Do Cd, Cu, Ni, Pb, and Zn Biomagnify in Aquatic Ecosystems?*

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*Additional material for this chapter can be found on http://extras.springer.com

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D.M. Whitacre (ed.), *Reviews of Environmental Contamination and Toxicology Volume 226*, Reviews of Environmental Contamination and Toxicology 226,
DOI 10.1007/978-1-4614-6898-1_4,

1 Introduction

Trophic transfer (biotransference—Dallinger et al. 1987) results from passage of a contaminant through food chains as a result of uptake only from water (bioconcentration), only from diet (dietary accumulation), or from a combination of these (bioaccumulation) (Biddinger and Gloss 1984; Davis and Foster 1958; Macek et al. 1979; Suedel et al. 1994). Trophic transfer factors (TTFs) are analogous to bioaccumulation (accumulation) factors, the original terms used to describe steady-state tissue residues in an organism resulting from both water and dietary uptake pathways (Boroughs et al. 1957). TTFs are the same as biomagnification factors and also meet the definition of biomagnification when TTFs exceeding 1.0 are observed through three or more trophic levels as a result of at least two trophic transfers (Biddinger and Gloss 1984). Most investigators have assumed TTFs result mainly from dietary accumulation (Baptist and Lewis 1967; Mathews and Fisher 2008; Reinfelder et al. 1998), although it is not possible to distinguish aqueous from dietary uptake in field studies. Moreover, the relative importance of the diet and aqueous uptake pathways is context-dependent, varying with exposure duration, metal bioavailability, and the species and their prey. Application of the aquatic TTF concept, as currently understood, may have first been proposed by Baptist and Lewis (1967), and the term had been widely adopted by the early 1990s (Baudin and Nucho 1992; Dillon et al. 1995; Garnier-Laplace et al. 1997; Suedel et al. 1994).

All the foregoing processes—bioconcentration, bioaccumulation, biomagnification, and trophic transfer—were well described and defined by the 1950s, albeit with differences in specific usage. Most of these terms were originally introduced by scientists studying the environmental fate of radionuclides (e.g., Baptist and Lewis 1967; Davis and Foster 1958; Krumholz and Foster 1957). The toxicological implications of biomagnification were established decades ago for many compounds, such as mercury in the late 1950s (McAlpine and Araki 1959), DDT in the 1960s (Burdick et al. 1964; Hunt 1966; Peakall 1969), and PCBs (polychlorinated biphenyls) and chlorinated insecticides in the early 1970s (Hunt 1966; Peakall and Lincer 1970). However, such was not the case for most metals. Biomagnification has been shown to be a predictor of aquatic hazard for certain nonpolar hydrophobic compounds having specific properties, such as log $K_{ow} > 6.0$, depuration rate half lives >40 days, and assimilation efficiencies >35% (Borga et al. 2011; Bruggeman et al. 1984; Fisk et al. 1998; Macek et al. 1979). Inorganic metals, in contrast, are hydrophilic, some are metabolically essential (Davis and Gatlin 1996; White and Rainbow 1985), and most are variably regulated and detoxified (Ju et al. 2011).

Trophic transfer and biomagnification historically were calculated similarly, but now are calculated in various ways. TTFs can be based on single or multiple transfers (steps) in a food chain, with each step representing a predator–prey interaction, such as algae → planktor or oyster → carnivorous snail. For many years, biomagnification typically was calculated the same way. Both of these methods differ from that used to calculate trophic magnification factors (Borga et al. 2011), which is the antilog of a linear regression slope relating trophic level to log tissue concentration in field-based food web studies. A third method for calculating trophic transfer

uses a biokinetic model that measures the influences of exposure concentration, assimilation efficiency, and growth (Reinfelder et al. 1998; Luoma and Rainbow 2005). Because trophic transfer is chemical- and species-specific (Wang 2002), it follows that trophic transfer and biomagnification may be food chain-specific, hence varying between lab studies and field studies.

In this paper, we evaluate published data in which single and multiple trophic transfers of five metals (Cd, Cu, Pb, Ni, and Zn) were studied in freshwater and marine food chains. We examine whether the aquatic toxicity of bioaccumulated metals may be related to TTFs, and we compare TTFs measured in the laboratory and field with those estimated using biokinetic models. In performing this review, we had the following objectives: First, to compare TTFs generated from lab and field data on tissue residues in predator and prey. Second, to compare these TTFs to those estimated using a standard biokinetic model (see review of Reinfelder et al. 1998). Third, we sought to determine whether relationships existed between TTF magnitude and metal concentration in prey. Fourth, we evaluated relationships between TTF magnitude and toxicity, which is the key reason that biomagnification in aquatic food webs is of concern (Meador 2006). The final objective was to consider whether TTFs and tissue residues for metals that were required for metabolism (Cu, Ni, and Zn) differed from those that were not required (Cd and Pb) (Brown 2005).

2 Methods

Relevant studies from the peer-reviewed literature cogent to our topic were identified using online searches (e.g., Google Scholar, SCIRUS, and ISI Web of Knowledge). We focused on Cd, Cu, Pb, Ni, and Zn because these are relatively data rich and represent essential (Cu, Ni, Zn) and non-essential (Cd and Pb) elements.

2.1 Laboratory Data

Trophic transfer data were compiled from dietary accumulation studies conducted in the laboratory (Online Resource 1). In these studies, measurements of metal concentration in the diet were made.

We compiled TTF data from studies in which the metal was incorporated into a natural food or was spiked into a processed food, such as a pellet. These data reflected tests having varying exposure durations, diet types and rations, some of which do not occur in nature. These differences may be consequential because metal bioavailability and assimilation efficiency will vary between diet types from a variety of factors: differences in the form in which the metal is stored, species-specific differences in metal homeostatic mechanisms (Wallace and Lopez 1997; Wallace et al. 2003; Ju et al. 2011), and differences in metal exposure history

(Rainbow et al. 2006). Only data in which the metal was measured in the consumer and its food were used. The TTFs were based on whole body metal concentrations so that comparisons across species and trophic levels could be normalized to the most commonly measured tissue type. We also evaluated whether TTF magnitudes and toxicity were related where both were measured.

A typical laboratory study design was to expose algae to a metal in an aqueous medium and then to feed the algae to a planktivore. In lab studies with carnivores, prey often were exposed via water or diet or both, then fed to the predator either live or in a processed form (e.g., as freeze-dried pellets). Trophic transfer factors were compiled from studies in which both single (e.g., alga → herbivore) and multiple (e.g., alga → herbivore → carnivore) steps in food chains were evaluated. Although the latter data were more relevant for evaluating metal biomagnification potential, one-step TTF data facilitated evaluation of relationships between TTFs and exposure concentration as well as those between TTFs and toxicity. Variability in these relationships is expected when the exposure concentration of a given metal influences the kinetics of uptake and depuration, and ultimately, TTF magnitudes in a species (Reinfelder et al. 1998) and toxicity (Cheung et al. 2006; Croteau and Luoma 2009).

All dietary and whole body tissue concentrations were expressed as dry weights. In some cases, typically fish, residues had to be calculated from wet weight concentrations using measured or assumed (75%) moisture contents. The moisture contents of whole body fish appeared to be relatively consistent, with reported values of 71, 75, and 77% ($n = 2{,}051$), corresponding to 25th, 50th, and 75th quartiles, respectively (Seiler and Skorupa 2001).

Relationships between $\log_{10}$ TTFs and $\log_{10}$ dietary metal concentrations were plotted and the slopes tested for statistical significance ($a = 0.05$) using linear regression. A significant negative slope—an inverse relationship—indicates that the metal concentration tends to be lower in the consumer than in its food. A significant positive slope indicates that a metal's concentration tends to be greater in the consumer than in its food. Slopes may be positive or negative, reflecting inherent differences among species (Schmidt et al. 2011), and the properties of the environment from which the species were sampled (Borga et al. 2011). Moreover, one-step increases in a metal concentration neither meet the definition of biomagnification (encompassing at least three trophic levels), nor that of trophic magnification.

2.2 Laboratory Biokinetic Data

TTFs were also estimated from biokinetic models that were parameterized, using values from the literature. Steady-state metal concentrations from waterborne and dietary exposures were estimated using the following equation (Reinfelder et al. 1998):

$$C_{ss} = \frac{(k_u \times C_w) + (\mathrm{AE} \times \mathrm{IR} \times C_f)}{k_e + k_g}, \tag{1}$$

where, C_{ss} = steady-state metal concentration (μg g^{-1}); k_u = uptake rate constant (L g^{-1} day^{-1}); C_w = metal concentration in water (mg L^{-1}); AE = assimilation efficiency from ingested particulate matter (%); IR = ingestion rate of the matter (g g^{-1} day^{-1}); C_f = metal concentration in food (μg g^{-1}); k_e = efflux rate constant (day^{-1}); and k_g = growth rate constant (day^{-1}).

The dietary component of (1) was re-arranged to calculate the TTF as follows (Wang and Fisher 1999):

$$\mathrm{TTF} = \frac{\mathrm{AE} \times \mathrm{IR}}{k_e + k_g}. \tag{2}$$

The assumption of steady state for some of the metals evaluated may be questioned, especially for temporally dynamic detoxification processes like metallothionein induction and granule formation (Vivjer et al. 2004). Mathematically, all organisms will reach steady state, although in some rare instances (e.g., Zn for barnacles) time to steady state may exceed the organism's lifespan. Equation 1 is simply the solution for a series of differential equations describing uptake and loss of metals at any instantaneous point in time. The general form of the equation used to estimate trophic transfer is valid whether solved for steady state or as an instantaneous measurement. Indeed, the measurements made to estimate TTF for the biokinetic data are short term and not in steady state. Hence the demonstration of steady state is unnecessary for purposes of this review.

Values reported in the literature for terms in (2) were used to generate species-specific TTFs. When unavailable, values for the same species that had been reported in another study (often by the same laboratory) were substituted. In a few cases, in which species-specific IR data were unavailable, a mean IR for the taxonomic group (e.g., bivalves, copepods) was substituted. Taking this step probably had minor effects on biokinetic TTF estimates, because IR generally is not a controlling parameter of TTF and the variability in IR among taxonomic groups generally is low (Luoma and Rainbow 2005; Wang and Rainbow 2008). Similarly k_g was reported infrequently, but with few exceptions does not greatly influence TTF magnitude (Luoma and Rainbow 2005; Wang and Rainbow 2008). Finally, most of the terms in (1) and (2) (k_u, AE, IR, k_e, k_g) are variable functions rather than constants, because exposure concentration influences k_u, k_e, and AE; the organism's exposure history influences k_u, k_e, and AE; and food density influences IR. No attempt was made to normalize these functions to a constant condition because, in most cases, the data needed to parameterize the functions were unavailable. As a result, some of the variations within and among species will be attributable to these sources.

Upon compilation of the biokinetic TTF estimates, species were assigned subjectively to trophic levels and food chains. The food chain assignments were dictated by the species for which biokinetic data were available. Initially, data were pooled into different taxonomic groups—e.g., copepods, bivalves, trophic level 3 fish and trophic level 4 fish. Within a trophic level, the mean (± standard error of the mean if n was ≥3) of available $\log_{10}$-transformed TTFs was quantified. This allowed for evaluation of specific food chain types (e.g., benthic vs. pelagic). Where both

biomagnification potential and variation within taxonomic group TTF were high, the data for individual species were examined to identify possible reasons for the variability. Freshwater and marine biokinetic data were compiled and are presented in Online Resources 2 and 3.

2.3 Field Data

Field bioaccumulation data were compiled for lakes, streams, estuaries, and coastal marine waters (see Online Resource 4). Studies typically comprised food chains of varying lengths and trophic levels, including primary producers, secondary consumers, and predators. We focused generally on studies in which trophic levels were assigned through measurement of stable isotope ratios of nitrogen (^{15}N:^{14}N; $\delta^{15}N$) and carbon (^{13}C:^{12}C; $\delta^{13}C$). As summarized in Croteau et al. (2005), $\delta^{15}N$ is a tool for inferring the relative trophic position of an individual species in a food web, and $\delta^{13}C$ can be used to identify food sources provided they have distinctive isotopic signatures. Food web associations also were inferred from reported dietary preferences of the species (e.g., Timmermans et al. 1989; Barwick and Maher 2003), and when trophic levels could be surmised (e.g., primary producer, primary consumer, secondary consumer). These choices augmented the database with information from a wider variety of sites and food webs. Where possible, linear regression was used to assess slopes and the statistical significance of the relationships between log whole body tissue concentration and trophic levels and/or stable isotope ratios (Online Resource 4). Otherwise, the statistics referenced are those reported in the studies.

3 Results

3.1 Laboratory Data

Laboratory-based TTFs were highly variable for each metal, ranging over two to three orders of magnitude (Online Resource 1). The TTFs for Cd, Cu, Pb, and Zn decreased with increased dietary exposure concentration (the slopes of the relationships between TTFs and dietary exposure concentration were significant, $p \leq 0.003$). TTF variability in relation to whole body concentration was greatest for Ni, possibly reflecting limited data, low TTF magnitude (TTFs generally ≤ 0.1) and differences among taxa (Fig. 1a–e). Metal-specific regressions for taxonomic groups (i.e., arthropod, fish, annelid, etc.) were typically less variable, and statistically significant ($p < 0.05$) for Cd, Cu, Pb, and Zn, indicating that the overall inverse relationship did not result from pooling data from different taxonomic groups.

Ranges of minimal nutritional requirements for Cu and Zn for fish and some invertebrates (Brown 2005) are shown in Fig. 1b, e. The TTF data for Cu and Zn in fish extend above and below the ranges. These data suggest that some of the Cu and Zn TTFs >1 were associated with nutritional requirements.

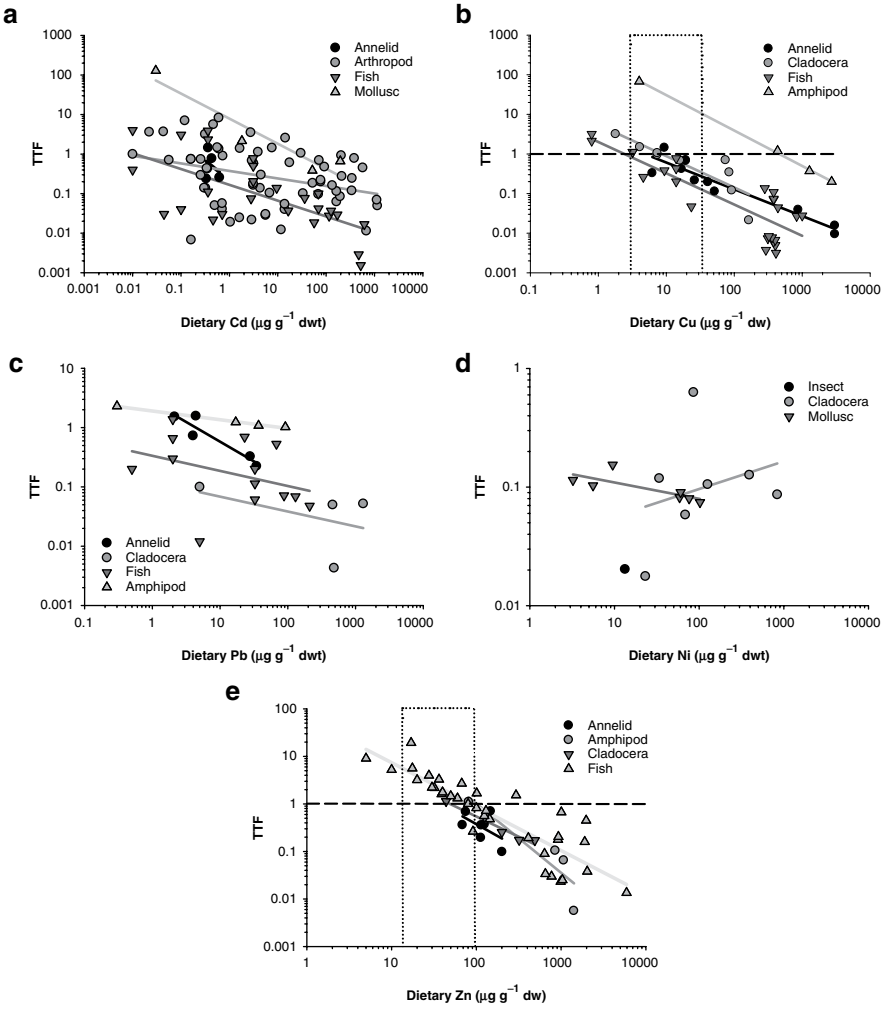

Fig. 1 Relationship between trophic transfer factors for different taxonomic groups and dietary exposure concentration from laboratory studies: (**a**) cadmium, (**b**) copper, (**c**) lead, (**d**) nickel, and (**e**) zinc. The *horizontal dashed line* indicates a TTF of 1. *Solid lines* represent regressions of TTF vs. dietary metal for individual taxa. The *dotted boxes* in (**b**) and (**e**) identify the range nutritional requirements for fish and some invertebrates (from Brown 2005)

Dietary metal toxicity was not more likely when the consumer had bioaccumulated a higher metal concentration than that in its food (Fig. 2a–e; Online Resource 1). Toxicity was defined as a significant adverse effect (i.e., reduced survival, growth, or reproduction) relative to the control. Toxicity based on whole body concentrations appeared unrelated to whether the organism bioaccumulated metal concentrations higher than those in its food, because there were insignificant relationships ($p = 0.2–0.7$) between TTF magnitude and toxicity for Cd, Cu, Pb, and Zn (Fig. 2a–c, e). Almost equal proportions of Cd TTFs >1 was associated with each of the three

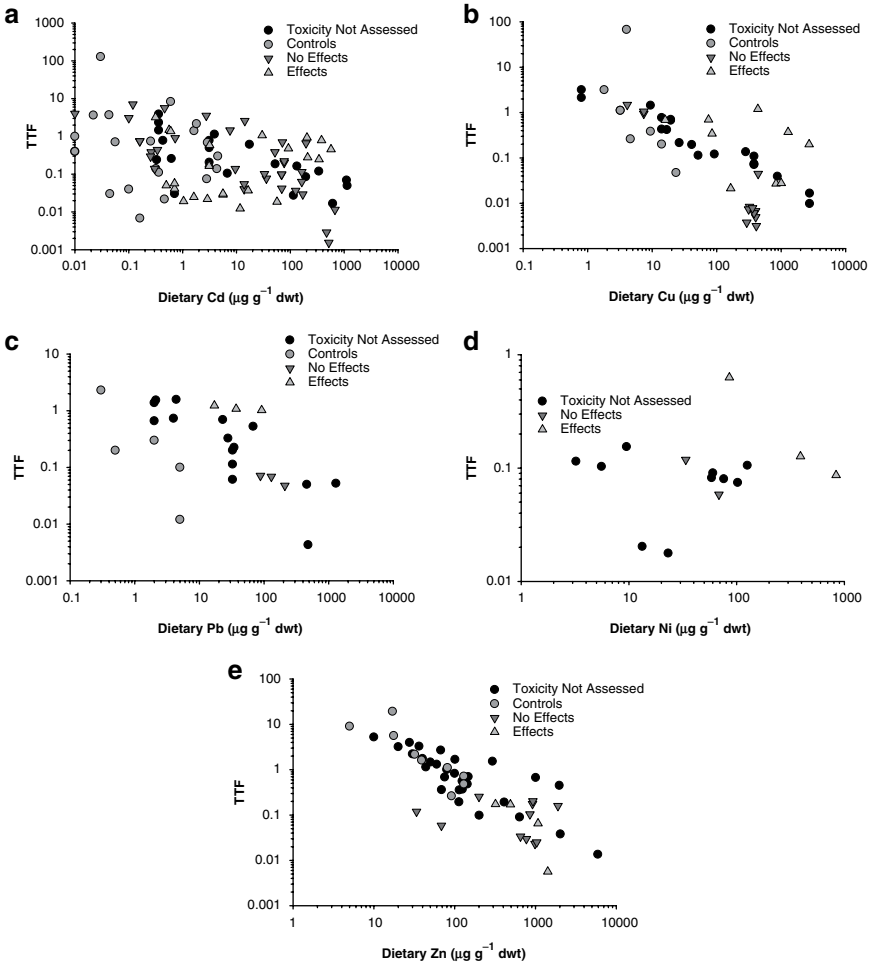

Fig. 2 Relationship between presence–absence of adverse effects, trophic transfer factors and dietary exposure concentration from laboratory studies: (**a**) cadmium, (**b**) copper, (**c**) lead, (**d**) nickel, and (**e**) zinc. The *different symbols* distinguish data associated with effects or lack thereof, and include controls and bioaccumulation studies in which toxicity was not evaluated explicitly, but occurred nonetheless

groups—controls, no effect, and effects (Fig. 2a). For Cu, only one of the nine data points associated with effects had a TTF >1.0 (Fig. 2b). All three data points associated with Pb toxicity had TTFs of 1.0–1.2 (Fig. 2c), all from a study in which the freshwater amphipod *Hyalella azteca* was fed rabbit chow equilibrated with aqueous Pb (Besser et al. 2005). Approximately 75% of the remaining Pb TTF data points in Fig. 2c were <1. None of the Ni TTFs exceeded 1.0 (Fig. 2d), and all of the Zn TTFs >1.0 were associated with control organisms or with studies in which toxicity was not evaluated (Fig. 2e). TTFs were well below 1.0 for the few studies in which dietary Zn toxicity was observed.

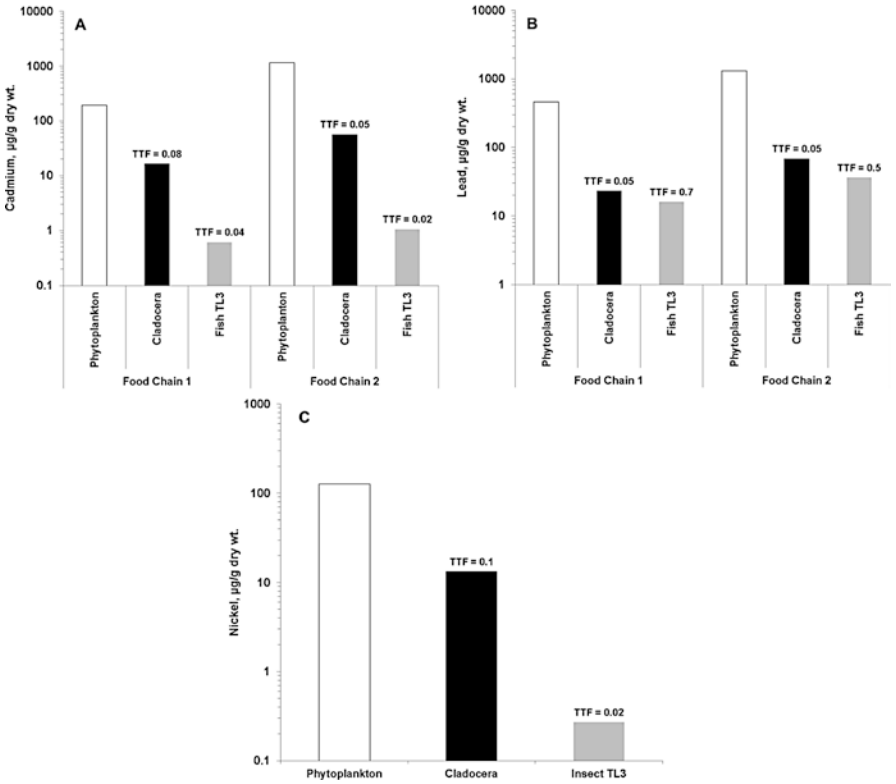

Fig. 3 Trophic transfer data from laboratory-simulated food chain studies for freshwater systems. (**a**) Cadmium, (**b**) lead, and (**c**) nickel. Geomean value for each taxonomic group. *White bars* = metal conc. in phytoplankton, *Black bars* = metal conc. in TL2, *Light gray bars* = metal conc. in TL3. Cadmium data from Ruangsomboon and Wongrat (2006); lead data from Vighi (1981); and nickel data from Ponton and Hare (2010)

Most (93%) of the TTFs summarized in Figs. 1a–e and 2a–e were from studies in which a single trophic transfer was evaluated. In the remaining studies, two or more transfers were evaluated, providing a more complete picture of trophic transfer and facilitating comparison of results to those from biokinetic modeling and field studies. In freshwater, phytoplankton were exposed to aqueous concentrations of Cd, Pb, and Ni and were then fed to cladocerans, which in turn were fed to fish or a predatory insect. Tissue concentrations decreased with increasing trophic level (Fig. 3a–c). From trophic level 1 (TL1) to TL2, the TTFs were similar (0.05–0.1) for Cd, Pb, and Ni. From TL2 to TL3, they declined for Cd (0.07–0.03), declined for Ni (0.1–0.02), and remained unchanged for Pb (0.05–0.6). Results of the single marine study that used Cd were similar to those in freshwater, namely TTFs of 0.1 for the first trophic transfer and one of 0.03 for the next transfer (Fig. OR1-1 in Online Resource 1).

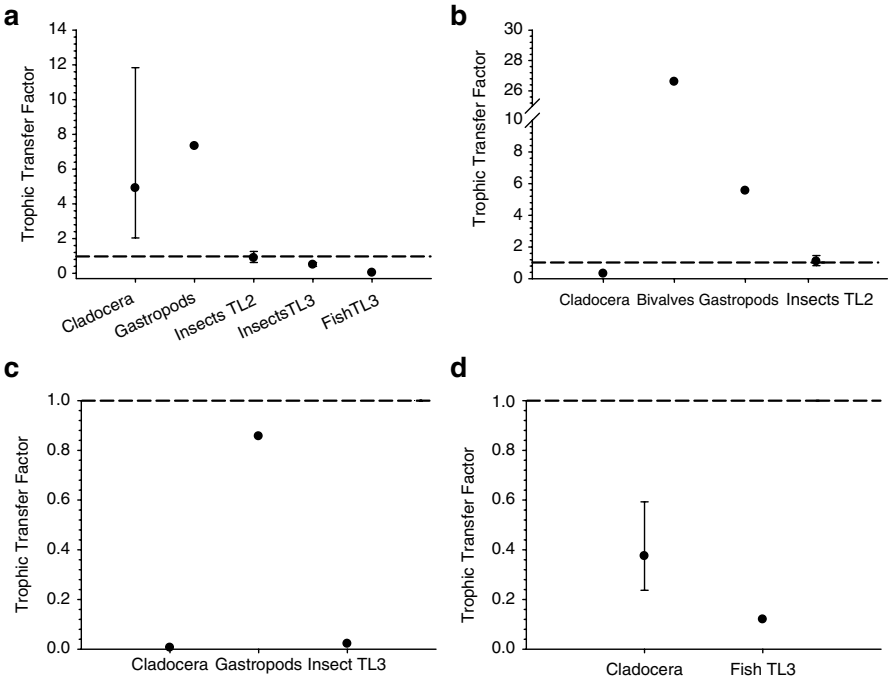

Fig. 4 Trophic transfer factor estimates from biokinetic data for freshwater studies. (**a**) Cadmium, (**b**) copper, (**c**) nickel, and (**d**) zinc. Geomean value for each taxonomic group, except when $n \geq 3$, geometric mean ± standard error of the mean. *Dashed lines* indicate TTF = 1

TTFs from one-step trophic transfers were also applied to simulated food chains because laboratory data for three or more trophic levels were limited ($n=4$; Figs. OR1-2 and OR1-3 in Online Resource 1). Using these data, TTFs also tended to decline with increasing trophic level for Cd, Cu, and Ni. However, zinc did not: declining slightly in freshwater food chains (ANOVA, $p=0.07$, $n=5$ and 9 for TL2 and TL3, respectively) and increasing slightly in the marine food chain (ANOVA, $p=0.37$, $n=4$, 7, and 8 for TL2, TL3, and TL4, respectively). Comparatively high TTFs were almost always associated with low dietary exposure concentrations (Fig. 1). Moreover, TTFs >1 for essential metals were associated with organisms assimilating metal to meet minimal nutritional requirements (Fig. 1b, e; Brown 2005).

3.2 *Biokinetic Data*

Overall, the biokinetic data for metal exposures in freshwater were much more limited than those in saltwater (Online Resource 2). With few exceptions, only a single TTF estimate was available for any taxonomic group, and only three trophic levels could be assessed (Cd, Ni, and Zn) (Fig. 4a, c, d). Copper TTF estimates were only

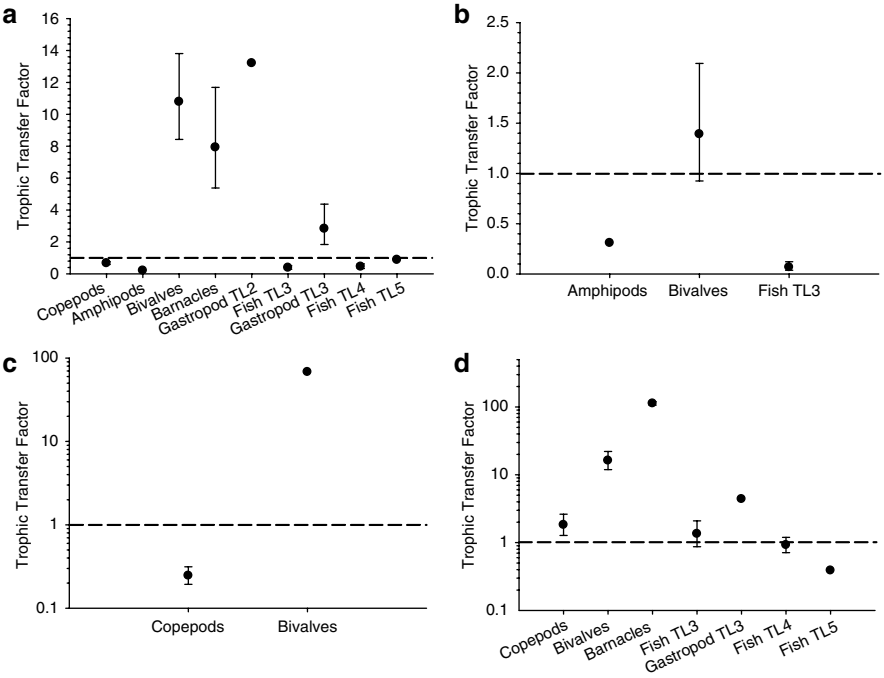

Fig. 5 Trophic transfer factor estimates from biokinetic data for marine studies. (**a**) Cadmium, (**b**) copper, (**c**) nickel, and (**d**) zinc. Geometric mean value given for each taxonomic group, except when $n \geq 3$, geometric mean ± standard error of the mean. *Dashed lines* indicate TTF = 1

available for TL1 to TL2 (Fig. 4b). Given the limited data, it is not possible to draw conclusions regarding the potential for metal biomagnification based on biokinetic data alone for freshwater organisms. The data suggest TTFs >1 from TL1 to TL2 for Cd and Cu, but not for Ni and Zn (Fig. 4a–e). Cadmium TTFs were >1 for both cladocerans and gastropods. Copper TTFs were low (0.1) for cladocera and high (6–27) for gastropods and bivalves. These observations appear to be consistent with the understanding that aquatic organisms in general do not regulate Cd, while crustaceans regulate Cu and mollusks generally do not (Rainbow 1997a, b).

In marine systems, the biokinetic data allowed a more robust assessment of biomagnification potential (Online Resource 3). Up to five trophic levels, multiple taxonomic groups, and multiple species within groups were examined. Trophic transfer factors for Cd and Zn suggest that the potential exists for biomagnification in carnivorous gastropods at both TL2 and TL3, when they prey upon bivalves, barnacles, or herbivorous gastropods in three-step food chains (Fig. 5a, d). Generally, this was not the case for TL3 fish, for which mean TTFs were <1 for Cd and Cu and averaged 2.2 for Zn (Fig. 5 a, b, and d). At TL4 (fish) and TL5 (shark), TTFs were ≤1 for both Cd and Zn. Biokinetic data for Ni were only available for TL1 to TL2, so no conclusions could be drawn (Fig. 5c). The high TTFs for Ni (9.3 and 496) estimated in the single study of Ni in bivalves contrasted with those (<1) for TL2 copepods fed algae, allowing no general conclusion.

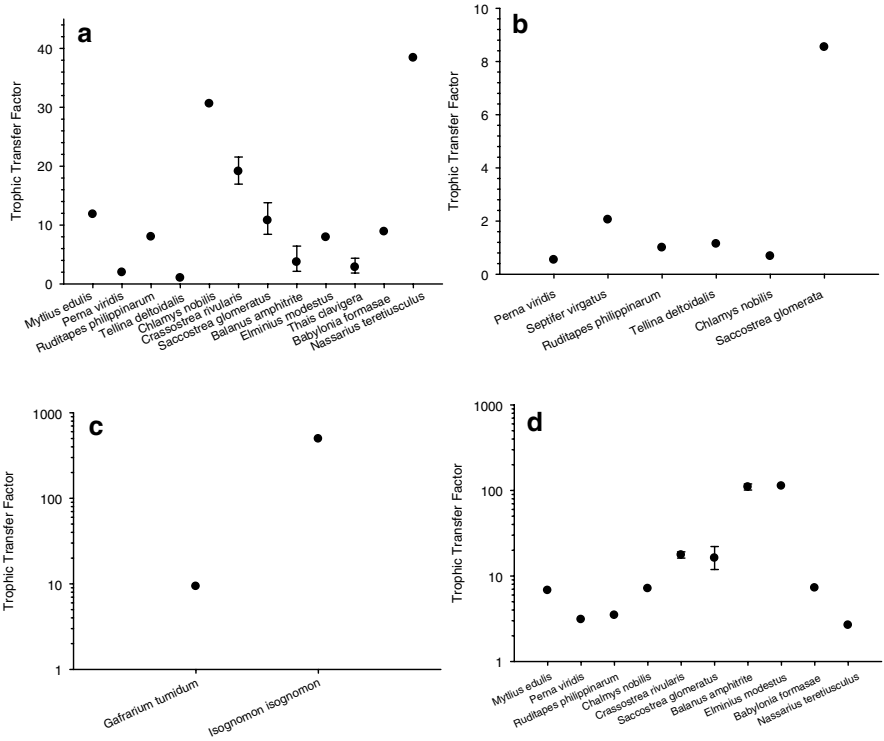

Fig. 6 Trophic transfer factor estimates from biokinetic data for accumulator species in marine systems. (**a**) Cadmium, (**b**) copper, (**c**) nickel, and (**d**) zinc. Geometric mean value for each species. When $n \geq 3$, mean ± SEM

Because of the potential importance of metal biomagnification in barnacles and mollusks in marine systems, we estimated TTFs for these taxa using biokinetic data (Fig. 6a–d). Bivalve TTFs consistently were higher in oysters and scallops (Ostreoida and Pterioida) than in mussels (Mytiloida) and clams (Veneroida) for all metals: Cd, Cu, Ni, and Zn. Both barnacle species had similar TTFs, perhaps not surprising because they are both within the family Balanidae. There were differences in Cd TTFs for the three carnivorous gastropods, with *Thais clavigera* having a distinctly lower mean TTF (1.5) than *Babylonia formosae* (TTF = 8.9) and *Nassarius teretiusculus* (TTF = 38).

3.3 Field Data

The majority of authors performing field studies (75% of 25 papers) that addressed metal concentrations at multiple trophic levels of aquatic organisms reported little evidence for the biomagnification of Cd, Cu, Pb, Ni, or Zn among primary

producers, primary consumers, and predators, including fish (Online Resource 4). Studies in which metal biomagnification was reported were generally limited to specific macroinvertebrate food webs; in fact, only two studies, both involving Zn, provided evidence of biomagnification in fish.

Several studies, in which trophic levels were defined using stable isotopes, provided evidence of significant ($p \leq 0.05$) biomagnification of certain metals in macroinvertebrates, but not fish (Online Resource 4). Examples of Cd biomagnification were limited to invertebrate food chains, and one involving a predatory flatworm (*Dugesia tigrina*) had a mean Cd concentration approximately three times greater than other macroinvertebrates within the same food web (Croteau et al. 2005). Another example involved herbivorous mollusks and predacious mollusks occupying TL 2 and 3 (Cheung and Wang 2008), whose results were consistent with the biokinetic estimates presented above. The best evidence of biomagnification in this last study involved Cd in two of the three habitats sampled, namely rocky intertidal habitats. Analysis of the δ^{15}N-log$_{10}$ Cd data that were reported, which were based on all species sampled in each intertidal habitat, indicated positive slopes ($b = 0.16$–0.24) that were statistically significant ($p = 0.002$–0.011) for both bays. For Cu and Zn, Jara-Marini et al. (2009) observed a significant ($p < 0.05$) linear relationship between Cu concentrations and δ^{15}N values from phytoplankton up to a secondary consumer crab, but the relationship was insignificant ($p > 0.05$) when secondary and tertiary consumer fish were included. The highest Zn concentrations were several-fold greater in filter-feeding oysters and barnacles than in other higher trophic level macroinvertebrates, such as snails, polychaetes, shrimp, and crab. Field data from Timmermans et al. (1989) and Quinn et al. (2003) both suggested that Zn biomagnified—but not Cd, Cu, and Pb—in insects occupying multiple trophic levels. The conclusion of Quinn et al. (2003) concerning zinc biomagnification might deserve further qualification as, based on re-analysis of their data, the slopes of the TMF regressions were significant only for one of the four stream/year combinations studied. Zinc biomagnification [TMF = 0.43 (95%CL = 0.3–0.6)] was only significant in insects from the uncontaminated stream in 1999 and was not significant ($p = 0.13$) the next year, 2000 [TMF = 0.09 (95%CL = −0.02 to 0.2)]. Biomagnification did not occur in insects from the stream receiving acid mine drainage in either year.

Other studies have failed to confirm Zn biomagnification in the field. Farag et al. (1998), for example, observed significantly ($p \leq 0.01$) lower Zn concentrations in detritivorous, omnivorous and carnivorous benthic macroinvertebrates from the metals-contaminated Coeur d'Alene River (Idaho) than in herbivorous benthic macroinvertebrates. Similarly, Watanabe et al. (2008) found insignificant correlations ($p > 0.05$) among Zn concentrations and δ^{15}N values in macroinvertebrates collected from three of four locations in a creek below an abandoned mining area in Japan.

There were two field studies in which Zn concentrations in fish were greater than in lower trophic levels. However, it appears that these higher Zn concentrations in fish are due to essentiality requirements, because the Zn concentrations in the food web were relatively low. In the first study, Saiki et al. (1995) analyzed Zn in several food web organisms collected from the mining-impacted locations in the upper Sacramento River (USA) and in reference tributaries. In reference tributaries, mean

Zn concentrations in fish were similar to or greater than those measured in macroinvertebrates and the aquatic plant *Elodea canadensis* (i.e., TTFs > 1.0) At the mining-impacted locations, however, mean Zn concentrations in fish were always less than the mean concentrations in macroinvertebrates and waterweed (i.e., TTFs < 1.0). The increased Zn concentration in fish relative to lower trophic levels collected from reference streams, but not in mining-impacted streams, likely reflects internal regulation of Zn by the fish. In the second study (Campbell et al. 2005), Zn concentrations in Arctic cod (*Boreogadus saida*) collected from northern Baffin Bay (between Ellesmere Island, Canada, and Greenland) were greater than in the food web. Because this study area is not contaminated with metals, the higher Zn residues in the cod probably reflect physiological requirements.

4 Conclusions and Discussion

Our review of the freshwater and saltwater literature concerning trophic transfer and biomagnification suggested several conclusions that we summarize below.

4.1 Overall Findings Concerning Biomagnification Potential

Cadmium, Cu, Ni, Pb, and Zn generally do not biomagnify in food chains consisting of primary producers, macroinvertebrate consumers and fish. Yet, there are specific food chains in which biomagnification of these metals occurs. First, biomagnification may occur in certain marine food chains consisting of bivalves, herbivorous gastropods, and barnacles at TL 2 and carnivorous gastropods at TL3. Trophic transfer factors for all three groups of taxa at TL2 were consistently >1 for these four metals (Online Resource 3). Moreover, their gastropod predators at TL3 had Cd and Zn TTFs significantly >1. Depending on the subcellular metal distribution in these gastropods, the possibility of direct toxicity to the snails at TL3 or to their predators at TL4 warrants further study.

Secondly, biomagnification of Zn in fish (TTFs of 1–2) may occur in specific circumstances. The authors of four biokinetic studies reported TTFs of 1.1–6.0 for fish feeding on planktonic crustacean and clams, and, in one, a TTF of 0.2 (Online Resource 3). Yet all but one laboratory-derived TTF >1, for a TL3 fish, was associated with dietary Zn concentrations ≤100 μg/g dry wt, the upper end of the essential range for dietary Zn (Fig. 1e). Thus, it is possible that the test fish may have been deficient in Zn. In addition, some of the values used to parameterize the biokinetic model may be suspect: The highest Zn TTFs for fish of 4.9 and 6.0 did not quantify K_g, which can affect biokinetic results because it can be comparable to efflux rate (Baines et al. 2002; Dutton and Fisher 2010). This may have produced an overestimate of the TTF (Xu and Wang 2002; Zhang and Wang 2007). Overall, it appears that Zn TTFs between 1 and 2 are possible for fish.

In field studies with fish, Zn biomagnification only occurred in uncontaminated reference sites where prey contained generally ≤105 μg Zn/g dry wt (Campbell et al. 2005; Saiki et al. 1995). Zn biomagnification was neither observed in reference streams where macroinvertebrate prey had 235–977 μg Zn/g dry wt (Farag et al. 2007), nor in mining-impacted streams with macroinvertebrate Zn concentrations ranging from 430 to 1,600 μg/g dry wt (Saiki et al. 1995). Overall, the weight of evidence suggests Zn biomagnification is more likely to occur in waters where ambient Zn concentrations are deficient or less than optimal.

4.2 Congruence of Lab, Field, and Modeled TTF Estimates

We assessed trophic transfer in aquatic systems using three independent methodologies: laboratory food chain, biokinetic modeling and field studies. In general they yielded similar conclusions. The one exception to method congruence was the relationship between lab and modeled TTFs for freshwater cladocerans exposed to dietary Cd. The majority (79%, $n = 24$) of the lab Cd TTFs for cladocerans were <1. Modeled TTFs for *Daphnia* ranged from 1.3 to 4.7, except for a TTF of 0.21 that was based on a lower ingestion rate and higher elimination rate than the other daphnid studies. Despite the uncertainty in Cd TTFs for cladocerans, all three methodologies indicate that the TTFs for organisms (*Chaoborus* and two species of fish) consuming cladocerans are always <1, thus signifying no biomagnification.

4.3 The Inverse Relationship Between TTF and Metal Concentrations

There was an inverse relationship between TTF and exposure concentration for Cd, Cu, Pb, and Zn. This finding is consistent with previous reviews of bioconcentration factors, bioaccumulation factors, and TTFs for metals (DeForest et al. 2007; McGeer et al. 2003). Moreover, the inverse relationships were most pronounced for the essential metals Cu and Zn and more variable for the non-essential metals Cd and Pb. The underlying mechanisms for the inverse relationship vary with metal and species, reflecting variations among species in metal regulation and subcellular storage strategies (Phillips and Rainbow 1989; Rainbow and White 1989; Rainbow et al. 1990). For essential metals like Cu and Zn, internal tissue concentrations may be regulated over a fairly wide range of exposure concentrations, with TTFs decreasing as dietary exposure increases. For aquatic organisms that detoxify metals by storage (e.g., granules), TTFs increase with increasing dietary exposure, but not necessarily proportionally. This phenomenon appears to be partially explained by decreases in assimilation efficiencies as exposure concentration increases (e.g., Reinfelder et al. 1998; Guan and Wang 2004; Croteau and Luoma 2008; Lapointe et al. 2009). The effect on assimilation efficiency may result from Michaelis–Menten type saturation kinetics for metal transport proteins in the digestive epithelia (Bury et al. 2003).

4.4 The Relationship Between TTFs and Toxicity

Our analysis also failed to demonstrate a relationship between the magnitude of TTFs and dietary toxicity to consumers/predators. Consequently, TTFs for the metals examined may not be an inherently useful predictor of potential hazard (i.e., toxic potential) to aquatic organisms. Perhaps, as our scientific understanding develops, it will be possible to use other metrics, such as the biologically effective dose, to estimate effects of assimilated metal. This is the not possible presently because of many unknowns, such as the fraction of metal that is bioavailable to organisms in the next trophic level, which is highly species-specific. For example, fish cannot digest metal granules sequestered by bivalves but predatory snails can. The biologically effective dose has not been defined for metals and, based on the limited data available, is unlikely to be consistent across taxa (Adams et al. 2011).

4.5 Extrapolation of Results to the Field

Finally, we note that the laboratory and biokinetic studies reported above have focused on highly controlled studies of structured, simple food chains, where the predator has no choice of prey type. They also have tended to focus on trophic levels 1–3 and mainly invertebrates. Many aquatic food webs in nature encompass not only more trophic levels but are unstructured (Isaacs 1973), wherein species feed at multiple trophic levels as prey availability varies over time and space as a result of changes in prey body size, energy content, densities, etc. (Petchey et al. 2008). These complexities raise uncertainties about the degree to which lab and biokinetic modeling results can be extrapolated to the field. Yet, this meta-analysis indicated congruence between the lab and field studies and the biokinetic modeling. The field results are especially compelling. For example, the authors of one field study of an unstructured food web off the Southern California coast in the 1970s failed to detect biomagnification of Cd, Cu, and Zn in food webs encompassing five trophic levels from zooplankton to Great White Shark (Schafer et al. 1982) (Fig. 7a). Yet clear-cut evidence of organic mercury's biomagnification was observed in the same food web (Fig. 7b). Their results support this paper's inferences regarding the lack of biomagnification of Cd, Cu, Ni, Pb, and Zn in most aquatic food chains.

4.6 Data Variability and Additional Uncertainties

Most of the studies of biomagnification have not accounted for variability within species, over time or between habitats. In addition, biokinetic data were limited in some cases, precluding conclusions concerning the potential for metal biomagnification solely from these data. Data limitations were especially notable for Ni, although 91% ($n=23$) of the TTFs for this metal compiled in Online Resources 1, 2, and 3 were <1.0.

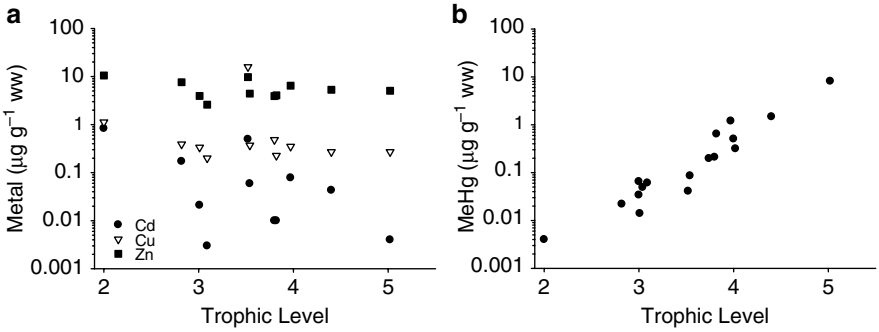

Fig. 7 Tissue residues (mostly muscle) of (**a**) Cd, Cu, and Zn and (**b**) methylmercury, in relation to trophic level in 11 species (9 fish, zooplankton, and squid) from a coastal pelagic food chain off Southern California. Data from Table 2 of Schafer et al. (1982)

Another set of uncertainties involve how background tissue concentrations for essential metals influence the results of field studies, and whether it is possible to distinguish true increases in metal residues due to trophic transfer from inherent differences between species. Unfortunately, background metal concentrations in tissues are rarely measured. This hinders interpretation of data from lab and field studies, but not biokinetic studies that use radio-isotopes, where TTFs are based on accumulation and efflux of new metal, and therefore are not subject to interference from background metal concentrations.

In the field, more variability can be expected because the food webs are more temporally and spatially dynamic, and unstructured. Sampling food webs is difficult because spot sampling reflect what species are present and possess sufficient mass to accommodate the analyses sought. Moreover, variability among samples of the same specimens is rarely integrated into regressions of $\delta^{15}N$ or TL vs. log metal residue. Sampling location, variation between years and variation in species composition have the potential to materially influence results. For example, in a study of Cu, Fe, and Zn in insects occupying TL 2–3, the relationship between log metal residue and TL (or $\delta^{15}N$) differed between years and locations (control vs. mine drainage) sampled (Quinn et al. 2003). The data of Cheung and Wang (2008) were similar: Cd biomagnified in invertebrates collected at two rocky intertidal habitats, but not in a soft-bottomed, subtidal habitat. Metal residues within and between taxa vary widely, of course, and means or values from single samples typically constitute the dependent variable in the TL-log metal regressions. For example, such variation, indexed in terms of coefficient of variations, ranged from about 14–69% for Cd in specimens from Butterfly and Clearwater bays. Yet the independent variable, TL or $\delta^{15}N$, which in typical regression is assumed to be measured without error, does vary: coefficients of variation ranging from 1 to 6% for $\delta^{15}N$ measurements in the Cheung and Wang (2008) study and from 1 to 16% in the Jara-Marini et al. (2009) study. Despite these sources of error, many of them were not measured or integrated into the studies. Yet, overall, the congruence of the multiple lines of evidence increases confidence in the conclusions of this assessment.

5 Summary

In this review, we sought to assess from a study of the literature whether five inorganic metals (viz., cadmium, copper, lead, nickel, and zinc) biomagnify in aquatic food webs. We also examined whether accumulated metals were toxic to consumers/predators and whether the essential metals (Cu and Zn and possibly Ni) behaved differently from non-essential ones (Cd and Pb). Biomagnification potential was indexed by the magnitude of single and multiple trophic transfers in food chains. In this analysis, we used three lines of evidence—laboratory empirical, biokinetic modeling, and field studies—to make assessments. Trophic transfer factors, calculated from lab studies, field studies, and biokinetic modeling, were generally congruent. Results indicated that Cd, Cu, Pb, and Zn generally do not biomagnify in food chains consisting of primary producers, macroinvertebrate consumers, and fish occupying TL 3 and higher. However, biomagnification of Zn (TTFs of 1–2) is possible for circumstances in which dietary Zn concentrations are below those required for metabolism. Cd, Cu, Ni, and Zn may biomagnify in specific marine food chains consisting of bivalves, herbivorous gastropods, and barnacles at TL2 and carnivorous gastropods at TL3. There was an inverse relationship between TTF and exposure concentration for Cd, Cu, Pb, and Zn, a finding that is consistent with previous reviews of bioconcentration factors and bioaccumulation factors for metals. Our analysis also failed to demonstrate a relationship between the magnitude of TTFs and dietary toxicity to consumer organisms. Consequently, we conclude that TTFs for the metals examined are not an inherently useful predictor of potential hazard (i.e., toxic potential) to aquatic organisms. This review identified several uncertainties or data gaps, such as the relatively limited data available for nickel, reliance upon highly structured food chains in laboratory studies compared to the unstructured food webs found in nature, and variability in TTFs between the organisms found in different habitats, and years sampled.

Acknowledgments This assessment was partially funded by Rio Tinto. KVB was supported by the SETAC/ICA Chris Lee Award for Metals Research. This manuscript was improved based on the reviews performed by Drs. Jim Meador and Alan Mearns, and the Journal editor. We are grateful for their efforts.

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