

TRENDS IN METALS IN URBAN AND REFERENCE LAKE SEDIMENTS ACROSS THE UNITED STATES, 1970 to 2001

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Abstract—Trends in metals concentrations in sediment cores from 35 reservoirs and lakes in urban and reference settings were analyzed to determine the effects of three decades of legislation, regulation, and changing demographics and industrial practices in the United States on concentrations of metals in the environment. Decreasing trends outnumber increasing trends for all seven metals analyzed (Cd, Cr, Cu, Pb, Hg, Ni, and Zn). The most consistent trends are for Pb and Cr: For Pb, 83% of the lakes have decreasing trends and 6% have increasing trends; for Cr, 54% of the lakes have decreasing trends and none have increasing trends. Mass accumulation rates of metals in cores, adjusted for background concentrations, decrease from the 1970s to the 1990s, with median changes ranging from −46% (Pb) to −3% (Hg and Zn). The largest decreases are from lakes in dense urban watersheds where the overall metals contamination in recently deposited sediments has decreased to one-half its 1970s median value. However, anthropogenic mass accumulation rates in dense urban lakes remain elevated over those in lakes in undeveloped watersheds, in some cases by as much as two orders of magnitude (Cr, Cu, and Zn), indicating that urban fluvial source signals can overwhelm those from regional atmospheric sources.

Keywords—Metals Sediment Trends Lakes Cores

INTRODUCTION

Sediment contamination by metals in the United States is widespread [1], particularly in urban areas [2]. Is this contamination increasing or decreasing? On one hand, since the 1970s, the United States has taken numerous actions to control pollution. These actions include the establishment of the U.S. Environmental Protection Agency (1970); the passage of the Clean Air Act (1970), the Safe Drinking Water Act (1974), and the Toxic Substances Control Act (1976; <http://www.epa.gov/epahome/laws.htm>); and the phasing out of lead in gasoline (1973). Conversely, since 1970, demographics and lifestyles in the United States have changed in ways expected to deliver more contaminants to the environment: The population has increased by 42% (1970–2002), the aerial extent of urbanized land has increased by 90% (1970–2000) [3], and the number of vehicle miles driven has increased by 150% (1970–2001; [4], <http://www.fhwa.dot.gov/ohim/hs01/>).

One approach to reconstructing historical trends in metals in aquatic systems is the analysis of sediment cores collected from lakes, reservoirs, estuaries, tidal flats, floodplains, peat bogs, or the oceans. Use of sediment coring to reconstruct trends in metal pollution has a long history [5]. Analysis of sediment cores has been used around the globe to determine the historical contribution of localized sources to aquatic-sediment contamination, including mining [6,7], smelters [6,8], and municipal and industrial discharges [9]. In other cases, sediment cores have been used to reconstruct histories of long-range atmospheric deposition in remote areas where no local sources are present (e.g., the Swiss Alps [10], the Indiana Dunes, USA [11]). Some studies have investigated trends in individual metals, primarily lead and mercury, over extensive

spatial scales (e.g., Pb in Sweden [12], the Canadian arctic [13], and the midcontinental and eastern United States [14]; Hg in the Great Lakes Region and Alaska, USA [15]).

The study presented here was undertaken to identify generalized trends in a suite of metals of environmental concern (Cd, Cr, Cu, Hg, Pb, Ni, and Zn) at a national scale. The study is part of the National Water-Quality Assessment program of the U.S. Geological Survey, one of whose goals is assessment of trends in water quality across the United States. For this study, sediment cores were collected from water bodies in or near 17 major metropolitan areas and from a few remote locations; land use in the watersheds ranges from undeveloped to entirely urbanized (Fig. 1; Table 1). Concentrations of metals in sediments deposited from 1970 to the date of collection were tested statistically to determine if there was a significant trend, either increasing or decreasing.

METHODS

Study design

Sediment cores were collected from 35 lakes in the United States between 1996 and 2001 (23 reservoirs and 12 natural lakes, hereafter referred to as lakes except where the distinction is relevant), age-dated, analyzed chemically, and tested for trends. The objectives were to evaluate contaminant trends in freshwater, aquatic sediments in urban and undeveloped reference settings across the United States and to develop hypotheses regarding the causes of those trends. The National Water-Quality Assessment design provided a national framework for identifying potential study areas [16]. The selection of urban areas in this study was based on the combination of National Water-Quality Assessment study units, metropolitan statistical areas (<http://www.census.gov/epcd/www/g97geo2.htm>), and ecoregions [17]. Urban areas were selected to represent broadly the diversity of ecoregions where a majority of

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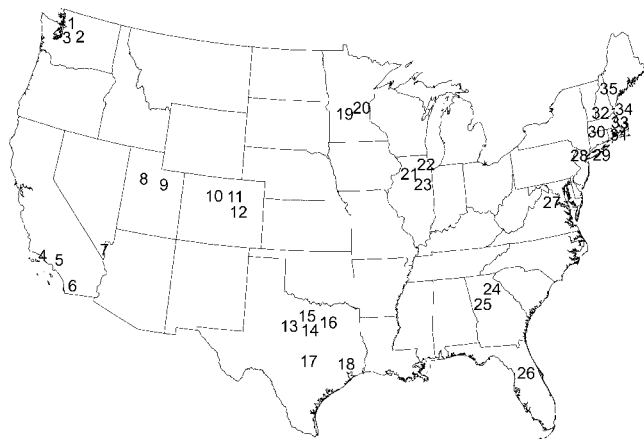


Fig. 1. Locations of lakes and reservoirs where sediment cores were collected (USA). Numbers correspond to map numbers in Table 1.

United States cities and urban populations are located. Lakes in one or more cities in the five most populous (summing urban population only) level II ecoregions and eight of the 11 most populous ecoregions were sampled. Although it is not a probabilistic design, it does provide a geographically diverse coverage of major urban areas of the country.

The 35 lakes are a subset of 58 lakes sampled by the U.S. Geological Survey between 1992 and 2001 [18]. The 35 lakes presented here (Table 1) were selected because they are representative of target land-use settings (urban and reference), their sediment-core profiles do not appear to be unduly affected by diagenesis and postdepositional sediment mixing, and the age-control for the cores was judged to be reliable for trend testing of the 35-year period of interest (see Van Metre et al. [18] for a detailed discussion of methods and age-dating). Land use in the watersheds was categorized as dense urban (>52% urban land use; 13 lakes), light urban (6–43% urban; 13 lakes), or reference (<1.5% urban; 9 lakes), as determined from the 1992 U.S. Geological Survey National Land Cover Data (<http://edc.usgs.gov/products/landcover/nlcd.html>). In urban settings, watersheds with residential and commercial land uses were favored, although those sites that are integrators of large urban watersheds (e.g., Charles River, Lake Mead) contain some heavy industry and point sources in their watersheds. Lakes with small drainage-area to surface-area ratios and undeveloped watersheds were chosen as reference lakes to assess trends in atmospheric fallout. Three of the nine reference lakes are water-supply reservoirs in protected watersheds, and five of the lakes and their watersheds are in county, state, or national parks; the remaining reference lake (Big Round Top) has 1.5% developed land, consisting of one road and a few houses, and no evident agriculture or grazing.

Core collection

Cores were collected in most cases from the deepest part of the lake or in the downstream part of the reservoir where postdepositional disturbance was assumed to be at a minimum [18]. Collection devices included box corers (Wildco, Buffalo, NY, USA), piston corers (Benthos, North Falmouth, MA, USA), gravity corers (Benthos), and core liners pushed directly into the sediment. In all cases the sample was collected inside a clean polycarbonate liner. Cores were extruded vertically and subsamples were analyzed for major and trace elements, ^{137}Cs , and, in some cores, ^{210}Pb and grain-size. The sediment was

not sieved. Organochlorine compounds and polycyclic aromatic hydrocarbons also were analyzed and are reported elsewhere [19].

Analytical methods

For major and trace element analyses, samples were freeze-dried and ground to a powder. Elemental concentrations were determined on concentrated-acid ($\text{HCl-HNO}_3\text{-HClO}_4\text{-HF}$) digests (near-total digestions) either by inductively coupled plasma-atomic emission spectrometry [20] or by inductively coupled plasma/mass spectrometry [21]. For samples using inductively coupled plasma-atomic emission spectrometry, Cd was analyzed by graphite furnace atomic absorption spectrometry [22]. Concentrations of Hg were determined by cold-vapor atomic absorption spectroscopy [23]. Quality assurance was provided by analyzing several standard reference materials, an environmental duplicate, and a blank sample with each batch of up to 20 samples. The two methods used for elements both performed well on the basis of analyses of four of the same standard reference materials. Median relative percent difference for all elements for all standard reference materials was 2.0% for inductively coupled plasma-atomic emission spectrometry and 4.4% for inductively coupled plasma/mass spectrometry. Cesium-137 activities were counted on freeze-dried samples in fixed geometry with a high-resolution intrinsic germanium detector γ -spectrometer, using a method similar to that described by [24]. Lead-210 activities were measured by high-precision γ -ray spectrometry [25]. Cadmium was not analyzed for two lakes, and Hg was not analyzed for four lakes.

Age-dating and trend analysis

Sampling and analytical methods, detailed descriptions of age dating for each core, an assessment of the quality of age control, and a discussion of factors affecting dating are presented for 33 of the 35 cores in [18]. In brief, the primary basis for age dating 23 of the cores was the ^{137}Cs profile. For eight of the cores, dating was based on ^{210}Pb profiles using either the constant input concentration model or the constant rate of supply model [26]. The two lakes included here that are not presented in Van Metre et al. [18], Mills Lake and Lake Elbert, were dated using ^{210}Pb and the constant input concentration model. The interface with prelacustrine sediment provided a date marker in most reservoirs and served as the primary basis for dating cores from four reservoirs constructed after 1964. Dates were assigned to individual samples on the basis of dry mass accumulation. For cores with no evidence to the contrary, a constant mass accumulation rate (MAR) of sediment was assumed between date markers. Thirty of the 35 cores had constant MARs over the time period of the trend testing. Although confidence intervals cannot be assigned to the dates corresponding to individual samples in the cores, the consistency of multiple corroborative date markers, such as the DDT and Pb peaks, suggests that most dates are probably within a few years of the actual deposition dates. The consistency of Pb peaks (1974.4 ± 5.7 years) in cores dated using constant MARs, relative to the 1972 peak in atmospheric emissions of lead in the United States, supports the use of constant MARs based on the ^{137}Cs peak in 1963 to 1964.

Two processes that can affect metal profiles in cores, potentially obscuring anthropogenic trends, are changes in geologic source material and diagenesis, including chemical alterations and postdepositional sediment mixing [27,28]. These processes were evaluated for all the cores collected for the

Table 1. The U.S. sampling sites and watershed characteristics. Map number refers to Figure 1

Map no.	Lake name	Nearest urban area	State	Date sampled	Lake (L) or reservoir (R)	Water depth at coring site (m)	Watershed area (km ²)	% Urban land use	Land-use type
1	Lake Ballinger	Seattle	WA	06/08/1998	L	9.9	13.7	73.1	Dense urban
2	Tolt Reservoir	Seattle	WA	06/11/1998	R	18.3	47.3	0	Reference
3	Lake Washington	Seattle	WA	06/09/1998	L	62.5	1,471	37.6	Light urban
4	West Street Basin	Los Angeles	CA	11/12/1998	R	1.2	3.30	79.8	Dense urban
5	R.R. Canyon Lake	Los Angeles	CA	11/10/1998	R	11.3	1,859	8.3	Light urban
6	Sweetwater Reservoir	San Diego	CA	09/24/1998	R	16.2	470	9.9	Light urban
7	Lake Mead, Las Vegas Bay	Las Vegas	NV	05/11/1998	R	105.2	5,245	7.9	Light urban
8	Great Salt Lake, Farmington Bay	Salt Lake City	UT	04/07/1998	L	1.2	10,313	11.0	Light urban
9	Red Butte Reservoir	Salt Lake City	UT	04/09/1998	R	7.6	19.7	0	Reference
10	Lake Elbert	Denver	CO	09/16/1999	L	5.5	1.06	0	Reference
11	Mills Lake	Denver	CO	09/14/1999	L	6.7	12.10	0	Reference
12	Sloans Lake	Denver	CO	08/19/1997	L	1.1	8.24	80.1	Dense urban
13	Lake Como	Fort Worth	TX	03/08/2001	R	7.8	2.70	93.9	Dense urban
14	Echo Lake	Fort Worth	TX	03/06/2001	R	4.6	2.60	95.5	Dense urban
15	Fosdic Lake	Fort Worth	TX	03/07/2001	R	2.4	1.20	83.7	Dense urban
16	White Rock Lake	Dallas	TX	07/06/1994	R	4.6	264	66.5	Dense urban
17	Town Lake	Austin	TX	08/26/1998	R	8.7	405	25.0	Light urban
18	Lake Houston	Houston	TX	07/10/1997	R	13.4	2,828	6.7	Light urban
19	Palmer Lake, West Lobe	Minneapolis	MN	07/30/1997	L	0.6	64.2	51.9	Dense urban
20	Lake Harriet	Minneapolis	MN	07/29/1997	L	21.3	6.07	60.6	Dense urban
21	Lake in the Hills	Chicago	IL	07/19/2001	R	8.5	24.0	14.9	Light urban
22	Beck Lake	Chicago	IL	07/17/2001	R	4.0	3.26	21.3	Light urban
23	Shoe Factory Road Pond	Chicago	IL	07/18/2001	L	0.5	0.02	0	Reference
24	Berkeley Lake	Atlanta	GA	05/19/1999	R	15.2	3.01	28.1	Light urban
25	Lake Panola	Atlanta	GA	05/18/1999	R	5.2	0.54	1.1	Reference
26	Lake Killarney	Orlando	FL	03/16/1999	L	7.5	6.34	63.9	Dense urban
27	Lake Anne	Washington, DC	VA	06/24/1996	R	8.2	2.28	34.4	Light urban
28	Orange Reservoir	Newark	NJ	09/18/1997	R	3.0	11.7	42.5	Light urban
29	Newbridge Pond	New York City	NY	09/22/1997	R	1.8	7.91	96.0	Dense urban
30	Big Round Top	Boston	RI	07/25/2000	R	1.2	23.3	1.5	Reference
31	Harris Pond, Middle	Boston	MA	07/26/2000	R	5.0	82.8	10.6	Light urban
32	Upper Mystic Lake	Boston	MA	08/31/2000	L	1.4	66.2	67.3	Dense urban
33	South Reservoir	Boston	MA	09/01/2000	R	13.9	1.90	0.2	Reference
34	Charles River, Lower	Boston	MA	07/28/2000	R	9.8	787	71.8	Dense urban
35	Crocker Pond	Boston	ME	08/30/2000	L	2.7	0.81	0	Reference

National Water-Quality Assessment study, and cores for which these processes were judged to have had a large influence on chemical profiles were excluded from the analysis presented here. Indications of mixing include a flat profile in excess ^{210}Pb in the upper part of the core and a rounded peak or no peak in ^{137}Cs . Alternatively, consistent decreases in ^{210}Pb with increasing depth, pronounced peaks in ^{137}Cs , and large ratios of peak to top of core ^{137}Cs activities are indications of a relative lack of mixing. Large vertical variations in contaminant concentrations (e.g., Pb, Hg, DDT, and polychlorinated biphenyls) also are evidence of a relative lack of mixing in cores included in this analysis.

Normalization of metals data to an aluminosilicate element such as Al or Ti sometimes is done to correct for diagenetic effects or for variations in geologic source [29]; if the reference elements are not highly variable or trending, however, use of the raw data is preferable, so data for this study were not normalized. Of the 35 lakes presented here, Al and Ti had the same direction of trend (decreasing in all cases) for nine lakes. For these nine lakes, metals trends are not uniform, but rather have about the same proportions of increasing, decreasing, and no trends as other sites. Lack of commonality between metals trends and Al and Ti trends in these nine cores suggests the metals trends are not simply a result of changes in bulk sediment properties.

Diagenetic processes such as oxidation of organic matter, dissolution of Fe and Mn oxides at depth in a core, and reprecipitation of Fe and Mn oxides near the sediment-water interface can affect profiles of some elements in some settings [28], usually resulting in a profile with an apparent increasing trend. In these 35 lake cores, trends in the seven metals presented here do not correlate with trends in organic carbon, Fe, or Mn, and decreasing trends in the metals are much more common than increasing trends. The limited role of diagenesis in affecting trends in these cores can be attributed in part to the relative nonreactivity of these metals and in part to the high sedimentation rates in many of the reservoirs and lakes sampled, which limit sedimentary diagenesis and preserve metal signals [30].

Temporal trends in concentration of the seven metals were analyzed using Kendall's tau with a criterion for statistical significance of $p < \alpha = 0.1$ [31]. Positive and negative taus signify increasing and decreasing trends, respectively. The tau value is an indication of the amount of noise in the trend: A purely monotonic trend has a tau value of 1.0 (or -1.0), and tau values for trends with one or more values deviating from a monotonic trend will be between -1.0 and 1.0. The starting time of 1970 for trend evaluation was chosen because it corresponds to the initiation of important environmental legislation or regulatory actions in the United States, including the National Environmental Policy Act of 1969, the Clean Air Act (1970), and the phasing out of lead from gasoline (1973). By focusing on this period, recent trends can be evaluated using a consistent approach nationally.

In this study, we chose to base trend analyses on concentration profiles and not contaminant MAR profiles as is sometimes done [15,32]. We chose concentrations because biota are exposed to concentration, not load or flux; 30 of the 35 lakes have constant sediment MARs, meaning that trends in concentrations and metal MARs will be identical; and an analysis of differences in trend results between concentrations and metal MARs for the five lakes with variable sediment MAR suggested more representative results were obtained using con-

centrations. About the same proportion of increasing, decreasing, and no trends result for these five lakes as for the other 30 lakes if concentrations are trend tested; however, if metal MARs are trend tested, the result in almost every case is a trend in the same direction as the trend in sediment MAR. We therefore concluded that anthropogenic contaminant releases in these watersheds were better represented by concentrations, although metal MARs also are presented and discussed.

RESULTS

For these 35 lakes, representing urban and reference watersheds across the United States, sites with decreasing trends outnumber sites with increasing trends for all metals (Fig. 2; full data can be accessed at <http://pubs.usgs.gov/ds/2006/166/>). Considering the possibility of a trend for each metal in each lake as one case, decreasing trends or no change account for 45 and 43% of total cases, respectively, and increasing trends account for only 12%. By metal, the percentage of lakes with decreasing trends is in the following order: Pb (83%) > Cr > Cd > Hg \approx Ni > Cu = Zn (31%). The percentage of lakes with increasing trends is in the following order: Cr (0%) < Pb = Ni < Cd < Hg \approx Cu < Zn (29%) (Fig. 2). For four metals (Cu, Hg, Ni, and Zn), lakes with no trend in concentration outnumber those with either increasing or decreasing trends.

Core profiles

Examples of three core profiles for each land-use type and the associated Kendall's tau values, where trends are statistically significant, illustrate several of the generalities present in the data set (Fig. 3). First, variation over time, between lakes, between metals, and between land uses is evident. The different trends seen between lakes (e.g., decreasing Cd in Mills Lake vs increasing Cd in Harris Pond) and in the same lake for different metals (e.g., decreasing Ni and increasing Zn in Lake Ballinger) are consistent with the hypothesis that the cores are recording trends in anthropogenic inputs rather than the effects of mixing, diagenesis, or changes in sedimentation rate. The relation between lakes in terms of degree of contamination varies between metals as well; for example, Shoe Factory Road Pond has higher concentrations of Cd and Ni than Lake Panola, but lower concentrations of Zn. Second, the relation between tau and trends is visually evident: A tau of 1.0 or -1.0 corresponds to a completely monotonic increasing or decreasing trend, whereas a low tau corresponds to numerous departures from a monotonic trend (e.g., Pb at Lake Panola). However, a high tau value does not indicate the steepness of the increase or decrease: The same tau value can be associated with two different magnitudes of change (e.g., Ni in Shoe Factory Road Pond vs Ni in Lake Ballinger). Third, even at the relatively short time-scale evaluated (25-30 years), some complex trends cannot be captured with a monotonic trend test (e.g., Pb in Lake Panola, Hg in Lake Ballinger), but in general a monotonic trend test of the 1970 to 2000 time period identifies most of the recent trends in the metals contaminant record.

Concentrations and mass accumulation rates

To investigate the magnitude of change since the 1970s, for each core the mean concentration for 1970s and 1990s sediment was computed and the change expressed as a percentage (Table 2). The median change in decadal mean concentration for all metals considered together is -7%. For in-

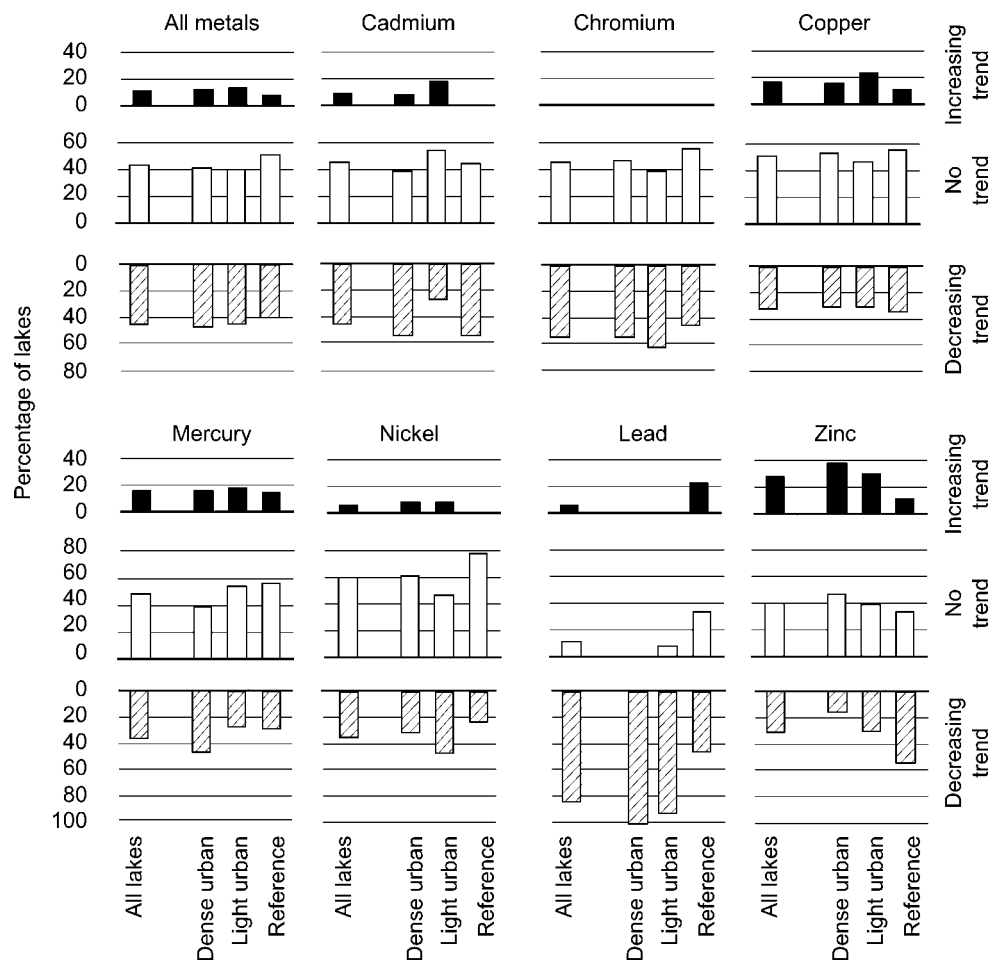


Fig. 2. Percentage of lakes sampled (USA) with statistically significant increasing trends, decreasing trends, and no trend since 1970.

dividual metals, the magnitudes of the decreases are in the order $Pb (-28\%) > Cd > Cr \approx Ni > Cu \approx Hg > Zn (+2\%)$. Note that the median percent change for individual lakes does not always agree with the percent change in the median of all lakes (Table 2). Although median changes are sometimes small for a metal when lakes are grouped, changes in many individual lakes are much larger. For example, the median change in Cd concentrations among all lakes is a decrease of 15%, but eight of the 35 lakes have decreases of more than 30%. Conversely, Zn, with a median change of 2%, increases by more than 10% in 10 lakes and by more than 35% in five lakes.

The concentration of a metal measured in a sediment sample has a naturally occurring (background) component and, in some cases, an anthropogenic component. If background concentrations are known, they can be subtracted from total concentrations to estimate the anthropogenic concentration. For 28 of the 35 cores collected in this study, background concentrations were estimated using older, predevelopment lacustrine sediment from the deepest part of the core (15 lakes or reservoirs), prereservoir soil from the bottom of the core (2 reservoirs), or background concentrations from a nearby core or cores (11 lakes or reservoirs). The use of older lacustrine sediment in the core was the preferred method; however, in many lakes the core did not extend back in time far enough to represent predevelopment conditions. In some of these lakes, it was determined that reasonable estimates of background concentrations could be made using background concentrations from a nearby core. The primary conditions for using

this approach were location in a similar geologic setting and relatively similar major element chemistry (e.g., Al, Ca, Fe, K, Ti) between the cores. Because a consistent method could not be used, the background concentrations should be considered approximations. Subtracting background concentrations from 1970s and 1990s concentrations yields estimates of anthropogenic concentration for the 28 cores (Table 2). In cases where total concentration was within 5% of background concentration (\sim within analytical uncertainty), anthropogenic concentrations were taken as zero.

The median change in anthropogenic concentrations (1970s–1990s) for all metals considered together is -18% , more than twice the change of -7% computed for unadjusted concentrations. For individual metals, the magnitude of the decreases (medians) are in the order: $Pb (-46\%) > Cr > Cd \approx Ni > Cu > Zn > Hg (0\%)$. This order is similar to that for total concentrations. For the four metals (Cd, Cr, Ni, and Pb) that had ratios of decreasing to increasing trends of 5:1 or greater, the median change in anthropogenic concentration is much greater than the median change in total concentration. This is reasonable, as proportional decreases computed with adjusted data will be greater than those computed with total concentration, and trends are dominantly in the same direction (decreasing). For the other three metals (Cu, Hg, and Zn), small average changes in both total and anthropogenic concentrations are consistent with a more similar number of increasing and decreasing trends.

Anthropogenic mass accumulation rates (MAR_A) for each

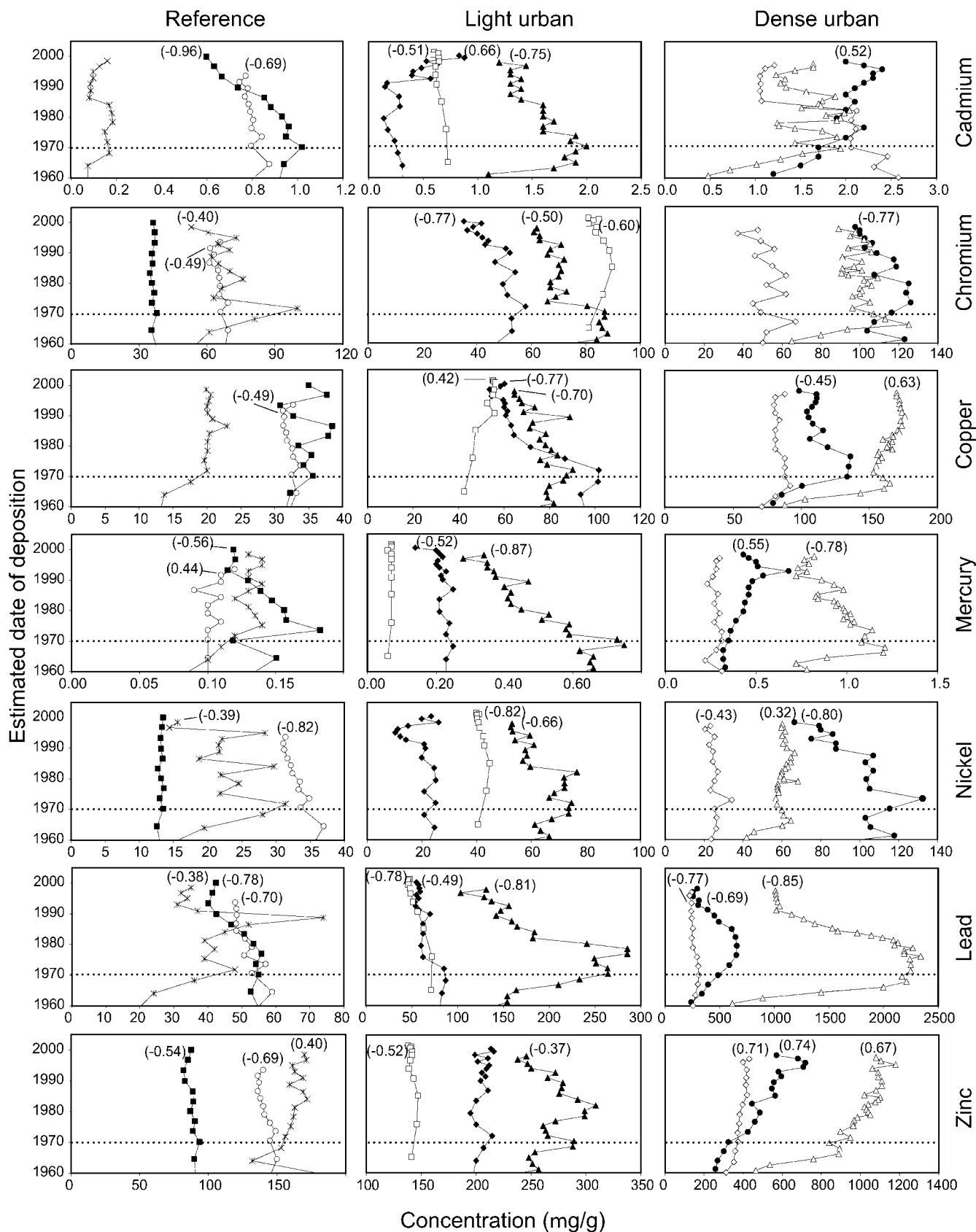


Fig. 3. Representative core profiles for reference, light urban, and dense urban watersheds. Trends were tested from 1970 (dashed line) to top of core. Positive and negative values of tau corresponding to increasing and decreasing trends, respectively, are shown next to those cores for which they were statistically significant ($p < 0.1$). Reference lake cores shown are for Lake Panola (GA, USA) (*), Mills Lake (CO, USA) (■), and Shoe Factory Road Pond (IL, USA) (○); light-urban lake cores shown are for Harris Pond (MA, USA) (◆), Beck Lake (IL, USA) (□), and Lake Washington (WA, USA) (▲); dense-urban lake cores shown are for Sloans Lake (CO, USA) (◇), Newbridge Pond (NY, USA) (△), and Lake Ballinger (WA, USA) (●). Note differences in x-axis scales by metal and land use.

Table 2. Median decadal concentrations, anthropogenic concentrations, and anthropogenic mass accumulation rates (MAR) for metals by land-use type

Metal	Land-use setting	Median concn. ($\mu\text{g/g}$)			Median background concn. ($\mu\text{g/g}$)	Anthropogenic concn. ($\mu\text{g/g}$)			Anthropogenic MAR ($\mu\text{g/cm}^2\text{-year}$)		
		1970s	1990s	Median % change among lakes		1970s	1990s	Median % change among lakes	1970s	1990s	Median % change among lakes
Cd	All	0.78	0.65	-15	0.14	0.53	0.34	-29	0.14	0.06	-29
	Dense urban	2.07	1.60	-20	0.14	1.74	1.23	-44	0.20	0.22	-44
	Light urban	0.54	0.49	-7	0.16	0.17	0.18	-29	0.16	0.10	-29
	Reference	0.76	0.64	-15	0.14	0.53	0.22	-20	0.01	0.01	-20
Cr	All	73	65	-7	52	22	14	-34	5.8	2.2	-15
	Dense urban	91	75	-12	50	59	22	-44	20.8	11.6	-44
	Light urban	73	65	-4	54	19	5	-29	4.1	1.2	-3
	Reference	50	47	-6	39	0	0	-7	0.0	0.0	0
Cu	All	46	58	-3	16	29	29	-7	10	9	-10
	Dense urban	86	83	-4	14	37	38	-7	23	16	-7
	Light urban	83	68	-6	25	57	46	-5	14	11	-5
	Reference	28	34	0	16	4	7	-12	0	0	-19
Hg	All	0.16	0.14	-2	0.040	0.091	0.088	0	0.023	0.022	-3
	Dense urban	0.38	0.30	-7	0.040	0.110	0.105	-16	0.067	0.044	-16
	Light urban	0.07	0.07	-2	0.033	0.044	0.044	-1	0.023	0.022	-7
	Reference	0.16	0.13	2	0.055	0.077	0.079	3	0.004	0.005	3
Ni	All	32	31	-6	22	9.2	6.3	-29	2.5	0.8	-22
	Dense urban	37	33	-11	22	10.4	8.6	-47	8.1	4.3	-47
	Light urban	36	31	-6	24	14.1	9.4	-37	2.5	0.8	-37
	Reference	26	20	-1	13	4.2	5.7	0	0.2	0.2	-8
Pb	All	115	73	-28	21	64	37	-46	27	14	-46
	Dense urban	483	214	-49	20	353	194	-49	178	59	-49
	Light urban	86	56	-35	22	49	22	-55	14	6	-55
	Reference	53	48	-10	23	24	28	-16	1	1	-16
Zn	All	190	216	2	72	127	176	-5	29	34	-3
	Dense urban	350	343	8	53	262	253	5	90	86	5
	Light urban	184	203	3	79	63	64	0	26	30	0
	Reference	134	134	-7	83	24	29	-22	1	0	-12

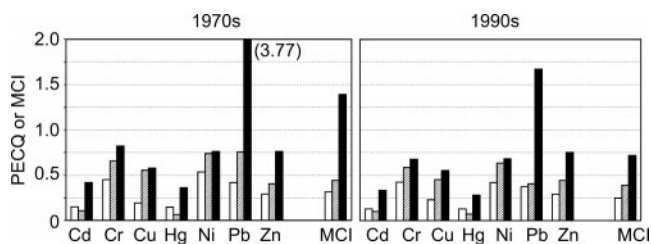


Fig. 4. Median probable effect concentration quotient (PECQs) and metals contamination indices (MCIs) for sediment deposited in the 1970s and 1990s, by land use type. Reference lakes are shown in white, light urban lakes in crosshatch, and dense urban lakes in black.

metal were computed for the 1970s and 1990s by multiplying decadal anthropogenic concentrations in each core by the average sediment MAR for the decade. Because sediment MAR was modeled as constant over the period from 1970 to the top of the core for most lakes (24 of the 28 with background concentrations), proportional changes in median values of anthropogenic concentrations and MAR_A are similar or identical (Table 2).

To evaluate the environmental relevance of metals contamination in these lake sediments, metals concentrations are compared to corresponding probable effect concentrations (PECs) [33]. The PECs are a consensus of six different published sets of sediment quality guidelines, which were based on toxicity to a number of different benthic taxa; a concentration of a metal in bed sediment above the corresponding PEC is expected to cause adverse effects to benthic biota in freshwater ecosystems (bioaccumulation is not considered). To facilitate comparison between metals, the concentration of each metal is normalized by dividing by its PEC to obtain a PEC quotient (PECQ) for 1970s and 1990s sediment in each lake. The frequency with which a PEC is exceeded ($PECQ > 1$) in 1990s sediment follows the pattern $Pb (43\%) > Zn = Cu > Ni > Hg = Cr > Cd (3\%)$. For each lake a metals contamination index (MCI), indicating the overall degree of metals contamination for the 1970s and 1990s, was computed by summing the individual metal PECQs and dividing by the number of metals, similar to the mean PECQ of [33]. The decrease in the median MCI between the 1970s and the 1990s for reference and light urban lakes was relatively small (from 0.31–0.27, and from 0.44–0.41, respectively), but the change for dense urban lakes was large (from 1.39–0.67; Fig. 4).

DISCUSSION

The results of a study of this scope suggest some broad generalizations about trends in metals contamination of freshwater aquatic sediment across the United States and their causes. The overall decrease in metals contamination seen is consistent with reported decreases in emissions (<http://www.epa.gov/tri/index.htm>) and with the results of many previous studies that have focused on individual metals or on smaller spatial scales (e.g., [6,10,12,15,34]), and extends them to a suite of metals at a subcontinental scale. With two important exceptions (Hg and Zn), the median decrease in anthropogenic concentrations reported here is in the same range as those reported in other studies [6,12,32,34–37]. This is noteworthy in light of the range of land uses, watershed sizes, and geographic settings represented here, and suggests that the trends determined do indeed represent national trends in the target land-use setting.

Interpretation of concentrations and mass accumulations of metals

Variation in concentrations at individual sites and between sites can reflect natural variations (e.g., mineralogy), dilution of contaminated sediment by clean sediment, and anthropogenic loading rates. In theory, the effects of the first two can be removed by subtracting background concentrations to obtain anthropogenic concentrations and then converting them to MAR_A .

Comparison of differences in magnitude of anthropogenic concentrations and MAR_A between reference and urban land uses can indicate contaminant source and transport pathway. If anthropogenic concentrations at urban and reference sites are similar, then a widespread atmospheric source is suggested. If, however, the anthropogenic concentration at urban sites is significantly elevated, then additional local watershed sources are indicated. Furthermore, if the difference in MAR_A between urban and reference sites is enhanced relative to the difference in anthropogenic concentrations, then dominance of fluvial transport of the contaminant over direct atmospheric deposition is indicated. Direct atmospheric deposition results in an MAR_A that is independent of sedimentation rate, and sedimentation rate is inversely related to concentration, whereas input of contaminants by a fluvial pathway results in an MAR_A that is directly proportional to sedimentation rate [38].

Cadmium, Cr, Cu, Pb, and Zn have much greater anthropogenic concentrations in dense urban lakes than in reference lakes (ratios of about 5:1 to 10:1 for 1990s median values; Table 2). Further, differences in MAR_A between dense urban lakes and reference lakes (ratios of about 50:1 or greater) are much greater than the differences in anthropogenic concentrations, a result of the higher sedimentation rates in the urban lakes. The relative differences between concentrations and MAR_A as a function of land use indicate that there are local watershed sources contributing these metals to the urban lakes and that most of the contaminant input is fluvial. In contrast, anthropogenic concentrations of Hg are only slightly higher in dense urban lakes than they are in reference lakes (ratio of 1.3:1), yet MAR_A for Hg in urban lakes are about eight times greater than in reference lakes. This suggests that the source of Hg is atmospheric, but the dominant transport pathway to the urban lakes is fluvial, i.e., fallout on the watershed and transport to the lake is a dominant pathway for input to the lakes. This is consistent with what is known about atmospheric sources of Hg, but demonstrates the importance of fluvial pathways in urban settings. Nickel has land-use relations that are intermediate between Hg and the other metals, with ratios in anthropogenic concentrations of approximately 1.5:1 and in MAR_A of approximately 26:1, suggesting mostly regional atmospheric sources and relatively smaller local urban sources than the other metals.

The magnitude of change from the 1970s to the 1990s, when corrected for background and converted to mass accumulation rate, is enhanced for some metals in some lakes but not all. In most cases where the temporal change in concentrations is small (Cu, Hg, and Zn), the percent change in anthropogenic concentrations and MAR_A also is small (Table 2). In those cases where temporal change in concentrations is large (Cd, Cr, Ni, and Pb), the changes in anthropogenic concentrations and MAR_A are proportionally much larger, especially in urban settings. These also are the metals and settings where the proportion of decreasing trends is greatest (Fig. 2). The

greater relative change in MAR_A implies that the changes are caused by changes in anthropogenic source strength. For Cd, Cr, Ni, and Pb, the median percent change in dense urban lakes in anthropogenic concentrations and MAR_A is a decrease of more than 40%. These are very large changes, considering they occur over only 30 years.

Effect of land use on trends

Strength and direction of trends in concentrations of some metals are affected by land-use type, in particular Pb and Zn (Fig. 2). For Pb, although the overall direction of trend is decreasing in all land-use settings, the signal is strongest in dense urban settings (100% decreasing) and weakest in reference settings (44% decreasing). The opposite is seen for Zn: Increasing concentrations outnumber decreasing concentrations by 2.5:1 in dense urban settings, but the reverse is seen in reference settings (1:5). These results suggest that, for these two metals, urban-related local sources and fluvial pathways are distinct from regional or global atmospheric sources. For the other metals, the ratio of decreasing to increasing trends is not related to land use, suggesting that the change is being driven by decreases in regional or global atmospheric sources. For Cr and Ni, however, the evidence is somewhat mixed regarding urban versus regional sources. The direction of trends in both is not related to land-use type (Fig. 2), but the change in anthropogenic concentrations and MAR_A is related (Table 2). Large magnitude decreases in urban settings relative to much smaller magnitude but systematic (monotonic) decreases in reference settings suggest distinct urban and regional sources that have both declined or that declining urban sources (e.g., industrial emissions) have a much greater local impact than regional impact.

Lake sediments remain more contaminated in urban settings as evaluated by the PECs and MCI, but the difference in sediment quality as it relates to metals in urban and reference lakes is narrowing (Fig. 4). In 1990s sediment, the median PECQ for Cr, Cu, Ni, Pb, and Zn increases with increasing urbanization, and the median MCI for the three land-use settings increases from 0.27 (reference) to 0.41 (light urban) to 0.67 (dense urban). This represents a decrease in the MCI since the 1970s for all land-use types, particularly for dense urban, for which the MCI has decreased to about half its 1970s value of 1.39. Most of this change is attributable to decreases in Pb (Fig. 4), for which the median PECQ has decreased from 3.77 in the 1970s to 1.67 in the 1990s. In dense urban lakes, Pb accounts for more metals contamination, as indicated by PECQs, than any of the other six metals (Fig. 4). The median 1990s PECQ in dense urban settings follows the pattern Pb (1.67) > Zn > Ni = Cr > Cu > Cd > Hg (0.28).

Evaluation of trends in individual metals

Differences in trends between land uses illustrate the sometimes-competing effects of national-scale reductions in atmospheric releases versus inputs from localized sources. In general, trends in reference lakes are expected to record changes in regional- to national-scale atmospheric deposition. Differences in trends between reference and urban lakes for a given contaminant can indicate the contribution of local sources on sediment quality.

Lead

The effect of the removal of Pb from gasoline is clear: 83% of the lakes sampled had decreasing trends in Pb. The direction

of the trends and the magnitude of the decreases in anthropogenic concentration (Table 2) are consistent with numerous studies in urban and remote settings in Europe and North America documenting decreases in anthropogenic Pb from 30 to 79% since the 1970s (e.g., [12,14,34,39]). Further, this study demonstrates the strength of the urban Pb source signal: The frequency of lakes with decreasing trends and the percent change increases from reference to light urban to dense urban settings (Fig. 2; Table 2).

Although the number of decreasing trends and the percent decrease in concentration for Pb greatly exceed those for any other metal, Pb continues to contribute the greatest metals contamination of the seven metals investigated on the basis of comparison to PECs, particularly in dense urban watersheds (Fig. 4). This may be a result in part of the time necessary for erosion of legacy Pb from the watershed [40], but local sources, such as municipal waste incineration [34], exterior paint [41], and roofing materials [42] also may be contributing Pb contamination to the urban environment.

Cadmium, chromium, nickel, and copper

These four metals are associated with industrial processes, and, in locations around the globe affected by wastewater or industrial emissions, the four metals often trend similarly [43,44]. Atmospheric sources of Cd, Cr, Ni, and Cu include smelting, waste incineration, and combustion of fossil fuel, and they are used in a wide range of industrial processes, including tanning, chrome plating, wood preserving, metal production and plating, and dye and pigment production; in the United States, release of emissions and disposal of waste from these industries now is controlled [45].

In the cores analyzed here, decreasing trends in Cd, Cr, and Ni outnumber increasing trends by 5:1 or more. The results for Cr are particularly striking in that no lake had an increasing trend. The median percent decreases in anthropogenic concentrations of the three metals across all land uses from the 1970s to the 1990s (Table 2) are similar to those reported in studies of sediments from urban areas (e.g., Mersey Estuary in England [37] and Central Park in New York City, USA [34]). In contrast to Pb, the relative proportions of decreasing trends for these three metals do not appear to be related to land use, suggesting that the regional atmospheric signal has decreased. Further, the relative changes in anthropogenic concentrations and MAR_A for these three metals are much greater in dense urban lakes than reference lakes, suggesting that local sources also have declined. This might be because of the strong association of these three metals with smokestack emissions; many industries are located in urban areas, so reductions in these emissions could lead to pronounced decreases in urban lakes closer to the source and smaller reductions in more distant reference lakes.

For Cd, decreasing trends and decreases in atmospheric releases might be attributable to an important change in industrial practices. Cadmium occurs in zinc ore and as an impurity in zinc metal. Since 1950, there has been a gradual transition from the production of zinc metal by smelting to production by electrolysis, although smelting still is in use [45]. Far less Cd is released to the atmosphere from electrolytic refining than by smelting (<http://www.inchem.org/>), and from 1988 to 2002 reported atmospheric emissions of Cd from primary metals production decreased by a factor of 24 (<http://www.epa.gov/tri/index.htm>). Furthermore, as zinc metal refined by electrolysis contains Cd at concentrations seven to 25

times lower than zinc metal refined by smelting (0.02% compared to 0.15–0.5% by weight) [46], less Cd is expected to leach from products, such as galvanized roofing, that contain Zn refined by electrolysis than from those that contain Zn refined by smelting.

Although Cu in the environment has many of the same sources as Cd, Cr, and Ni, Cu in these 35 cores has relatively fewer decreasing trends and more increasing trends. Reported decreases in atmospheric emissions of Cu from 1988 to 2002 are similar to those for Cr and Ni (<http://www.epa.gov/tri/index.htm>), yet the median percent decrease in anthropogenic concentrations is much smaller (Table 2). Anthropogenic concentrations and MAR_A of Cu are much higher in the lakes with light and dense urban watersheds than in the reference lakes, but the frequency of increasing and decreasing trends is about the same across all three land uses. Although vehicle brakepad wear has been cited as an important source of Cu in urban areas (<http://www.epa.gov/OWOW/info/NewsNotes/issue53/national53.html>), we cannot attribute trends in the cores presented here to this source, which should result in fewer decreasing trends in the more urbanized watersheds.

Mercury

Mercury does not display the national-scale systematic trends seen for Pb, Cd, Cr, and Ni in the lakes investigated by this study. One-half of the lakes investigated have no Hg trend, and decreasing trends outnumber increasing trends by only 2:1, similar to the results for Cu. In dense urban areas, there were more decreasing trends than in light urban or reference settings. These results are consistent with reports of declines in Hg accumulation rates at urban and some reference lakes in Minnesota, USA, and no trend in other lakes in Minnesota as well as in Alaska, USA [15]. The authors attributed these differences to reductions in regional emissions but not in global emissions, or alternatively to geographic location of Hg emissions sources. The median change of 0% in anthropogenic concentration and -3% in MAR_A in the lakes presented here is in contrast to results of many studies that have reported decreases in Hg since the 1970s in the United States [6,32] and Europe [37,47]; this might be because of the number of lakes and variety of geographic settings sampled for this study. Some of the individual lakes in settings similar to those sampled for other studies had similar decreases in Hg concentration. Total concentrations in urban settings have been reported to decrease from 30 to 65% (e.g., Lake Ontario, Canada [36]; Mersey Estuary [37]) and some of the sites in dense urban watersheds sampled for this study (West Street Basin, Fosdic Lake, Charles River, Lake Washington, USA) had decreases from 35 to 70%.

The median percent change in anthropogenic concentrations of Hg from the 1970s to the 1990s increased slightly in reference settings, was zero in light urban settings, and decreased in dense urban settings. This suggests that regional and global atmospheric contributions to Hg in lake sediments are not changing, but that fluvial urban point and nonpoint sources are decreasing. These results are consistent with national emissions data from 1988 to 2002, which show a reduction of only 13% for atmospheric emissions of Hg, but an eightfold reduction of Hg emissions to water (<http://www.epa.gov/tri/index.htm>).

The PEC for Hg is exceeded in only three lakes (two dense urban and one light urban), and Hg accounts for a smaller proportion of the MCI than any other metal in all land-use

settings (Fig. 4). However, more than 75% of all United States fishing advisories have been issued at least in part because of Hg contamination [48], a reminder that PECs, which evaluate toxicity rather than bioaccumulation, are not the only measure of environmental concern.

Zinc

In contrast to the other metals, in dense urban watersheds, the number of increasing trends in Zn exceeds the number of decreasing trends, even though reported releases of Zn to air and water have been decreasing since they were first recorded by the Toxics Release Inventory in 1988 (<http://www.epa.gov/tri/index.htm>). The direction of trends is related to land use, with decreasing trends outnumbering increasing trends by 5:1 in reference watersheds, equal in number in light urban watersheds, and increasing trends outnumbering decreasing trends by 2.5:1 in dense urban watersheds (Fig. 2). Median anthropogenic concentrations of Zn are more than two times higher in light urban lakes than in reference lakes and about an order of magnitude higher in dense urban lakes than in reference lakes; Zn concentrations in 1990s sediment exceeded the PEC in 38% of lakes in dense urban watersheds.

The median change in total Zn concentrations from the 1970s to the 1990s was 8, 3, and -7% for dense urban, light urban, and reference lakes, respectively. These results are similar to those reported by Callender and Rice [49], who found that Zn concentrations had remained nearly constant since the 1970s in six reservoirs along an urban gradient. They attributed their results in part to increased vehicle traffic. Tires have been recognized for several decades as a source of Zn to the environment [50] and are hypothesized to be a major and perhaps controlling source of particulate Zn in urban runoff and impounded sediments [51]. It is notable that a large decrease in Zn concentrations reported by [34] was for a lake in a dense urban area receiving only atmospheric inputs (Central Park, New York) and no road or parking lot runoff. Other sources of Zn in the urban environment include galvanized metal, batteries, smelting, coal combustion, and waste incineration. In an urban watershed in Texas, USA, galvanized metal roofs were estimated to contribute more than 50% of the particulate Zn loading to the stream [42].

Implications of metals trends

The lakes presented here have a wide range of watershed areas, land uses, climates, and topography, yet the trends tell a consistent story: A preponderance of decreasing trends in metals are evidence that actions taken since the 1970s to improve environmental quality have had some positive effects. This is particularly notable given that the amount of urban land use in many of these watersheds has increased since the 1970s. The greatest improvements are seen in urban areas and are attributable to decreases in local urban point and nonpoint sources. The median magnitude of decrease in anthropogenic concentration, not unexpectedly, is greatest for Pb (-46%), but the median decrease for Cd, Cr, and Ni also are high (-29%, -34%, and -29%, respectively). Interestingly, technological advancements are responsible for much of the decrease in releases of Pb and possibly of Cd, but decreases in anthropogenic concentrations of Cr and Ni have no single identified source. In contrast, widespread decreasing trends are not seen for Cu, Zn, and Hg, and increasing trends outnumber decreasing trends in Zn in urban watersheds.

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