Contaminant Trends in Reservoir Sediment Cores as Records of Influent Stream Quality

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FIGURE 1. Site locations in Fort Worth, TX and Boston, MA. The watersheds of the reservoirs sampled are shown as shaded areas.

When reconstructing water-quality histories from lake and reservoir cores, it is sometimes assumed that the chemical signatures in the cores reflect historical water quality in the influent streams. To investigate this assumption, concentrations of metals, PAHs, and organochlorine compounds in sediment cores were compared to those associated with an influent-stream suspended sediment for three reservoirs in Fort Worth, TX, and two reservoirs in Boston, MA, U.S.A., and interpreted in light of land-use and regulation histories. In evaluating relations between suspended sediments and cores, three levels of preservation were indicated: (1) influent concentrations and historical trends are preserved in cores (metals at all sites; some organic contaminants at some sites); (2) some loss occurs during transport and initial deposition but relative historical trends are preserved in cores (some organic contaminants at some sites); and (3) neither stream concentrations nor relative historical trends are preserved (dieldrin and p,p'-DDT). The degree of preservation of influent concentration histories varied between lakes, particularly for PAHs. The results support the use of sediment cores to infer streamwater-quality histories for many contaminants but indicate that reservoir-bottom sediment samples might underestimate concentrations of organic contaminants in some streams.

Introduction

Sediment in streams and lakes often contains particle-associated contaminants (PACs) at levels of concern, particularly in urban areas (*1–3*). Many PACs, which include trace elements, organochlorine compounds (OCs), and polycyclic aromatic hydrocarbons (PAHs), pose a threat to biota in aquatic systems because they are persistent, bioaccumulative, and (or) toxic (*4*). Transport of PACs is assumed to be dominated by movement on suspended sediments (*5*), but because little historical data on suspended sediments exist, numerous researchers have relied on streambed-sediment sampling and sediment coring to evaluate the occurrence of and to identify trends in PACs in aquatic systems (*1, 6–9*). The study presented here investigates the extent to which reservoir sediment cores record concentrations of and historical trends in contaminants associated with suspended sediment in influent streams.

Research on the relation between suspended and bottom sediment has been carried out mostly in estuaries and other large water bodies, with inconclusive results. In two studies
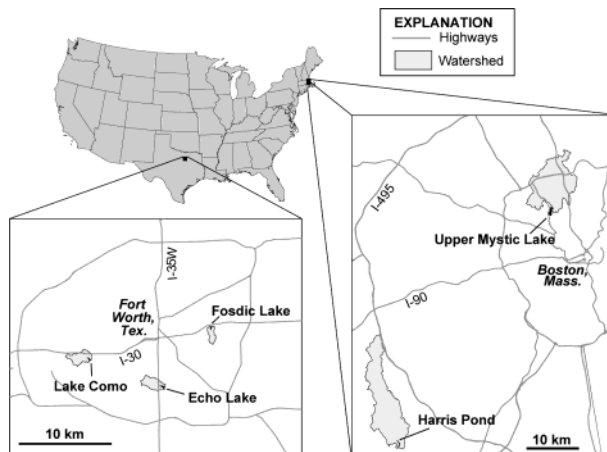
of the Baltic Sea, for example, one study reported concentrations of PACs in settling particulate matter similar to those in surficial bottom sediment (*10*) and the other found lower PCB concentrations on settling particles than in bottom sediment (*11*). PAH concentrations were lower on settling particles than in bottom sediment in the Humber Estuary, U.K., but were somewhat higher in suspended sediment from two influent rivers (*12*). In contrast, concentrations of trace elements and OCs on bottom sediment in the Great Lakes were found to be higher than those in suspended sediment from 17 tributaries on the Canadian side of the lakes (*13*).

The study presented here differs from the studies described above in both scale and hydrologic setting. Contaminant loading to large water bodies usually is from several sources, which can include multiple tributary streams, point-source discharges, and atmospheric fallout (*14*). The large tributaries that feed the water bodies respond relatively slowly to rainfall, and transport distances and particle residence times are long. Once in a large, deep water body, the residence time for settling particles is on the scale of weeks to as much as a year, sedimentation rates are low, and resuspension is common (*14*); as a result, the sediment geochemistry often is controlled by contaminant cycling within the system. In contrast, for small, shallow reservoirs such as those investigated for this study, large drainage-area to surface-area ratios result in fluvially dominated PAC loading, often from a single stream (*8*). The streams generally respond quickly to rainfall, and transport distances and particle residence times are short. Once in the reservoir, settling times are brief, and high sedimentation rates lead to rapid burial of sediment, limiting resuspension and diagenesis (*15*). Relations between stream suspended-sediment chemistry and bottom-sediment chemistry in such systems have not, to our knowledge, been described before.

The study presented here investigated the transport and fate of PACs in small stream-reservoir systems in two urban areas with contrasting hydrologic and climatic settings: Fort Worth, TX, and Boston, MA, U.S.A. Sediment cores from five reservoirs and suspended sediment from the influent streams were analyzed for PACs (Figure 1). Concentrations at the tops of the cores are compared to those associated with suspended sediment in the streams, and trends in the cores are evaluated in relation to historical releases of PACs and historical land use in the watersheds.

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Experimental Section

Site Selection. The five reservoirs investigated (Echo Lake, Fosdic Lake, and Lake Como in Fort Worth, Upper Mystic Lake, and Harris Pond in the Boston area; Figure 1) have small surface areas (0.03−0.64 km²), with large drainage-area to surface-area ratios (22−590). Upper Mystic Lake was a natural lake until 1864, when a dam was constructed raising the water level by 2 m. Each of the reservoirs is fed by one main influent stream. The reservoirs are shallow (1.4−7.8 m depth at the coring sites; mean depths are not available), so particle settling times are short. The watersheds of four of the reservoirs are heavily urbanized with 67% or more urban land use which includes residential, commercial, and some industrial land uses (*16, 17*). The watershed of the fifth reservoir, Harris Pond, is only recently undergoing urban development, with urban land use of 11% in 1992 (*17*). The two urban areas sampled have contrasting hydrologic settings. The unnamed streams feeding the three Fort Worth reservoirs are ephemeral, and those feeding the two Boston reservoirs, Mill Creek for Harris Pond and the Aberjona River for Upper Mystic Lake, are perennial. Suspended-sediment concentrations are much higher in Fort Worth (median of 203 mg/L) than in Boston (median of 11 mg/L), and the climate in Fort Worth is warmer and drier.

Sample Collection. Three cores were collected from locations distributed along the longitudinal axis of each reservoir except at Upper Mystic Lake, where two cores were collected from the upstream embayment of the lake (only one was analyzed for metals). A 6.7-cm diameter gravity corer with a polybuterate liner was used in Fort Worth and for one core from Harris Pond and a 50-cm × 14-cm × 14-cm box corer with a polybuterate liner was used for the other Boston cores. Cores were sectioned into discrete intervals from 1- to 10-cm thick and analyzed chemically. Subsampling equipment and box-core liners were cleaned between each sample by rinsing with native water, washing with phosphate-free detergent, and rinsing again with native water. Gravity-core liners were washed prior to use and only used once. One core from each lake was selected for more detailed vertical (and therefore temporal) sampling: 9−31 samples and 9−13 samples were analyzed from each of these cores for major and trace elements and hydrophobic organic compounds (HOCs), respectively. For the other cores from each lake, only two or three samples, from the top, middle, and (or) bottom of the core were analyzed chemically.

Suspended-sediment samples were collected during runoff events from the influent streams (Table 1; Figure 1). A water-level sensor and an automatic sampler equipped with a peristaltic pump and seven 9-L high-density polyethylene containers (Fort Worth sites) or a 200-L Teflon-bag-lined plastic barrel (Boston sites) was installed at each stream near the lake inflow. Tubing and containers were cleaned between events with phosphate-free detergent, repeated distilled/deionized water rinses, a methanol rinse, and a final distilled/deionized water rinse. The Teflon bags were used once and discarded. Sample containers were not acid-rinsed; however, it is unlikely that any trace metals contamination from the container walls would compromise detected concentrations of metals on suspended particles, as concentrations in particles typically exceed those in water by several orders of magnitude. Sampling intervals during storm events ranged from 20 min to 13.5 h (median of 1 h) in Fort Worth and from 2 to 6 days in Boston. As many as seven discrete samples were combined to make a flow-weighted composite sample at the Fort Worth sites. Flow-weighted composite samples were generated by the Boston samplers on the basis of preprogrammed stage-discharge ratings. Whole-water samples were stored chilled until samples were filtered. The time interval between completion of sample collection and filtering was from a few hours to 3 days. Sediment was isolated by filtration using 0.45-μm PTFE-membrane filters (*18*).

Chemical Analysis. All samples for analysis of major and trace elements from Fort Worth and the suspended-sediment from New England were freeze-dried and completely digested using a mixture of hydrochloric-nitric-perchloric-hydrofluoric acids and analyzed by inductively coupled plasma/mass spectrometry (ICP/MS) (*19*). Sediment core samples from New England were freeze-dried and completely digested using nitric-hydrofluoric acids in microwave pressure vessels and analyzed by inductively coupled plasma-atomic emission spectrometry (ICP/AES) (*20*) and by graphite furnace atomic adsorption spectrometry (GF/AAS) (arsenic and cadmium, only) (*21*). Mercury in all samples was analyzed by cold vapor atomic absorption spectrometry (*20*). Samples for analysis of OCs and PAHs were extracted, isolated, and analyzed using the procedures of refs *22* and *23*. In brief, sediment was extracted overnight with dichloromethane in a Soxhlet apparatus. Two aliquots of the extract were injected into a polystyrene-divinylbenzene gel permeation column and eluted with dichloromethane. The first aliquot was analyzed for PAHs and alkyl-PAHs by capillary-column gas chromatography with detection by selected ion monitoring mass spectrometry. The second aliquot was analyzed for OCs by dual capillary-column gas chromatography with electron capture detection. ΣPAH reported here is the sum of 18 parent PAHs plus the homologous series of alkyl-PAHs, and combustion PAH is the sum of 10 4- and 5-ringed parent PAHs (*24*). Chlordane reported here is technical chlordane, and ΣPCB is the sum of the quantified Aroclor equivalents 1242, 1254, and 1260. ΣDDT reported here is the sum of p,p'-DDT, p,p'-DDD, and p,p'-DDE. In computing sums, nondetections were treated as zero. Cesium-137 activity was measured by counting freeze-dried sediments in fixed-geometry with a high-resolution, intrinsic germanium detector gamma-spectrometer (*25*). Activity concentrations of ^{210}Pb and ^{226}Ra were measured by high-precision gamma-ray spectrometry (*26*).

Quality Assurance. Quality assurance data and laboratory method reporting levels (MRLs) are available in the Supporting Information. Quality assurance for major and trace element analyses was provided by analyzing several standard reference materials (SRMs), an environmental duplicate, and a blank sample with each batch of up to 20 samples. The two methods used for elements both performed well, based on analyses of four of the same SRMs. Median relative percent difference (RPD) for all elements for all SRMs was 2.0% for ICP/AES (and GF/AAS for Cd and As) and 4.4% for ICP/MS. Nine bottom-sediment duplicate samples from the New England lakes analyzed by ICP/AES had a median RPD of 3.2%, compared with a median RPD of 2.0% for 4 bottom-sediment duplicate samples from Fort Worth analyzed by ICP/MS. Median RPD for elements was 1.8% for 18 suspended-sediment samples analyzed using ICP/MS by this study and a related study of suspended sediment in Austin, TX (*18*).

Quality assurance for organic-compound analyses was provided by analyzing an environmental duplicate sample, a blank sample, a spiked sample, and a certified reference material (CRM) and by monitoring the recovery of surrogate compounds with each set of 12 environmental samples (*22, 23*). Median spike recoveries for sample sets that included samples from this study were 72% for PAHs and 87% for OCs. Although the methods were the same for suspended and bottom sediments, sample mass was limited for suspended-sediment samples, affecting reporting levels and precison and limiting the number of duplicates analyzed. Six environmental duplicates for organic compounds analyzed from this and a related study of suspended sediment in Austin, TX (*18*) had median RPDs of 36% for chlorinated hydrocarbons

TABLE 1. Selected Chemical Data for Suspended Sediment and Tops of Cores

site and sample[a]		concentration (µg/g)			concentration (µg/kg)					
		chromium	lead	zinc	chlordane	dieldrin	ΣPCB	p,p′-DDT	ΣDDT	ΣPAH
Lake Como										
stream										
	8/30/2001	74	147	637	410	58	230	<30	18	95 000
	9/20/2001	64	133	657	740	94	290	<42	16	88 000
	11/9/2001	65	172	590	750	66	<2010	<67	22	73 000
	1/23/2002	57	121	421	84	6.3	50	<5.0	4.3	46 000
core										
upper	0−10 cm (2 yr)	51	131	229	150	5.7	60	2.7	15	30 000
middle	0−10 cm (2 yr)	62	127	247	140	6.2	46	<1.3	12	18 000
lower	0−5 cm (1 yr)	68	124	262	150	12	37	<1.5	8.9	11 000
Echo Lake										
stream										
	5/28/2001	55	80	269	79.0	6.1	60	10	17	24 000
	8/17/2001	68	146	375	220	10	200	130	170	54 000
	9/20/2001	60	166	607	260	28	110	42	61	51 000
	10/11/2001	69	212	554	220	23	140	78	110	68000
core										
upper	0−5 cm (2 yr)	54	137	292	130	5.1	110	12	46	33 000
middle	0−8 cm (4 yr)	63	134	307	99	1.7	140	2.3	28	18 000
lower	0−5 cm (2 yr)	72	124	297	130	3.3	160	3.2	29	18 000
Fosdic Lake										
stream										
	8/11/2001	89	127	596	<1100	<110	<3300	<110	<330	12 000
	9/18/2001	81	72	184	380	34	<180	18	30	12 000
	10/10/2001	78	80	374	450	<12	<360	13 000	14 000	18 000
	12/6/2001	93	85	340	300	23	<1980	<150	20	30 000
core										
upper	0−10 cm (4 yr)	64	123	218	140	5.1	89	3.0	22	28 000
middle	0−5 cm (2 yr)	87	108	223	140	9.0	99	3.0	22	16 000
lower	0−10 cm (4 yr)	79	105	225	170	6.5	110	<0.5	21	27 000
Harris Pond										
stream										
	3/21 to 3/27/01	46	76	161	<610	<61	320	<61	35	44 000
	5/22 to 5/24/01	51	103	507	<110	<11	<330	23	65	40 000
core[b]										
upper	0−6 cm (6 yr)	37	59	203	27	<2.5	100	<2.5	12	15 000
middle	0−2 cm (2 yr)	35	55	213	22	<4.0	170	<4.0	34	22 000
lower	0−6 cm (6 yr)	37	41	155	47	5.0	110	<3.5	18	17 000
Upper Mystic Lake										
stream										
	3/21 to 3/23/01	275	328	798	400	6.6	280	65	130	140 000
	5/22 to 5/24/01	368	515	1610						
	8/29 to 8/30/02	419	588	1870	490	<20	320	59	130	180 000
core[c]										
upper	0−2 cm (2 yr)	379	563	1930	420	<6.8	230	24	110	120 000
lower	0−8 cm (8 yr)				450	<2.0	310	33	130	140 000
PEC[d]										
		111	128	459	17.6	61.8	676	62.9	572	

[a] Sample date for stream or coring location in reservoir (upper, middle, and lower part), sample interval, and approximate time interval represented based on average mass accumulation rate of core. [b] Chromium, lead, and zinc measured from upper, middle, and lower cores in 0−3, 0−1, and 0−3 cm intervals, respectively. [c] Chromium, lead, and zinc measured from upper core 0−1 cm interval. [d] Probable effect concentration (PEC) (MacDonald et al., 2000).

and 22% for PAHs. The median RPDs for duplicate bottom-sediment samples for this study were 8.5% for 14 OC samples and 8.2% for 18 PAH samples.

Age Dating. Details of age dating of the cores are presented in the Supporting Information. In brief, the ^{137}Cs peak of 1964 was used as a primary depth-date marker in cores from four lakes, and a ^{210}Pb age model was used at Upper Mystic Lake. The reservoir construction date was used for cores that penetrated to the prereservoir land surface. Age assignments were based on assumed constant mass-accumulation rates (MARs) between depth-date markers or MARs derived from the ^{210}Pb model.

Results and Discussion

The extent to which sediment cores from these reservoirs have recorded historical concentrations of contaminants associated with influent suspended sediment is evaluated using two lines of evidence. First, contaminant concentrations at the tops of cores are compared to those of influent suspended sediment, to see to what degree concentrations are preserved during transport and deposition. Second, trend profiles in the cores are evaluated on the basis of historical use of the compounds and historical land use in the watersheds, to assess the level of preservation of contaminants following deposition. Selected chemical data are presented in Table 1, and full chemical data are available in Supporting Information and are presented for the Fort Worth sites in ref *16*.

Sample Variability. In comparing suspended sediment samples to core samples, event variability (for suspended sediments) and spatial variability (for the core samples) were considered. Antecedent conditions, location and intensity of rainfall, recent land disturbance, recent releases of contaminants, and many other factors might affect event
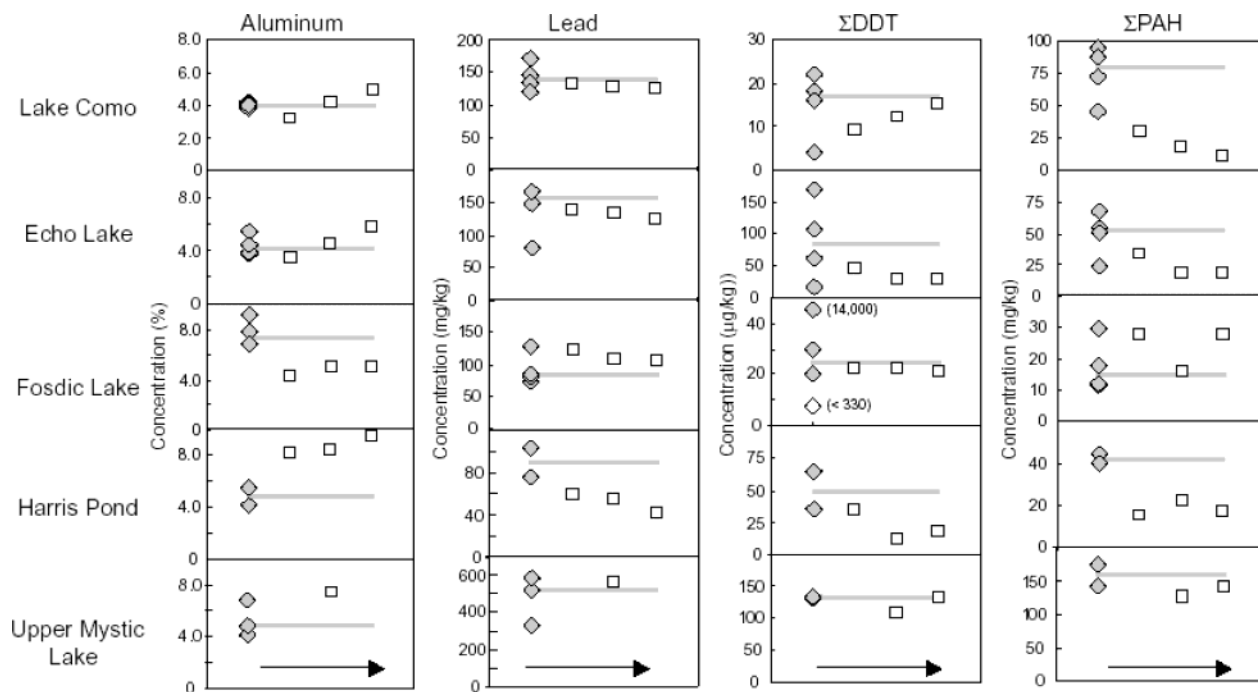
FIGURE 2. Comparison of concentrations of aluminum and selected contaminants in suspended sediment (diamonds) and top-of-core sediment (squares) at each lake. The horizontal lines are the median of suspended sediment concentrations. An arrow indicates downstream direction.

concentrations in suspended sediments. Previous work on suspended sediment in urban streams in Austin, TX, demonstrated that interevent variability at individual sites was the least for metals, intermediate for PAHs, and greatest for OCs (*18*, *27*). To evaluate the interevent variability, a simple measure of variation was computed at each site for each of the metals, ΣPAH, chlordane, dieldrin, ΣPCB, and ΣDDT as the ratio of the range to the median concentration (r/m). For this study, interevent variability was least for ΣPAH (median $r/m = 0.3$), intermediate for metals (median $r/m = 0.4$), and greatest for OCs (median $r/m = 0.9$).

Reservoirs are expected to integrate variability in concentrations of influent PACs to some degree, but physical processes will introduce spatial variability in sediment properties down-reservoir through size-sorting. Spatial variability in sediment size, as reflected by aluminum concentration at the tops of the cores (an indication of clay content), is shown in Figure 2: in all cases, sediment size decreases (aluminum concentration increases) in the down-reservoir direction. Spatial variability in sediment size may translate to variability in contaminant concentrations. Concentrations of PACs might also vary spatially within a reservoir because of point sources, multiple tributaries, bank-slumping, and other factors. Variability in contaminant concentrations between the tops of cores from individual lakes was less than that for suspended sediments for metals (median r/m of 0.2) and OCs (median r/m 0.5) but more than that of suspended sediments for PAHs (median r/m of 0.4).

Reservoir bottom sediments likely will be most affected by sediment inputs from large runoff events. The suspended-sediment samples presented here are from mostly small-to-medium-sized events. The four events sampled in Fort Worth represent less than 7.5% of the rainfall that occurred in Fort Worth during the 1-year sampling period (*16*); however, there was no relation between contaminant concentrations and storm-runoff volume (testing lead, ΣDDT, and ΣPAH; all p-values in Spearman's rank correlations greater than 0.2). The events sampled for the two Boston lakes represent 15% of the rainfall during the 18-month sampling period at Upper Mystic Lake and 33% of the rainfall

during the 4-month sampling period at Harris Pond. One large event was sampled at these sites: the March 2001 storm (120 mm of rain over 3 days) was a 100-year flood (Ann Chalmers, USGS, written commununication). At both sites, metals concentrations in suspended sediment were lower for the large event. At Upper Mystic Lake, concentrations at the tops of the cores were more similar to suspended sediment for the smaller events than for the large event, while at Harris Pond the opposite was true. At both sites PAH concentrations in the suspended sediments for the events were similar and at Upper Mystic Lake, OC concentrations were generally similar; however, at Harris Pond, OC concentrations were smaller for the larger event.

To quantify relations between suspended sediment and top-of-core samples for each site, the ratios of all combinations of individual top-of-core concentrations to suspended-sediment concentrations were computed and expressed as a percentage (TC/SS). The means and standard deviations of the TC/SS for each site are shown in Figure 3. A mean TC/SS between 75% and 125% was chosen to indicate "similar" concentrations between cores and suspended sediments. The intervals used to represent top-of-core sediment, and the approximate time span represented by the intervals, are listed in Table 1.

Metals. Concentrations of metals (and the metalloid arsenic) at the tops of cores are similar to those of influent suspended sediment in about half the cases, with the other half evenly distributed above and below the similar range (Figure 3). The amount of variability was comparable among the sites (r/m from 0.31 to 0.51 in suspended sediment and from 0.15 to 0.33 in top-of-core sediment). Good analytical precision for the metals indicates that virtually all of the variability in concentrations is environmental (Figure 2). In most cases TC/SS within one standard deviation of the mean extends into the similar range (Figure 3), thus, the interevent and intrareservoir variability could account for the lack of similarity for some metals. There was no systematic divergence of TC/SS from 100% at any site or for any metal, suggesting there is no consistent site-specific or metal-specific diagenetic gain or loss. There was more variability in metals
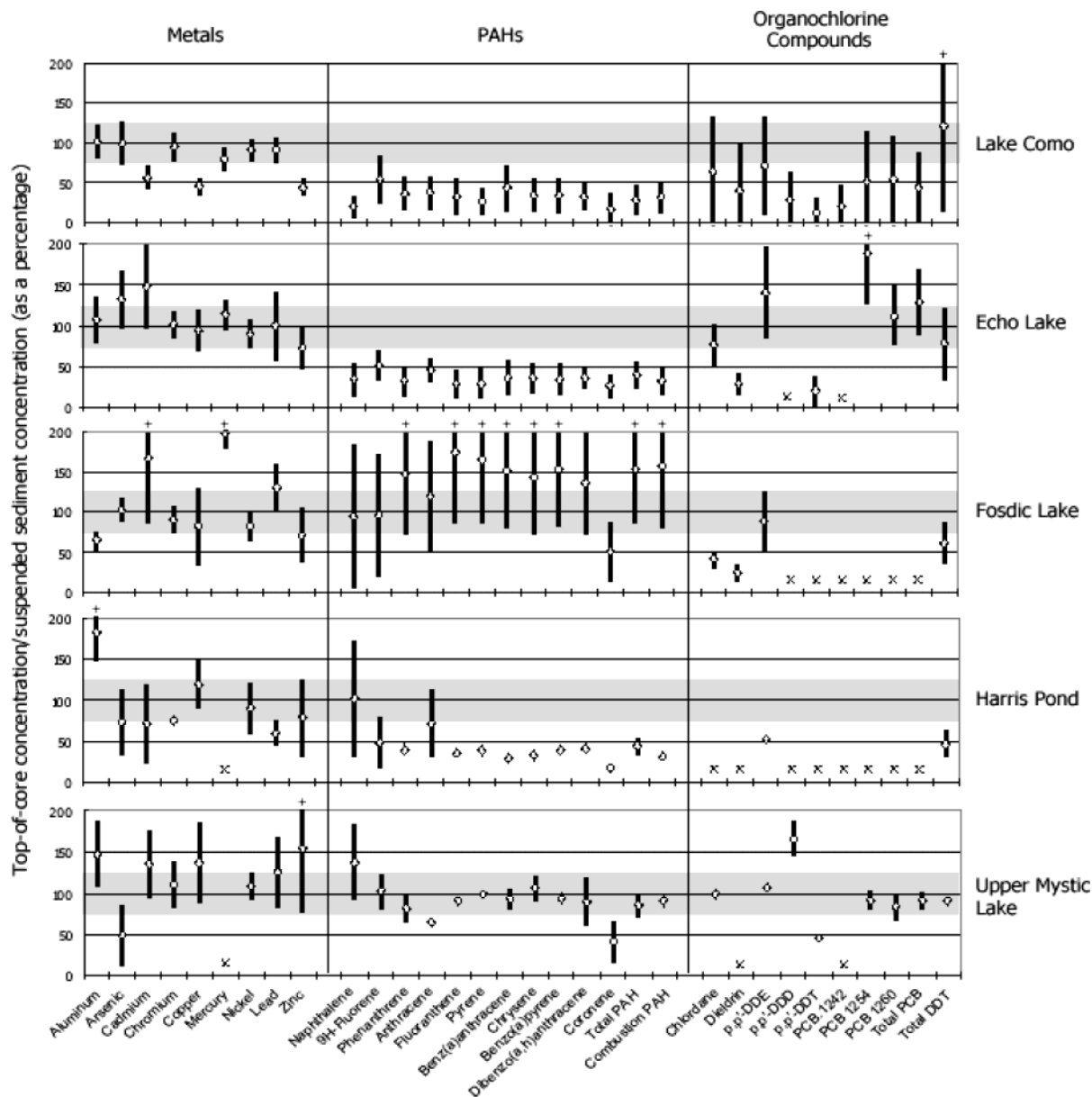
FIGURE 3. The ratio of top-of-core concentrations to suspended-sediment concentrations (TC/SS) for selected elements and organic compounds, expressed as a percentage. The diamond symbol is the mean of all computed TC/SS; combined interevent and intercore variability are reflected in the lengths of the bars, which are one standard deviation about the mean. "+" above the graph or "−" below the graph indicates that the bar extends beyond the y-axis in that direction. The "x" symbol indicates insufficient detections for comparison.

concentrations in suspended sediments than between cores collected at the same site, consistent with the concept that cores integrate short-term variability in suspended sediment. The two metals with the least variability in the influent suspended sediment, chromium and nickel, were similar between tops of cores and influent suspended sediment in every case. The highest interevent variability was seen for Zn, Cd, and Pb; metals that have been shown to be strongly related to urban land use (16, 28, 29). We hypothesize that the metals with lower interevent variability are mostly contributed from the mineral matrix of the sediment, which is not expected to vary much, and that higher variability may indicate more anthropogenic contribution.

Trend profiles of lead in the cores can be evaluated in the context of historical use, for which data are readily available (Figure 5). Lead emissions in the United States peaked in 1972 just prior to phasing out leaded gasoline, and numerous studies have documented corresponding lead peaks in sediment cores (34, 7). Lead concentrations peak in the 1970s

in the five lakes investigated for this study, and peak concentrations between lakes vary by more than an order of magnitude, consistent with historical land use in the watersheds (Figure 4). Given that sample variability and TC/SS of the other metals are similar to those of lead, we suggest that trends in those metals might also be preserved.

PAHs. Concentrations of PAHs associated with influent suspended sediment were similar to those in the sediment cores only at Upper Mystic Lake (Figure 3). TC/SS values were low (about 30%) at Lake Como, Echo Lake, and Harris Pond, and at all sites except Fosdic Lake, the TC/SS fell within a surprisingly small range, particularly given the analytical uncertainty. The only site where top-of-core concentrations exceeded those in suspended sediment (mean TC/SS > 1.25 for most PAH), Fosdic Lake, also was the site with the greatest variability in concentrations (r/m of 1.2, twice that of any other lake). The overlap of the concentration range in suspended sediments and cores (Figure 2) and the relatively high variability in TC/SS suggests that concentrations in
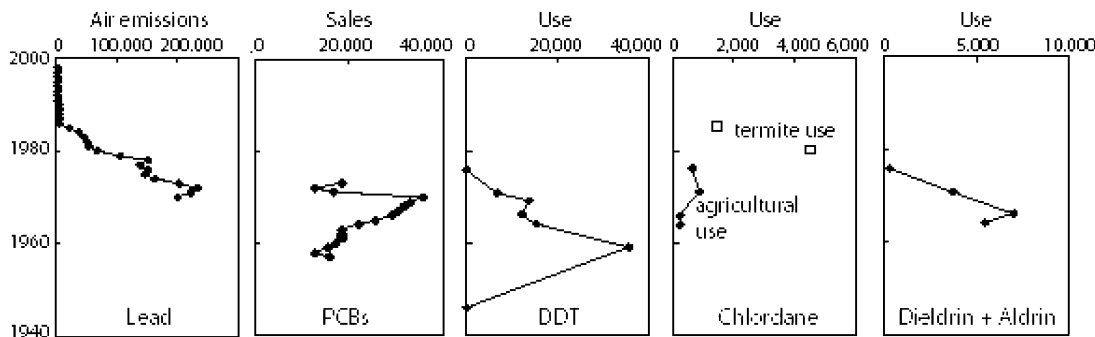
FIGURE 4. Concentrations and trends in cores and suspended sediment. Circles are core samples and squares are suspended-sediment samples from the influent stream. Nondetections are shown as open symbols at the reporting level, which varied on the basis of mass of sediment available for analysis. Information on peak domestic (U.S.) emissions, sales, or use and phase-out or ban are included where available.

suspended sediments might be preserved at the tops of cores at this site.

The differences between sites in degree of preservation of PAHs during transport and deposition is difficult to explain. Given the hydrologic differences between Texas and Massachussets, one might expect to find differences in relations between cores and suspended sediments between the two

settings, yet differences occur within both hydrologic settings. The watersheds of Lake Como, Echo Lake, and Fosdic Lake are similar in size, geology, and climate. The watershed of Fosdic Lake, however, is the smallest of the three, and land use is almost entirely residential and commercial, whereas land use in the watersheds of the other two lakes includes interstate highway and industrial. Fosdic Lake is the only

FIGURE 5. Data on domestic (U.S.) historical emissions of lead (*30*), sales of PCBs (*31*), agricultural use of DDT, chlordane, and aldrin and its metabolite dieldrin (*32*), (*33*), and termite use of chlordane (*33*). All data are in megagrams per year.

one of the three to show a strong trend in PAH in the core (Figure 4). Interestingly, PAH loss in Lakes Como and Echo during transport is not greater for the lower molecular-weight PAH (Figure 3), despite their higher solubility; the ratio of the sum of 2- and 3-ringed PAH plus homologues to combustion PAH in suspended and top-of-core sediment is very similar (*16*). In fact, there is no systematic variation in PAH TC/SS with molecular weight at any of the lakes (except for coronene, which is consistently low (Figure 3)), although PAH solubilities range over about 4 orders of magnitude. In the New England lakes, PAH TC/SS were near 100% at Upper Mystic Lake but were low at Harris Pond. Here, the lake with the least PAH loss is larger and more developed (including a large proportion of industrial land use) than the other, the opposite of what was seen in Fort Worth. Thus, any explanation regarding lake size, watershed size, or degree of development does not seem to hold for both lakes.

Evaluation of PAH trends in these cores in light of historical land use suggests that relative trends (i.e., the shapes of the occurrence profiles) might be preserved in cores. PAH concentrations in cores from the Fort Worth lakes increase by factors of two to four in sediment deposited from the 1950s to the 1970s, coincident with urban development, and remain at the higher concentrations or increase in sediment deposited since that time (*16*) (Figure 4). At Fosdic Lake, PAH concentrations increase by 30-fold up to the mid-1990s and then decrease to present; the difference between trends at this lake and other Fort Worth lakes, given their similar age of development and climate, suggests an unidentified source in the Fosdic Lake watershed that may have been eliminated. PAH concentrations in the core from Harris Pond vary little over time, consistent with the historically rural setting of the watershed. The ΣPAH profile seen in Upper Mystic Lake, with a peak about 1960 followed by a decrease and a subsequent increase, is similar to PAH profiles seen in other lakes with urban land-use dating back before 1950 (*2*, *35*). The abrupt increases at the tops of cores from Echo Lake, Harris Pond, and Upper Mystic Lake could be a result of degradation or desorption losses soon after deposition.

Profiles of PAH assemblages suggest that PAH might be relatively stable down-core. If PAH were degrading down-core, a shift to proportionally less lower-molecular-weight PAH should occur with depth in the core, because degradation kinetics favor more rapid degradation of lower-molecular-weight compounds (*36*, *37*). Instead, PAH assemblages generally shift to favor lower-molecular-weight compounds deeper in the cores, as indicated by increases in the ratio of the sum of 2- and 3-ringed PAH plus homologues to combustion PAH with depth (Figure 6) (*2*). This change implies a shift to predominantly combustion sources of PAH coincident with urban development. At Echo Lake, the peak in ΣPAH concentration in about 1980 is caused by petrogenic sources, and the peak at Fosdic Lake in about 1996 has a combustion source. However, these profiles do not rule out
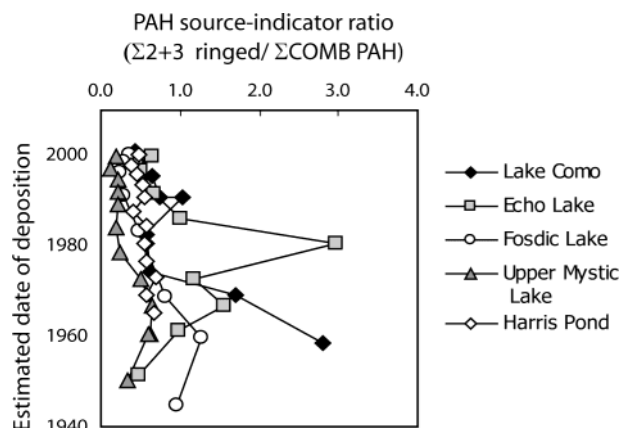

FIGURE 6. Trends in a PAH source-indicator ratio in sediment cores, computed as the sum of 2- and 3-ringed PAH plus homologues divided by combustion PAH.

the possibility that past PAH inputs were even more elevated in 2- and 3-ring PAH that degraded after burial, resulting in deep sediment samples only slightly elevated in noncombustion PAH.

Organochlorine Compounds. TC/SS for OCs are highly variable among constituents and sites (Figure 3), at least in part because of analytical uncertainty, which was the greatest for this contaminant group. Small sample masses for some suspended-sediment samples resulted in high reporting levels, frequent nondetections, and high RPDs between duplicates. Additional variation in occurrence of OCs in suspended sediment might result from the fact that the source is erosion of contaminated soils, which could vary greatly depending on location, duration, and intensity of rain events. Variability in OCs in suspended sediment samples (median $r/m = 1.3$) was more than twice that in the core samples (median $r/m = 0.5$) for the Fort Worth sites; however, the opposite was true for the New England sites (median r/m of 0.2 and 0.5, respectively).

In the context of event variability, one sample merits specific mention. The suspended sediment sample collected at Fosdic Lake on October 10, 2001 (six months after the cores were collected) had a ΣDDT concentration of 14 100 μg/kg, 92% of which was p,p'-DDT, and a toxaphene concentration of 12 000 μg/kg (*16*). The only other sample with detectable p,p'-DDT from this site had a ΣDDT concentration of 30 μg/kg, 60% of which was p,p'-DDT. These surprisingly high concentrations and the predominance of p,p'-DDT suggest an accidental or intentional release of an unweathered product. It is unknown how frequently such extreme events occur or to what extent they contribute to the continuing occurrence of DDT and other OCs in newly introduced aquatic sediment.

The relative preservation of OCs associated with suspended sediments is similar to that of PAHs for some lakes

(Figure 3). At Upper Mystic Lake, OCs and PAHs appear to be well represented at the tops of cores, and many OCs at Lake Como, like PAHs, show transport losses. This pattern, however, does not hold for Echo and Fosdic Lakes; at Echo Lake OCs are better preserved than PAHs and at Fosdic Lake, the opposite is true. Little can be concluded for Harris Pond, where the only OCs detected in suspended sediments were the DDTs, except that DDE and ΣDDT shows transport losses, similar to most PAHs. Two OCs, p,p'-DDT and dieldrin, are not well represented in any of the cores with mean TC/SS ranging from 12 to 46% where it can be computed.

Where OCs have similar concentrations in top-of-core and suspended-sediment samples, logical historical trends are seen in the cores (Figures 3 and 4). For example, concentrations of ΣDDT in the two media are similar at Como, Echo, and Upper Mystic Lakes, and at Fosdic Lake the mean TC/SS is 90% if the one extremely high ΣDDT concentration for suspended sediment is excluded. In these cores, ΣDDT concentrations peak in the 1960s, soon after use of DDT peaked in the United States (Figure 5), then decrease to 10–20% of peak concentrations, a pattern seen in numerous U.S. reservoirs and lakes (8, 38). The only site for which transport losses of ΣDDT are indicated is Harris Pond, where no ΣDDT peak is recorded in the core. The lack of a trend is reasonable in light of the history of the watershed, which has only recently begun to develop and has no history of agriculture. It is unknown why ΣDDT might be more likely to be lost in transport at this site than at the other four. Concentrations of PCBs in suspended sediments are similar to those at the tops of cores from Upper Mystic and Echo Lakes, and core PCB concentrations peak in sediment deposited about 1970, consistent with historical peak use in 1970 and trends seen elsewhere (38) (Figures 4 and 5). In the same two reservoirs, TC/SS for chlordane are near 100%. While chlordane trends seem reasonable, with peaks in the 1970s when urban and agricultural uses were permitted and decreases to about one-half of peak concentrations at the tops of the cores, historical-use data are sparse and inconsistent, making a trend assessment difficult (Figure 5). The decrease is more gradual than that seen for other OCs, consistent with continued urban uses until at least 1990 (33). We therefore propose that stream suspended-sediment concentrations and trends in selected OCs might, in some cases, be preserved in downstream reservoir cores.

Trend profiles and TC/SS of some OCs suggest that in other cases relative trends, but not historical concentrations, are reflected in cores. Although PCBs were infrequently detected in suspended sediment from Fosdic Lake and Harris Pond and TC/SS were low for PCBs at Lake Como, historical trends in PCBs in all three reservoir cores make sense in light of historical use, with peaks in the 1960s and decreases to the tops of the cores (Figure 4). Chlordane concentrations at Lake Como and Harris Pond peak between the late 1960s and early 1980s and then decrease to about one-half and one-quarter, respectively, of the peak concentration by 2000, trends that are consistent with regulatory history (Figures 4 and 5) (33). Stability of chlordane in sediment cores has been suggested by the relatively stable and racemic chiral chlordane signatures seen in some cores, including the core from Lake Como (39). At Fosdic Lake, however, chlordane concentrations increase to the top of the core (2001) (Figure 4). There is no reason to expect that chlordane use in this watershed was low in the 1960s–1980s and increased through the 1990s, as the core profile suggests. Interestingly, similar chlordane profiles were reported for White Rock Lake in Dallas, TX (40) and in ponds adjacent to Clear Creek south of Houston, TX (41), raising the possibility of chlordane degradation or desorption over decadal time periods in some lake sediments.

Profiles of p,p'-DDT and dieldrin in cores are different from those of the other OCs, with low or undetected concentrations in the deeper parts of the cores (except for Upper Mystic Lake), small to sharp increases at the very tops of the cores (Figure 4), and much higher concentrations in suspended sediments (Table 1). Interpreting these results as increasing loading to streams and lakes would be inconsistent with historical use and documented historical occurrence, e.g., refs 42 and 43. DDT use peaked in the early 1960s and was discontinued in 1972; agricultural use of dieldrin and its parent, aldrin, peaked in 1966 and was canceled in 1970; termite use was voluntarily canceled in May 1987 (44). Instead, relatively high concentrations in suspended sediment, low TC/SS, and the virtual disappearance with depth in the cores suggest preservation of p,p'-DDT and dieldrin in soils, continuing inputs of eroded soils to streams, desorption during transport, and degradation after deposition and burial. This hypothesis is consistent with what is known of the fates of these two contaminants: degradation of p,p'-DDT occurs slowly in aerated soils but more rapidly in the presence of water (33, 45) and dieldrin is persistent in soils (46). The relation between concentrations of p,p'-DDT and its metabolites p,p'-DDD and p,p'-DDE supports the hypothesis of degradation of p,p'-DDT: for suspended sediment samples in which p,p'-DDT was detected, the compound accounts for 44–92% of ΣDDT compared to only 1–26% in top-of-core sediments, and the proportion decreases with depth in the cores. In contrast, trends in ΣDDT in cores, composed primarily of the more stable p,p'-DDD and p,p'-DDE, appear to be relatively conservative once isolated from the water column, as discussed above.

Contaminant Fate Processes and Implications for Reconstruction of Historical Trends. Metal concentrations and trends appear to be relatively well preserved in cores, but many HOCs are at lower concentrations in cores than in suspended sediment, suggesting loss during transport and (or) soon after deposition. Where losses are occurring, several processes could be involved, including desorption as soils and street dust come into equilibrium with water, desorption as organic matter is solubilized or degraded, and bacterially mediated degradation of the contaminant. Many researchers have noted that HOCs in sediment can be operationally divided into a "rapidly extractable" fraction and a "sequestered" fraction, e.g., refs 47 and 48. Based on the results of this investigation, we hypothesize that some of the rapidly extractable fraction associated with soils and street dust, the precursors of aquatic sediment, is lost to the water column during transport and soon after deposition. We are unaware of any studies directly addressing this question for soils and suspended sediments in small urban streams, but in studies using weathered estuary sediments (47) it was found that from 36 to 70% of PAHs desorbed over a 3-month period and that one-half of the desorption occurred in a few hours to days. Desorption from unweathered sediments, such as those investigated here, would be expected to be greater than that from weathered aquatic sediments, which might already have lost much of their organic matter and the associated rapidly extractable fraction. In addition, it has been reported that the organic matter with which HOCs are associated is altered when soils are transformed into sediment, resulting in significant differences in the partitioning of HOCs between soil and sediment (49). Thus, it is conceivable that the introduction to water of soil and street dust particles contaminated with HOCs results in some rapid desorption and that, once deposited and isolated from the water column, HOCs remaining in the sediment are less subject to desorption. It is not obvious, however, why these processes might occur in some watersheds and not others.

The results of this study highlight the difficulties encountered in using sediment cores to infer stream quality,

even in settings relatively amenable to this kind of analysis, in part because of sampling and analytical variability and in part because of natural processes. However, we believe that the results support the judicious use of reservoir sediment coring to evaluate historical contaminant trends in riverine systems and indicate that the sampling of suspended sediments in combination with cores can provide additional understanding of fate processes.

Acknowledgments

Supporting Information Available

Descriptions of age dating of cores and full chemical data on environmental and quality-control samples and other information. This material is available free of charge via the Internet at http://pubs.acs.org.

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