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Dynamics of trace metal concentrations in an intertidal rocky shore food chain

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Numerous studies have measured the concentrations of various trace metals in marine organisms (for a review see Eisler, 1981; Neff, 2002), often in response to concerns about trace metal contamination in seafood or in an attempt to employ marine organisms as biological monitors of coastal contamination. In these studies, marine organisms are typically collected from polluted and unpolluted environments and their concentrations of metals are quantified. The main objectives of these studies are to examine whether the organisms are contaminated with the metals and whether there are any spatial or temporal trends in metal contamination in the coastal or estuarine environment. Few studies have attempted to mechanistically interpret the metal body concentrations in these animals (Langston and Spence, 1995; Wang et al., 1996; Blackmore, 2000; Rainbow, 2002; Luoma and Rainbow, 2005). Over the past decade, the development of kinetic modeling has rekindled interest in the mechanistic interpretation of metal concentrations in marine invertebrates. In addition, a few studies have also attempted to address potential trophic interactions in accounting for the variability of trace metal concentrations in predators (Blackmore, 2000, 2001; Blackmore and Morton, 2002).

Trophic transfer has increasingly been recognized as an important pathway for metal accumulation in marine invertebrates (Wang and Fisher, 1999; Wang, 2002). Biomagnification occurs when the metals are transported through a food chain at increasing concentrations in the animals at higher trophic levels. Metal biomagnification has long been recognized as occurring with Hg (mainly in its methylated form, methylmercury) and cesium (Wang, 2002). Evidence has largely come from measurements in fish or other higher level organisms (e.g., birds, ducks).

There have been fewer studies of intertidal rocky shore food chains. Several studies have found that metal concentrations in predatory snails from intertidal rocky shores were unusually high (Blackmore, 2000; Jeng et al., 2000). There is thus considerable interest in examining the trophic interaction and any metal biomagnification in such food chains. Intertidal rocky shores host diverse species of invertebrates that differ tremendously in their metal accumulation patterns and thus metal concentrations, even among the closely related species such as bivalves (e.g., mussels and oysters).

In this study, the concentrations of five trace metals/metalloids (Ag, Cd, Cu, Se, and Zn) were measured monthly for one year in a predator-prey chain on an intertidal rocky shore in Hong Kong. The relationships among metals, species and seasons were investigated, with special emphasis on potential biomagnification of metals in the top predator. The animals were collected from a rocky shore in Clear Water Bay, where the dominant prey species included the black mussels *Septifer virgatus*, the oyster *Saccostrea cucullata*, and the barnacle *Tetraclita japonica*; the predators included the snail *Morula musiva*. Another top predator typical of such rocky shores is the starfish, which

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was only occasionally observed in this area. Clear Water Bay is in the eastern part of Hong Kong and subjected to significant influence from ocean currents. The bay can be considered relatively pristine, without significant impact from anthropogenic activity. The salinity of the bay is rather constant throughout the different seasons (typically 25–32 ppt).

The invertebrates were collected from an exposed shore in a rocky area. All species except the oyster *S. cucullata* were collected from June 2003 to June 2004. The oysters were collected from July 2003 to June 2004. For the barnacles, five bodies were combined into one sample, because the mass of an individual organism was too small for metal analysis. For the other species, 6–8 replicate individuals of similar body sizes were sampled each month. The samples were collected randomly from the site, then placed in polythene bags and frozen at −20 °C until metal analysis.

In the laboratory, the animals were dissected using stainless steel knives and briefly rinsed with nanopure distilled water. The bodies were dried at 60 °C in an acid-cleaned test tube. The dry mass of each replicate was measured after the mass had reached a constant weight. Concentrated HNO_3 was added and digestion was performed in a heating block. The digests were then diluted with nanopure distilled water for metal analysis. The digests were analyzed for Ag, Cd, Cu, Se, and Zn using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin–Elmer, Elan 6000). Further dilution was made for the Cu and Zn measurements, since the concentration of the samples was too high for the ICP-MS. Throughout the metal analysis, oyster standards (Standard Reference Material 1566 Oyster tissue, National Institute of Standards and Technology, Gaithersburg, MD) were used for checking the methodology. Comparisons of measurements performed on the standards with their certified values are shown in Table 1. Recoveries were 90–110% for Cd, Cu, Se, and Zn. For Ag, the recovery was somewhat lower, i.e., 83%. All the metal concentrations were expressed based on the dry weights of tissues.

Over the one-year sampling period, the tissue dry weights of the mussels and oysters were much lower during August–November period than during the winter season, which is likely caused by the reproductive cycle of these bivalves (Fig. 1). The dry weights of the barnacles were also lower in the summer season (July–September) than during the other seasons, again probably caused by reproduction.

Table 1
Comparison of the certified metal concentrations in the oyster standard reference and the measured values ($\mu g\ g^{-1}$)

	Certified values ± std	Measured values ± std	% Recovery
Ag	0.666 ± 0.009	0.554 ± 0.077	83.1
Cd	2.48 ± 0.08	2.233 ± 0.079	90.0
Cu	71.6 ± 1.6	67.2 ± 2.3	93.8
Se	2.06 ± 0.15	2.27 ± 0.32	110
Zn	1424 ± 46	1405 ± 97	98.7

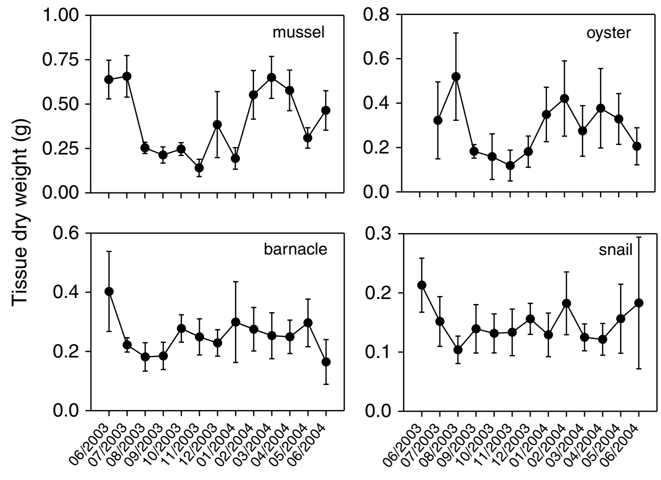

Fig. 1. Seasonal variations in tissue dry weight of the collected invertebrates. For barnacles, each measurement represents five bodies. Mean ± SD ($n = 6–8$).

Table 2
Size allometric coefficients (b) of metal concentrations in the black mussel *Septifer virgatus* and the rock oyster *Saccostrea cucullata*

	Septifer virgatus		*Saccostrea cucullata*	
	b	r^2	b	r^2
Ag	−0.676	0.235^{***}	−0.575	0.277^{***}
Cd	−0.272	0.155^{***}		NS
Cu		NS		NS
Se		NS		NS
Zn	−0.202	0.131^{**}	−0.239	0.174^{***}

r^2: Correlation coefficient. No relationship was found for the barnacles and snails. NS: not significant.
** Significant at the $p < 0.01$ level.
*** Significant at the $p < 0.001$ level.

There was no clear pattern of tissue dry weight for the snails through the seasons. It should be noted that only 6–8 replicates were collected at each sampling time, and efforts were made to select comparable body sizes in each monthly sampling.

The metal concentrations were first correlated with the tissue dry weight of the animals using an allometric power function (Boyden, 1974, 1977). Significant correlations between metal concentration and tissue dry weight were found for Ag, Cd, and Zn in the mussels, and Ag and Zn in the oysters (Table 2). No significant correlation was found for the barnacles or snails, presumably because the body tissue weights were within a narrow range (0.16–0.4 g for each composite of five individual barnacles, and 0.10–0.21 g for snails) throughout the different seasons. Interestingly, the allometric coefficients for Cd and Zn in the two bivalves were −0.20 to −0.28, whereas they were much higher for Ag (−0.575 to −0.676), indicating a higher dependence of Ag concentration on body size in bivalves. Numerous studies have measured the size dependence of metal concentrations in such bivalves, but often over a much wider range of body sizes (Boyden, 1977; Wang