

# The retention of cadmium and zinc in appendicularian houses

Appendicularians  
Cadmium  
Zinc  
Larvaceans  
Vertical transport

Appendiculaires  
Cadmium  
Zinc  
Logettes  
Flux vertical

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## ABSTRACT

The discarded houses of appendicularians can be important components of marine snow and might therefore be instrumental in mediating the vertical flux of metals from surface waters in oceanic ecosystems. Their significance in this regard depends on the retention of metals in these organic debris. To assess this, an experiment was conducted in which the release of cadmium and zinc from discarded houses of the appendicularian *Oikopleura longicauda* was studied using gamma-emitting radiotracers. The retention curves of the two metals conformed with a single exponential decay loss model. The retention half-times were of the order of two days, suggesting that sinking appendicularian houses would not transport these metals to deep ocean waters but could contribute to their flux out of surface waters.

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## RÉSUMÉ

Rétention du cadmium et du zinc dans les logettes abandonnées par les appendiculaires

Les logettes abandonnées par les appendiculaires peuvent constituer une partie importante de la neige marine et, à ce titre, pourraient servir de vecteur dans le flux vertical des métaux. En effet, l'importance de ces débris organiques dépend de leur capacité de rétention des métaux. Afin d'établir l'influence de ces logettes dans le transport des métaux des couches superficielles vers les profondeurs, une série d'expériences a été conduite pour décrire la perte de cadmium et de zinc par les logettes abandonnées par l'appendiculaire *Oikopleura longicauda*, en utilisant comme traceurs des isotopes émetteurs gamma. Les courbes de rétention des deux métaux correspondent à un modèle de décroissance à un compartiment, indiquant la présence d'un réservoir pour chaque métal dans les débris. Les demi-vies des éléments dans la logette sont de deux jours. Cette courte période suggère que la sédimentation des logettes abandonnées ne permet pas le transport des métaux vers les couches profondes mais contribue cependant au flux hors de la couche superficielle.

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## INTRODUCTION

Sinking biogenic debris plays a pivotal role in the vertical transport of metals and other materials in oceanic ecosystems (Fowler and Knauer, 1986). Different kinds of debris from crustacean zooplankton, including fecal pellets, cast exoskeletons, and sinking carcasses, have been implicated in the vertical transport of materials, partly because of their relatively rapid sinking rates (tens to hundreds of meters per day; Fowler and Knauer, 1986).

Comparatively little information exists, however, on the relative contribution that debris from gelatinous zooplankton can make toward the vertical flux of materials, despite the fact that gelatinous zooplankton can dominate the zooplankton community in large areas, often including subtropical waters (Alldredge and Madin, 1982; Taguchi, 1982; Alldredge and Silver, 1988). Gorsky *et al.* (1984), in a series of laboratory experiments focusing on the transuranic element, americium, demonstrated that discarded houses of appendicularians are capable of vertically transporting this and presumably other particle-reactive metals to intermediate depths in the water column. Moreover, discarded houses of appendicularians can be prominent components of marine snow (Silver and Alldredge, 1981; Alldredge and Silver 1988). Marine snow can dominate the flux of materials in different oceanic regions (Hebel *et al.*, 1986; Alldredge and Silver, 1988). Hebel *et al.* (1986) reported highly enriched concentrations of eight different transition metals in marine snow collected from surface waters of Monterey Bay, California.

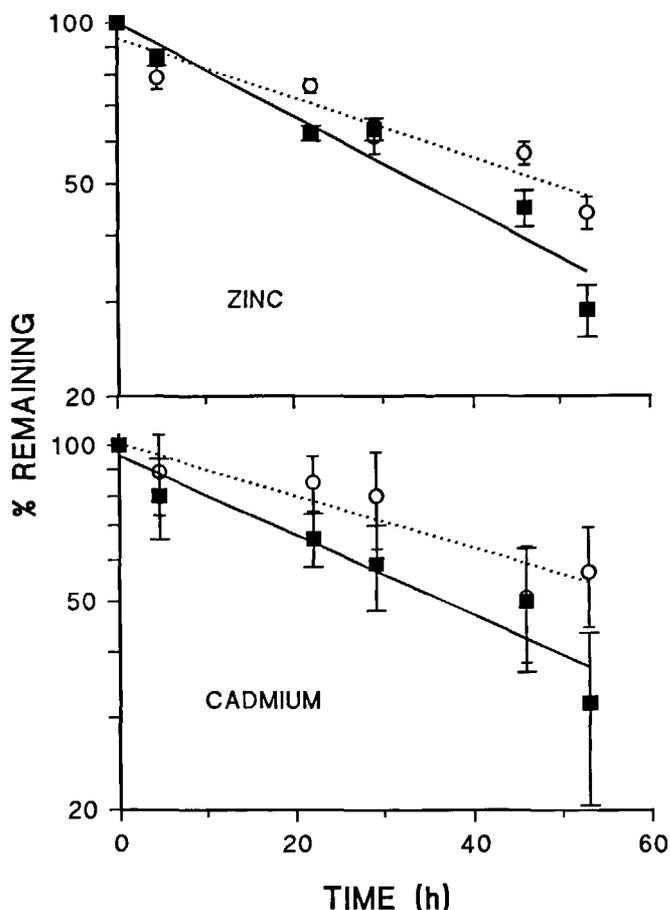
While there have been an increasing number of studies determining the retention of metals in fecal pellets of crustacean zooplankton (Fowler and Knauer, 1986; Fisher *et al.*, in press), we are unaware of any assessments of the retention times of metals in debris of gelatinous animals, other than the study of Gorsky *et al.* (1984). We have therefore conducted a laboratory experiment to determine the retention time of two metals of geochemical and potential toxicological interest, cadmium and zinc, in discarded houses of the appendicularian *Oikopleura longicauda*.

## MATERIALS AND METHODS

To assess the retention of cadmium and zinc in discarded houses of *Oikopleura longicauda*, animals were first allowed to graze on radiolabeled phytoplankton cells. To prepare radiolabeled food, an axenic unialgal culture of *Dunaliella tertiolecta* (clone DUN), a naked chlorophyte, was exposed to  $^{109}\text{Cd}$  and  $^{65}\text{Zn}$  in sterile-filtered (using sterile 0.2  $\mu\text{m}$  Nuclepore polycarbonate membranes) Mediterranean surface seawater (SFSW). The cell density  $- 1.42 \times 10^5 \text{ ml}^{-1}$  - remained essentially constant over the 72 hour incubation period.  $^{109}\text{Cd}$  was added to give a final concentration of  $1378 \text{ Bq ml}^{-1}$  (25.8 nM Cd added);  $^{65}\text{Zn}$

was added to give  $599 \text{ Bq ml}^{-1}$  (15.6 nM Zn added). The  $^{109}\text{Cd}$  ( $t_{1/2} = 462$  days) and  $^{65}\text{Zn}$  ( $t_{1/2} = 244$  days) were taken from stock solutions in 0.1 N HCl obtained from Amersham plc (UK). Cells were incubated at  $16^\circ\text{C}$  under cyclic illumination 14:10 L:D provided by cool-white fluorescent lamps (approx.  $200 \mu\text{Ein m}^{-2} \text{ s}^{-1}$ ).

After 72 hours, aliquots of cells were sampled to determine their radioactivity, using the procedures described by Fisher *et al.* (1983). At this time, cells had accumulated 80.4 % of the Cd and 41.0 % of the Zn, corresponding to volume/volume concentration factors of  $3.2 \times 10^5$  and  $5.4 \times 10^4$  for Cd and Zn, respectively. The cells were harvested out of the radioactive seawater by centrifugation (9220 g, 10 mn,  $10^\circ\text{C}$ ) and resuspended into 4 l of unlabeled SFSW to give a cell density of  $2 \times 10^3 \text{ ml}^{-1}$  in the feeding suspension (corresponding to  $30 \mu\text{g dry wt l}^{-1}$  or  $182 \mu\text{m}^3 \text{ l}^{-1}$ ). To this feeding suspension, 30 individuals of *Oikopleura longicauda*, collected from Villefranche Bay three hours prior to the experiment, were added to the feeding suspensions and allowed to graze for twenty eight hours under dim light. Following this feeding period, 115 discarded appendicularian houses were collected by gentle pipetting using



Figure

Retention of  $^{65}\text{Zn}$  and  $^{109}\text{Cd}$  in discarded houses from the appendicularian *Oikopleura longicauda*. The radioactivity (Bq) of each radioisotope in the houses (expressed on a per discarded house basis) was compared with the radioactivity of the houses at the beginning of the depuration period; values expressed are percentages of the initial radioactivity. Each data point is shown with its propagated error. In all cases, 100 % of the radioactivity was found to be in a single pool. ■—■: samples incubated in the dark; ○---○: samples incubated in the light.

a wide-bore glass pipet (Gorsky *et al.*, 1984). The houses were divided as follows: 65 houses were placed into 10 ml unlabeled SFSW, counted for their radioactivity (4.55 Bq  $^{109}\text{Cd}$  house $^{-1}$  and 3.99 Bq  $^{65}\text{Zn}$  house $^{-1}$ ), washed by serially transferring them through 1 l of unlabeled SFSW, and transferred into 1 l of unlabeled SFSW in which they were incubated for 53 hours at 16°C in the dark. The other 50 houses (5.98 Bq  $^{109}\text{Cd}$  house $^{-1}$  and 5.76 Bq  $^{65}\text{Zn}$  house $^{-1}$ ) were treated identically but were incubated in the light. Periodically, samples were taken by collecting all the houses by pipet into 10 ml of SFSW, counting their radioactivity, and returning them to a fresh batch of 1 l SFSW for further incubation. At each sample time, 10 ml of seawater was also taken by pipet and its radioactivity determined, to assess the released radioactivity. Twelve naked animals (*i.e.*, without houses) were also collected and allowed to depurate in 1 l of SFSW.

The radioactivity of samples was determined by gamma counting with a high purity Ge detector linked to a Cosynus multi-channel analyzer and a computer with spectra analysis software (Intertechnique, Grenoble). The detector was calibrated for energy and counting efficiency with appropriate standards for each of the geometries used. Photon emissions of  $^{109}\text{Cd}$  were detected at 88 KeV and of  $^{65}\text{Zn}$  at 1115 KeV. Propagated counting errors were calculated using the radioactive counts of the material at each sample time and at the beginning of depuration; expressed as a percentage of the initial counts, they amounted to < 4 % for samples containing  $^{65}\text{Zn}$  and  $\leq 17$  % for samples containing  $^{109}\text{Cd}$ .

## RESULTS AND DISCUSSION

Both zinc and cadmium were released from discarded *Oikopleura longicauda* houses (Fig.), indicating that these metals were not irreversibly bound to these gelatinous houses or, more precisely, the trapped *Dunaliella tertiolecta* cells within them. There were no significant differences between the two metals with respect to their retention in the houses (Fig.), and retention half-times were on the order of two days.

The loss curves for both metals conformed with a single exponential decay loss model, with 98 % of the zinc in dark-incubated material (95 % Confidence Interval: 91-105 %), 96 % of the zinc in light-incubated material (95 % C.I.: 87-106 %), 98 % of the cadmium in the dark (95 % C.I.: 90-105 %), and 101 % of the cadmium in the light (95 % C.I.: 90-111 %) being in single pools. The regression coefficients ( $r^2$ ) for the single exponential decay of zinc were 0.93 in the dark and 0.90 in the light; for cadmium they were 0.92 in the dark and 0.87 in the light. For zinc, the retention half-time in the material incubated in the light, 54 hours (95 % C.I.: 41-79 hours), was 1.5 times that in material incubated in the dark, 36 hours (95 % C.I.: 30-45 hours). For cadmium, the retention half-time in the

light-incubated material, 62 hours (95 % C.I.: 45-96 hours) was similarly greater than that in the dark, 39 hours (95 % C.I.: 32-50 hours). The greater retention of the metals in light-incubated material may reflect growth in the light of undigested *Dunaliella* cells trapped within the houses, leading to greater suspended particulate surface area, as well as possible recycling of released metal.

The retention half-times of these transition metals in discarded *O. longicauda* houses (36 to 62 hours) were comparable to their retention half-times in phytoplankton cells (*Dunaliella tertiolecta* and *Thalassiosira pseudonana*) (Fisher, unpublished results), indicating that the gelatinous houses themselves did not appreciably sorb any of the metal released from the labeled algae trapped within the houses. Similarly, appendicularian houses displayed little sorption of americium, a particle-reactive transuranic element (Gorsky *et al.*, 1984). The retention half-times of cadmium and zinc were much shorter than that of americium, where retention half-times in *O. dioica* houses were about nine days under similar experimental conditions. It is noteworthy that the americium depuration curves also indicated only a single compartment for this isotope in the debris (*i.e.*, a single exponential described the release of this element from the houses; Gorsky *et al.*, 1984). Retention of americium by *O. dioica* fecal pellets was comparable to that of discarded houses (Gorsky *et al.*, 1984).

Given the retention half-times for cadmium and zinc and the sinking rates of < 100 m day $^{-1}$  for appendicularian houses in surface waters (Gorsky *et al.*, 1984; Alldredge and Silver, 1988), it is readily apparent that this form of biogenic debris is unlikely to transport these transition metals to great depths in the oceanic water column, but would rather be expected to transport these metals no more than a few hundred meters, by which time they would have released most of their original metal. Moreover, the settling velocities of these materials would be expected to decrease with time, largely due to decomposition of the debris, as well as their sinking into colder, denser waters. The discarded houses in this experiment lost much of their structural integrity after twenty two hours incubation, by which point they appeared to be amorphous mucilaginous entities. The extent to which sinking houses or their contents can scavenge metal from the dissolved phase during their descent in the water column was not studied here, although recent experiments demonstrated that marine snow collected from sediment traps can effectively scavenge a broad spectrum of dissolved metals, including cadmium and zinc (Fisher *et al.*, in press), possibly explaining the metal enrichment observed in marine snow (Hebel *et al.*, 1986). By scavenging metal, sinking appendicularian houses and their contents could contribute to the flux of metals out of surface waters.

Metal measurements in gelatinous zooplankton are rare. Cadmium, copper and lead measurements in gelatinous macroplankton (tunicates, cnidarians, and ctenophores) from the Mediterranean showed no significant differences among the phyla while zinc was lower in tunicates than in

cnidarians; in general concentrations were lower than in crustacean zooplankton, indicating that many of the metals ingested together with the food are defecated or otherwise released by these gelatinous zooplankton (Romeo *et al.*, 1987). Consistent with this idea, Krishnaswami *et al.* (1985) showed that tunicate fecal pellets were highly enriched in several trace metals and accounted for a greater flux of metals from Mediterranean surface waters than did molts and fecal pellets from crustaceans zooplankters.

The naked animals, which contained a mean of 6.75 Bq  $^{109}\text{Cd}$  and 0.22 Bq  $^{65}\text{Zn}$  animal $^{-1}$  prior to depuration, lost virtually all of their radioisotopes within 4.5 hours and no detectable radioactivity was associated with them at this time. Thus, carcasses of *Oikopleura longicauda* indivi-

duals settling in the water column would not be expected to contribute significantly to the vertical flux of these metals.

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