



## Delineating metal accumulation pathways for marine invertebrates

Wen-Xiong Wang<sup>a,\*</sup>, Nicholas S. Fisher<sup>b</sup>

<sup>a</sup>Department of Biology, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

<sup>b</sup>Marine Sciences Research Center, State University of New York, Stony Brook, NY 11794-5000, USA

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### Abstract

Delineating the routes of metal uptake in marine invertebrates is important for understanding metal bioaccumulation and toxicity and for setting appropriate water and sediment quality criteria. Trace element biogeochemical cycling can also be affected if the rates of metal uptake and regeneration by marine animals are dependent on the routes of metal accumulation. In this paper we review recent studies on the pathways of metal accumulation in marine invertebrates. Both food and water can dominate metal accumulation, depending on the species, metal and food sources. Trace elements which exist in seawater primarily in anionic forms (e.g. As and Se) are mainly accumulated from food. For metals that tend to associate with protein, uptake from water can be an important source. Kinetic modeling has recently been used to quantitatively separate the pathways of metal uptake in a few marine invertebrates. This approach requires measurements of several physiological parameters, including metal assimilation efficiencies (AE) from ingested food, metal uptake rates from the dissolved phase, and metal efflux rates (physiological turnover rates) in animals. For suspension feeders such as mussels and copepods, uptake from the dissolved phase and food ingestion can be equally important to metal accumulation. Metal AE and partition coefficients for suspended particles, which are dependent on many environmental conditions, can critically affect the exposure pathways of metals. For marine surface deposit feeding polychaetes such as *Nereis succinea*, nearly all metals are obtained from ingestion of sediments, largely because of their high ingestion rates and low uptake from solution. The bioavailability of metals from food and the trophic transfer of metals must be considered in establishing water and sediment quality. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Metals; Exposure pathway; Invertebrates; Kinetic modeling

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\* Corresponding author.

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## 1. Introduction

Marine invertebrates are exposed to metals from both dissolved and particulate phases. Metals dissolved in water may be accumulated by direct adsorption to body surfaces. Particulate metals can be accumulated by animals following ingestion and digestion of food. Separation of these two exposure pathways is fundamental for understanding factors controlling metal bioavailability and for setting water and sediment quality criteria. While some earlier studies suggested that food could contribute significantly to metal uptake in marine invertebrates [see reviews by Luoma (1989, 1983)], most bioassays exposed marine invertebrates to chemical contaminants only in the dissolved phase — food ingestion was not considered a major source for metal accumulation and toxicity in these toxicity tests. Toxicity derived from laboratory tests for sensitive species was then used for the development of water quality criteria (WQC) and sediment quality criteria (SQC) by applying a 'safety factor' to lethal contaminant concentrations. If food ingestion is an important pathway by which a metal is accumulated in marine animals, however, these water or sediment quality criteria may be inadequate in protecting marine life. In addition to these environmental interests, separation of the routes of metal uptake is also important for understanding metal trophic transfer and the biogeochemical cycling of metals in marine systems. For example, differences in metal regeneration following different routes of uptake may affect the fates of metals in marine systems.

Two approaches have been generally employed to model metal accumulation in aquatic invertebrates (Landrum et al., 1992; Luoma and Fisher, 1997). The first approach assumes an equilibrium partitioning of contaminants among various compartments (e.g. water, sediments and animals; DiToro et al., 1991). In this model, the exposure pathway is not important when there is an equilibrium among various compartments. Thus, metal concentrations in animals can be predicted based on measurements of concentrations in the aqueous phase. Equilibrium between aqueous phase

and food phase (e.g. living components) may be easily reached, particularly for microorganisms with relatively short life spans (Fisher et al., 1983), but between animal and food or water it may take a much longer period, making it difficult to simulate in laboratory studies. This approach may therefore be less predictive of metal accumulation in natural waters, although its simplicity has great appeal for environmental regulators. A second approach is the bioenergetic-based kinetic modeling which treats contaminant accumulation as a first-order physiological process (Thomann, 1981; Landrum et al., 1992; Luoma and Fisher, 1997; Wang and Fisher, 1997a). In the model, metal-specific physiological parameters can be measured experimentally and then incorporated to predict metal concentrations in animals. The model generally assumes steady-state conditions, but it can also be applied to study metal accumulation under non-steady-state conditions resulting from temporal variations of metal input into a body of water. This kinetic model has only just recently been applied to understanding metal bioaccumulation and bioavailability, largely because of the development of realistic experimental techniques for measuring metal assimilation efficiency from ingested food and uptake rate constants from the dissolved phase.

In most previous studies, the relative importance of different exposure pathways of metals for invertebrates has been assessed by: (1) direct experimental measurements, in which metal uptake rates from each pathway are compared; (2) an indirect, mass balance method in which metal uptake rates from water exposure or food exposure only are compared with uptake rates from combined food and water exposure; and (3) comparison of tissue distribution of metals observed in the laboratory with observations in nature by assuming that tissue distribution is dependent on the uptake pathway. Application of experimental results from such studies to field situations can be problematic, however, usually because experimental conditions do not reflect those prevailing in natural waters.

Recent studies have combined kinetic modeling and experimental measurements to delineate the

exposure pathways of metals in several invertebrate species (Luoma et al., 1992; Thomann et al., 1995; Wang et al., 1996; Reinfelder et al., 1997; Wang and Fisher, 1998a). Key physiological and geochemical parameters described in the kinetic model can account for metal accumulation in these animals (Luoma et al., 1992; Wang et al., 1996; Fisher et al., submitted). It is therefore possible to construct a simple mathematical model to predict metal accumulation for a variety of natural conditions if these parameters are accurately quantified. Furthermore, the relative importance of each uptake pathway can then be quantitatively assessed by comparing influx rates into the animals from each source. Because the variability of each physiological parameter can be measured over a wide range of environmental conditions, the kinetic model is more flexible than empirical studies for delineating metal exposure pathways under different field conditions.

Numerous studies have been conducted in which the accumulation of metals in marine animals was examined experimentally. Earlier experimental studies have been reviewed by Luoma (1983, 1989). In most of the earlier, descriptive studies, a mass balance method was used to compare metal uptake from each exposure pathway. Often, results of different laboratories have been contradictory, and few generalizations have been possible. Reasons for contradictory results may be due to different experimental protocols and conditions as well as differences in the animal species tested (or their physiological states), although sometimes it is not possible to account for discrepancies due to inadequate descriptions of experimental conditions. Some examples of these descriptive studies which reported on dominant uptake pathways for silver, arsenic, cadmium, polonium, chromium, selenium and zinc are given in Table 1. In this paper we review recent studies on the exposure pathways of metal uptake for marine invertebrates, emphasizing studies employing both experimental and modeling approaches. We consider both suspension and deposit feeders because representatives of these groups have been used in biomonitoring programs of environmental contamination and in toxicity testing.

## 2. Separation of uptake pathways using a kinetic modeling approach

Empirical studies are typically conducted using simple experimental conditions that may not reflect prevailing natural conditions (which often vary temporally and spatially). By combining kinetic modeling and experimental measurements it is possible to consider the variations in each factor controlling metal bioaccumulation, thereby greatly expanding the applicability of laboratory findings to natural waters. Thomann (1981) developed a model of contaminant accumulation in aquatic food chains in which the influx rate from food is determined by multiplying the contaminant concentration in ingested food particles by the ingestion rate and assimilation efficiency of ingested contaminant, and the contaminant influx rate from solution is determined by multiplying the contaminant concentration in the dissolved phase by the animal's filtration rate and the absorption efficiency of the dissolved contaminant in the animal. The loss rates of metal following uptake from either pathway are also considered. This model has been recently applied to consider metal accumulation in several marine invertebrates, including marine copepods, bivalves and deposit feeding polychaetes (Luoma et al., 1992; Thomann et al., 1995; Wang et al., 1996, 1997, 1998; Wang and Fisher, 1998a). In this model, metal uptake over time is described by the following first-order equation:

$$\frac{dC}{dt} = (k_u \cdot C_w) + (AE \cdot IR \cdot C_f) - (k_e + g) \cdot C \quad (1)$$

where,  $C$  is the metal concentration in the animals ( $\mu\text{g g}^{-1}$ ),  $t$  is the time of exposure (days),  $k_u$  is the uptake rate constant from the dissolved phase,  $C_w$  is the metal concentration in the dissolved phase ( $\mu\text{g l}^{-1}$ ),  $AE$  is the metal assimilation efficiency from ingested particles,  $IR$  is the ingestion rate of the animal ( $\text{mg g}^{-1} \text{day}^{-1}$ ),  $C_f$  is the metal concentration in ingested particles ( $\mu\text{g mg}^{-1}$ ),  $k_e$  is the efflux rate constant (per day), and  $g$  is the growth rate constant (per day).

This model considers metal uptake from both

Table 1  
Empirical studies of the relative importance of food and water in the overall metal accumulation in aquatic invertebrates<sup>a</sup>

Metal	Animal	Food	Exposure pathway dominated by	Reference
Ag	<i>Crassostrea virginica</i>	Phytoplankton	Water	Abbe and Sanders (1990)
	<i>Palaemonetes pugio</i>	Sediments	Water	Abbe and Sanders (1990)
	<i>Crassostrea gigas</i>	Detritus	Water	Connell et al. (1991)
As	<i>Eurytemora affinis</i>	Phytoplankton	Water	Martoja et al. (1988)
	<i>Balanus improvisus</i>	Phytoplankton	Food	Sanders et al. (1989)
	<i>Crassostrea virginica</i>	Phytoplankton	Food	Sanders et al. (1989)
Cd	<i>Pseudodiaptomus coronatus</i>	Phytoplankton	Food	Sanders et al. (1989)
	<i>Chaoborus punctipennis</i>	Zooplankton	Food	Sanders et al. (1989)
	<i>Mytilus edulis</i>	Phytoplankton	Water	Sick and Baptist (1979)
		Phytoplankton	Water	Munger and Hare (1997)
		Phytoplankton	Water	Borchardt (1983)
		Phytoplankton	Water	Janssen and Scholz (1979)
		Phytoplankton	Water	Riisgård et al. (1987)
	<i>Macoma balthica</i>	Bacteria	Water	Harvey and Luoma (1985)
	<i>Capitella</i> sp.	Sediment	Food	Selck et al. (1998)
Cr	<i>Pseudechinus novaezealandiae</i> (larvae)	Phytoplankton	Food	Bremer et al. (1990)
Po	<i>Palaemon serratus</i>	Mussel	Food	Carvalho and Fowler (1994)
Se	<i>Meganyctiphanes norvegica</i>	Mussel	Food	Fowler and Benayoun (1976)
	<i>Pudiatapes philippinarum</i>	Phytoplankton	Food	Zhang et al. (1990)
Zn	<i>Macoma balthica</i>	Bacteria	Water	Harvey and Luoma (1985)
	<i>Orchestia gammarellus</i>	Phytoplankton	Food	Weeks and Rainbow (1993)

<sup>a</sup>In most studies, metal accumulation was compared following exposure to water, food and water + food treatments.

the dissolved phase and food (Fig. 1). Both sources can of course be further divided, e.g. solute uptake can include porewater and overlying water for infaunal invertebrates, and food can include phytoplankton, detritus, and inorganic particles or sediments. The model assumes that uptake from each phase is directly proportional to the metal concentration in that phase (Fig. 1). Additive uptake from each phase is also assumed (Luoma and Fisher, 1997), thus:

$$C_{ss,w} = (k_u \cdot C_w) / (k_{ew} + g) \quad (2)$$

$$C_{ss,f} = (AE \cdot IR \cdot C_f) / (k_{ef} + g) \quad (3)$$

$$C_{ss} = C_{ss,f} + C_{ss,w} \quad (4)$$

where  $C_{ss,w}$  ( $\mu\text{g g}^{-1}$ ) and  $C_{ss,f}$  ( $\mu\text{g g}^{-1}$ ) are the metal concentrations in the animals obtained from water and food, respectively,  $k_{ew}$  and  $k_{ef}$  are the efflux rate constants following uptake from water and food, respectively, and  $C_{ss}$  is the metal concentration in the animals ( $\mu\text{g g}^{-1}$ ) at steady state. This kinetic model has been recently tested in marine bivalves and copepods by comparing the model predicted metal concentrations with metal concentrations measured independently in field collected samples (Luoma et al., 1992; Wang et al., 1996, 1997; Fisher et al., submitted). For example, the predicted tissue concentrations for Ag, Cd, Se and Zn were almost identical to measured concentrations in the mussel *Mytilus edulis* collected from San Francisco Bay and Long Island Sound (Wang et al., 1996). Thus, it appears that the model takes into consideration all the

processes which govern metal accumulation in these animals. With this model, it is also possible to quantify the fraction of metal uptake from food ( $R_f$ ) and water ( $R_w$ ):

$$R_f = C_{ss,f}/C_{ss} \quad (5)$$

$$R_w = C_{ss,w}/C_{ss} \quad (6)$$

In Eq. (3),  $C_f$  can be calculated from  $C_w$  multiplied by the metal partition coefficient ( $K_d$ ) for suspended particles, assuming an equilibrium partitioning between solute and particulate phases (Fig. 1). If metal efflux rates are comparable following uptake from water and food, Eqs. (5) and (6) can be calculated as:

$$R_f = 1/[1 + k_u/(AE \cdot IR \cdot K_d)] \quad (7)$$

$$R_w = 1 - R_f \quad (8)$$

The biological and geochemical parameters ( $k_u$ , AE, IR, and  $K_d$ ) identified in this model are thus critical in determining the relative importance of water vs. food in the overall metal accumulation. If the variabilities of these parameters can be reasonably quantified, the model will allow predictions under various conditions typically encountered by the animals in the field. Sensitivity analysis can also be performed to assess the im-

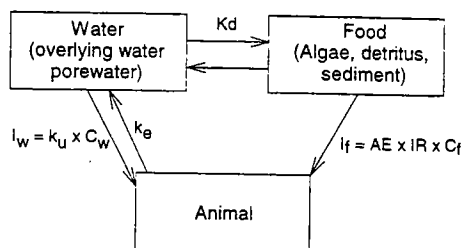


Fig. 1. Exposure pathways of metal uptake in marine invertebrates and the parameters describing the rate of metal uptake from each pathway.  $I_w$ : influx rate from the dissolved phase;  $k_u$ : uptake rate constant from the dissolved phase;  $C_w$ : metal concentration in the dissolved phase;  $k_e$ : efflux rate constant;  $I_f$ : influx rate from the food source; AE: metal assimilation efficiency from ingested food; IR: ingestion rate of the animal;  $C_f$ : metal concentration in ingested food;  $K_d$ : metal partition coefficient in food.

portance of each parameter in affecting  $R_f$  and  $R_w$  (Fisher et al., 1996; Wang et al., 1996).

One disadvantage of the kinetic model is that it requires measurements of several parameters that are highly dependent on the physiological conditions of the animals and on environmental conditions. There is no generic value for each species–metal combination. For example, AEs for any particular metal can vary as a function of food quantity (Wang et al., 1995), quality (Decho and Luoma, 1994; Wang and Fisher, 1996a), and chemical composition (Wang and Fisher, 1996b), although exceptions are noted (Fisher and Teyssié, 1986). Uptake rate constants from the dissolved phase are related to aqueous chemistry, including dissolved organic carbon concentration (DOC) and salinity (Wright, 1995; Wang et al., 1996). Filtration rates of animals may also influence uptake rate constants (which are a function of metal absorption efficiency from the dissolved phase and filtration rate). Efflux rate constants can be dependent on the route of metal exposure (Wang and Fisher, 1998a). Metal  $K_d$  values in food particles can vary by at least an order of magnitude over temporal and spatial scales (Fisher and Wang, 1998; Lee and Luoma, 1998). Consequently, variability of each parameter needs to be considered in developing a realistic kinetic model for marine animals.

We now consider specific examples of studies which experimentally determined key parameters regarding metal accumulation in invertebrates that were used in kinetic models. Timmermans et al. (1992) estimated the rate constants of Cd and Zn uptake in the water mite *Limnesia maculata* and the caddisfly larva *Mystacides* sp., including  $k_u$ ,  $C_w$ , AE, IR, and  $C_f$ . Based on these measurements, they predicted that approximately 65% of Zn and only 6% of Cd in *L. maculata* were obtained from the dissolved phase, whereas for *Mystacides* sp. 76% of Zn and 38% of Cd were from the dissolved phase. In these animals, therefore, food ingestion was a more important source for Cd uptake whereas solute uptake was more important for Zn. In prawns, Carvalho and Fowler (1994) measured uptake rate constants and calculated that dissolved Po in seawater should account for only 1–2% of the total body burden. In

these studies, however, variations of each parameter were not considered.

Luoma et al. (1992) measured the AE and  $k_u$  of Se (including selenite and elemental selenium) and then used the kinetic model to predict Se accumulation in marine clams (*Macoma balthica*) using concentrations of Se in suspended particles and in solution in San Francisco Bay. The Se concentrations in clams predicted by the model were comparable to those found in the estuary. The model further predicted that > 95% of Se in the clams was obtained from food, primarily because of the very high AE (e.g. 90% from ingested diatoms) and the very low  $k_u$  of selenite. Most previous assessments of Se toxicity employed selenite in solution, whereas Se was accumulated in these animals mostly through trophic transfer. Thus, regulations derived from toxicity tests with Se in water would underestimate actual Se exposures of the clams by more than 20-fold, and may thus be irrelevant to natural systems.

Table 2 summarizes the measured  $k_u$ , AE, IR,  $k_{ew}$ ,  $k_{ef}$ , and  $K_d$  of Ag, Cd, Co, Se and Zn in the mussel *M. edulis*, the copepod *Temora longicornis*,

and the polychaete *Nereis succinea*. Both mussels and copepods are suspension feeders which can accumulate metals from the dissolved phase and seston (including algae and inorganic particles). Metal associated with sediments may also become potentially available to mussels following sediment resuspension. *N. succinea* is a surface deposit feeder primarily feeding on surface toxic sediments including any biological components associated with surface sediments. Metal-specific physiological parameters in these invertebrates and their variability's under diverse environmental conditions have been systematically determined. Metal AEs in each animal were measured for different food types, and the ranges of values are given in Table 2. In general, there was no consistent taxonomic difference in metal AEs among different groups. AEs of Cd and Zn in copepods were approximately two times higher than AEs in mussels and worms, whereas the AE of Co in worms was 2–4 times higher than AEs in mussels and copepods.

The uptake rate constant of metals from the dissolved phase is often measured by exposing

Table 2

Physiological and geochemical parameters used in the kinetic modeling of the exposure pathways of metals in the mussel *Mytilus edulis*, the copepod *Temora longicornis*, and the polychaete *Nereis succinea*<sup>a</sup>

Animal		Ag	Cd	Co	Se	Zn
<i>M. edulis</i>	AE (%)	10 (4–34)	20 (11–40)	30 (14–43)	60 (15–72)	30 (16–48)
	$k_u$ ( $l\ g^{-1}\ day^{-1}$ )	1.794	0.365	0.124	0.035	1.044
	$k_{ef}$ ( $day^{-1}$ )	0.034	0.014	0.010	0.022	0.015
	$k_{ew}$ ( $day^{-1}$ )	0.019	0.011	0.018	0.026	0.020
	$K_d$ ( $l\ kg^{-1}$ )	$1.5 \times 10^5$	$5 \times 10^3$	$5 \times 10^3$	$1 \times 10^4$	$2 \times 10^4$
	IR ( $g\ g^{-1}\ day^{-1}$ )	0.27	0.27	0.27	0.27	0.27
<i>T. longicornis</i>	AE (%)	10 (8–20)	40 (33–53)	15 (14–21)	55 (50–60)	60 (52–64)
	$k_u$ ( $l\ g^{-1}\ day^{-1}$ )	10.42	0.694	0.606	0.024	3.290
	$k_{ef}$ ( $day^{-1}$ )	0.294	0.297	0.281	0.155	0.079
	$k_{ew}$ ( $day^{-1}$ )	0.173	0.108	0.122	0.155	0.108
	$K_d$ ( $l\ kg^{-1}$ )	$1.5 \times 10^5$	$5 \times 10^3$	$6 \times 10^3$	$3 \times 10^4$	$6 \times 10^4$
	IR ( $g\ g^{-1}\ day^{-1}$ )	0.42	0.42	0.42	0.42	0.42
<i>N. succinea</i>	AE (%)	20 (10–30)	20 (10–30)	65 (40–80)	40 (30–50)	35 (20–50)
	$k_u$ ( $l\ g^{-1}\ day^{-1}$ )	1.853	0.010	0.016	0.006	0.064
	$K_d$ ( $l\ kg^{-1}$ )	$1 \times 10^4$	$2 \times 10^3$	$2 \times 10^5$	$1 \times 10^3$	$2 \times 10^4$
	IR ( $g\ g^{-1}\ day^{-1}$ )	3.5	3.5	3.5	3.5	3.5

<sup>a</sup>Data for mussels are from Wang et al. (1996), for copepods from Wang and Fisher (1998a), and for polychaetes from Wang et al. (1999).

animals to a range of metal concentrations for a short period of time. Several studies also derived uptake rate constants from bioconcentration factors obtained by exposing animals for longer periods (Timmermans et al., 1992; Thomann et al., 1995). Advantages of employing short-term exposure in quantifying metal influx rate have been discussed (Wang et al., 1996; Luoma and Fisher, 1997). In general, influx rate from the dissolved phase increases linearly in a log-log relationship with increasing metal concentration in the dissolved phase for both plants (Fisher et al., 1984; Fisher, 1985; Gstoettner and Fisher, 1997) and animals (Bjerregaard et al., 1985; Luoma et al., 1992; Wang et al., 1996, 1998; Wang and Fisher, 1998a), indicating that metals are primarily transported by passive diffusion and facilitated transport (Capene and George, 1981; Simkiss and Taylor, 1989). Uptake rate constants are typically much higher in copepods (except for Se) than in mussels and worms, presumably a result of their smaller body sizes (higher surface area to volume ratio which enhances diffusion and transport). Body size has been demonstrated to be important in determining the uptake rate constant in mussels, although the absorption efficiency (which can be calculated by dividing the uptake rate constant by the filtration rate of an animal) is relatively independent of body size (Wang and Fisher, 1997b). In the kinetic model, uptake from the dissolved phase is normally considered to be from one total pool and metal speciation and its influence on metal uptake are not considered. However, metal speciation can clearly affect metal accumulation in aquatic organisms (Campbell, 1995), and future modeling efforts need to take dissolved speciation of metals into account.

The route of exposure has no major influence on the efflux rate of metals in mussels, but in copepods efflux rates are highly dependent on the source of metal exposure (Table 2). In this group of animals, non-essential metals (e.g. Ag, Cd) are regenerated at a much faster rate after food ingestion than after solute uptake. Further, efflux in copepods is consistently higher than that in mussels or other macroinvertebrates (Reinfelder et al., 1998), presumably as a result of their higher weight specific metabolic rates associated with

smaller body sizes. Efflux rates in copepods are also dependent on food quantity, where regeneration of non-essential elements (e.g. Ag, Cd) increase with food concentration but regeneration of essential elements (e.g. Se, Zn) remains independent of food concentration (Wang and Fisher, 1998b).

Typically, in model calculations, maximum reported ingestion rates (IR) are used, but the influence of IR variation can also be evaluated by sensitivity analysis (Wang and Fisher, 1998a). Because of the low nutritional value of sediments, the daily weight-specific ingestion rates in deposit feeders are at least two times their body weights (Cammen, 1980; Lopez and Levinton, 1987), and greatly exceed those of suspension feeders. In suspension feeders, ingestion rates generally increase with increasing seston concentration up to a maximum, above which rates remain relatively constant (Conover, 1978; Widdows et al., 1979).

The growth rate constants ( $g$ ) have been ignored in mussel and worm modeling because they are much lower than the efflux rate constants in adults. In copepods,  $g$  values have been incorporated into the kinetic model (Wang and Fisher, 1998a), although  $g$  should be ignored in adult copepods as there is no growth once individuals develop into the adult stage (Fisher et al., submitted). In these crustacean zooplankton any growth is manifested by molting during the naupliar and copepodite developmental stages. When  $g$  is ignored in the model, the predicted metal concentrations in copepods are close to concentrations measured in field-collected samples (Fisher et al., submitted).

Metal  $K_d$  values determined from laboratory-cultured phytoplankton can be employed for modeling metal accumulation in copepods because phytoplankton cells are the dominant food source for these animals (Kleppel, 1993).  $K_d$  values in natural seston have been used for modeling metal accumulation in mussels. Bioconcentration factors in marine phytoplankton are relatively well quantified (Fisher and Reinfelder, 1995), whereas partition coefficients in seston have been quantified for only a few estuarine systems (e.g. Cutter, 1989; Kuwabara et al., 1989; Lee and Luoma, 1998). Metal  $K_d$  values in sediment, the

food source for *N. succinea*, are lower than those in seston and phytoplankton for Cd and Se, but are much higher for Co, presumably due to bacterial activity in the sediment (Lee and Fisher, 1993).

The proportion of total metal uptake in three invertebrates deriving from ingestion of food has been calculated as a function of AE and  $K_d$ , using parameters in Table 2 (Figs. 2 and 3). In modeling the influence of each parameter, numeric means of other parameters were employed (Table 2). In mussels, with the exception of Se which is accumulated almost exclusively from food, both food ingestion and solute uptake can contribute to overall metal accumulation (Wang et al., 1996). Uptake from the dissolved phase is important for metals (e.g. Cd, Ag, and Zn) that tend to be transported by a facilitated process (e.g. requiring ligand binding before be-

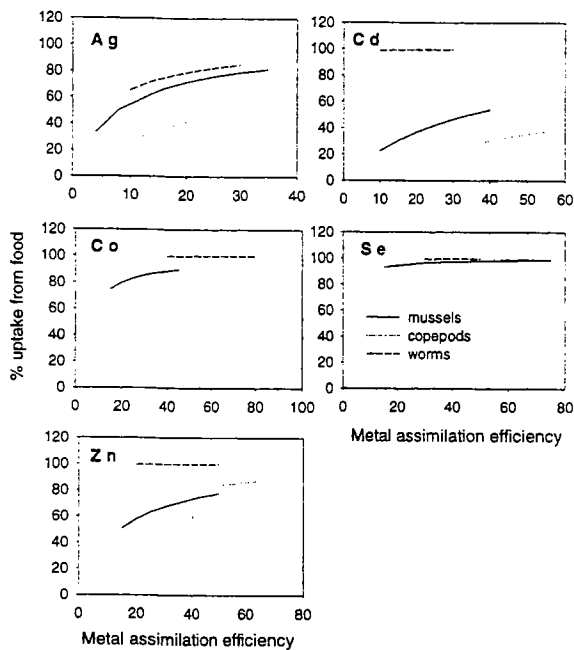


Fig. 2. The percentages of metal in three species of marine invertebrates (mussel *Mytilus edulis*, copepod *Temora longicornis*, and polychaete *Nereis succinea*) due to uptake from food ingestion as a function of change in metal assimilation efficiency (AE). In modeling the influence of AE on the route of metal uptake, mean numeric values of other parameters were employed (Table 2; see also Wang et al., 1996; Wang et al., 1999; Wang and Fisher, 1998a).

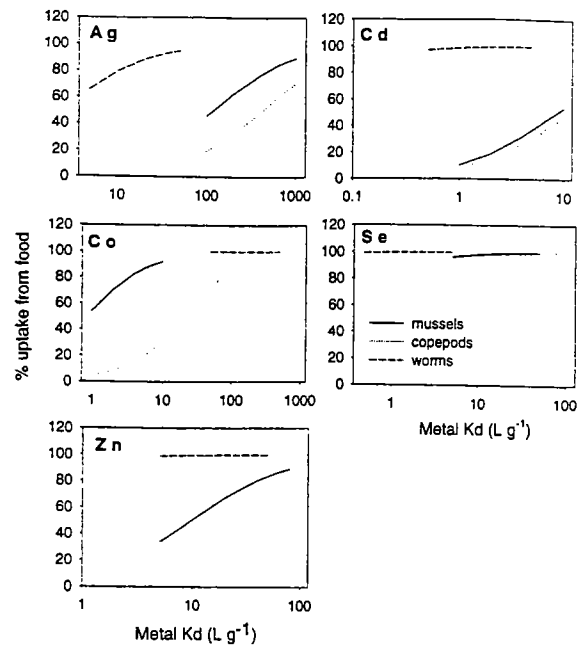


Fig. 3. The percentages of metal in three species of marine invertebrates (mussel *Mytilus edulis*, copepod *Temora longicornis*, and polychaete *Nereis succinea*) due to uptake from food ingestion as a function of change in metal partition coefficient ( $K_d$ ). In modeling the influence of AE on the route of metal uptake, mean numeric values of other parameters were employed (Table 2; see also Wang et al., 1996; Wang et al., 1999; Wang and Fisher, 1998a).

ing transported intracellularly). Using the mean numeric value for each parameter (Table 1), the percent of uptake from the food source would be 56% for Ag, 37% for Cd, 85% for Co, 98% for Se, and 67% for Zn.

Model analyses can lead to some non-intuitive and often surprising conclusions. For example, it had previously been suggested that most lanthanides and actinides are probably accumulated mostly from the dissolved phase because these elements typically have very low AEs in marine animals (Fowler, 1982). While this seems a very plausible conclusion, modeling has nevertheless shown that > 80% of  $^{241}\text{Am}$  in marine mussels is accumulated from food, despite its very low AE in mussels (1–6%) (Wang et al., 1996; Wang and Fisher, 1997a). This is primarily because Am is such a particle-reactive element, leading to high Am concentrations on food particles and there-



fore a high Am influx from the particulate phase. Conversely, the importance of Co uptake from ingested food is a result of relatively high AE values (10–30%), which can offset the low Co concentration in food particles due to its low  $K_d$  in marine phytoplankton (Fisher and Reinfelder, 1995). For Cd, the low AE from ingested food coupled to its relatively weak particle reactivity in seawater lead to a low Cd influx from ingested food, thus the dominance of its uptake from the dissolved phase. Ag is very particle-reactive and thus food is enriched in this metal, but it also has a very high absorption efficiency from solution, so the route of metal exposure can vary greatly under different environmental conditions.

Both water and food can contribute significantly to metal uptake in copepods (Figs. 2 and 3; Wang and Fisher, 1998a). Under most conditions that are likely encountered by copepods in the field, > 98% of Se and > 50% of Zn in copepods are derived from ingested food, but > 50% of Cd, Co and Ag body burden are derived from uptake from the dissolved phase. The dominance of solute uptake of Ag, Cd, and Co is due to a 2–3 times greater metal efflux following uptake from food than from water. In addition, the high  $k_u$  of these metals in copepods may also contribute to the dominance of solute uptake. For Zn,  $k_u$  is three times higher in copepods than in mussels, but its AE and  $K_d$  values (from pure phytoplankton cells) are also higher, resulting in a dominance of food ingestion in its uptake.

In contrast to mussels and copepods, the kinetic model consistently demonstrates that > 98% of the Cd, Co, Se and Zn body burden in the worm *N. succinea* derives from sediment ingestion, and this is primarily due to the very high IR, very low  $k_u$  and relatively high AE values (Wang et al., 1998; Wang et al., 1999). Uptake from the solute phase (including both from porewater and overlying water) contributes little to the overall metal accumulation in these animals (Figs. 2 and 3). Ag is the only metal which shows considerable uptake from the dissolved phase, but its overall accumulation is also dominated by ingestion of sediment particles (65–95%). Previously it was suggested that sediment is the major source for metal accumulation based on the strong correla-

tions between metal concentrations in sediments and in deposit feeding invertebrates (Luoma, 1983, 1989; Bryan and Langston, 1992). The modeling study using *N. succinea* unequivocally demonstrates that sediments should not be ignored as a direct and important route for metal accumulation in deposit-feeding animals.

The work with *N. succinea* has important implications for setting sediment quality criteria. It has been proposed, for example, that sediment quality criteria consider that sediment acid volatile sulfide (AVS) controls metal porewater concentrations and that metal toxicity results from uptake from interstitial water only (DiToro et al., 1992; Ankley et al., 1996). The sediment is considered to be in equilibrium with porewater and to indirectly affect metal accumulation due to the controls of AVS on porewater metal concentrations. Ankley et al. (1996) therefore proposed to use a toxicity assay based on dissolved exposure for the development of sediment quality criteria. However, both modeling (Wang et al., 1998) and experimental studies (Selck et al., 1998) have shown that ingestion of sediments can be a dominant route of metal accumulation for at least a few important benthic invertebrates such as *N. succinea* and *Capitella* sp. Assuming that metal AE is as low as 1% (lower than any AE measured for deposit feeders), (Wang et al., 1999) calculated that 88% of Cd, 100% of Co, 85% of Se and 92% of Zn come from sediment ingestion, suggesting that the route of metal exposure is not particularly sensitive to a change in metal AE and  $K_d$ . The low  $k_u$  and high IR values of deposit feeding animals have rarely been considered in most studies. Additional studies are warranted on the feeding physiology of other deposit-feeding animals and their ability to accumulate metals from both porewater and overlying water before broad generalizations are possible on how these animals accumulate metals.

More studies have focused on determining metal AEs than on the effects of environmental conditions on  $k_u$  and  $k_e$ . Nevertheless, uptake rates from the dissolved phase in mussels have been shown to increase with decreasing salinity but are less affected by dissolved organic carbon concentration in seawater (Wang et al., 1996).

Change in  $k_u$  as a function of aqueous chemical properties can be incorporated into modeling analyses, but this has not been performed as salinity and DOC can additionally affect metal concentrations in the particles. The influences of environmental conditions on metal uptake from the dissolved phase in copepods and worms have not yet been studied (Wang and Fisher, 1998a). Particle concentration, which can specifically affect IR, AE and possibly  $K_d$ , plays a less important role in affecting the exposure pathways in mussels (Wang and Fisher, 1997a).

Kinetic modeling can also distinguish the contribution of different species of a metal to a metal's overall accumulation in marine invertebrates (Wang et al., 1997, 1998). Examples are given here for Cr [Cr(III) and Cr(VI)] and Hg [Hg(II) and CH<sub>3</sub>Hg(II)]. Because different metal species can have very different toxicological effects, it is important to delineate the species of metal that is accumulated in these organisms. For example, Cr(VI) is highly soluble (as oxyanion chromate) and toxic due to its oxidation of intracellular compounds (Nieboer and Jusys, 1988), whereas Cr(III) forms insoluble Cr(OH)<sub>3</sub> and is relatively nontoxic to organisms. Methylmercury has higher mobility, bioavailability and toxicity than inorganic Hg(II) in aquatic organisms. Biomagnification of CH<sub>3</sub>Hg(II) in aquatic food webs is the best documented example among metals (Watras and Bloom, 1992; Westcott and Kalff, 1996). Many studies have found that even though CH<sub>3</sub>Hg(II) comprises only a small fraction (typically < 1%) of the total Hg in sediments (Gagnon et al., 1996, 1997), concentrations in fish and

mammals can increase by several orders of magnitude and most of the Hg in the muscle tissue of these animals is methylated (Bloom, 1992; Wagemann et al., 1997).

Wang et al. (1997, 1998) used <sup>51</sup>Cr(III) and <sup>51</sup>Cr(VI) radiotracers to measure their respective AE,  $k_u$  and  $k_e$  values in marine mussels, and <sup>203</sup>Hg(II) and CH<sub>3</sub><sup>203</sup>Hg(II) to measure their respective AE and  $k_u$  in the worm *N. succinea*. These values and other parameters required in the kinetic model are summarized in Table 3. Bioavailability of Cr(VI) to mussels from both dissolved and particulate phases is much higher than Cr(III), as indicated by approximately an order of magnitude higher AE and threefold higher  $k_u$ , but the  $K_d$  of Cr(VI) is at least two orders of magnitude lower than Cr(III). Because Cr(III) concentrations in the dissolved phase are generally undetectable at high salinity (> 18 ppt) (Beaubien et al., 1994; Abu-Saba and Flegal, 1995) and its uptake rate from the dissolved phase is much lower than Cr(VI), the contribution of dissolved Cr(III) is negligible for the overall Cr accumulation in mussels (Wang et al., 1997). The contribution of Cr(VI) from the particulate phase is also negligible because of its low particle-reactivity and thus low concentration in food particles (Wang et al., 1997). Thus, only dissolved Cr(VI) and particulate Cr(III) are significant sources for Cr accumulation in mussels. Using environmentally relevant Cr(VI) concentrations in the dissolved phase and Cr(III) concentrations in particles, Wang et al. (1997) calculated that 13–38% of the Cr body burden in mussels in San Francisco Bay is due to Cr(VI) uptake from the dis-

Table 3  
Physiological and geochemical parameters used in the kinetic modeling of the exposure pathways of metals in mussels and polychaete<sup>a</sup>

Animal	Metal	AE (%)	$k_u$ (l g <sup>-1</sup> day <sup>-1</sup> )	$k_{ef}$ (day <sup>-1</sup> )	$k_{ew}$ (day <sup>-1</sup> )	$K_d$ (l kg <sup>-1</sup> )
<i>M. edulis</i>	Cr(III)	0.7 (0.2–1.3)	0.034	0.010	0.012	$7 \times 10^4$ ( $10^4$ – $10^5$ )
	Cr(VI)	6 (0.7–10.4)	0.100	nd	0.011	$3 \times 10^2$ ( $2 \times 10^2$ – $5 \times 10^2$ )
<i>N. succinea</i>	Hg(II)	20 (7–22)	1.26	0.027	nd	$2 \times 10^4$ ( $10^4$ – $10^5$ )
	CH <sub>3</sub> Hg(II)	70 (43–75)	2.77	0.014	nd	$2 \times 10^3$ ( $10^3$ – $10^4$ )

<sup>a</sup> nd, not measured. Values in parentheses are the range observed for each parameter. Data for mussels are from Wang et al. (1997), and for polychaetes from Wang et al. (1998).

solved phase, and 62–87% is from Cr(III) ingestion on particles.

Methylmercury is more bioavailable to deposit-feeding worms than Hg(II) from both solute and sediment phases. Its AE and  $k_u$  are approximately 3.5 and two times higher than Hg(II), but its  $K_d$  is an order of magnitude lower than Hg(II). The efflux rate constants of CH<sub>3</sub>Hg(II) are approximately two times higher than Hg(II) (Wang et al., 1998).

To quantitatively separate the sources of Hg [Hg(II) and CH<sub>3</sub>Hg(II)] uptake in worms, a bioconcentration factor (BCF) is first calculated as:

$$\text{BCF} = C_{\text{ss}}/C_w = (k_u + \text{AE} \cdot \text{IR} \cdot K_d)/(k_e + g) \quad (9)$$

Thus, the relative importance of Hg vs. CH<sub>3</sub>Hg(II) in the overall Hg accumulation can be calculated:

$$R_{\text{Hg}} = \text{BCF}_{\text{Hg}} / [\text{BCF}_{\text{Hg}} + (\text{BCF}_{\text{CH}_3\text{Hg}} \cdot C_{w,\text{CH}_3\text{Hg}}/C_{w,\text{Hg}})] \quad (10)$$

$$R_{\text{CH}_3\text{Hg}} = 1 - R_{\text{Hg}} \quad (11)$$

where,  $R_{\text{Hg}}$  and  $R_{\text{CH}_3\text{Hg}}$  are the fractions of total Hg in the worm from Hg(II) uptake and CH<sub>3</sub>Hg(II) uptake, respectively, and  $\text{BCF}_{\text{Hg}}$  and  $\text{BCF}_{\text{CH}_3\text{Hg}}$  are the bioconcentration factors of Hg(II) and CH<sub>3</sub>Hg(II) in the worm.  $R_{\text{Hg}}$  and  $R_{\text{CH}_3\text{Hg}}$  can be calculated from Eqs. (9) and (10) as a function of the ratio of  $C_{w,\text{CH}_3\text{Hg}}/C_{w,\text{Hg}}$  in the solute phase (including porewater and overlying water).

Using the kinetic parameters in Table 3, Wang et al. (1998) calculated that > 70% of the Hg(II) body burden in worms derives from sediment ingestion, whereas for CH<sub>3</sub>Hg(II) the relative importance of dissolved source and sediment is dependent on its AE and  $K_d$ . Again the dominance of sediment Hg(II) over solute Hg(II) results from the high ingestion rate of the worms, despite the relatively high rate of Hg(II) uptake rate from the solute phase. For CH<sub>3</sub>Hg(II), the very high  $k_u$  (the highest recorded for any metal) can counteract the high AE and relatively weak particle-reac-

tivity. In coastal sediments, CH<sub>3</sub>Hg(II) in porewater is typically 10–30% of the total dissolved Hg (Gagnon et al., 1996). Using this range, the model predicts that approximately 5–17% of the total Hg in worms is from CH<sub>3</sub>Hg(II) accumulation (Wang et al., 1998), consistent with field measurements in the polychaete *Nereis diversicolor* (18%; Muhaya et al., 1997). Therefore the model indicates that even though CH<sub>3</sub>Hg(II) is typically < 1% of the total Hg in sediment and < 30% of the total Hg in porewater, it can constitute an important source for Hg accumulation because of its high  $k_u$  and AE and low  $k_e$  values. The relative importance of CH<sub>3</sub>Hg(II) uptake can of course depend on the types of sediment ingested by the animals and the depth at which the animals feed because the ratio of CH<sub>3</sub>Hg(II) to Hg(II) can increase with sediment depth due to methylation by anaerobic bacteria (Gagnon et al., 1996).

### 3. Significance of exposure pathways

With a few exceptions (e.g. Se is only from ingested food), both uptake from the dissolved phase and from food should be considered in evaluating metal accumulation in suspension feeders. Any water quality criteria based on biological responses to solute exposure only would be inadequate for the protection of aquatic life. Many biological and environmental factors can affect the relative importance of food vs. water as sources for metal accumulation in these animals. The modeling examples shown here employed only the mean numeric value of each parameter, and it is likely that their values would change under different environmental conditions. Modeling studies could well have important implications for setting new water and sediment quality criteria. Toxicity tests, for example, would need to consider metal exposure from food as well as water; currently only solute exposure is typically evaluated. Differences in exposure pathways may affect metal toxicity, but this has rarely been considered in toxicity tests (Taylor et al., 1998). Metal transfer to higher trophic levels may depend on metal binding following different routes

of exposure (Wallace and Lopez, 1996). In copepods, metals accumulated from the dissolved phase often associate with exoskeleton (Wang and Fisher, 1998a), and consequently are less bioavailable to fish than metals in internal tissues (Reinfelder and Fisher, 1994). In mussels, Ag from food may bind with metal-rich granules (Ag<sub>2</sub>S) in the cell lining of the digestive tract, whereas Ag from the dissolved phase is stored in the kidneys in an insoluble form (George et al., 1986; Wang et al., 1996). Exposure pathways can influence trace element biogeochemical cycling in aquatic systems, but this has been little studied. In copepods, metal excretion rate and the decomposition rate of carcasses, which can both affect the cycling and residence time of metals in the water column, are related to the pathway of metal uptake (Wang and Fisher, 1998a). Excretion rates of Cd, Co and Ag are approximately two times lower following uptake from the dissolved phase than uptake from food. Following metal assimilation, small zooplankton release metals into the dissolved phase at very high rates and may lengthen the residence times of metals in surface waters (Wang and Fisher, 1998b). In addition, metals which display high AEs in zooplankton also have longer oceanic residence times than do metals with lower AEs (Fisher and Reinfelder, 1995).

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