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Accumulation of heavy metals in food web components across a gradient of lakes

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Abstract

Recent studies have emphasized the need for understanding the accumulation and fate of metal contaminants at different trophic levels and across a broad spectrum of lake types. To address both issues, metal concentrations (Hg, Zn, Cd, As, and Pb) were measured in the water, two size fractions of zooplankton, and fish from 20 lakes in contaminated to pristine watersheds in the northeastern United States. Our goals were to examine links between watershed characteristics and aqueous metal levels in lakes and relationships between aqueous concentrations, metal burdens in different plankton groups and in fish. Two pairs of metals, (1) Hg and Zn and (2) As and Pb, exhibited strong similarities both in the factors that predict their concentrations in water and in the patterns of accumulation in particular trophic levels. Aqueous concentrations of Hg and Zn were highest in cool water lakes, whereas As and Pb were highest in more eutrophic lakes in agricultural areas. Aqueous Cd concentrations were closely correlated with the land-use variables, percentage of agricultural land, and road densities. Similarly, Hg and Zn both biomagnified from small plankton (45–202 μm) to macrozooplankton (>202 μm) and from macrozooplankton to fish. In contrast, bioaccumulation of both As and Pb diminished with increasing trophic level. Although aqueous metal and zooplankton metal levels were not significant predictors of As and Pb levels in fish, metal levels in zooplankton were predictive of Hg and Zn in fish, suggesting that sources of bioaccumulation differ for different metals. Our findings demonstrate the importance of investigating upper and lower trophic levels separately, to fully understand metal transfer pathways in aquatic food webs.

Metals transferred through aquatic food webs to fish, humans, and other piscivorous animals are of environmental and human health concern. High levels of Hg in fish from apparently pristine lakes have resulted in the adoption of conservative fish consumption advisories in many states (Håkanson et al. 1988; DiFranco et al. 1995; USEPA 1997; Yeardley et al. 1998). However, pathways of metal movement from land to water and then through aquatic food webs are not well understood. This makes it difficult to extrapolate findings from single systems to other lakes or to account for the significant variation in metal levels found in the fish from different lakes within the same geographic regions. Our broad goal is to elucidate factors across a variety of lake types that determine metal levels in water, in fish, and in the zooplankton, which are the primary dietary conduit of metal from water to pelagic feeding fish.

Although knowledge of metal movement in freshwater systems has grown significantly in recent years, there are still large gaps in our understanding. For example, most past studies of metals focus on a few taxa, single metals, or transfer mechanisms in a small portion of the food web (Prahalad and Seenayya 1989; Spry and Wiener 1991; Miller et al. 1992). Moreover, certain metals have been studied almost exclusively in marine systems (e.g., arsenic transfer in natural food webs; Eisler 1994; Suedel et al. 1994; but *see* Chen and Folt in press). Lack of consistency among studies has made it difficult to compare transfer processes of different metals, to generalize findings across systems, or to predict metal movements through food webs in freshwater lakes. Metal movement in the lower trophic levels in freshwater systems is particularly poorly understood, because of technical limitations and less information on the structure of these communities.

To address these gaps, we compared concentrations of five potentially toxic metals in three trophic levels (small plankton, macrozooplankton, and fish) across a gradient of lake types. Our gradient included 20 lakes that varied in factors (size, water chemistry, trophic status, and food-web composition) affecting metals in fish, plankton, and water. None of the lakes were considered ''contaminated'' and most are used recreationally for boating, swimming, and fishing. Key environmental and land-use variables were also used to characterize each lake, allowing for a more comprehensive analysis of factors affecting metals entering the food web.

We examined five metals, four of which (Hg, Cd, As, and Pb) are in the top 10 of the Hazardous Substances Priority List (Agency for Toxic Substances and Disease Registry 1999). Zn was included because earlier evidence suggests its similarity to Hg in many of our sample lakes (Stemberger and Chen 1998). For each metal, we tested (1) whether metal levels in zooplankton and fish could be simply predicted from aqueous metal concentrations and (2) the extent to which levels in particular zooplankton fractions could be used to forecast levels in fish. Aqueous concentrations were

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also correlated with lake characteristics (pH, nutrient status, etc.) and land use in the area surrounding each lake and compared with metal levels in zooplankton and fish. Two plankton size fractions, small (45–202 μm) and large (>202 μm), were analyzed separately. These fractions comprise organisms that are likely to be consumed very differently by pelagic fish. For example, perch, sunfish, and juvenile bass are highly size selective and prey most heavily on large zooplankton. Thus, the value of each plankton fraction as a predictor for fish metal burdens is likely to differ.

One of our specific goals was to examine links between watershed characteristics and aqueous metal levels in lakes, since metal concentrations in water depend in part on water chemistry and watershed influxes. A few studies have correlated aqueous concentrations of metals with other chemical parameters (Turner et al. 1985; Stephenson and Mackie 1988; Watras et al. 1998). For instance, aqueous Hg has been related to dissolved organic carbon (DOC) and other metals (Watras et al. 1998), and aqueous Cd, Pb, and Zn have also been related to pH, dissolved oxygen, carbonate, and nutrients (Turner et al. 1985; Stephenson and Mackie 1988; Prahalad and Seenayya 1989). However, the direct relationship between land use variables and aqueous concentrations of metals has rarely been addressed.

Another specific goal was to examine links between metal concentrations in water and burdens in different plankton groups and in fish. It is generally accepted that metal concentrations at any trophic level result from a combination of bioconcentration (uptake from the water) and bioaccumulation (uptake from the diet) processes particular to each metal and taxa. However, there is very little information on the factors determining metal concentrations in zooplankton (but *see* Munger and Hare 1997; Hare and Tessier 1998 for Cd and USEPA 1997; Lawson and Mason 1998; Watras et al. 1998 for Hg). Nor is there is a general consensus for the relative influence of water versus diet on metal levels in fish, although, in most cases, diet is thought to contribute significantly to the total burden (Langston and Spence 1995). In the case of Hg, variation in fish metal concentrations are particularly strongly influenced by food web structure, which indicates that plankton (via diet) is a crucial determinant of mercury burdens in fish (Cabana et al. 1994; Stemberger and Chen 1998). However, Hg levels in fish also have been correlated with environmental variables such as lake and watershed areas, pH, DOC, and acid neutralizing capacity (ANC) (Håkanson et al. 1988; Driscoll et al. 1995).

In summary, the key elements of this study are the focus on metal concentrations in four ecosystem components (water, two size fractions of plankton, and fish), the comparison across a 20-lake gradient, and the concurrent assessment of five metals with potentially different modes of transfer. By examining all metals in the same lakes, we avoid problems associated with comparing across studies. General features of the accumulation of each metal emerge from a variety of lake types, which increases our power to extrapolate from these lakes to additional systems.

We asked four questions for each metal: (1) to what extent do environmental and land use parameters predict metal concentrations in the water; (2) to what extent do metal levels in either water or a small plankton predict metal concentrations in the macrozooplankton; (3) to what extent do metal levels in either water or potential foods (small and large plankton) predict metal concentrations in fish; and (4) how do these metals compare with respect to bioconcentration and biomagnification in zooplankton and fish across lakes?

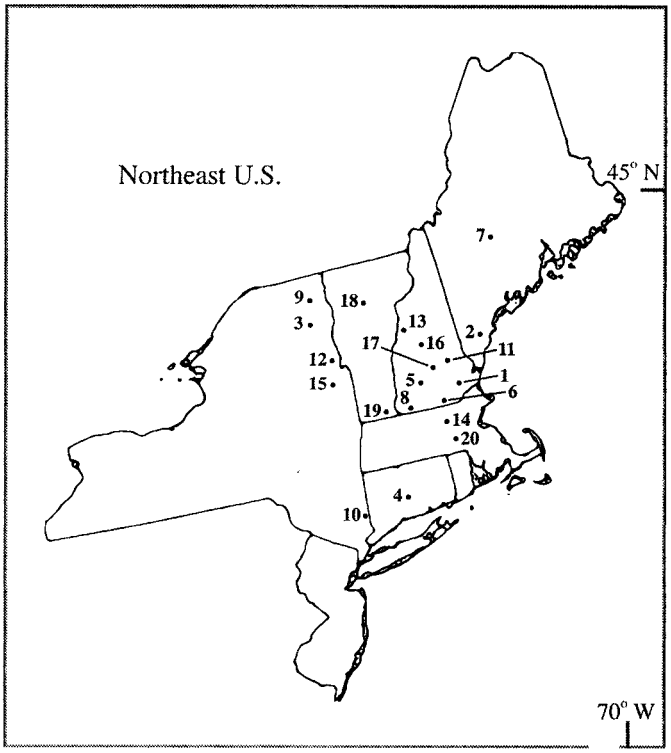

Fig. 1. Locations of the 20 study lakes: (1) Canobie Lake, (2) Chaffin Pond, (3) Clear Pond, (4) Community Lake, (5) Gregg Lake, (6) Horseshoe Pond, (7) Ingham Pond, (8) Island Pond, (9) Lake Placid, (10) Lower Kohanza Reservoir, (11) Mirror Lake, (12) Palmer Pond, (13) Post Pond, (14) Queen Lake, (15) Schroon Lake, (16) Tewksbury Pond, (17) Turkey Pond, (18) Waterbury Reservoir, (19) Weatherhead Lake, and (20) Williams Lake.

Methods

Data were collected in the fall of 1995–1996 from 20 lakes in the northeastern United States (Fig. 1). Metal concentrations in two size fractions of plankton and water were measured, and fish metal and land use data were obtained from the 1992–1993 surveys conducted by the USEPA Environmental Monitoring and Assessment Program (EMAP). Fifteen of the lakes were chosen from EMAP lakes sampled in 1992–1993, and the others were included to expand the range of lake types. None of the lakes were in watersheds with known metal point sources. We selected lakes that had similar food web structures (equal chain length) and were within 300 miles of Dartmouth College, Hanover, NH. Each lake was sampled once (except for Tewksbury Pond, which was sampled twice), and heavy metal levels were measured in water and plankton samples. Environmental variables were also measured (chlorophyll, dissolved oxygen [DO],

temperature, pH, conductivity, and DOC), and phytoplankton and zooplankton taxonomy were identified. Both minimum and maximum temperature and DO were determined from a vertical profile of the water column on one sampling date.

Water and plankton protocols—All water and plankton samples were collected during August through October 1995–1996 from a fiberglass rowboat by use of trace metal clean technique and nonmetallic sampling gear. Prior to field sampling, Teflon® sample vials and sampling apparatus were acid cleaned in sequential concentrated nitric acid, dilute HCl, and trace metal–grade dilute nitric acid baths. Field sampling was conducted with great care, to minimize contamination by use of previously established protocols (Patterson and Settle 1976). Dissolved aqueous samples were taken by use of a peristaltic pump drawing water through acid-cleaned LDPE tubing from 1-m depth and filtered through acid-cleaned 0.45-μm Teflon® filters. A blank aqueous sample was also taken at each location by use of ultraclean water pumped and filtered through the same apparatus. Aqueous samples were acidified in the field to pH 1 with ultrapure nitric acid and analyzed directly without further digestion.

Plankton were collected with vertical tows in the deepest portion of the lake from 0.5 m above of the bottom to the surface using a cone net (202-μm nylon mesh) for macrozooplankton and a Wisconsin net (45-μm nylon mesh) for small plankton. The 45–202 μm fraction was additionally filtered through a 202-μm mesh filter, to remove the larger organisms. In some lakes, tows were dragged through an anoxic zone at the bottom, but care was taken to not collect samples with any bottom sediment. Plankton taxonomy samples were anaesthetized for 1–3 min in CO_2-charged water and preserved in buffered formalin sucrose (Stemberger and Lazorchak 1994). These size cutoffs were chosen in order to separate a large zooplankton fraction containing adult copepods and cladocerans (>202 μm) from a fraction that contained both large phytoplankton and small zooplankton (45–202 μm). Taxonomic groups found in the small fraction included phytoplankton, rotifers, and small crustaceans, whereas the large fraction included cladocerans, calanoid and cyclopoid copepods, and aquatic insect larvae. Metal concentrations per plankton biomass (μg metal g^{-1} of plankton) were calculated from separate metal samples and biomass samples because weight could not be measured directly without contaminating metal samples. Plankton biomass was estimated from three replicate tows, which were filtered onto preweighed Whatman filters, dried at 60°C, and weighed. Plankton metal samples were filtered in situ onto acid cleaned Teflon® filters, and filter blanks were taken by filtering ultraclean water through the same-sized Teflon® filters. Metal samples were digested for analysis with an aqua regia solution (2 : 1 Seastar nitric acid and hydrochloric acid) and heated to 70°C for 8–10 h. After digestion, Teflon® filters were removed, and the sample was centrifuged to separate undigested material from the metal in solution. Finally, the sample was split into glass and Teflon® vials for analysis of mercury and arsenic (glass) and cadmium, lead, and zinc (Teflon®) and stored at 4°C. Teflon® vials (Savillex) showed significant Hg losses after several weeks of storage, whereas the samples stored in glass vials remained stable for >6 months.

All metal samples were analyzed in the Dartmouth Superfund Trace Metal Core Facility by use of a magnetic sector–inductively coupled plasma-mass spectrometer (ICP-MS ELEMENT, Finnigan MAT). Cd, Pb, and Zn were determined with a standard liquid sample introduction system (microconcentric nebulizer MCN-2, CETAC, and cooled Scott-type spray chamber). Relative determination limits (10 s blank SD) were 0.05–0.10 μg L^{-1} for Zn and 0.005–0.01 μg L^{-1} for Cd and Pb. Hg and As were analyzed by use of cold vapor/hydride generation ICP-MS (Klaue and Blum 1999), with determination limits of 0.3–0.5 ng L^{-1} (10 s blank SD). All samples were quantified with matrix-matched National Institute of Standards and Technology (NIST)-traceable standard solutions (HPS, Charleston; VHG, Manchester). External quality control was achieved by digesting and analyzing identical amounts of rehydrated (90% water) standard reference materials (DORM-2, NRC-CNRC Canada, and Prawn CRM, China). Recovery rates ranged from 95–100% for Zn, Cd, Pb, and Hg and 85–90% for As. The lower recovery rates for As with hydride generation can be explained by incomplete mineralization of the dominant arsenobetaine component in the reference materials, which was expected to be negligible for the zooplankton samples. Redigestion of the reference materials with perchloric acid at 120°C for 4 h yielded recovery rates of 95–100%. Plankton subsamples were also redigested and reanalyzed, to insure that all the As was extracted, but no significant differences from the initial analysis in As concentrations were observed.

Fish tissue analysis—Concentrations of metals in fish tissue, aqueous concentrations of nitrogen and phosphorus, watershed area, lake area, and land use data (percent of watershed as urban agricultural, disturbed, forested, or wetland and road density) were obtained from the USEPA-EMAP program (Paulsen et al. 1991). Fish were sampled by EMAP personnel using gill nets, trap nets, minnow traps, and beach and minnow seines and frozen at −20°C (Whittier et al. 1997). Generally, 3–5 whole fish were homogenized for a composite tissue sample (Yeardley et al. 1998). Top trophic species (largemouth bass, smallmouth bass, rainbow trout, yellow perch, pumpkinseed sunfish, etc.) were preferred for analysis, but sizes and species that were in the composite varied. Metals in fish tissue were analyzed by use of ICP-MS for Cd, As, Pb, and Zn, and Hg was determined by use of cold vapor–atomic absorption spectrometry (Yeardley et al. 1998). EMAP metal concentration data (μg g^{-1} wet weight) were converted to dry weight under the assumption of an 88% weight reduction (Dumont et al. 1975).

Data analysis—Statistical analyses were conducted by use of both measured and derived variables. Measured variables included environmental, lake, and land use factors (Table 1) and metal concentrations of zooplankton and fish (μg metal g^{-1} animal). Most measured variables were $\log_{10}(x + 1)$ transformed, to correct for nonnormal distributions of the data and to adjust for 0 values. Land use variables based on percentages were not transformed. Derived variables for

Table 1. Environmental, lake, and land use characteristics used in correlation analysis of aqueous metal concentrations. Selected environmental data and land use data from EMAP-SW Program (Paulsen et al. 1991). DOC, dissolved organic carbon.

Environmental variables	Lake characteristics	Land-use variables
Average DOC	Elevation	Road density
Secchi depth	Lake area	% total area urban
Minimum dissolved oxygen	Watershed area	% total area agricultural
Conductivity		% total area forested
pH		% total area wetland
Maximum temperature		% total area disturbed
		% total area with roads

each metal were calculated to estimate the degree of enrichment and bioaccumulation at each trophic level in each lake. Biomagnification factors (BMF) were calculated for plankton ([mean metal concentrations of macrozooplankton in μg g^{-1}]/[mean metal concentration of small plankton in μg g^{-1}]) and fish ([mean metal concentrations of fish in μg g^{-1}]/[mean metal concentration of macrozooplankton in μg g^{-1}]; USEPA 1997). Bioaccumulation factors (BAF) were calculated by use of (mean metal concentrations for each trophic group in μg g^{-1})/(mean metal concentration in water in μg g^{-1}) for each lake.

Metal concentrations in water, the two zooplankton size fractions, and fish were statistically compared by use of multiple least-squares regression. Significant relationships between land use and environmental factors and aqueous metal concentrations were determined with nonparametric Kendall's τ correlations. Derived variables (BMF and BAF) were analyzed by use of a nonparametric Wilcoxon test or log transformed and analyzed by use of one-way ANOVA, to compare the degree of enrichment between trophic levels and metals. Principal components analysis (PCA) was used to examine the relationships of metal concentrations in fish and zooplankton fractions. Multiple regressions, correlation analyses, and ANOVA were conducted using JMP (SAS 1995), and the PCA was done with CANOCO version 3.1 (Ter Braak 1988).

Provisos—There were several methodological constraints to our study. First, although it is recognized that methyl-Hg is the most biomagnified species, metal speciation for mercury or other metals was not addressed in this study, because our objective was to compare total concentrations of the five different metals across trophic levels. Our comparison of total metal concentrations distinguishes Hg as the most highly magnified of the five metals. Measures of methyl-Hg would no doubt show even higher levels of biomagnification (Mason et al. 1996; Watras et al. 1998) but not change our conclusions about the importance of biomagnification of Hg in these food webs. Second, we recognize that our gradient of lakes varies in many ways other than metal concentrations (e.g., trophic status, land use, size, depth, etc.). Nevertheless, significant consistent patterns of metal accumulation emerge across this gradient, which provides even stronger evidence that these patterns may be reflective of important transfer pathways in most lakes. Last, the fish data used in this study were from the EMAP-SW field program conducted in 1992–1993, whereas the plankton data were collected in 1995–1996. We feel that using both data sets in our analysis is appropriate because fish are longer-lived species and integrate metal signals over time, and our sampling of Tewksbury Pond in two separate years and additional analyses of EMAP-SW data (Stemberger unpubl. data) demonstrate that between-lake differences far exceed between-year differences within lakes. Therefore, we believe that the metal accumulation patterns in zooplankton and fish are reflective of pathways that appear to be consistent over time and space.

Results

Mean metal concentrations in water, two zooplankton size fractions, and fish were generally consistent with values previously reported for uncontaminated systems, but the maximum levels were indicative of contamination in some lakes (Surma-Aho and Paasivirta 1986; Lum 1987; Schmitt and Brumbaugh 1990; Eisler 1994; Tremblay et al. 1995; Table 2). In the following sections we present (1) the environmental and land use factors significantly correlated with aqueous metal concentrations, (2) the variables (food and water) in multiple-regression models that contributed significantly to the variance in metal burden of macrozooplankton and fish, and (3) derived variables (BMF and BAF) that were calculated to compare metals in terms of their accumulation in different trophic levels.

Predictors for metal in water—Aqueous metal concentrations were best predicted by certain environmental and land use variables. Significant correlations were similar for the pairs of metals, Hg–Zn and As–Pb (Table 3). Both Hg and Zn were negatively correlated with maximum temperature, whereas Pb and As concentrations in water were positively correlated with percentage of watershed in agricultural land use, high DOC, and high total nitrogen. Aqueous Pb concentrations also were higher in lakes with shallower secchi depth and higher minimum oxygen concentrations, whereas Zn was correlated with total phosphorus. In contrast, aqueous Cd concentrations were best predicted by only land use variables, agricultural land use, and road density.

Predictors for metal in macrozooplankton and fish—Concentrations of Hg, As, and Pb in macrozooplankton were best predicted by metal levels in small plankton, whereas no relationships among metal levels in the two zooplankton size

Table 2. Metal concentrations (unweighted averages) in water (μg L^{-1}), small plankton (small, 45–202 μm, μg g^{-1} dry weight), and macrozooplankton (large, >202 μm, μg g^{-1} dry weight); aq, aqueous concentration; SD, standard deviation; SE, standard error; 16a*, 1995 data, 16b*, 1996 data; ND, no data.

Lake	Hg (aq)	Zn (aq)	As (aq)	Cd (aq)	Pb (aq)	Hg (small)	Zn (small)	Cd (small)	As (small)	Pb (small)	Hg (large)	Zn (large)	Cd (large)	As (large)	Pb (large)
1	0.001	0.506	0.221	0.080	0.055	3.40	124	0.000	10.4	31.5	0.895	105	2.20	2.41	1.90
2	0.001	0.074	0.113	0.073	0.014	2.87	76.2	3.39	0.000	5.90	0.416	77.0	0.504	0.109	0.217
3	0.001	0.033	0.046	0.102	0.006	0.079	195	12.4	0.129	15.0	0.217	201	1.20	0.270	1.73
4	0.005	0.535	0.367	0.114	1.04	1.09	614	2.78	1.41	10.7	0.143	134	0.625	0.282	1.34
5	0.001	0.320	0.038	0.003	0.000	2.32	75.2	0.548	5.86	6.66	1.40	70.6	1.99	1.57	0.898
6	0.001	0.050	0.078	0.001	0.000	1.99	35.0	0.447	7.60	1.60	0.488	36.8	0.235	0.524	0.128
7	0.001	0.631	0.587	0.089	0.019	0.668	18.5	1.38	1.13	2.59	1.30	147	1.06	2.06	2.19
8	0.017	14.0	0.260	0.095	0.223	7.72	89.0	2.77	6.51	20.6	2.97	200	1.52	0.000	5.37
9	0.001	0.532	0.123	0.062	0.007	0.247	91.8	1.14	0.790	16.2	0.412	92.2	6.70	0.363	5.52
10	0.004	1.34	0.085	0.075	0.051	0.423	230	1.36	0.268	7.00	0.074	31.3	0.293	0.166	0.655
11	0.001	0.696	0.409	0.072	0.008	0.026	54.8	0.222	1.03	1.27	0.028	49.6	0.407	0.561	0.518
12	0.000	0.785	0.022	0.066	0.000	0.307	253	11.3	0.262	7.63	4.38	2870	1.94	0.000	47.8
13	0.017	10.1	0.260	0.022	0.001	0.099	8.90	0.103	0.480	0.224	0.190	52.3	0.217	0.947	0.245
14	0.002	0.524	0.107	0.096	0.048	0.082	43.2	0.278	0.926	7.73	0.512	84.6	0.431	0.307	12.6
15	0.006	0.665	0.000	0.051	0.025	0.208	92.5	2.03	0.095	5.95	0.388	94.7	4.81	0.103	1.33
16a*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.669	50.7	2.48	0.905	0.729
16b*	0.012	1.42	0.057	0.089	0.034	0.697	1040	1.29	2.23	36.9	0.036	330	0.477	0.165	0.911
17	0.017	5.54	0.260	0.013	0.340	29.4	648	6.86	9.91	57.0	7.48	427	1.86	2.99	16.5
18	ND	ND	ND	ND	ND	20.1	881	5.08	13.4	54.4	1.94	385	3.10	3.94	11.9
19	ND	ND	ND	ND	ND	0.334	16.5	0.082	0.401	0.727	1.13	21.2	0.507	0.480	1.59
20	0.021	0.703	0.096	0.061	0.020	0.115	51.1	0.817	1.41	28.2	0.081	64.9	0.354	0.462	2.22
Average concentration	0.006	2.14	0.174	0.065	0.105	3.61	232	2.72	3.22	15.9	1.20	249	1.57	0.886	5.53
SD	0.007	3.87	0.158	0.034	0.248	7.60	308	3.61	4.16	17.2	1.80	611	1.66	1.09	10.7
SE	0.002	0.940	0.038	0.008	0.060	1.84	74.6	0.875	1.01	4.17	0.437	148	0.402	0.264	2.60

Table 3. Results of nonparametric correlation using Kendall's τ for aqueous metal concentrations versus environmental and land-use variables. Only significant ($P<0.05$) variables are shown. DOC, dissolved organic carbon.

Metal	Variable	Kendall's τ b	n	P value
Hg	Maximum temperature	−0.5459	17	0.0043
Zn	Maximum temperature	−0.5683	17	0.0015
	Total *P*	0.4327	15	0.0256
Cd	Road density	−0.3828	15	0.0475
	% agricultural	0.4701		0.0297
As	DOC	0.3455	18	0.0480
	% agricultural	0.5775	13	0.0076
	Total *n*	0.4211	15	0.0292
Pb	DOC	0.3696	18	0.0335
	Secchi depth	−0.4356	18	0.0122
	Minimum DOC	0.3981	15	0.0413
	% agriculture	0.4270	13	0.0472
	Total *n*	0.3905	15	0.0425

Table 4. Results or least-squares multiple regression analyses for the relationship of metal concentration in macrozooplankton (>202 μm) with metal concentrations in water and small plankton (45–202 μm) and fish tissue with metal concentrations in water, small plankton, and macrozooplankton (>202 μm).

		Macrozooplankton		Fish	
Metal	Variables	P value (slope)	R^2	P value (slope)	R^2
Hg	Water	0.5062	0.420	0.2541	0.553
	45–202	0.0049* (+)		0.0345* (−)	
	>202			0.0058* (+)	
Zn	Water	0.5759	0.095	0.0073* (+)	0.645
	45–202	0.2679		0.3416	
	>202			0.3836	
Cd	Water	0.9093	0.004	0.0470* (+)	0.670
	45–202	0.8325		0.5003	
	>202			0.6435	
As	Water	0.0351* (+)	0.591	0.6530	0.118
	45–202	0.0017* (+)		0.5841	
	>202			0.8005	
Pb	Water	0.9708	0.293	0.7739	0.038
	45–202	0.0291* (+)		0.5560	
	>202			0.8433	

* $P < 0.05$.

fractions were found for Zn and Cd (Table 4). Arsenic concentrations in macrozooplankton were also positively related to As concentrations in water.

Metal concentrations in fish tissue were predicted by either metal levels in zooplankton (food) or water, depending on the metal (Table 4). For example, variance in the Hg concentrations in fish is significantly explained by concentrations of Hg in both micro- and macrozooplankton (negative for small plankton and positive for macrozooplankton) but not by Hg concentration in water. In contrast, Zn and Cd concentrations in fish were best predicted by their concentrations in water but not by either zooplankton size fraction. Finally, variance in As and Pb concentrations in either water or zooplankton did not significantly explain fish metal variance.

The PCA revealed additional and some similar relationships for metal concentrations in small plankton, macrozooplankton, and fish (Fig. 2). The first and second PCA axes explained 30.9% (eigenvalue = 0.309) and 22.1% (eigenvalue = 0.221), respectively, of the variance for metal concentrations in zooplankton and fish tissue. The first and second axes were most strongly characterized by Hg-Zn-Pb and As-Cd-Pb, respectively. Concentrations of Zn, Hg, and Pb in small plankton are located on similar axes to their respective macrozooplankton concentrations, suggesting a relationship between metal concentrations in the two size fractions. This pattern was also observed in the multiple regression analyses for Hg and Pb. Hg concentrations in the two fractions of zooplankton and fish were positively correlated. This relationship is similar to the multiple-regression results in which Hg concentrations in zooplankton explained a significant amount of the variance in fish Hg concentrations. However, in the regression analysis, Hg in small plankton was negatively associated with Hg in fish. Zn was similar to Hg, in that Zn concentrations in fish were related to zooplankton concentrations of Zn and also with Hg concentrations in fish. For Cd, As, and Pb, metal concentrations in zooplankton tissue were oriented differently from their respective metal concentrations in fish, demonstrating little or no relationship of fish concentrations with their food concentrations.

Trophic enrichment of metal—Metal-specific BMF calculated for fish and macrozooplankton identified differences in the degree to which the concentration of each metal in one trophic level exceeds the concentration in the next lower trophic level (Fig. 3). There were significant differences between metals in their magnitude of enrichment from small plankton to macrozooplankton (one-way ANOVA with pairwise comparisons, $P = 0.0182$). Hg, Zn, and Cd enriched from small plankton to macrozooplankton (BMF > 1.0), whereas As and Pb did not (BMF < 1.0). The zooplankton BMF for Zn was significantly greater than for Pb, As, and Cd, and the BMF for Cd was greater than for As. Metal enrichment from macrozooplankton to fish also differed significantly among metals (nonparametric Wilcoxon/Kruskal-Wallis, $P < 0.0001$). Hg and Zn enrich the most from zooplankton to fish, whereas Cd, As, and Pb appeared to diminish (BMF < 1.0) from lower to higher trophic levels.

Log-transformed BAFs were calculated for micro- and macrozooplankton and fish (Fig. 4). In general, log BAF values for Hg and Zn were higher than those of other metals but did not differ significantly across trophic levels. In contrast, BAFs for Cd, As, and Pb do exhibit differences between trophic levels. For Cd, there were significant differences in metal burden between size fractions, suggesting that the fish BAF was significantly lower than the two zooplankton BAFs (Wilcoxon, $P < 0.0001$). For As, the small plankton BAF was significantly greater than the two higher trophic levels ($P = 0.0113$); and Pb BAFs decreased significantly with each increasing trophic level ($P < 0.0001$).

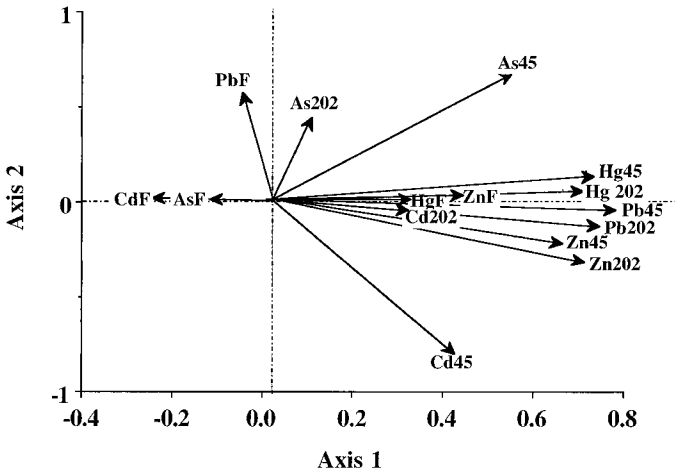

Fig. 2. PCA of metal concentrations for 20 northeastern lakes, showing relationships of fish metal burden to small plankton (45–202 μm) and macrozooplankton (>202 μm) metal concentrations. Each arrow represents the direction of increasing magnitude of a metal variable relative to the first two PC axes. The length of the arrow represents the amount of variance in the environmental variable, and the arrow tip indicates high-magnitude values. Values at the origin represent the mean value for the variable taken over the entire data set. Metals are represented as follows: Hg, Zn, Cd, As, and Pb. Size fractions of plankton are shown as 45 (45–202 μm) and 202 (>202 μm), fish as F.

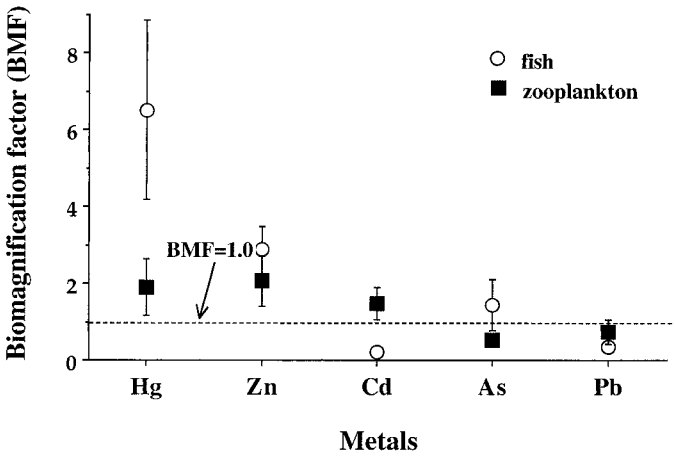

Fig. 3. Biomagnification factors (means of BMF ± SE) for fish and zooplankton. *See text* for calculation of derived variable. Values >1.0 show enrichment of the metal at the respective trophic level and values <1.0 show a diminution.

Discussion

Our findings demonstrate the value of comparing metal predictors and accumulation across a gradient of lake types in order to contrast pathways by which different heavy metals move from land to water and from water and zooplankton to fish. Studying metal movement several different ways greatly increased our power to detect relationships. The five metals we measured showed distinct patterns with respect to the environmental factors that correlate with their aqueous metal concentrations and the factors that predict their levels in various components of food webs (Table 5). Strong similarities between Hg and Zn (both are greatest in cool lakes and appear to biomagnify) and As and Pb (both are greatest in eutrophic agricultural lakes and appear to biodiminish with trophic level) were identified, suggesting that similar biological and geochemical mechanisms may determine their environmental fate. In contrast, Cd could not be consistently placed in a group with any of the other metals, which may be due its unique biological properties or to low variation in concentration across the study lakes. However, despite similarities among pairs of metals (Hg and Zn; As and Pb) in both water and fish, aqueous concentrations were not always good predictors of fish metal burdens. Lastly, our closer examination of the zooplankton food web revealed differences in the ways in which certain metals are accumulated in zooplankton and fish from food or water. Thus, our investigation of a suite of metals across multiple trophic levels and lake types allowed us to suggest possible biotic and abiotic factors that may influence fate of metals in aquatic food webs.

Predictors of metal concentrations in water—Aqueous metal concentrations in our 20 lakes were comparable to values for other north temperate lakes reported in the literature (Yan et al. 1990*a*; Yan and Mackie 1991; Driscoll et al. 1995, 1998). Hg concentrations for most of our lakes fell between 0.001 and 0.006 μg L^{-1}, which is the range of aqueous concentrations found in nearby lakes and streams in the Adirondacks of New York (Driscoll et al. 1995, 1998). Our Cd concentrations (0.001–0.114 μg L^{-1}) were also similar to the range of values measured in nonacidified Canadian lakes (0.002–0.112 μg L^{-1}; Yan et al. 1990*a*; Yan and Mackie 1991). However, both Hg and Cd concentrations in our study were generally higher than those measured in the Great Lakes (Hg, 0.0002–0.0163 μg L^{-1}; Cd, 0.0041–0.0082 μg L^{-1}; Mason and Sullivan 1997; Roditi et al. 2000). These differences may be due to relatively lower surface area : volume ratios in the Great Lakes, resulting in lower atmospheric inputs and greater removal of metals to the sediments (Mason and Sullivan 1997).

A key result of this study is correlation of land use and other environmental variables with aqueous levels of particular metals. These correlations identify factors that may be helpful for identifying lake types at greatest risk for metal contamination and also suggest similarities among certain metals. For example, Hg and Zn were both elevated in cool lakes, whereas As and Pb were highest in nutrient-enriched agricultural lakes. Past studies have correlated cool water temperatures with cold-water fish assemblages and longer food chains, which are also characteristics of lakes that biomagnify Hg (Cabana et al. 1994; Stemberger and Chen 1998; Stemberger and Miller 1998). However, predictors of Zn and Hg also differed in that total P was associated with Zn but not Hg. Although cooler water temperatures have been correlated with higher Hg in fish, warmer temperatures have been correlated with higher Zn in fish (Stemberger and Chen 1998). These similarities and distinctions between Hg and Zn may be related to their chemical characteristics and require further investigation. However, studying different metals across a range of lakes has revealed that certain wa-

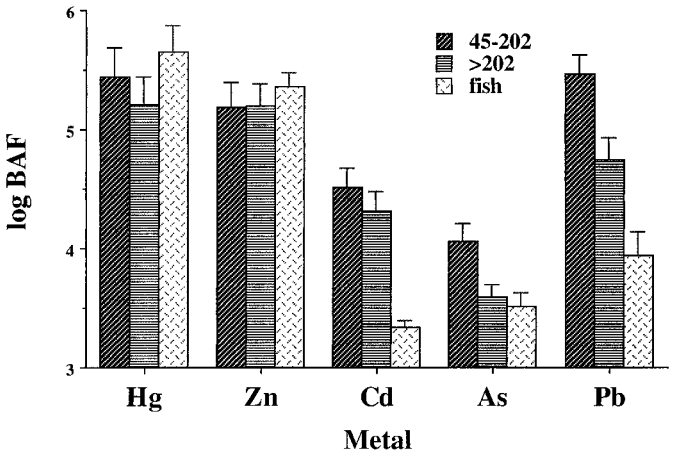

Fig. 4. Log-transformed bioaccumulation factors (means of BAF±SE) for each trophic level (small plankton [45–202 μm], macrozooplankton [>202 μm], and fish) of each metal. *See text* for calculation of derived variable.

Table 5. Predictors of metal concentrations in water, macrozooplankton (>202 μm), and fish in a gradient of lakes in the Northeast United States.

Metal	Water*	Macrozooplankton	Fish
Hg	Temperature	Small plankton†	Small plankton†, ‡ Macrozooplankton†, ‡
Zn	Temperature Chemistry	Small plankton‡	Water† Macrozooplankton‡
Cd	Land use	None†	Water
As	Land use Productivity	Water† Small plankton†	None†
Pb	Land use Productivity	Small plankton	None†

* Kendall's τ b nonparametric correlations.
† Least-squares multiple regression.
‡ Biomagnification calculation.

tershed characteristics are related to aqueous concentrations of different metals.

DOC was correlated with aqueous As and Pb but not with Hg, as was found by Watras et al. (1998). Although aqueous Pb has been associated with DOC (Turner et al. 1985), this has not been shown previously for As. The pH has been found to correlate with higher metal concentrations in other studies but was not found to be a significant predictor in this study (White and Driscoll 1987; Stephenson and Mackie 1988; Watras et al. 1998). This may have been due to the lack of strongly acidic lakes (range of pH 5.98–9.31) among our study sites. Finally, the correlations of Pb and As with agricultural land use and total N suggest associations with nutrient-enriched agricultural watersheds rather than industrial sources (Aurillo et al. 1995). This may not be surprising given the historical use of lead arsenate and arsenical sprays as insecticides throughout the United States and Canada (USDA 1949).

Predictors of metal concentrations in zooplankton—Our study is one of the few that demonstrates the importance of investigating lower trophic levels to understand the relationships in metal accumulation among water, plankton, and fish. Our primary finding was that metal in water was not an effective predictor for levels in macrozooplankton but metal in food was a good predictor. In fact, several lines of evidence suggest that concentrations of all these metals in small plankton and macrozooplankton were related probably through dietary transfer from the smaller to the larger size fraction. These trophic relationships differed significantly among metals, with some biomagnifying (Hg, Zn, and Cd) and others biodiminishing (As and Pb) with trophic level. However, laboratory or field experiments are necessary to determine precise mechanisms of trophic transfer.

The multiple regression analysis showed that concentrations of Hg, As, and Pb in the microzooplankton were good predictors of their concentrations in macrozooplankton. Two plausible scenarios to explain the predictive relationship of metals in small and large zooplankton are (1) that small plankton and macrozooplankton consist of similar taxa or get a large fraction of their metals by consuming similar diets, and/or (2) that macrozooplankton get a large portion of their metals by consuming small plankton. If scenario (1) predominates, concentrations of metals in the two size fractions should be nearly equal. However, the BMFs measured for zooplankton in these lakes revealed that the BMFs increased (BMF $>$ 1.0 for Hg) or decreased (BMF $<$ 1.0 for As and Pb) with trophic level depending on the metal. These results suggest that macrozooplankton derive metal from ingestion of smaller zooplankton (scenario [2]) and that Hg levels in large zooplankton biomagnify from their food sources (smaller zooplankton), whereas As and Pb biodiminish. Field evidence for biomagnification of Hg in zooplankton food webs has been shown (Mason and Sullivan 1997; Monson and Brezonik 1998; Watras et al. 1998) and diminution of both As and Pb have been demonstrated previously (As in the laboratory, Maeda et al. 1992; Maeda 1994; Kaise et al. 1997; Pb in streams and estuaries, Suedel et al. 1994; Chen and Folt in press).

Our multiple-regression analysis did not indicate a clear association between small plankton and macrozooplankton for either Zn or Cd. Yet, zooplankton BMFs provided evidence that the accumulation of Zn and Cd by zooplankton was similar to that for Hg. The BMFs for all three metals were >1, which is the first field evidence that Zn and Cd may biomagnify in a variety of aquatic food webs and lake types. Empirical field evidence for biomagnification of Zn and Cd has been lacking, although Timmermans et al. (1989) showed that Zn and Cd biomagnified between trophic levels when examined in specific trophic pairs of freshwater stream macroinvertebrates. Reinfelder et al. (1998) also suggested that Cd biomagnification might be expected for filter feeders or predators that assimilate Cd from their prey with assimilation efficiencies >20%. Moreover, Fisher and Reinfelder (1995) calculated concentration factors for Cd that increased from phytoplankton to zooplankton but decreased to fish, showing biomagnification in lower trophic levels. Unlike macrozooplankton in Canadian shield lakes, Cd burdens in

macrozooplankton in our study were not predicted by aqueous concentrations of Cd (Yan et al. 1990*a*,*b*). A clearer understanding of the trophic links and metal exposure pathways for the zooplankton is obviously needed to fully understand the role of the planktonic food web in the movement of metals to upper trophic levels.

Predictors of metal concentrations in fish—We provide clear evidence that metal burdens in fish are related to different potential sources depending on the metal and that similarities between metals also exist. Our findings showed that Hg and Zn concentrations in fish were both biomagnified and appeared to be related to metal concentrations in their food, whereas As and Pb in fish biodiminished but were not predicted by levels in water or food. Predictors of metals in fish and patterns of metal accumulation across trophic levels (shown by BMFs and BAFs) revealed similarities in the metal pairs Hg and Zn, and As and Pb. Despite the fact that the fish data were obtained from earlier years of sampling than the water and plankton data, accumulation and differences between metals in fish and plankton corroborated results in other studies.

Hg, Zn, and Cd: Prior studies have been most intensive for Hg in fish, which has been found at high levels in lakes with little or no measurable aqueous Hg. Our study has two key results related to predicting Hg levels in fish across lakes. First, the concentration of Hg in the water was not a good predictor of total Hg levels in fish. The lack of a strong correlation between metal in water and fish probably results from measurement constraints at the extremely low aqueous Hg levels found in most of these lakes and the potential for significant biomagnification in different lakes to far outweigh lake-to-lake differences in aqueous concentrations. These results do not mean that systems with much higher inputs of Hg are not expected to result in high burdens in fish. However, they show that over the range of inputs characterized by these lakes, accumulation of metal in the food web is a more important predictor of Hg in fish. Given that the study lakes covered a broad range of lake types and natural Hg levels, this result may be suggestive of the important predictors of Hg in fish in other systems.

Our second key result for Hg is that levels in macrozooplankton were strong positive predictors of Hg levels in fish. The BMFs for Hg in fish were also greater than all the other metals (BMFs $\approx$ 6.6), demonstrating significant biomagnification of Hg from macrozooplankton to fish. This relationship was expected, because large zooplankton are the primary food source for juvenile and adult fish, and fish are known to biomagnify mercury (in the form of methylmercury) from their diets (Mason and Sullivan 1997; Lawson and Mason 1998). Hg was also the only metal for which there was any significant relationship between the concentrations in small plankton and fish; Hg levels in fish were negatively related to Hg in small plankton. There may be several explanations for this result. First, fish do not generally prey upon microzooplankton (comprising small crustaceans, rotifers, and ciliates). Therefore, we expected to find a significantly weaker regression between metals in small plankton relative to macrozooplankton and fish. Further, biomagnification of Hg from small plankton to macrozooplankton (BMF $>$ 1) may further accentuate differences in the regressions of small plankton relative to macrozooplankton and fish. Finally, the weak negative relationship we found between metal in small plankton and fish may arise indirectly from differences in the food webs across these lakes. Lakes that are dominated by large-bodied zooplankton assemblages are likely to transfer Hg to fish more efficiently than lakes dominated by small zooplankton. This occurs because of high fish feeding rates on large zooplankton and also because large zooplankton such as *Daphnia* carry relatively higher Hg burdens than other taxa (Watras et al. 1998; Folt et al. unpubl. data). If lakes with relatively greater levels of Hg in the small plankton were also lakes dominated by small-bodied zooplankton, overall trophic transfer to fish would be low in those lakes, and a negative across-lake regression could arise. More detailed food-web studies are needed to discern these patterns.

Unlike Hg, we found that aqueous metal concentration was a good predictor for Zn and Cd levels in fish. This may occur because Zn and Cd are transition metals with divalent cations, for which uptake is thought to be proportional to the free ion concentration (Langston and Spence 1995). In general, there is less known about predicting Zn and Cd in fish. Both Cd and Zn differ from Hg in being more organically complexed in water than inorganically complexed, which may affect their trophic transfer. Field studies in contaminated sites have also found fish tissue concentrations of Zn and Cd to be correlated to aqueous concentrations (Miller et al. 1992). However, Zn and Cd differ metabolically: Zn is an essential metal and its uptake has been shown to be regulated, whereas Cd is a nonessential metal for which there is little evidence of regulation of accumulation (Dallinger and Kautzky 1985; Memmert 1987).

Neither Zn nor Cd concentrations in macrozooplankton across lakes explained a significant amount of variance in fish burdens (regression analysis). However, our PCA showed strong correlations between Zn concentrations in planktonic fractions and fish, similar to Hg. Moreover, our BMF data strongly suggest that Zn biomagnifies (BMFs $>$ 1) and that Cd potentially biodiminishes (BMFs $<$ 1) from macrozooplankton to fish. For Zn, this is additional novel field evidence of biomagnification of this metal in aquatic food webs. Other studies have also suggested that dietary inputs of Zn and Cd are important sources to fish (Spry et al. 1988; Timmermans et al. 1992; Langston and Spence 1995). The lack of a significant regression model simply means the *relative* difference between fish and zooplankton was not the same across lakes (i.e., there was no linear relationship), making zooplankton metal burden a weak quantitative predictor of fish metal burdens. In most lakes, however, Zn levels in fish were greater than levels in macrozooplankton. Finally, the diminution of Cd from macrozooplankton to fish (BMF $<$ 1.0) contrasts with biomagnification of Cd observed between small plankton and macrozooplankton.

We also compared the BAFs for each metal in zooplankton and fish. As expected from the BMFs, the BAFs for Hg and Zn, but not Cd, in fish were greater than in macrozooplankton. On the basis of other work (Mason and Sullivan 1997; Watras et al. 1998), we expect that an analysis of

methyl-Hg would have shown a much more pronounced difference across trophic levels than measures of total Hg. Our findings for trophic enrichment of Hg and Zn also corroborate results of Stemberger and Chen (1998), in which Hg and Zn were related to food web structure (across 38 lakes). They found a positive relationship between food chain length and metal levels in fish for both Zn and Hg. Their results suggest biomagnification of these metals, but metals in the zooplankton were not measured in that study.

As and Pb: Concentrations of As and Pb in fish were not well predicted by the metal levels in water, small plankton, or macrozooplankton. Nevertheless, despite the lack of a significant regression, we found strong evidence that trophic processes influenced the levels of these metals in fish. Both metals appeared to decrease from small plankton to fish (e.g., we found decreasing BAFs with increasing trophic level). Our results are consistent with past studies that have also documented diminution of As and Pb in some circumstances (Maeda et al. 1992; Suedel et al. 1994; Chen and Folt in press). In laboratory marine food chains, total As has been shown to decrease with increasing level in the food chain, whereas methylated-As forms (which are less toxic) increase (Maeda et al. 1992; Maeda 1994). This was probably occurring in our samples but could not be determined because we measured only total As. Other studies have also shown that Pb is poorly assimilated by zooplankton and decreases with trophic level in both marine and freshwater organisms (Spry and Weiner 1991; Suedel et al. 1994).

Sources of metal accumulation—Our study suggests that both diet and exposure to aqueous concentrations are sources of metals for zooplankton and for fish but that sources differ greatly among metals. Evidence for the importance of water as a metal source comes from the significant regressions of aqueous metal levels with various food web components (e.g., arsenic in small plankton and macrozooplankton and Zn and Cd in fish). Evidence for the importance of diet comes from significant relationships between metal concentrations in lower and higher trophic levels (e.g., Hg in macrozooplankton and fish and Pb in small plankton and macrozooplankton), particularly when water concentrations are not significantly related to either. A great deal of uncertainty exists about the dominant source (food vs. water) of metals to zooplankton and fish. Although we did not experimentally determine the sources for metals in macrozooplankton and fish, our identification of predictors of metal concentrations in each of these trophic components provides some indication of their possible sources.

Trophic transfer of metals may also relate to the degree of assimilation by grazers or predators; metals that are highly assimilated have greater potential to be biomagnified, although elimination rates will also determine the overall magnitude of transfer (Reinfelder et al. 1998). Assimilation rates are dependent on the chemical characteristics of each metal and the tissues in which they are retained. Recent studies have shown that metals found in the cytoplasm of algal cells (e.g., Hg, Zn, and Cd) are likely to be assimilated by grazers (Fisher and Reinfelder 1995; Mason et al. 1996). This may explain the positive enrichment (BMF $>$ 1.0) of Hg, Zn, and Cd we find in zooplankton. Wang and Fisher (1998) also found that the assimilation efficiency of Zn by marine copepods from phytoplankton was the highest relative to Cd, Co, and Se, and $>$50% of Zn was from ingested food. Efficient assimilation of Zn by zooplankton may help explain Zn biomagnification in zooplankton and fish in this study.

Finally, our study revealed differences in accumulation patterns and possible sources of metals between lower and upper trophic levels. For example, Cd appeared to biomagnify from small plankton to macrozooplankton but to diminish from macrozooplankton to fish. Thus, we contend that there are differences in metal accumulation between trophic levels that need to be investigated separately, to fully understand the metal transfer pathways in aquatic food webs.

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