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Nineteen trace elements in marine copepods collected from the coastal waters off northeastern Taiwan

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ABSTRACT

This study analyzed nineteen trace elements in marine copepods collected from the coastal waters off Northeastern Taiwan. The bioconcentration factors (BCF) of the analyzed elements in copepods are discussed. Owing to the upwelling intrusion of Kuroshio Water, the study area presented an enriched copepod community and the copepod abundance ranged within 106–4890 ind. m⁻³. The trace elements content in the analyzed copepods varied substantially, ranging from 0.01 to 780 mg kg⁻¹. and the average concentration followed the sequence: Sr > Fe > Zn > Cr > Li > Ni > Mn > Ba > Cu > Se > As > V > Pb > Rb > Cd > Co > Ga > Ag > Cs. The trace elements can be divided into five groups according to the concentration quantity in copepods: (1) Sr; (2) Fe, Zn, Cr, Li and Ni; (3) Mn, Cu, Ba, Se, As, V, Pb and Rb; (4) Cd, Co and Ga; (5) Ag and Cs. The concentration difference in each group is nearly one order of magnitude. The trace element concentrations in copepods seem to be in proportion to the dissolved concentrations in seawater. The trace element log BCF values ranged within 1.32–5.66. Transition metals generally have a higher BCF value than the associated minor elements, such as Ba, Sr, Li and Rb. The trace element BCF value in copepods is in inverse proportion to the dissolved concentrations in seawater.

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1. Introduction

Copepods are the most numerous primary consumers and are widely distributed throughout the ocean. Copepods make up about one third of the mean plankton biomass and half of the mean zooplankton abundance in the marine environment (Longhurst, 1985). As a result, copepods play an important role in the energy pathways between primary producers and secondary consumers. Many studies have shown that marine copepods have a great ability to accumulate trace elements (Xu and Wang, 2002; Zauke and Schmalenbach, 2006; Fang et al., 2006; Hsiao et al., 2006, 2010, 2011a). Thus, trace elements accumulation in marine consumers is of great concern to marine scientists who are interested in the fate and effects of contaminants and the trace element biogeochemical cycles in the marine environment.

Because of their toxicity to marine organisms above threshold availability and their persistence in the environment, trace elements pose potentially hazardous conditions in the aquatic environment (Kennish, 1997). As a result, the known marine copepod trace

elements content in the literature focused mostly on transition metals, such as Cd, Cr, Cu, Pb and Ni. Such knowledge has been well established in temperate and polar regions by Zauke and his coworkers (Ritterhoff and Zauke, 1997a, b; Kahle and Zauke, 2002, 2003; Zauke and Schmalenbach, 2006) and in sub-tropical regions by Fang and his coworkers (Fang et al., 2006; Hsiao et al., 2006, 2010, 2011a). Zauke and his coworkers produced results indicating that distinct trace element concentration ranges existed among the different zooplankton species that flourished within a given water body. The Cd-anomaly findings in polar region copepods and potential Cu metabolic deficiencies in the Antarctic Ocean suggest that no global trace element background values could be defined in copepods. Fang and his co-workers found considerable variation in the same metal content between intra and inter copepod species. The trace element concentrations in copepods found in sub-tropical regions were generally one to two orders of magnitude higher than those found in temperate and Polar Regions. The latter finding may be attributed to the pristine environment in Polar Regions and the body size effect (Fang et al., 2006; Hsiao et al., 2010, 2011a).

The study of trace elements, such as As, Li, Ba, Se, Sr etc. in marine copepods is very limited. This may be partly attributed to the toxicity of these elements in marine organisms being weaker than that of transition metals, such as Cd, Cu, Cr, Ni and Zn etc. Knowledge of

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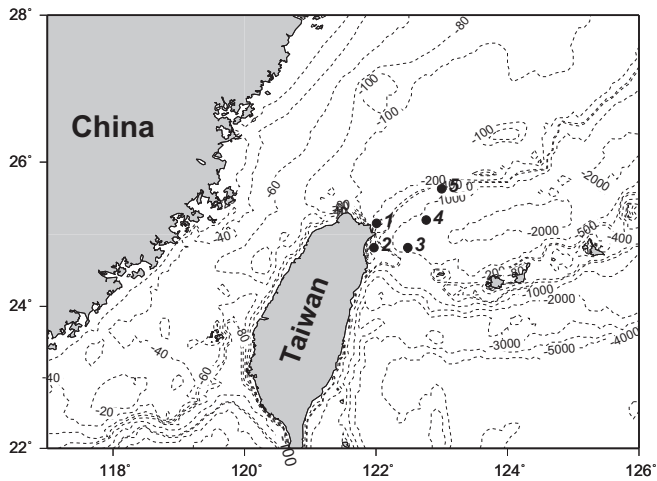


Fig. 1. Sampling stations. S1–S2: coastal waters off northeastern Taiwan, S3–S5: Kuroshio water.

trace element bio-accumulation in zooplankton is essential for better understanding of the food web and trace element biogeochemical cycles in the marine environment. In order to fill this knowledge gap we analyzed nineteen trace elements in different marine copepod species collected from the coastal waters off northeastern Taiwan where the Kuroshio Branch Current flows through. Hopefully the data collected in this research, especially for trace elements, can fill the knowledge gap.

2. Materials and methods

2.1. Sampling

The zooplankton samples were collected from five stations off the northeastern Taiwan coast extending to the Okinawa Trough onboard the R/V Ocean Research-II ship from August 10–12, 2011, as shown in Fig. 1. The zooplankton samples were collected using a zooplankton net with a 45-cm mouth diameter and 333 μm mesh size. The net was towed obliquely 1 m below the surface layer (surface tows) and at a deeper layer (deeper tows), depending on the topography of the studied stations. The deeper layer at stations 1 and 2 was about 30 m depth and at stations 3, 4 and 5 approximately 100 m depth. The sampling time was approximately 10 min at a vessel cruising speed of 2 knot. The zooplankton samples were preserved immediately in a freezer at $-20\text{ }^{\circ}\text{C}$ on board.

Station 1 is located on the northeastern Taiwan coast and station 2 is close to Kueishan Island where hydrothermal vents release hydrothermal fluids into the seawater containing higher concentrations of major trace elements, pure sulfur and extremely acidic thermal fluids, with pH values as low as 1.52 (Chen et al., 2005). Stations 3–5 are located primarily at the Okinawa Trough, which is the back arc basin of the Ryukyu subduction zone extending westward through an E–W trending graben caused by Luzon Plate subduction beneath the Eurasian Plate (Chen et al., 2005). The Kuroshio Current is the major current flowing through the Okinawa Trough. A portion of it intrudes into the East China Sea. The Kuroshio Current originates from the equatorial region east of the Philippines and diverges from the North Equatorial Current in the area east of the Philippines, forming a western boundary current flowing along the gyre margin (Nitani, 1972; Kawai, 1998). It flows northward along the east coast of Taiwan. The upper waters (0–500 m) of this boundary current flow northward into the Okinawa Trough through the Yonaguni Depression and pass along the outer edge of the East China Sea continental

shelf, forming the main track of the Kuroshio Current (Ujiie et al., 2003). The Kuroshio Current runs into the continental shelf-break off northeastern Taiwan and forms a year-round upwelling that brings high nutrient loads into the euphotic zone at the shelf break (Liu et al., 2003). As a result, a high zooplankton biomass is generally observed in the seawater around northeastern Taiwan (Lo et al., 2004; Hsiao et al., 2010, 2011a, b). High salinity and temperature characterize the Kuroshio waters as well as low nutrients in the surface layer (Liu et al., 2003).

2.2. Analysis

The copepod species were identified under a microscope after thawing. Though, the relative abundances of eight species of copepods were generally higher than 50%. Only four species, *Cosmocalanus darwini*, *Oncaea venusta*, *Temora turbinata*, and *Undinula vulgaris*, of copepods were analyzed for trace element concentrations because their quantities were sufficient and samples of the other four species were insufficient. The males and females of these copepod species were collected separately. Each sample had approximately 60–100 individuals and was washed with Milli-Q water three times to remove suspended particulate material prior to analysis. The copepod samples were then filtered out onto an acid-cleaned Nuclepore membrane (0.45 μm) that had been weighed prior to use. The copepod-loaded filters were dried in a laminar flow hood inside a clean room for 72 h. The weight of each copepod sample was obtained as the difference in the weight of the Nuclepore membrane with and without copepod samples. The copepod samples were then digested with 3 ml HNO_3 (65%, J.T. Baker Ultrex) in a Teflon centrifuge tube for 4 h in a $96\text{ }^{\circ}\text{C}$ water bath. Digested solutions were increased to 3-ml volumes using sub-boiled distilled water. The digestion procedure for the copepod samples was modified from the method of Ritterhoff and Zauke (1997a). The digested solution was properly diluted using sub-boiled distilled water and analyzed for the concentrations of nineteen elements (Ag, As, Ba, Cd, Co, Cr, Cs, Cu, Ga, Fe, Li, Mn, Ni, Pb, Rb, Se, Sr, V, and Zn) using the ICP–MS (Thermo X-series 2). The accuracy for the trace element analysis was checked using metals determination in a DORM-3 reference sample (National Research Council of Canada, NRCC) in triplicate. The ratio of measured concentration for each metal in DORM-3 to the certified values of the reference sample generally fell in the 0.85–1.06 range (Fig. 2) and the standard deviation of the triplicate analysis for each metal was generally less than 3% of the average value. This result suggests that the analytical results are acceptable. The DORM-3 reference sample provides certified values for only ten elements. Mercury and Sn were not analyzed in this study. Thus, the analytical accuracy of only eight elements can be checked with DORM-3 reference sample certified values.

3. Results

3.1. Copepod abundance

Fifty-one copepod species belonging to 22 families and 30 genera were recorded during this survey. The detailed taxon result is listed in Table 1. Fourteen copepod species, namely *Acrocalanus gibber*, *Acrocalanus gracilis*, *Canthocalanus pauper*, *C. darwini*, *Euchaeta rimana*, *Paracalanus aculeatus*, *Subeucalanus subcrassus*, *T. turbinata*, *U. vulgaris*, *Oithona plumifera*, *Corycaeus (Corycaeus) speciosus*, *Farranula gibbula*, *Oncaea mediterranea*, and *O. venusta*, were frequently observed at the studied stations with frequencies greater than 60% in all samples. However, only four copepod species, *C. darwini*, *O. venusta*, *T. turbinata*, and *U. vulgaris*, were analyzed for trace element concentrations because the amounts of

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