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Bioaccumulation of Trace Elements in Marine Organisms from Deep-Waters of Off-Sanninn and Off-Hokuriku, Japan

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Abstract—Twenty seven trace elements (Li, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Tl, Hg, Pb, Bi) and stable isotope ratios (δ^{13}C and δ^{15}N) were measured in deep sea organisms from Off-Sanninn and Off-Hokuriku, Japan to evaluate the trophic transfer of these elements. Concentrations of Al, Fe, In, Sb and Ba were positively correlated with δ^{15}N values suggesting that these elements were plausibly bioaccumulated through food web in the Off-Sanninn region. On the other hand, negative correlation between trace element concentrations and δ^{15}N values was not observed in the present study. This is an opposite trend compared with the previous studies in which many trace elements showed negative correlation with δ^{15}N values in Sagami Bay and Tohoku Bay. When only crustacean species were considered, concentrations of Al, V, Fe, Co, Mo, Ag, Sb and Pb were positively correlated with δ^{15}N values. This result suggests positively correlated with δ^{15}N values. This result suggests that these heavy metals are bioaccumulated through food web in crustacean species in both Off-Sanninn and Off-Hokuriku. Our results suggest possible ecotoxicological risk by these heavy metals with their increasing discharge to the marine environment.

Keywords: trace elements, bioaccumulation, stable isotope ratios (δ^{13}C and δ^{15}N), Japan Sea

INTRODUCTION

In recent years, human activities have emitted various trace elements into ambient environments (Pacyna *et al.*, 2001). The impact on the ecosystems by toxic elements is of great concern. Deep-sea plays a major role as the final reservoir and sink for environmental contaminants (Woodwell *et al.*, 1971). Moreover, deep-sea has a unique ecosystem, where the elements possibly bioaccumulate through food web. Hence, evaluating the behavior of trace elements in deep-sea ecosystem is very important to assess their ecotoxicological risk on marine organisms. There are several studies on the bioaccumlation of trace elements in marine ecosystems (Toyoshima *et al.*, 2007; Eric *et al.*, 2009; Hayase *et al.*, 2009; Asante *et al.*, 2010). Nevertheless general bioaccumulation pattern of heavy metals in marine organisms has not been established. Therefore, it is necessary to accumulate data from various marine ecosystems.

Stable isotopes have been increasingly employed to evaluate food web structure and energy pathways in aquatic ecosystems (Power *et al.*, 2002; Campbell *et al.*, 2003, 2004, 2005). $\delta^{15}N$ is an indicator of trophic level, while $\delta^{13}C$ is used to identify carbon sources in the food web (Wada *et al.*, 1991). If trophic level increases 1 level, $\delta^{15}N$ increases 3.4‰ and $\delta^{13}C$ increases 1‰ (Wada *et al.*, 1991). Stable isotopes can also be used to estimate the rate of biomagnification of a chemical across the entire food web. Therefore, the present study was conducted to evaluate the basic structure of a food web using $\delta^{15}N$ and $\delta^{13}C$ in the Off-Sanninn and Off-Hokuriku ecosystems and to discuss the trophic transfer of 27 trace elements in the biota of the ecosystems.

MATERIALS AND METHODS

Samples

Various deep-sea organisms, comprising demersal fishes, pelagic fish, crustaceans, cephalopods and bivalves were collected from Off-Sanninn and Off-Hokuriku, Japan, in May–June 2009 and July–September 2010. The collecting depth was 200 to 2100 m. Muscle tissues were collected from each organism and used for analysis.

Chemical analysis

Trace elements

Samples were freeze-dried and then digested in a microwave oven using nitric acid in a polytetrafluoroethylene (PTFE) tube. Concentrations of 26 trace elements (Li, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Tl, Pb and Bi) were measured by inductively coupled plasma-mass spectrometer (ICP-MS). Mercury concentration was determined by cold vapor atomic absorption spectrometer (CV-AAS).

Stable isotopes

Biological samples were dried for 24 hours at 60°C and powdered. For carbon isotope analysis, samples were treated with a 2:1 chloroform-methanol solution to remove lipid. Stable carbon and nitrogen isotopes were measured using a stable isotope ratio mass spectrometer (IR-MS).

RESULTS AND DISCUSSION

Food web structure

Demersal fishes and large crustaceans generally showed higher $\delta^{15}N$ than

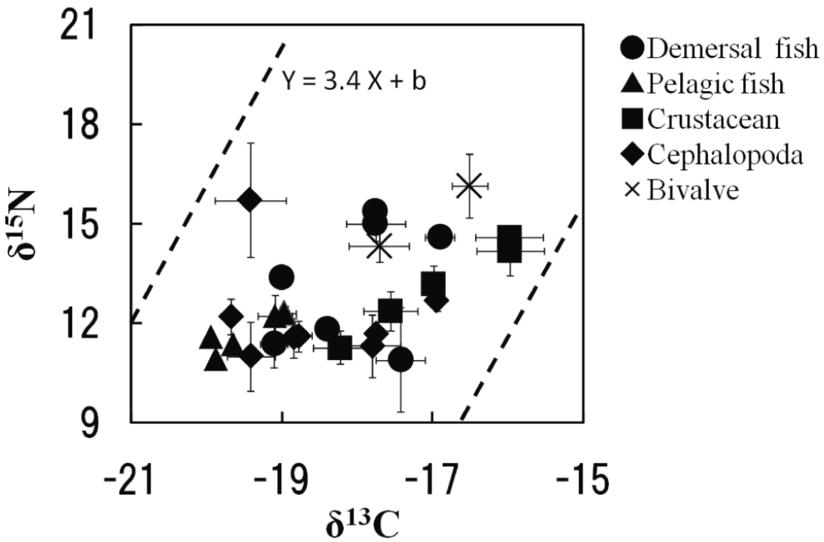

Fig. 1. Comparison of nitrogen vs. carbon delta values of deep-sea organisms collected from Off-Sanninn (average ± S.D.).

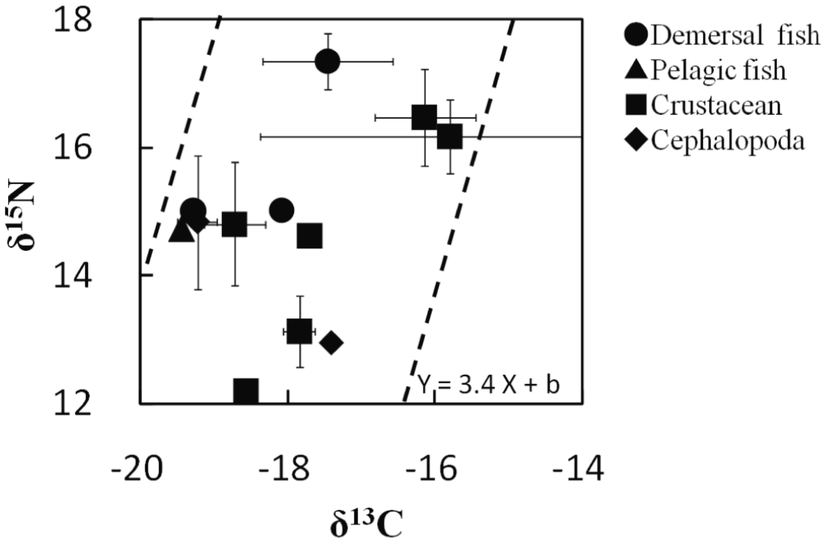

Fig. 2. Comparison of nitrogen vs. carbon delta values of deep-sea organisms collected from Off-Hokuriku (average ± S.D.).

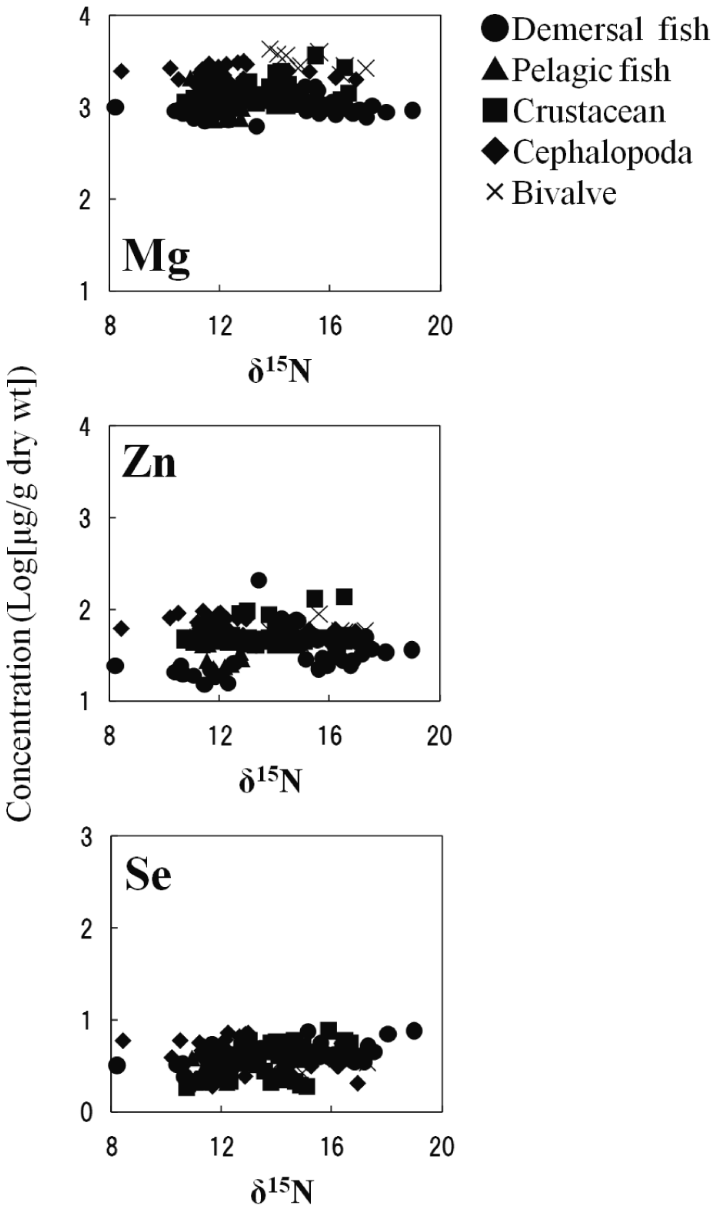

Fig. 3. Relationships between δ^{15}N and concentrations of trace elements in marine organisms in Sanninn (homeostasic type).

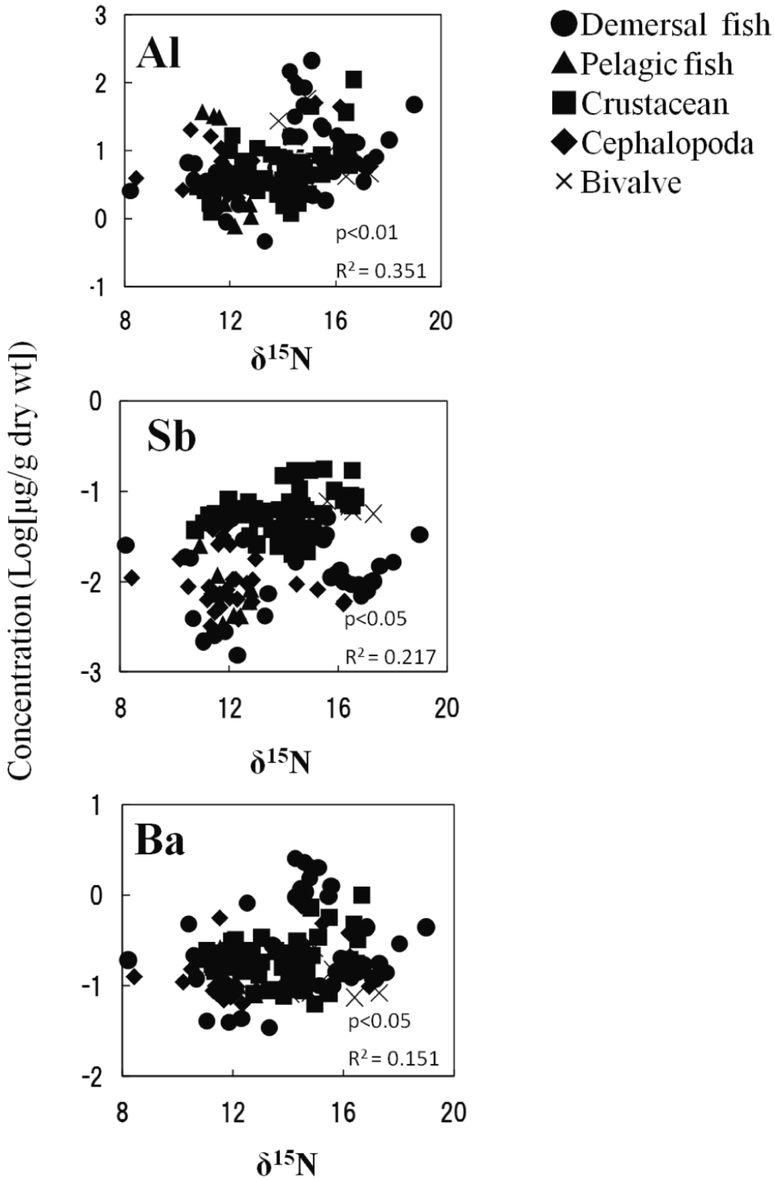

Fig. 4. Relationships between δ^{15}N and concentrations of trace elements in marine organisms in Sanninn (bioaccumulation type).

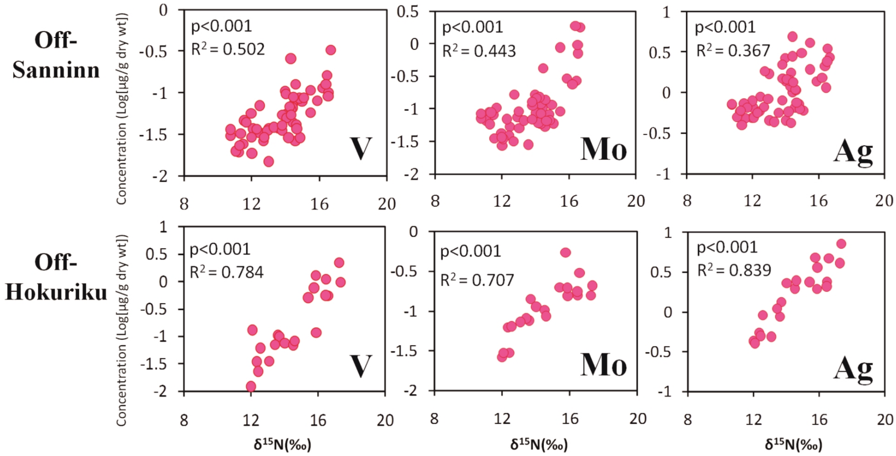

Fig. 5. Relationships between δ^{15}N and concentrations of trace elements in crustacean.

pelagic fishes, small crustaceans and cephalopods in the Off-Sanninn region. From the ranges of δ^{15}N observed in this study, demersal fishes and large crustaceans were from 3rd to 4th order consumers, whereas pelagic fishes, small crustaceans and cephalopods were 1st to 2nd order consumers. The δ^{15}N and δ^{13}C were positively correlated using Spearman's rank coefficient test ($p < 0.05$). The δ^{15}N of demersal fishes and large crustaceans were higher than pelagic fishes, small crustaceans and cephalopods in Off-Hokuriku. The δ^{15}N and δ^{13}C of all collected organisms were distributed along the line with the slope of 3.4 (Figs. 1 and 2). Hence, it seems that these organisms belong to the same food web.

Classification scheme for type of bioaccumulation

Concentration of many trace elements had significantly positive correlations with δ^{15}N using Spearman's rank coefficient test ($p < 0.05$) (Off-Sanninn: Al, Fe, In, Sb, Ba). Therefore, we tried to classify the bioaccumulation pattern to achieve a systematic understanding. Firstly, the trace elements with concentrations varying within one order throughout all the trophic levels were classified as "homeostasis type" (Fig. 3). Secondly, the trace elements which had a positive correlation with δ^{15}N value at statistically significant level were classified as "bioaccumulation type" (Fig. 4). Thirdly, the trace elements showing negative correlation with δ^{15}N value in statistically significant level were classified as "biodilution type". Finally, trace elements which could not be classified by any of the above criteria were classified as "species specific type".

Trophic transfer of trace elements

In Off-Sanninn, Mg, Ni, Zn, Se, Rb, Cs and Tl were classified as homeostasis type (Fig. 3). Since Mg, Zn, and Se are the essential elements (Machlin and

Bendich, 1987; Watanabe *et al.*, 1997; Shi *et al.*, 2002; Tubek *et al.*, 2008), concentrations of these elements tended to be maintained constant at all trophic levels. Rubidium and Cs were also classified into homeostasis type. Levels of these elements in the organisms are maintained by same the mechanism that controls major electrolytes such as Na and K (Sakurai, 2009).

Trace elements classified into bioaccumulation type were Al, Fe, In, Sb and Ba (Off-Sanninn) (Fig. 4). Since Fe is a well-known essential element, we expected that Fe may fall into homeostasis type. But this element was found to be classified into bioaccumulation type. This may be due to the increasing biological demand of Fe with increasing trophic level. But biological information for deep-sea organisms is unclear, so it must be more research about this. Reports on bioaccumulation patterns of Al, Sb, Ba and In are scarce. Thus, further data collection is needed.

No trace element was classified into biodilution type in this study. However, many trace elements were classified into biodilution type in previous studies (Toyoshima *et al.*, 2007; Eric *et al.*, 2009; Hayase *et al.*, 2009). For example, in Sagami Bay, V, Cu, Rb, Mo, Ba and Pb were classified into biodilution type (Toyoshima *et al.*, 2007). In Off-Tohoku, V, Mn, Fe, Co, Cu, Mo, Sb and Pb were classified into this type (Hayase *et al.*, 2009). In those studies, target samples were mainly pelagic fishes. In the present study, major portion of the samples were crustaceans and demersal fishes. This may be the reason for the discrepancy in the bioaccumulation patterns, and suggest the possibility that ecologically different species have different accumulation pattern in the food web.

In this study Cu, Sr, Cd, Sn and Bi were classified as species specific type. Generally, cephalopods are known to accumulate Cd, and Cu is used for hemocyanin in crustaceans, cephalopods and bivalves (Bustamante *et al.*, 2003). These elements were considered not to relate trophic levels.

Bioaccumulation patterns in crustaceans

When we focus only on crustacean species, many trace elements showed clear bioaccumulation trend (Fig. 5). In Off-Sanninn region, Al, V, Fe, Co, Ni, Mo, Ag, Pb and Bi were bioaccumulated, whereas, V, Cr, Mn, Fe, Co, Ni, As, Rb, Mo, Ag, Sb, Pb and Hg were bioaccumulated in Off-Hokuriku region. Silver and Fe were known to accumulate in the epithelial tissue in the form of granules in crustaceans (Ahearn *et al.*, 2004). This particular mechanism may affect bioaccumulation pattern. Some reports suggested that large crustaceans mainly feed on small crustaceans and makes a simple food chain in Off-Sanninn and Off-Hokuriku (Minami., 1999). Clear positive correlation observed here indicates biomagnification would be apparent in the case of many metals when crustaceans are the dominant organisms in an ecosystem.

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