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Environmental Monitoring of Trace Elements Using Marine Mammals as Bioindicators —Species-specific Accumulations and Temporal Trends—

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Abstract—The distribution of 21 trace elements (V, Cr, Mn, Co, Cu, Zn, Se, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Tl, Hg, Pb, Bi) were investigated in the liver of melon-headed whale (*Peponocephala electra*) stranded and collected along Japanese coasts during 1982–2006. Mean Cd, total-mercury (T-Hg) and organic mercury (O-Hg) levels were 37.8 μg g^{-1} dry wt., 493 μg g^{-1} dry wt. and 21.4 μg g^{-1} dry wt., respectively. These metal concentrations were relatively high in this species than those in other marine mammals. As for temporal trend analysis, 10 element levels (V, Cr, Mn, Co, Cu, Zn, Sr, Mo, Cs, O-Hg) in the liver increased temporally.

Keywords: mercury, marine mammals, rare metals, temporal trends

INTRODUCTION

Increasing human activities on global scale lead to the release of various trace elements into the environment. Cetaceans, pinnipeds and large-size fishes which are in higher trophic level accumulate multiple chemical pollutants. The odontocete, melon-headed whale, inhabits open seas between the subtropics and the temperate zone, this species may be an available bioindicator for investigating the expansion of trace element pollution. In the present study, the status of global contamination and temporal and spatial distribution of trace elements were elucidated, and the effect of human activities in open seas was evaluated utilizing the samples of melon-headed whales stocked in *es*-BANK of Ehime University, Japan.

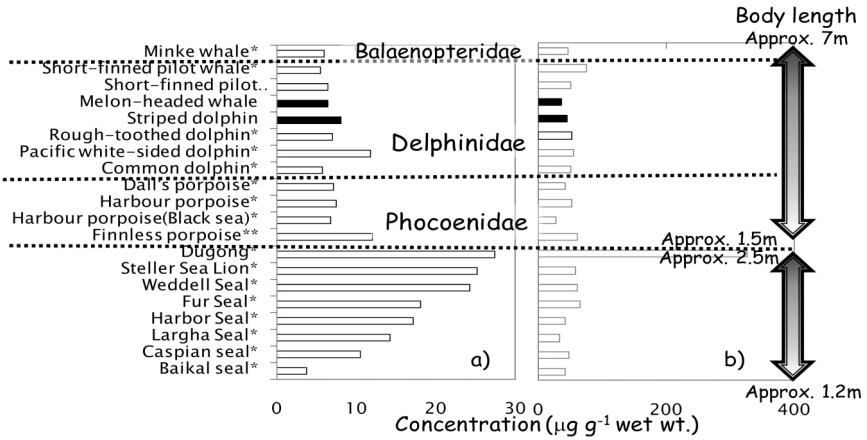

Fig. 1. Comparison of a) Cu and b) Zn concentrations in the liver of marine mammals.

MATERIALS AND METHODS

Samples

Totally 39 adult melon-headed whales (*Peponocephala electra*) (male: n = 16, female: n = 23) were collected at 3 coastal areas in Japan (Miyazaki, Ibaraki and Chiba) during 1982–2006. The body length of the specimens ranged from 211 to 270 cm and the mean value was 240 cm. All samples were packed in clean polyethylene bags and were kept at –20°C in the Environmental Specimen Bank (*es*-BANK) at Center for Marine Environmental Studies (CMES), Ehime University, Japan (Tanabe, 2006) until chemical analyses.

Chemical analysis of trace elements

Twentyone elements (V, Cr, Mn, Co, Cu, Zn, Se, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Tl, Hg, Pb and Bi) were measured according to Ikemoto *et al.* (2004) with slight modification. Liver tissues were dried at 80°C for 16 h and uniformly homogenized. After weighting about 0.20 g of the dried fine sample into a Teflon vial, 3.5 ml of HNO_3 was added and pre-digested at room temperature for overnight, then digested in a closed microwave digestion system. Twenty trace elements (V, Cr, Mn, Co, Cu, Zn, Se, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Tl, Pb and Bi) were measured by ICP-MS (HP4500, Hewlett-Packard, Avondale, PA, USA). Mercury concentration was determined with CV-AAS (Model HG-3000, Sanso, Tsukuba, Japan). Standard reference materials, SRM1577b (bovine liver; National Institute of Standards and Technology, Gaithersburg, MD, USA) and DOLT-3 (National Research Council Canada, Ottawa, ON, Canada), were used to assess the accuracy of the analysis. Recoveries of all the elements ranged from 76.5–119% of the certified values.

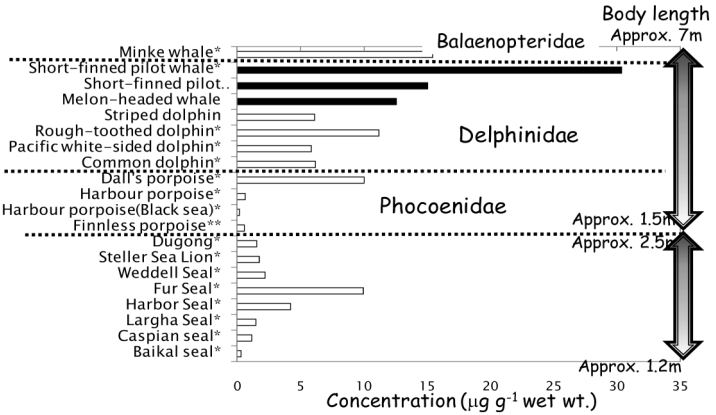

Fig. 2. Comparison of mean Cd concentrations in the liver of marine mammals.

Organic Hg concentration was determined with CV-AAS with a modified method of Uthe *et al*. (1972). Briefly, dried fine samples were mixed with 10 ml of 0.1M $CuSO_4$ and 5 ml of 3M acidic NaBr to release O-Hg followed by extraction of O-Hg into the toluene phase. Part of the toluene phase was removed, and 0.005M $Na_2S_2O_3$ 2 ml was added to it. The aqueous phase of $Na_2S_2O_3$ was removed and digested with HNO_3. The accuracy of the method was assessed by using standard reference material, DORM2 (National Research Council Canada, Ottawa, ON, Canada). The recovery of O-Hg ranged from 99.8 to 101%.

Statistical analysis

The data were compared regarding temporal trends using the Mann-Whitney U-test, p-value < 0.05 was considered statistically significant. All of the statistical analyses were executed by the Statcel 2 program (Yanai, 2004).

RESULTS AND DISCUSSION

Species specific accumulation of trace elements in marine mammals

Trace element levels in the liver of melon-headed whale were compared with those of 19 marine mammals (Horai *et al*., 2006). The mean Cu level was higher in pinnipeds than in cetaceans. Moreover, the mean level was higher in the species which has larger body length in pinnipeds (Fig. 1a). With regard to Zn level, it was the highest in dugong. The mean concentration in the liver of dugong was 326 μg g^{-1} WW, whereas it was 37.1 μg g^{-1} WW in the liver of melon-headed whale (Fig. 1b). This value was much higher than in other species. Dugong is the only herbivore among the marine mammals investigated. Therefore food habit may be reflected on Zn level. Mean Cd level in the liver of melon-headed whale was 12.6 μg g^{-1} WW. As shown in Fig. 2, the food habit of the species which have high Cd

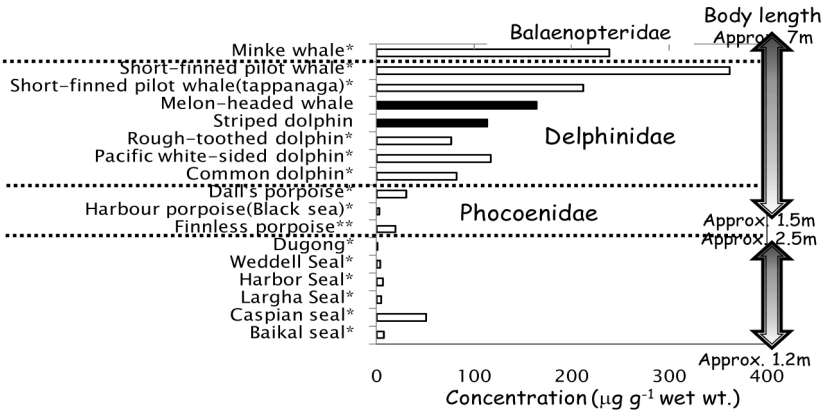

Fig. 3. Mean concentrations of T-Hg in the liver of marine mammals. *Unpublished data; **Furukawa (2005).

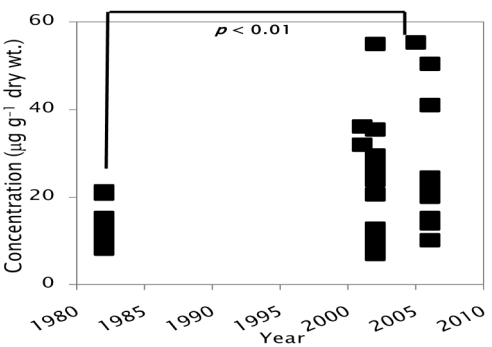

Fig. 4. Temporal trend of O-Hg level in the liver of melon-headed whale.

in the liver such as short-finned pilot whale and melon-headed whale, are cephalopods. Cadmium level in cephalopods is relatively higher than that in fish (Agusa *et al*., 2005; Bustamante *et al*., 2008). Therefore Cd concentration in a body may be reflected the food habit. On the other hand, mean T-Hg level in liver may be reflected on body length (Fig. 3). The mean T-Hg level high ordered short-finned pilot whale, melon-headed whale and striped dolphin in delphinidae. This order was same to body length. Moreover, T-Hg level was higher in delphinidae than in phocoenidae, and the level was higher in cetaceans which has no fur than that in pinnipeds which has fur. Mercury level may also be depended on fur because fur is an organ to excrete Hg from the body.

Temporal trend analysis of trace elements

With regard to temporal trend analysis, Co and Ag levels in the liver of melon-headed whale and world's production of these metals. These two metal concentrations significantly increased in this species as human activities. Moreover level of O-Hg which is known for its marked increase of emission from developing Asian countries also increased in this species temporally (Fig. 4).

In conclusion, Cd level in the liver of melon-headed whale was high as its diets is mainly cephalopods. Total Hg level was relatively higher in cetaceans which has no fur than in pinnipeds which has fur. It indicates that fur may play a major role on Hg excretion by molting. With regard to temporal trend analysis of trace element in the liver of melon-headed whale, Co and Ag concentrations increased temporally, and the patterns were consistent with world production of these metals. Furthermore, O-Hg level also increased temporally.

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