawaters and some marine organisms, and their geographical distribution in seawater and bioaccumulation processes are also discussed in comparison with other marine ecosystems.

### 2. Materials and Methods

Sample collection sites of the Antarctic seawaters and marine organisms are shown in Fig. 1.

Seawater: Four samples, Nos. 1-4 (Fig. 1) of the Antarctic seawater were pumped up by suction from under the fast ice (0-1 m), mainly around Syowa Station (69°00'S,



Fig. 1. Sample collection sites of the Antarctic and other ocean waters, and the Antarctic organisms.

Seawater (•): Antarctic (Nos. 1–12), western North Pacific (Nos. 13–31), Bering Sea (Nos. 32–35), Japan Sea (Nos. 36–38). Organism ( $\bigcirc$ ): Antarctic krill, fishes (Noto-thenioidei, Myctophid), southern minke whale; ( $\times$ ): Copepod, bivalve, fishes (T. bernacchii, P. borchgrevinki), Adélie penguin, Weddell seal.

39°35'E) during the wintering of JARE-22 (January 1981–January 1982). Six seawater samples, Nos. 5, 7–8, and 10–12, were collected from surface water (0–0.5 m) using polyethylene bucket on the Japanese factory ship, NISSHIN MARU No. 3, during the austral summer (December 1985–March 1986). Two samples of seawater, Nos. 6 and 9, were pumped up by suction from surface water (0–1 m) during the crusing periods of the First International BIOMASS Experiments (FIBEX, November 1980– March 1981).

Most of the seawater samples were immediately filtered through a 0.45  $\mu$ m membrane filter (Toyo, TM-2) using a vaccum filtration apparatus, acidified to pH<1 with H<sub>2</sub>SO<sub>4</sub>, and stored in carefully cleaned polyethylene bottles at 4–15°C until analysis. Two samples from the FIBEX Program were filtered through an acid-washed glass fiber filter (Toyo, GC-50).

Organisms: Planktonic copepod, bivalve (Admussium colbecki), two species of fish (Trematomus bernacchii, Pagothenia borchgrevinki), Adélie penguin (Pygoscelis adeliae), and Weddell seal (Leptonychotes weddelli) were collected around Syowa Station during the wintering of JARE-22. Samples of the copepod were collected from surface water using a plankton net, and the fish samples were caught by fishing. Samples of the Adélie penguin were collected by asphyxiation at the breeding site in Rumpa (island) about 18 km south of Syowa Station. Samples of the Weddell seal were electrocuted at Tottuki Point, about 13 km northeast of Syowa Station.

Southern minke whale (*Baraenoptera acutorostrata*) were collected from the catch hauled up on the Japanese factory ship, NISSHIN MARU No. 3, in the Antarctic during the austral summer (November 1980–February 1981; November 1984–March 1985; December 1985–March 1986). The Antarctic krill (*Euphausia superba*) and two species of fish (*Notothenioidei*, myctophid) were collected from the stomach contents of the southern minke whales hauled up on the Japanese factory ship (December 1985–March 1986).

All specimens were immediately frozen below  $-20^{\circ}$ C until measurements. Body length, body weight, sex and basic morphometric data were recorded for all the specimens. Age of the Weddell seal was determined by counting the growth layers of cannine teeth, and for the southern minke whale the number of growth layers in the earplug was counted by the method of BEST (1982). Samples of the bivalve, fishes, penguin, seal and minke whale were dissected, and the weights of organs and tissues were measured. All tissue samples were stored in polyethylene bags at  $-20^{\circ}$ C until analysis. For moisture determination, all tissue samples were dried at  $80^{\circ}$ C for 12 h.

Metal analysis: For the analysis of metals in seawater, 5-L of seawater samples was adjusted to pH 6 with ammonium acetate buffer and passed through Chelex-100 resin (Bio Rad Lab., 200–400 mesh) column for collecting metals (KAWABUCHI *et al.*, 1976). The metals chelated on the resin were eluted with 2-N HNO<sub>3</sub>, and the solutions were made up to a known volume with 2-N HNO<sub>3</sub>. The concentrations of Fe, Zn, Cu, Ni, Pb, and Cd were determined by flame atomic absorption spectrophotometry (AAS). Hg was measured after acid digestion of the chelex-100 resin by cold vapor AAS. For the analysis of Mn, 500-ml of the seawater sample was treated with methyl isobutyl ketone-diethyl dithiocarbamate (DDTC-MIBK), and Mn in the extract was determined by AAS. Corrections for background interference were made

by running appropriate blanks. The accuracy of those methods has been determined in this laboratory by spiking seawater with known amounts of Fe, Zn, Cu, Pb, Ni, Cd, Mn and Hg. Recoveries of 90.0 to 98.0% were obtained.

For the determination of metals in organisms, the dried or wet tissues were homogenized, and 1 to 10/g samples were digested with a mixture of nitric, perchloric and sulfuric acids. The resultant solutions were diluted to a known volume with deionized water and transferred to acid-washed test tubes with teflon screw-caps. The concentrations of Fe, Mn and Zn were determined by AAS. Cu, Pb, Ni, and Cd were measured by AAS, after DDTC-MIBK treatment. The presence of Hg was determined by cold-vapor AAS. It consisted of the mineralization of samples with a nitric, perchloric and sulfuric acid mixture in a flask equipped with a Liebig condenser and followed by KMnO<sub>4</sub> digestion. The excess of KMnO<sub>4</sub> was reduced with a 20% hydroxylamine hydrochloride solution and the mercury was reduced to Hg<sup>0</sup> with tin (II) chloride. Determinations were made with a Shimadzu AA-680 spectrophotometer.

### 3. Results and Discussion

### 3.1. Concentration levels and distribution of heavy metals in Antarctic seawater

Table 1 shows heavy metal concentrations in the Antarctic seawaters with those of the western North Pacific, Bering Sea and Japan Sea waters.

Although the metal concentrations in the Antarctic seawaters varied within the locations sampled, their variations as a whole were very small when compared to those in the western North Pacific, Bering Sea and Japan Sea waters. The average concentrations of heavy metals in the Antarctic waters were in the order of  $Zn \cdot Fe > Mn > Cu > Pb \cdot Ni > Cd > Hg$  (ANOVA, p < 0.05), and this order agreed well with those in the other ocean waters (Table 1).

Concentration data on heavy metals in the Antarctic waters are very scarce. ORREN and MONTEIO (1985) reported the concentrations ( $\mu$ g/L) of Cu (0.062–0.110), Zn (0.35–1.01) and Cd (0.1–0.14) in the surface waters collected during two surveys (1980, 1981) in the Southern Ocean south of South Africa. These values were slightly high for Cd, very low for Cu, and nearly the same for Zn when compared with our results. Since the sampling and analytical procedures were different between the two works, further investigation is needed for discussing whether these differences are true.

When compared to the results obtained by us on other ocean waters, as shown in Table 1, significant differences of Fe, Zn, Cd and Hg concentrations were observed (Mann-Whitney U-test, p < 0.05). The concentrations of Fe, Zn, and Hg in the Antarctic water were significantly lower than those in the other waters, and especially the difference for Hg was apparent when compared with the area, Nos. 19–25 (Table 1), along the Kuroshio current of the western North Pacific. NISHIMURA *et al.* (1983) examined latitudinal variation of surface mercury concentration in the ocean, and reported that the maximum concentration occurred at 40°N and decreased at each latitude from 40°N to 30°S. This variation provides evidence that atmospheric Hg

No.	Position	Date	Fe	Mn	Zn	Cu	Pb	Ni	Cd (×10 <sup>-2</sup> )	Hg (×10 <sup>-3</sup> )
Antarc	Antarctic									
1	69°13′S, 39°40′E	Oct. 14, '81	0.60	0.70	1.26	1.17	0.40	0.40	6.0	4.0
2	69 00 S, 39 35 E	Jan. 3, '82	1.50	0.60	1.12	1.08	0.30	0.50	3.0	2.0
3	68 55 S, 39 50 E	July 3, '81	0.62	0.60	0.64	0.18	0.30	0.40	5.0	7.0
4	68 55 S, 39 50 E	Nov. 24, '81	0.87	0.60	0.98	0.30	0.30	0.30	4.0	7.0
5	65 32 S, 108 07 E	Mar. 21, '86	0.34	0.63	0.41	0.24	0.26	0.30	7.0	8.6
6	64 52 S, 124 37 E	Jan. 1, '81	· <u> </u>	0.79	—	—	0.43	0.54	9.3	_
7	66 08 <b>S,</b> 144 60 E	Jan. 7, '86	1.10	0.43	0.69	0.40	0.22	0.34	6.1	7.0
8	66 18 S, 148 69 E	Feb. 17, '86	0.77	0.54	0.73	0.48	0.40	0.39	6.9	—
9	66 36 S, 162 16 E	Jan. 31, '81	—	0.90	—	_	0.49	0.54	7.5	2.0
10	64 01 S, 160 08 W	Jan. 7, '86	0.48	0.51	0.82	0.38	0.21	0.44	7.4	8.4
11	64 27 S, 152 17 W	Dec. 25, '85	0.57	0.63	1.17	0.38	0.28	0.41	7.9	7.4
12	65 18 S, 125 27 W	Dec. 4, '85	0.52	0.46	0.90	0.54	0.31	0.41	10.2	4.9
1–12	Overall mean		$0.74 {\pm} 0.34$	$0.61 \pm 0.13$	$0.87 {\pm} 0.27$	$0.52{\pm}0.34$	$0.33 {\pm} 0.09$	$0.41{\pm}0.08$	$6.7{\pm}2.1$	$5.8 \pm 2.5$
Wester	stern North Pacific <sup>a</sup>									
13-	22°57′N- 38°08′N	Mar. 5, '81	(0.67-3.17)	(0.53-0.90)	(0.72–1.91)	(0.34-0.94)	(0.26-0.80)	(0.14-0.56)	(1.0-7.0)	(5.0-20.0)
18	133 01 E-175 02 E	June 9, '85	$1.19 \pm 0.93$	$0.63 \pm 0.18$	$1.28 \pm 0.53$	$0.49 {\pm} 0.26$	$0.49 {\pm} 0.23$	$0.34 {\pm} 0.16$	$3.5 \pm 2.1$	$8.8 \pm 6.1$
19–	40°00'N- 45°01'N	May 16, '80	(0.25 - 3.32)	(0.48-0.93)	(0.53-1.59)	(0.41-0.49)	(0.21-0.70)	(0.30-0.37)	(1.0-4.0)	(8.0-23.0)
25	144 01 E-177 24 E	Oct. 11, '84	$1.42 \pm 1.36$	$0.67 \pm 0.23$	$1.04 \pm 0.41$	$0.44 {\pm} 0.44$	$0.50 \pm 0.18$	$0.32 \pm 0.03$	$2.5 \pm 1.2$	$17.7 \pm 5.5$
26-	43°29'N- 51°32'N	May 18, '80	(1.58-3.16)	(0.36–1.41)	(0.84-1.58)	(0.30-0.47)	(0.25-0.50)	(0.30-0.47)	(5.0-8.5)	(6.0-7.0)
31	156 38 E-179 54 E	Aug. 16, '84	$2.21 \pm 0.55$	$0.74 \pm 0.41$	$1.35 \pm 0.27$	$0.40 \pm 0.07$	$0.40 \pm 0.09$	$0.41 \pm 0.07$	$7.0 \pm 1.2$	$6.5 \pm 0.7$
Bering Sea <sup>b</sup> $a^{b}$										
32-	52°26′N- 62°00′N	Aug. 16, '85	(0.89-3.68)	(0.48-0.84)	(0.78–1.36)	(0.27-0.57)	(0.16-0.39)	(0.26-0.42)	(6.0-7.0)	(6.0-7.0)
35	175 47 E-175 00 W	Sep. 5, '85	$1.83 \pm 1.26$	$0.69 \pm 0.16$	$1.18 \pm 0.27$	$0.41 \pm 0.12$	$0.27 \pm 0.10$	$0.35 \pm 0.07$	$6.3 {\pm} 0.5$	$6.5 {\pm} 0.6$
Japan	Seaª	• •		$\begin{array}{cccccccccccccccccccccccccccccccccccc$						
36-	41°05'N- 45°08'N	June 27, '85	(1.31-3.05)	(0.47-0.96)	(1.04–1.25)	(0.30-0.75)	(0.24-0.37)	(0.31-0.41)	(3.0-4.0)	(5.0-7.1)
38	136 57 E-142 55 E	July 6, '85	$2.23 \pm 0.87$	$0.65 {\pm} 0.27$	$1.15 \pm 0.11$	$0.49 {\pm} 0.23$	$0.30 {\pm} 0.07$	$0.36 {\pm} 0.05$	$3.7 \pm 0.6$	$6.1 \pm 1.1$

Table 1. Concentrations  $(\mu g|L)$  of heavy metals in the Antarctic and other ocean waters.

<sup>a</sup> The data were cited from HONDA, 1985.

<sup>b</sup> The data were cited from FUJISE, 1987.

is emitted mainly from continental areas either naturally or anthropogenically, and the mercury is added to the sea surface by atmospheric route. On the contrary, the fact observed here that the lowest level of Hg was in the Antarctic water suggests that the amount of atmospheric Hg added to the Antarctic water is much less. This situation may also account for low concentrations of Fe and Zn in the Antarctic water. In fact, the average concentrations of Hg, Fe, and Zn in snow collected by us in Antarctica were 2–15 times lower than those in rain collected over the western North Pacific and Kuroshio current. The relationships between Hg, Fe and Zn concentrations in the snow, rain and seawater will be published elsewhere in detail.

Furthermore, the concentration of Cd in the Antarctic water  $(6.7\pm2.1\times10^{-2} \mu g/L)$ , nearly the same as those in the Bering Sea  $(6.3\pm0.5\times10^{-2} \mu g/L)$  and the area, Nos. 26-31  $(7.0\pm1.2\times10^{-2} \mu g/L)$ , Table 1) of the western North Pacific, was twice those in other waters  $(3.1\pm1.5\times10^{-2} \mu g/L)$ . This geographical distribution of Cd was generally in contrast to that of Hg, and therefore, the locational differences of Cd cannot be explained by atmospheric route as in the case of Hg. ORREN and MONTEIO (1985) examined vertical distribution of Cd concentration in the Antarctic waters, and reported that there was a surface depletion increasing to a mid-water maximum whose depth varied and below which the concentration remained nearly constant. They also reported that the surface values for Cd were higher than those found in the North Atlantic (YEATS and CAMPBELL, 1983) and the Pacific (BRULAND, 1980; BOYLE *et al.*, 1977), which may be accounted for by the upwelling of Cd-enriched deep water to the surface. This may again account for relatively high values of Cd in this study.

## 3.2. Metal concentrations in the Antarctic marine organisms

Table 2 shows the concentrations of heavy metals in the Antarctic marine organisms. The metal concentrations were generally high in liver and mid-intestinal gland tissues and low in muscle. However, highest concentration of Cd was found in kidneys of the Adélie penguin, southern minke whale and Weddell seal, and Zn, Pb, and Hg showed high concentrations in gestinal organ of the Antarctic bivalve.

In the correlation coefficients between the metal concentrations and the size of the animals (Table 3), only in the case of fishes were there some significant (p < 0.05) positive or negative correlations. The correlations were negative for Mn, Zn, Cu, Pb, and Ni in all tissues, whereas they were positive for Fe, Cd, and Hg, except for muscular Fe and Cd, and hepatic Fe and Hg. Similar correlations were also found with the Antarctic fish, *P. borchgrevinki* (HONDA *et al.*, 1983). Furthermore, in our earlier reports (HONDA *et al.*, 1986, 1987; YAMAMOTO *et al.*, 1987a), we already reported the reproductive process-related variations of certain metals in the Adélie penguin, and the age-dependent increases of Fe, Cd, and Hg concentrations in the southern minke whale and Weddell seal. YAMAMOTO *et al.* (1987b) examined seasonal and size-related changes of heavy metals in the Antarctic krill, and found no size-related change of the metal concentrations, but there was an increase of Cu concentration throughout the austral summer, *i.e.*, from December to February and elevated levels of Cd and Ni during the period from January to mid-February.

Data on heavy metals in the Antarctic plankton and fishes are scarce. SOSZKA

Species	Tissue	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Hg (×10 <sup>-1</sup>
Plankton									
Copepod	Whole	208	5.83	100	12.5	1.67	1.42	1.25	0.58
E. superba	Whole	(5.55-27.1)	(1.25 - 5.90)	(26.3-64.1)	(6.70–102)	(0.07 - 2.74)	(0.41 - 6.13)	(0.32 - 8.35)	(0.19-0.91)
n=76		14.4	3.27	44.5	54.1	0.46	1.87	1.90	0.36
Bivalve									
A. colbecki	A.m.	(48.8-59.1)	(2.50-9.20)	(44.3-73.2)	(1.51-7.94)	(0.11-3.69)	(0.33-1.73)	(1.68-28.8)	(0.13-0.81)
n=27		263	5.15	58.4	3.97	1.60	0.88	13.4	0.38
2.0–7.0 cm	M.i.g.	(453–1227)	(2.71–12.4)	(24.6-60.0)	(11.1–21.1)	(0.56-2.60)	(1.28–2.48)	(70.9–109)	(0.12-0.54)
		851	7.94	49.1	16.3	1.39	1.76	80.1	0.26
	G.o.	(42.5–308)	(1.25-8.33)	(60.4-97.4)	(3.50-12.1)	(0.77-13.3)	(0.46-2.92)	(1.43–15.2)	(0.29-1.30)
		101	4.46	86.4	5.65	4.14	1.18	4.92	0.41
	Whole	(230-880)	(1.50–11.0)	(40.0–105)	(5.50-14.6)	(1.00-3.15)	(0.68 - 2.10)	(26.0-49.0)	(0.26-0.42)
		578	8.15	83.7	10.6	2.51	1.41	34.0	0.31
Fish									
T. bernacchii	Muscle	(0.95-8.25)	(0.11-0.37)	(4.89–11.2)	(0.13-0.91)		(0.01-0.17)	(0.01-0.16)	(0.02-0.65)
n=30		2.12	0.22	7.78	0.29	—	0.07	0.05	0.17
6.8–22.4 cm	Liver	(14.9–102)	(0.31–1.40)	(15.9–110)	(0.27-6.33)	_	(0.06-0.49)	(0.08-6.18)	(0.14-2.90)
		44.9	0.81	43.2	2.00	_	0.20	1.90	0.68
	Whole	(6.93-46.5)	(0.73–1.85)	(11.0-20.6)	(0.27-0.70)	(0.04-0.19)	(0.03-0.26)	(0.06-0.34)	(0.04-0.31)
-		14.9	1.17	14.6	0.43	0.06	0.11	0.15	0.11
P. borchgrevinki	Muscle	(1.42–5.95)	(0.10-0.46)	(4.27-8.15)	(0.17–1.39)	(0.02-0.28)	(0.02-0.23)	(0.01-0.04)	(0.02-0.09)
n=22		2.84	0.24	5.65	0.43	0.12	0.08	0.02	0.05
9.5–22.5 cm	Liver	(10.0–114)	(0.42–2.94)	(22.4–34.2)	(0.92–5.88)	(0.04–0.96)	(0.04-0.66)	(0.30-2.46)	(0.05-0.26)
		43.2	1.30	28.1	2.47	0.29	0.19	0.85	0.09
	Whole	(4.04–9.25)	(0.33–1.03)	(8.73–13.7)	(0.38–1.07)	(0.02–0.31)	(0.05–0.12)	(0.01-0.12)	(0.01-0.05)
		6.51	0.61	11.1	0.65	0.15	0.08	0.06	0.03
Notothenioidei	Whole	(3.71–7.00)	(0.31-0.51)	(9.02–11.2)	(0.44–1.90)	(0.01-0.07)	(0.04-0.17)	(0.05–0.23)	(0.12-0.26)
<i>n</i> =7		5.81	0.41	10.0	1.08	0.03	0.10	0.12	0.17
11.8–18.5 cm									
Myctophid	Whole	(10.8–13.8)	(0.68–0.74)	(9.35–10.1)	(1.92–2.65)	(0.05-0.13)	(0.11-0.12)	(0.22–0.23)	(0.44-0.45)
n=2		12.3	0.71	9.73	2.29	0.09	0.12	0.23	0.45
7.5–7.7 cm									

Table 2. Concentrations (range/mean,  $\mu g/wet g$ ) of heavy metals in the Antarctic marine organisms.

.

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	10 <sup>- 1</sup> )
Bird and Mammal P. adeliaeMuscle $(109-204)$ $(0.21-0.35)$ $(18.9-27.2)$ $(2.20-3.05)$ $<0.01$ $<0.01$ $(0.04-0.46)$ $(0.09-0)$ $n=10$ 1430.3021.42.720.240.21AdultLiver $(233-1670)$ $(1.57-2.90)$ $(31.9-73.4)$ $(3.26-6.06)$ $<0.01$ $<0.01$ $(0.99-8.46)$ $(0.58-4)$ $733$ 2.1947.84.703.851.80Kidney $(162-360)$ $(0.95-2.18)$ $(29.6-71.4)$ $(2.89-4.51)$ $<0.01$ $<0.01$ $(23.8-93.4)$ $(0.69-4)$ $220$ 1.6048.53.6051.01.83Whole $(68.7-163)$ $(0.60-1.02)$ $(27.1-35.7)$ $(1.89-2.20)$ $<0.01$ $<0.01$ $(0.33-1.07)$ $(0.24-0)$ $102$ 0.8030.82.060.600.39R suptamentationMuscle $(10.5, 67.5)$ $(0.60, 0.10)$ $(6.90, 25.7)$ $(0.42, 0.78)$ $<0.01$ $(0.01, 0.20)$ $(0.04, 0.20)$	
P. adeliaeMuscle $(109-204)$ $(0.21-0.35)$ $(18.9-27.2)$ $(2.20-3.05)$ $<0.01$ $<0.01$ $(0.04-0.46)$ $(0.09-0)$ $n=10$ 143 $0.30$ $21.4$ $2.72$ $0.24$ $0.21$ AdultLiver $(233-1670)$ $(1.57-2.90)$ $(31.9-73.4)$ $(3.26-6.06)$ $<0.01$ $<0.01$ $(0.99-8.46)$ $(0.58-4)$ $733$ $2.19$ $47.8$ $4.70$ $3.85$ $1.80$ Kidney $(162-360)$ $(0.95-2.18)$ $(29.6-71.4)$ $(2.89-4.51)$ $<0.01$ $<0.01$ $(23.8-93.4)$ $(0.69-4)$ $220$ $1.60$ $48.5$ $3.60$ $51.0$ $1.83$ Whole $(68.7-163)$ $(0.60-1.02)$ $(27.1-35.7)$ $(1.89-2.20)$ $<0.01$ $<0.01$ $(0.33-1.07)$ $(0.24-0)$ $102$ $0.80$ $30.8$ $2.06$ $0.60$ $0.39$	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	.33)
AdultLiver $(233-1670)$ $(1.57-2.90)$ $(31.9-73.4)$ $(3.26-6.06)$ $<0.01$ $<0.01$ $(0.99-8.46)$ $(0.58-4)$ $733$ $2.19$ $47.8$ $4.70$ $3.85$ $1.80$ Kidney $(162-360)$ $(0.95-2.18)$ $(29.6-71.4)$ $(2.89-4.51)$ $<0.01$ $<0.01$ $(23.8-93.4)$ $(0.69-4)$ $220$ $1.60$ $48.5$ $3.60$ $51.0$ $1.83$ Whole $(68.7-163)$ $(0.60-1.02)$ $(27.1-35.7)$ $(1.89-2.20)$ $<0.01$ $<0.01$ $(0.33-1.07)$ $(0.24-0)$ $102$ $0.80$ $30.8$ $2.06$ $0.60$ $0.39$ B suptamentationMuscle $(10.5, 67, 5)$ $(0, 60, 0, 19)$ $(6, 90, 25, 7)$ $(0, 42, 0, 78)$ $<0.01$ $(0, 91, 0, 20)$ $(0, 94, 0, 91, 0, 20)$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.65)
Kidney $(162-360)$ $(0.95-2.18)$ $(29.6-71.4)$ $(2.89-4.51)$ $<0.01$ $<0.01$ $(23.8-93.4)$ $(0.69-4)$ $220$ $1.60$ $48.5$ $3.60$ $51.0$ $1.83$ Whole $(68.7-163)$ $(0.60-1.02)$ $(27.1-35.7)$ $(1.89-2.20)$ $<0.01$ $<0.01$ $(0.33-1.07)$ $(0.24-0)$ $102$ $0.80$ $30.8$ $2.06$ $0.60$ $0.39$ B support that $(10.5, 67.5)$ $(0.60, 0.19)$ $(6.90.25.7)$ $(0.42.0.78)$ $<0.01$ $(0.01.0.20)$ $(0.04.0.20)$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.02)
Whole $(68.7-163)$ $(0.60-1.02)$ $(27.1-35.7)$ $(1.89-2.20)$ $<0.01$ $<0.01$ $(0.33-1.07)$ $(0.24-0)$ $102$ $0.80$ $30.8$ $2.06$ $0.60$ $0.39$ R sourcestrate       Muscle $(10.5, 67.5)$ $(0.60, 0.19)$ $(6.90, 25.7)$ $(0.42, 0.78)$ $<0.01$ $(0.01, 0.20)$ $(0.04, 0.20)$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.47)
$R_{\text{contended}}$ Muscle (10.5.67.5) (0.60.0.10) (6.00.25.7) (0.42.0.78) <0.01 <0.01 (0.01.0.20) (0.04.0.	
<b><i>B. acuiorosiraia</i></b> Muscle $(10.3-07.3)$ $(0.00-0.19)$ $(0.30-23.7)$ $(0.42-0.78)$ $< 0.01$ $< 0.01$ $(0.01-0.20)$ $(0.04-0.19)$	.62)
n=37 35.5 0.12 9.64 0.54 0.05 0.19	
1-45.5 y Liver $(35.2-4482)$ $(1.60-4.89)$ $(30.2-70.1)$ $(4.25-11.2)$ <0.01 <0.01 (2.32-41.7) (0.26-1)	.63)
880 2.93 46.7 6.03 15.4 0.72	
Kidney (20.2–114) (0.61–1.37) (23.3–60.1) (1.87–3.75) $<0.01$ (3.50–85.0) (0.05–1	. 32)
52.9 0.91 32.7 2.54 21.2 0.33	
Whole $(12.3 - 149)$ $(0.18 - 0.40)$ $(14.6 - 50.4)$ $(0.59 - 1.10)$ $< 0.01$ $< 0.01$ $(0.10 - 0.90)$ $(0.03 - 0.01)$	. 50)
56.2         0.27         20.1         0.73         0.31         0.15	
L. weddellii Muscle $(237-267)$ $(0.13-0.14)$ $(33.7-39.6)$ $(0.85-1.02)$ < 0.01 < 0.01 $(0.01-0.03)$ (1.10-1	.60)
<i>n</i> =2 252 0.14 36.7 0.94 0.02 1.40	•
11.9-13 y Liver $(389-940)$ $(1.80-1.86)$ $(41.7-47.0)$ $(15.0-25.8)$ $<0.01$ $<0.01$ $(0.96-1.31)$ $(31.0-8)$	5.0)
665 1.83 44.4 20.4 1.14 58.0	
Kidney (159-618) (0.90-1.12) (27.4-30.7) (5.12-11.0) <0.01 <0.01 (2.89-9.93) (3.80-9	. 60)
389 1.01 29.1 8.06 6.41 6.70	
Whole $(141-229)$ $(0.15-0.20)$ $(19.7-20.1)$ $(1.08-1.36)$ < 0.01 < 0.01 $(0.05-0.10)$ $(1.20-2)$	. 50)
185 0.18 19.9 1.22 0.08 1.90	

Table 2 (continued).

A.m.: Adductor muscle, M.i.g.: Mid-intestinal gland, G.o.: Gentinal organ. The concentrations of heavy metals in the copepod, krill, and bivalve are shown as  $\mu$ g/g on dry basis. The contents of moisture in the copepod, krill, and bivalve were 82.0%, 77.4±0.93% and 77.5±2.55%, respectively. The whole body concentrations of metals in the fishes, penguin, seal, and minke whale were calculated from the weights of organs and tissues and their respective metal concentrations.

Heavy Metals in Antarctic Marine Ecosystem

• ....

	icitg int					
	Species	Tissue	Fe	Mn	Zn	Cu
	A. colbecki	Whole	n.s.	n.s.	n.s.	n.s.
	E. superba	Whole	n.s.	n.s.	n.s.	n.s.
	T. bernacchii	Whole	n.s.	-0.610*	-0.612*	0.563*
		Muscle	-0.700*	-0.658*	n.s.	-0.551*
		Liver	-0.602*	-0.598*	-0.630*	-0.901**
_	Notothenioidei	Whole	n.s.	-0.680*	-0.590*	-0.612*
	Species	Pb	Ni	Cd	Hg	
	A. colbecki	n.s.	n.s.	n.s.	n.s.	
	E. superba	n.s.	n.s.	n.s.	n.s.	
	T. bernacchii	-0.801**	-0.699**	0.598*	0.700**	
		-0.590*	-0.590*	-0.602*	n.s.	
		-0.610*	-0.612*	0.500*	n.s.	
	Notothenioidei	-0.700*	-0.698*	0.586*	0.598*	

Table 3. Correlation coefficients between the metal concentrations in organisms and the body length.

n.s.: Not significant.

\*: Significant level, p < 0.05.

\*\*: Significant level, p < 0.01.

et al. (1981) examined some trace elements in the Antarctic krill collected at the Scotia Sea and in the areas  $(52-69^{\circ}S, 92-26^{\circ}W)$  of the Bellingshausen Sea and the Weddell Sea, and reported that their concentrations were found to be: Zn-123 (65.0-370), Pb-3.4 (0.8–11.5), and Cd-2.5 (1.24–4.6)  $\mu g/dry g$ . The value for Cd was in the same range as our results, while for Zn and Pb the values were about 3 and 6 times higher, respectively. Also, according to STOEPPLER and BRANDT (1979), the heavy metal concentrations ( $\mu$ g/wet g) in the Antarctic krill with shells collected at the Scotia Sea on November 1, 1978, were Cu-6.60 (2.90-11.0), Ni-0.30 (0.24-0.37), Cd-0.17 (0.07-0.36), and Hg-<0.02. The values for Cu, Ni, and Cd were significantly (p < 0.05) lower than those in this study, which might be because the krill used in the study of STOEPPLER and BRANDT was collected in the early period of the austral summer, and so might have contained relatively low concentrations of Cu, Ni, and Cd. They also reported the concentrations of metals in fillets of three species of fish, Noto thenia rossi, Notothenia gibberifrons and Dissostichus, and their concentrations ( $\mu$ g/wet g) were as follows: Cu-(0.13-0.22), Pb-(0.07-0.15), Ni-<0.1, Cd-(0.002-0.005), and Hg-(0.012-0.070). The value for Cd was about one order of magnitude lower than those found in this study.

When comparing the metal levels among birds and marine mammals, information on the age and/or growth stage is essential, because of the age- and growth-related variations of metal concentrations (HONDA, 1985). In the present study, the concentrations of Cd and Hg in the muscle and liver tissues of the southern minke whales and Weddell seals were similar to those in the Weddell seals and Leopard seals (*Hydrurga leptonyx*) previously reported by WAGEMANN and MUIR (1984), but the value for Hg was 1–2 order of magnitude lower than those in the sperm whale (*Physeter catodon*) reported by NAGAKURA *et al.* (1974). Furthermore, YOSHIYAMA *et al.* (1979) and MISHIMA *et al.* (1977) reported the concentrations of Zn, Cu, Pb, Cd, and Fe in the muscle, liver and kidney tissues of two adult Adélie penguins, and young and adult Weddell seals. Their values for Pb (0.015–0.03  $\mu$ g/wet g) were higher than those in our results (<0.01  $\mu$ g/wet g), while for Cd the values (<0.005–0.002  $\mu$ g/wet kidney g of the Adélie penguin) were about 4 order of magnitude lower compared with those (23.8–93.4  $\mu$ g/wet kidney g of the Adélie penguin) found in this study.

### 3.3. Bioaccumulation of heavy metals

For understanding bioaccumulation phenomena of heavy metals, consideration of metal concentrations in the whole body basis is essential. So the whole body concentrations of heavy metals in the Antarctic marine organisms were calculated from the weights of organs and tissues and their concentrations, and the results are shown in Table 2.

The average whole body concentrations of metals were, as a whole, in the order of  $Zn \cdot Fe > Cu \cdot Mn > Cd > Pb \cdot Ni > Hg$ , and this order agreed nearly with those in the Antarctic seawater (Table 1). This suggests that accumulations of metals in marine organisms are affected by metal concentrations in the seawaters. When bioaccumulation factors of the metals were calculated from the concentrations of metals in the whole body of the organisms and the seawaters (Fig. 2), their values were high with Fe ( $4.4 \times 10^3 - 2.5 \times 10^5$ ) and Zn ( $1.0 \times 10^4 - 3.6 \times 10^4$ ), and continued in order to Cd ( $9.0 \times 10^2 - 1.1 \times 10^5$ ), Hg ( $1.2 \times 10^3 - 3.3 \times 10^4$ ), Cu ( $8.3 \times 10^2 - 2.4 \times 10^4$ ), Mn ( $3.0 \times 10^2 - 3.0 \times 10^3$ ), Pb ( $3.0 \times 10 - 1.7 \times 10^3$ ) and Ni ( $2.0 \times 10 - 1.0 \times 10^3$ ). Although this order was nearly the same as those in the western North Pacific and Bering Sea ecosystems



Fig. 2. Bioconcentration factors of heavy metals in the Antarctic marine organisms.
1: Copepod, 2: E. superba, 3: A. colbecki, 4: T. bernacchii, 5: P. borchgrevinki, 6: Notothenioidei, 7: Myctophid, 8: P. adeliae, 9: B. acutorostrata, 10: L. weddellii.



Fig. 3. Bioaccumulation process of Hg in the Antarctic (1) and western North Pacific (0) ecosystems.

Horizontal and vertical lines indicate the average and the range, respectively. Data for the western North Pacific were cited from HONDA, 1985.

previously reported by HONDA (1985) and FUJISE (1987), the values for Hg were about two order of magnitude lower than those in the western North Pacific.

It is well known that a bioaccumulation process of Hg depends upon food chain, and high trophic animals contain higher content of Hg than that in lower trophic animals. Such bioaccumulation process was found in both the western North Pacific and Antarctic marine ecosystems (Fig. 3). But, when compared to the western North Pacific, the Antarctic ecosystem is relatively simple in the food web and short in the length of food chain with krill as key species. This accounts for the lower bioaccumulation factor of Hg in the Antarctic organisms compared with those in the western North Pacific. Also, low absolute values of Hg in the Antarctic organisms are due to a low concentration of Hg ( $5.8 \pm 2.5$  ng/L) in the Antarctic seawater than those ( $17.7 \pm$ 5.5 ng/L) in the western North Pacific.

The bioaccumulation factors of metals varied widely with animal species (Fig. 2). Mn, Ni, and Pb showed higher values in the low trophic animals, such as planktonic copepod, krill and bivalve, and its trend is in great contrast to the bio-accumulation process of Hg mentioned above. Furthermore, Fe, Zn, Cu, and Cd showed species- and metal-specific accumulations: The bioaccumulation factor of Fe was high in the bivalve, Adélie penguin and marine mammals, and low in the

plankton and fishes; high value for Zn was found in the Adélie penguin and marine mammals; and high values for Cd and Cu were in the bivalve. These bioaccumulation factors were nearly the same as those in animals from other ocean waters, even though they contained different concentrations of metals (HONDA, 1985). This probably mean that the accumulations of Fe, Zn, Cu, and Cd are species-specific in these animals. However, the bioaccumulation factor of Fe in the Antarctic fishes was about one order of magnitude lower than those found in fishes from other ocean waters (HONDA, 1985), which is due to a low concentration of blood cell in the Antarctic fishes for adapting themselves to the cold water condition. Also, the bioaccumulation factor of Cd in the fishes, Adélie penguin and marine mammals were 1.5-2 times higher compared with those in the western North Pacific, which can be explained by relatively high concentration of Cd in the krill, the food item of these animals.

Consequently, bioaccumulations of heavy metals in the Antarctic ecosystem are characterized by a high bioaccumulation of Cd and low bioaccumulation of Hg based on the short food chain with krill as key species, and also by a low bioaccumulation of Fe in fishes as a result of adaptation to the cold water condition.

### Acknowledgments

Materials used in the present report were obtained from the 22nd Japanese Antarctic Research Expedition (JARE-22) and Japanese Antarctic whaling expeditions. The authors are grateful to Prof. Y. YOSHIDA, leader of JARE-22, National Institute of Polar Research, for his kind arrangement, and also to Dr. S. OHSUMI and Mr. S. WADA, Far Seas Fisheries Research Laboratory, for offering the tissue samples of minke whale. We also wish to acknowledge the assistances of Mr. M. SATO, chief of meat production of NISSHIN MARU No. 3, Nippon Kyodo Hogei Ltd, and Mr. N. KURIHARA, Radio Research Laboratories, and also other members of the whaling expedition and JARE-22 for their cooperation. This work was supported, in part, by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (Project Nos. 58030020, 59030053 and 60030060).

#### References

- BEST, P. B. (1982): Seasonal abundance, feeding, reproduction, age and growth in minke whales off Durban (with incidental observation from the Antarctic). Rep. Int. Whaling Comm., 32, 759-786.
- BOYLE, E. A., SCLATER, F. R. and EDMOND, J. M. (1977): The distribution of dissolved copper in the Pacific. Earth Planet. Sci. Lett., 37, 38-54.
- BRULAND, K. W. (1980): Oceanographic distributions of cadmium, zinc, nickel and copper in the North Pacific. Earth Planet. Sci. Lett., 47, 176–198.
- DENTON, G. R. W., MARSH, H., HEINSOHN, G. E. and BARDON-JONES, C. (1980): The unusual metal status of the dugong, *Dugong dugon*. Mar. Biol., **57**, 201–219.
- FUJISE, Y. (1987): Hokubu Kita-Taiheiyô san ishiiruka no jûkinzoku chikuseki ni kansuru kenkyû (Study on heavy metal accumulations in dall's porpoises from the northern North Pacific).
  Ph. D. thesis, Hokkaido Univ., 109 p.
- HONDA, K. (1985): Kaisan-honyûrui no jûkinzoku no seibutsu nôshuku ni kansuru kenkyû (Study on bioaccumulations of heavy metals in marine mammals). Ph. D. thesis, Univ. Tokyo,

101 p.

- HONDA, K., SAHRUL, M., HIDAKA, H. and TATSUKAWA, R. (1983): Organ and tissue distribution of heavy metals, and their growth-related changes in Antarctic fish, *Pagothenia borchgrevinki*. Agric. Biol. Chem., **47**, 2521–2532.
- HONDA, K., YAMAMOTO, Y., HIDAKA, H. and TATSUKAWA, R. (1986): Heavy metal accumulations in Adélie penguin, *Pygoscelis adeliae*, and their variations with the reproductive processes. Mem. Natl Inst. Polar Res., Spec. Issue, 40, 443-453.
- HONDA, K., YAMAMOTO, Y., KATO, H. and TATSUKAWA, R. (1987): Heavy metal accumulations and their recent changes in southern minke whales *Baraenoptera acutorostrata*. Arch. Environ. Contam. Toxicol., 16, 209–216.
- IWASHIMA, K., FUJITA, M., ABIKO, T. and YAMAGATA, N. (1977): Syowa Kiti shûhen no biryô genso no bunpu (I); Taikichû no ryûshi-jô hiso ganryô (Distribution of trace elements around Syowa Station (I); Particulate arsenic content). Nankyoku Shiryô (Antarct. Rec.), 59, 2–9.
- KAWABUCHI, K., KANKE, M., MURAOKA, T. and YAMAUCHI, M. (1976): Ion-exchange concentration on a chelating resin and atomic absorption spectrophotometric determination of heavy metals in geochemical samples. Bunseki Kagaku (Jpn. Anal.), 25, 213–218.
- KNOX, G. A. (1970): Antarctic marine ecosystems. Antarctic Ecology, Vol. 1, ed. by M. W. HOLDGATE. London, Academic Press, 69–96.
- LANDY, M. P. and PEEL, D. A. (1981): Short-term fluctuations in heavy metal concentrations in Antarctic snow. Nature, 291, 144-146.
- MISHIMA, M., YAMAGATA, N. and TORII, T. (1977): Syowa Kiti shûhen ni seisoku suru seibutsu no seitai-nai kinzoku bunseki (Concentrations of trace metals in tissues of several animals around Syowa Station). Nankyoku Shiryô (Antarct. Rec.), 58, 145–153.
- NAGAKURA, K., ARIMA, S., KURIHARA, M., KOGA, T. and FUJITA, T. (1974): Mercury content in whales. Bull. Tokai Reg. Fish. Res. Lab., 78, 41-46.
- NISHIMURA, M., KONISHI, S., MATSUNAGA, K., HATA, K. and KOSUGA, T. (1983): Mercury concentration in the ocean. J. Oceanogr. Soc. Jpn., 39, 295–300.
- NRIAGU, J. O. (1979): Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature, 279, 409-411.
- ORREN, M. J. and MONTEIO, P. M. S. (1985): Trace element geochemistry in the Southern Ocean. Antarctic Nutrient Cycles and Food Webs, ed. by W. R. SIEGFRIED *et al.* Berlin, Springer, 30–37.
- SANO, M., NAKAI, N. and TORII, T. (1977): Nurume-ike no biryô kinzoku no enchoku bunpu (Vertical distributions of some trace metals in Lake Nurume, Antarctica). Nankyoku Shiryô (Antarct. Rec.), 58, 108-115.
- SOSZKA, G. J., SUPLIŃSKA, N. M., BARAŃSKI, A., GRZYBOWSKA, D. and PIETRUSZEWSKI, A. (1981): Trace metals, fluorine and radionuclides in antarctic krill *Euphausia superba* Dana. Pol. Polar Res., 2, 109–117.
- STOEPPLER, M. and BRANDT, K. (1979): Comparative studies on trace metal levels in marine biota. II. Trace metals in krill, krill products, and fish from the Antarctic scotia Sea. Z. Lebensm. Unters. Forsch., 169, 95–98.
- WAGEMANN, R. and MUIR, D. C. G. (1984): Concentrations of heavy metals and organochlorines in marine mammals of Northern waters; Overview and evaluation. Can. Tech. Rep. Fish. Aquat. Sci., **1279**, 1–97.
- WATANUKI, K., TORII, T., MURAYAMA, H., HIRABAYASHI, T., SANO, M. and ABIKO, T. (1977): Geochemical features of Antarctic lakes. Nankyoku Shiryô (Antarct. Rec.), 59, 18–25.
- YAMAMOTO, Y., HONDA, K., HIDAKA, H. and TATSUKAWA, R. (1987a): Tissue distribution of heavy metals in Weddell seals (Leptonychotes weddelli). Mar. Pollut. Bull., 18, 164–169.
- YAMAMOTO, Y., HONDA, K. and TATSUKAWA, R. (1987b): Heavy metal accumulation in Antarctic krill Euphausia superba. Proc. NIPR Symp. Polar Biol., 1, 198-204.
- YEATS, P. A. and CAMPBELL, J. A. (1983): Nickel, copper, cadmium and zinc in the north west Atlantic ocean. Mar. Chem., 12, 43-58.
- YOSHIDA, Y. and MUROZUMI, M. (1977): Mizuho hyôshô no suigin no rittai bunpu (Mercury profile

of Mizuho ice sheet, Antarctica). Nankyoku Shiryô (Antarct. Rec.), 59, 26-29.

YOSHIYAMA, T., TOKUOKA, S., KODAMA, T., AKAMIZU, H., NISHIDA, T., ETO, R., UMISA, H., MORIMOTO, K., NAKAMURA, T. and KODAMA, Y. (1979): Syowa Kiti syûhen no azarashi to pengin no seitai-nai jûkinzoku to PCB no bunseki (Concentrations of trace heavy metals and PCB in tissues of Weddell seal and Adélie penguin around Syowa Station). Hiroshima Igaku (J. Hiroshima Med. Assoc.), 32, 50-53.

(Received May 22, 1987; Revised manuscript received August 12, 1987)

.