# MODELING THE BIOACCUMULATION OF TRACE METALS IN MARINE HERBIVORES

Nicholas S. Fisher [1]*, Wen-Xiong Wang [1], and Samuel N. Luoma [2]
[1] Marine Sciences Research Center, State University of New York, Stony Brook, NY 11794-5000 USA
[2] Water Resources Division, US Geological Survey, Menlo Park, CA 94025 USA

## Abstract

We show that bioenergetic-based kinetic models can effectively be used to predict metal concentrations and delineate metal uptake pathways in marine herbivorous animals. Radiotracer experiments have been performed to determine key parameters of metal influx and efflux from diverse sources. These parameters were incorporated into kinetic models to understand the accumulation of cadmium, silver, selenium, cobalt, chromium, and zinc in marine copepods and bivalve molluscs. Sensitivity analyses underscore the importance of determining the assimilation efficiency of ingested metal as a first-order parameter which regulates the bioaccumulation of these metals in animals.

*Key-words : metals, bivalves, copepoda, models, bio-accumulation*

### Modeling approach

The metal content of an animal is a function of the uptake of the metal from the dissolved phase, metal uptake from ingested food, and retention of the metal in the animal, and can be described by the following first-order equation [1, 2]:

$$dC/dt = (\alpha_w * FR * C_w) + (AE * IR * C_f) - (k_e+g) * C \qquad (1)$$

where, C is the metal concentration ($\mu g\ g^{-1}$) in the organism at time t (d), $\alpha_w$ is the metal absorption efficiency from the dissolved phase, FR is the animal filtration rate ($L\ g^{-1}\ d^{-1}$), $C_w$ is the metal concentration in the dissolved phase ($\mu g\ L^{-1}$), AE is the metal assimilation efficiency from ingested food, IR is the ingestion rate ($mg\ g^{-1}\ d^{-1}$), $C_f$ is the metal concentration in the food ($\mu g\ mg^{-1}$), $k_e$ is the metal efflux rate constant ($d^{-1}$), and g is the growth rate constant ($d^{-1}$). Under steady state conditions, this equation becomes:

$$Css = \frac{(\alpha_w * FR * C_w) + (AE * IR * C_f)}{(k_e + g)} \qquad (2)$$

Metal influx rate from the dissolved phase can be expressed as:

$$I^w = \alpha_w * FR * C_w = k_u * C_w \qquad (3)$$

where $I_w$ is the experimentally determined influx rate from the dissolved phase ($\mu g\ g^{-1}\ d^{-1}$), and ku is the dissolved uptake rate constant ($L\ g^{-1}\ d^{-1}$), which is equal to $\alpha_w * FR$. If metal efflux rate constants are different following uptake from the dissolved and food sources, Eq. 2 can then be expressed as:

$$C_{ss} = \frac{(k_u * C_w)}{(k_{ew} + g)} + \frac{(AE * IR * C_f)}{(k_{ef} + g)} \qquad (4)$$

where $k_{ew}$ is the efflux rate constant for metal obtained from the dissolved phase ($d^{-1}$) and kef is the efflux rate constant for metal obtained from ingested food ($d^{-1}$).

### Review of parameters

Recent experimental progress in applying gamma-emitting radiotracer techniques to quantifying the assimilation of ingested metals and the absorption of dissolved metals in marine animals has resulted in a large data set for key parameters useful in the modeling of contaminant concentrations in aquatic organisms. Numerical values of the parameters in Eq. 4 for a variety of metals in marine bivalve molluscs and calanoid copepods have been compiled [2-9]. Table 1 summarizes representative values for $k_u$, $k_{ew}$, $k_{ef}$, and AE for diverse metals in the mussel *Mytilus edulis*. Table 2 summarizes values for these parameters in the calanoid copepod *Temora longicornis*.

AEs of trace elements in marine mussels depended greatly on the quantity and quality of food that the mussels ingested. For example, Ag AEs varied by a factor of 9 (4 *vs* 34%) when mussels ingested the prasinophyte Tetraselmis maculata and the dinoflagellate *Alexandrium tamarense*. Cr(VI) AEs also varied by a factor of 10 when mussels ingested diatoms and dinoflagellates [5]. For other metals, AEs generally varied by a factor of 3-6 depending on the particle type provided to the mussels [3]. Recent evidence suggests that several factors, including mussel digestive physiology (gut passage time, partitioning of extracellular and intracellular digestion), phytoplankton physiology (trace element cytoplasmic distribution in algal cells), and metal chemical behavior (metal desorption within the acidic environment of mussel gut), can all contribute to varying trace element assimilation in mussels [7]. The effect of each process on metal assimilation is also metal-specific. For Se, the cytoplasmic distribution within algal cells appears to be the sole determinant of Se assimilation in mussels, where a 1:1 relationship between Se assimilation in mussels and Se distribution in algal cytoplasm has been noted [2,4]. For Cd, metal desorption within the acidic gut environment influences its assimilation in mussels [4].

Table 1. Kinetic parameters for metal behavior in the mussel *Mytilus edulis*. Parameters presented are the mean uptake rate constant, $k_u$ ($L\ g^{-1}\ d^{-1}$), of metal from the dissolved phase; mean absorption efficiency, $\alpha_w$ (%), of metal from the dissolved phase; mean efflux rate constant, kew ($d^{-1}$), of metal following 6 d uptake from the dissolved phase; mean efflux rate constant, $k_{ef}$ ($d^{-1}$), of metal following 7 d uptake from diatom food; and assimilation efficiency, AE (%), of ingested metal. AE values are for seven different algal foods. Details are given elsewhere [2, 3, 5].

| **Metal** | **$k_u$ ($L\ g^{-1}\ d^{-1}$)** | **$\alpha_w$ (%)** | **$k_{ew}$ ($d^{-1}$)** | **$k_{ef}$ ($d^{-1}$)** | **AE (%)** |
|---|---|---|---|---|---|
| Ag | 1.794 | 1.533 | 0.019 | 0.034 | 4-34 |
| Am | 0.398 | 0.340 | 0.019 | 0.020 | 1-6 |
| Cd | 0.365 | 0.312 | 0.011 | 0.014 | 11-40 |
| Co | 0.124 | 0.106 | 0.018 | 0.010 | 20-43 |
| Cr(III) | 0.034 | 0.029 | 0.012 | 0.010 | 0.2-1.3 |
| Cr(VI) | 0.100 | 0.085 | 0.011 | nd | 1-10 |
| Se | 0.035 | 0.030 | 0.026 | 0.022 | 15-72 |
| Zn | 1.044 | 0.892 | 0.020 | 0.015 | 16-48 |

Table 2. Kinetic parameters for metal behavior in the copepod *Temora longicornis*. Parameters presented are the mean uptake rate constant, $k_u$ ($L\ g^{-1}\ d^{-1}$), of metal from the dissolved phase; mean efflux rate constant, $k_{ew}$ ($d^{-1}$), of metal following 2 d uptake from the dissolved phase; mean efflux rate constant, $k_{ef}$ ($d^{-1}$), of metal following 2 d uptake from diatom food; and assimilation efficiency, AE (%), of ingested metal. From Wang *et al.* [12].

| **Metal** | **$k_u$ ($L\ g^{-1}\ d^{-1}$)** | **$k_{ew}$ ($d^{-1}$)** | **$k_{ef}$ ($d^{-1}$)** | **AE (%)** |
|---|---|---|---|---|
| Ag | 10.42 | 0.173 | 0.294 | 8 - 20 |
| Cd | 0.694 | 0.108 | 0.297 | 33 - 53 |
| Co | 0.606 | 0.122 | 0.281 | 14 - 20 |
| Se | 0.024 | 0.155 | 0.155 | 50 - 60 |
| Zn | 3.294 | 0.108 | 0.079 | 52 - 64 |

In contrast to marine mussels, metal assimilation in marine copepods is relatively independent of food quality and quantity [6]. Food concentration within a range of 16-800 $\mu g$ C $L^{-1}$ has little influence on the AEs of Cd, Co, and Se. AEs of Am and Zn are highest at low food concentration (16-56 $\mu g$ C $L^{-1}$) but remain relatively constant when the food concentration exceeds 160 $\mu g$ C $L^{-1}$. Different phytoplankton diets also have no major effect on metal assimilation in copepods. In these herbivores, the cytoplasmic distribution of metals is critical in affecting metal assimilation [9,10], where a 1:1 relationship between trace element AE and distribution in algal cytoplasm suggests a "liquid" digestive strategy. Because of the relatively rapid gut passage of food particles in copepods (gut passage time generally is less than 0.5 h [11]), gut passage time does not directly determine metal assimilation. Recent studies have also demonstrated that the time to complete digestion andassimilation of metals from ingested food particles in marine copepods (ca. 10 h) is much longer than the gut passage time [12]. In marine mussels, the time to complete digestion and assimilation (ca. 3 d) is also much longer than the metal gut passage time (1-2 d [3]).

For both copepods and mussels, dissolved uptake rate constants are highest for metals that bind preferentially with protein ligands and are ranked in the order of Ag>Zn>Cd>Co>Cr>Se. Using the metabolic blocker N-ethylmaleimide to specifically inhibit the sulfhydryl group of ligands, Wang and Fisher [13] found that uptake of dissolved Ag, Zn and Cd is significantly inhibited, indicating that transport of these metals is primarily governed by a protein ligand (*e.g.*, facilitated transport process). The degree of inhibition by this blocker was highest for Ag, followed by Zn and Cd, consistent with the order of dissolved uptake rate constants. In contrast to these metals, influx of Co is not inhibited by N-ethylmaleimide, indicating that its transport is primarily a passive diffusive process. Se may be taken up through an anionic channel analogous to a sulfate or phosphate channel. It also appears that Ag, Zn and Cd can be transported through the calcium channel [13].

According to Eq. 3, the dissolved uptake rate constant can be controlled by an animal's filtration activity and metal absorption efficiency from the dissolved phase. It is not known whether filtration rate and absorption efficiency are independent parameters such that absorption efficiency is independent of filtration activity. The change of uptake rate of dissolved Co and