Trends in Hydrophobic Organic Contaminants in Urban and Reference Lake Sediments across the United States, 1970–2001

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A shift in national policy toward stronger environmental protection began in the United States in about 1970. Conversely, urban land use, population, energy consumption, and vehicle use have increased greatly since then. To assess the effects of these changes on water quality, the U.S. Geological Survey used sediment cores to reconstruct water-quality histories for 38 urban and reference lakes across the United States. Cores were age-dated, and concentration profiles of polycyclic aromatic hydrocarbons (PAHs) and chlorinated hydrocarbons were tested statistically. Significant trends in total DDT, p,p'-DDE, and total PCBs were all downward. Trends in chlordane were split evenly between upward and downward, and trends in PAHs were mostly upward. Significant trends did not occur in about one-half of cases tested. Concentrations of p,p'-DDE, p,p'-DDD, and PCBs were about one-half as likely to exceed the probable effect concentration (PEC), a sediment quality guideline, in sediments deposited in the 1990s as in 1965–1975, whereas PAHs were twice as likely to exceed the PEC in the more recently deposited sediments. Concentrations of all contaminants evaluated correlated strongly with urban land use. Upward trends in PAH concentrations, the strong association of PAH with urban settings, and rapid urbanization occurring in the United States suggest that PAHs could surpass chlorinated hydrocarbons in the threat they pose to aquatic biota in urban streams and lakes.

Introduction

Federal environmental policy in the United States changed markedly in about 1970 with the establishment of the U.S. Environmental Protection Agency (1969) and the passage of the Clean Air Act (1970), the Safe Drinking Water Act (1974), the Toxic Substances Control Act (1976), and other laws (*1*). Improving water quality is one objective of these actions. Conversely, increases in population, urban development, energy use, and vehicle use in the United States could lead to degradation of water quality. Identifying water-quality trends can provide measures of the success or failure of mitigation efforts and can provide a warning of unanticipated degradation. Understanding trends also can improve our understanding of cause and effect relations between human activities and water quality and can aid in developing efficient strategies for reducing adverse human effects on the environment.

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The U.S. Geological Survey is using paleolimnology, the reconstruction of water-quality histories from age-dated sediment cores, to evaluate water-quality trends across the United States (*2*). Organic compounds that are chemically persistent and strongly hydrophobic often are preserved in the sediments, thus creating a partial record of historical water quality. Downward trends in polychlorinated biphenyls (PCBs) and DDT since the 1960s, for example, have been documented in a variety of environmental settings (*3, 4*). Trends in chlordane and polycyclic aromatic hydrocarbons (PAHs) have been presented by numerous investigators but are more variable (*5, 6*). Many studies have addressed trends in these hydrophobic organic compounds (HOCs); however, most are local in scale or focus on only a few water bodies in one region (e.g., *3–5, 7–9*).

This study determined trends in persistent HOCs since 1970 using sediment cores collected from 38 lakes across the United States. The study was conducted by the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program (*10*). The primary objectives were to identify trends in HOCs in urban and undeveloped reference settings across the U.S. and, to the extent possible, to determine the causes of those trends. To our knowledge, this study is the first attempt to apply a consistent paleolimnological approach to identifying trends in numerous HOCs across the United States.

Experimental Section

Study Design. Sediment cores were collected from 38 lakes in the United States between 1996 and 2001 (28 reservoirs and 10 natural lakes, hereafter referred to as lakes except where the distinction is relevant), age dated, analyzed chemically, and tested for trends (Figure 1; see Supporting Information for more information on lakes sampled). The NAWQA design provided a national framework for identifying potential study areas (*10*). The selection of urban areas in this study was based on the combination of NAWQA study units, metropolitan statistical areas (MSAs) (*11*), and ecoregions (*12*). Urban areas were selected to represent a diversity of ecoregions where a majority of 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. In some cases, areas were chosen for study in less populous ecoregions to better represent the geographic diversity of the country (e.g., Las Vegas, NV (Lake Mead) in the Southern Basin and Range was included and Detroit, MI in the Erie/Ontario Lake Plain was not). Although it is not a probabilistic design, it does provide a geographically diverse coverage of major urban areas of the country.

Lakes were chosen for sampling on the basis of lake and watershed size, age of the lake (~40 years or more for reservoirs), and the amount and age of development in the watershed. The majority of lakes sampled have relatively small watersheds (74% of the watersheds are less than 100 km^2), although drainage area to lake surface area ratios (DA:SA) varied greatly, with generally larger ratios for urban lakes and smaller ratios for reference lakes. This bias was by design, with an objective in sampling the urban lakes being to represent historical trends in anthropogenic inputs to urban streams and an objective in the reference lakes being to represent historical trends in atmospheric deposition. Contaminant inputs to lakes with large DA:SA ratios and development in the watershed are typically dominated by fluvial inputs of contaminants from one or a few streams (*13, 14*). Lakes with small DA:SA ratios often have contaminant
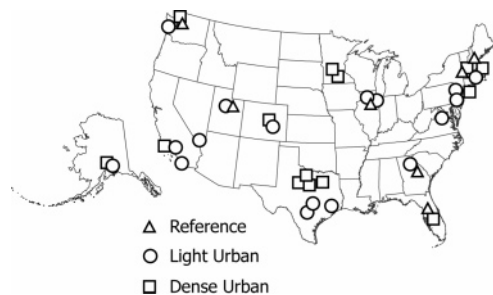
FIGURE 1. Locations of lakes sampled and land-use setting.

inputs that are dominantly from atmospheric fallout on the lake surface or watershed (*15*, *16*).

The 38 lakes used in this analysis are a subset of 56 lakes sampled by the USGS from 1992 to 2001. These 38 cores (one from each lake) were selected because (a) they are from lakes representative of target land-use settings, (b) a common suite of organic compounds was analyzed using consistent methods, and (c) their age-control and relative lack of postdepositional sediment mixing were judged to be reliable for trend testing of the 35-year period of interest (*2*). Land use in the watersheds was categorized as "dense urban" (>52% urban land use; 14 lakes), "light urban" (5−42% urban; 17 lakes), or "reference" (<1.5% urban; 7 lakes), as determined from the 1992 USGS National Land Cover Data (NLCD) (*17*). In urban settings, residential and commercial land uses were favored, and large point sources and heavily contaminated industrial areas were avoided. Three of the seven reference lakes are water-supply reservoirs in protected watersheds, and three others and their watersheds are in county or state 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.

Sampling. Cores were collected from the deepest part of the lake or in the middle or lower part of the reservoir, and sectioned into vertically discrete subsamples for analysis of major and trace elements, ^{137}Cs, ^{210}Pb (selected lakes only), organochlorine pesticides, PCBs, and PAHs (*2*). Gravity cores, piston cores, push cores (all 6.3 cm diameter polycarbonate tubes), and box cores (14-cm square polycarbonate liners) were collected. Cores were vertically extruded on site and sectioned into intervals ranging in thickness from 0.5 to 5 cm or more, depending on the assumed or known sedimentation rate at the site, sample mass requirements for chemical analyses, and site-specific objectives. Samples were transferred to baked glass jars and chilled pending shipment to the laboratory. Generally, sampling intervals were designed to represent from about 2 to 5 years of average sedimentation. The median number of samples per core was 12, and the median number of samples used for the trend-testing period, 1970 to top of core, was eight.

Chemical Analysis. Activities of ^{137}Cs were measured by counting freeze-dried sediments in fixed geometry with a high-resolution, intrinsic germanium detector gamma spectrometer, using a method similar to that reported by (*18*). Activities of ^{210}Pb were measured on freeze-dried sediments by high-precision gamma-ray spectrometry. Organochlorine pesticides, PCBs, PAHs, and alkyl-substituted PAHs (alkyl-PAHs) were extracted, isolated, and analyzed using the procedures of (*19*) and (*20*). Briefly, wet bottom sediment was extracted overnight with dichloromethane in a Soxhlet apparatus. The extract was reduced in volume and filtered. Two aliquots of the sample extract were quantitatively injected into a polystyrene-divinylbenzene gel permeation column and eluted with dichloromethane to remove sulfur and partially isolate the target analytes. The first aliquot was analyzed for PAHs and alkyl-PAHs by capillary-column gas chromatography with detection by full-scan mass spectrometry (MS)

or by selected ion monitoring MS. Nineteen parent PAHs, 10 specific alkyl-PAHs, and the homologous series of alkyl-PAHs for 2- to 7-ringed PAH were determined. The second aliquot was split into two sample fractions by combined alumina/silica adsorption chromatography, followed by Florisil adsorption chromatography for further cleanup of the second fraction. Both fractions were analyzed by dual capillary-column gas chromatography with electron capture detection for the determination of the organochlorine pesticides and PCBs. The organochlorine pesticides were reported as individual compounds with the exception of chlordane, which was reported as technical chlordane (estimated from concentrations of *trans*-nonachlor, *cis*-chlordane, and *trans*-chlordane), and PCBs, which were reported as individual Aroclor (1016/1242, 1254, or 1260) equivalents. Quality assurance was provided by analyzing duplicate samples (environmental samples split at the laboratory), laboratory blanks, and spiked reagent samples, and monitoring recovery of surrogate compounds. Median relative percent difference for chlorinated hydrocarbons was 11.8% for 41 duplicate samples and for PAHs was 11.9% for 40 samples (*2*).

Age Dating. 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 in ref *2*. The primary basis for age dating 26 of the cores was the ^{137}Cs profile, assigning the date of 1964 to the peak activity and, in a few cases, 1958 to a secondary peak (from testing in Nevada) and 1953 to the first occurrence. For six of the cores, dating was based on ^{210}Pb profiles using either the constant input concentration (CIC) model (four lakes) or the constant rate of supply (CRS) model (two lakes) (*2*, *21*). The interface with pre-lacustrine sediment provided a date marker in most reservoirs and served as the primary basis for dating cores from six reservoirs, supplemented in three cases by the peak in total lead dated as 1975 (*22*).

Dates were assigned to individual samples, between date markers or using ^{210}Pb models, based on accumulation of dry mass per unit area in the core. For cores with no evidence to the contrary, a constant mass accumulation rate of sediment (MAR) was assumed between date markers. Thirty-two of the 38 cores had constant MARs over the time period of the trend testing. The strongest evidence supporting constant MARs during this period is the timing of the lead peak. The mean date of the peak for these lakes is 1975 (standard deviation of 5 yr), consistent with the reported peak in emissions and concentration peaks in cores from urban lakes in the United States (*22*). Age assignments in most of these cores were corroborated by peaks in ΣDDT (total DDT, the sum of *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE) in the early 1960s. Although confidence intervals cannot be assigned to the dates corresponding to individual sample intervals in the cores, the consistency of multiple corroborative date markers suggests that most dates are probably within a few years of the actual deposition dates.

Postdepositional mixing can affect contaminant profiles in cores, potentially obscuring or altering anthropogenic trends (*23*). Mixing was evaluated for all of the cores collected for the NAWQA study, and cores for which it was judged to have had a large influence on trends were excluded from the analysis presented here. Pronounced peaks and systematic variations in chemical profiles in most of the cores, in particular for ^{137}Cs, ^{210}Pb, total Pb, total DDT, and total PCBs (*2*), indicate that postdepositional mixing has not obscured contaminant trends on a decadal time scale.

Trend Analysis. Trends in concentrations of ΣPAH (total PAH), nine individual PAHs, chlordane, *p,p'*-DDD, *p,p'*-DDE, ΣDDT, and ΣPCB (total PCB, the sum of Aroclors 1016/1242, 1254, and 1260) were tested statistically. For this paper, ΣPAH is the sum of 13 compounds used for the consensus-based
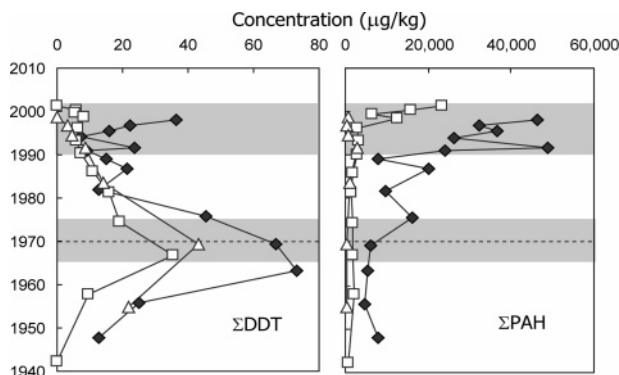
FIGURE 2. Trends in sediment cores from Lake Ballinger (◆), near Seattle, WA; Lake in the Hills (□), near Chicago, IL; and Sand Lake (△), near Orlando, FL. Dashed line (1970) is starting point of trend testing; shaded areas are periods used to compute decadal-mean concentrations.

sediment quality guidelines (*24*). The nine individual PAHs tested are those with a probable effect concentration (PEC) consensus-based guideline (*25*). Kendall's tau test was used to indicate whether there was a statistically significant relation (p-value < 0.1) between concentration and time from 1970 to the top of each core, representing 1996−2001. In a few cases, samples dated as late-1960s were included to increase sample count and improve statistical power. Trends also were evaluated by comparing mean concentrations of contaminants in sediment samples dated as deposited from 1965 to 1975 to those in samples deposited from 1990 to the top of the core. While not a statistical test, this comparison indicates the magnitude of change in concentration over a time period similar to that of the trend test. The starting period for these evaluations was chosen because it corresponds to the initiation of important environmental legislation or regulatory actions in the United States (*1*).

Nondetections were treated as zero values in summations (e.g., ΣPCB), in computing decadal mean concentrations, and in the Kendall's tau trend test, which gives them a lower rank in the test than detected values. If more than 60% of samples were nondetections, trend was not tested. Although 40% detections may seem to be a low rate to apply a trend test, significant trends occasionally were indicated if, for example, all of the detections occurred early in the time period with systematic decreases over time. Several other organochlorine pesticides were measured but rarely detected, including lindane, heptachlor, aldrin, endosulfan, methoxychlor, mirex, and toxaphene, and trends in these were not tested. Dieldrin and p,p'-DDT frequently were detected, but trends probably are not preserved in lake cores (*14*) so they were not tested.

Examples of contaminant profiles in selected cores and their relation to trend testing are shown in Figure 2 for ΣDDT and ΣPAH. Lake Ballinger is in a dense urban setting north of Seattle, WA. Lake in the Hills is in a light urban setting northwest of Chicago, IL, and has undergone rapid urbanization since about 1990. Sand Lake, an abandoned sand quarry, is a reference lake with a small watershed in a state park near Orlando, FL. Trends in concentrations of ΣDDT were significantly downward in two of these lakes, with p-values < 0.01; the trend in Lake Ballinger was not significant (p-value = 0.59). Trends in ΣPAH were upward in the two lakes in urban settings, with p-values < 0.01, whereas Sand Lake did not have a trend (p-value = 0.85). Although some details of the profiles are missed by the trend tests, the overall picture of trends in ΣDDT and ΣPAH in recent decades is reasonably represented. The magnitude of change since 1970 is also reasonably represented by the decadal-mean concentrations, indicated by shading on the graphs.
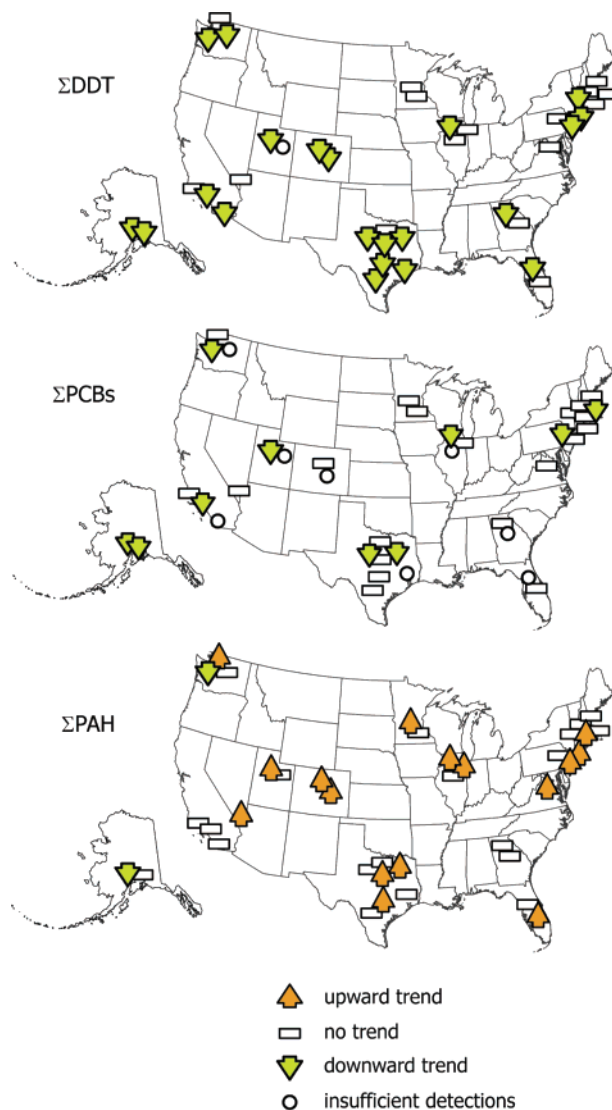

FIGURE 3. Trends in lake sediment cores from 1970 to 2001.

Results and Discussion

Trends. Two broad conclusions about trends are evident from these 38 lakes: DDT and PCB concentrations are decreasing, and PAH concentrations are increasing (Figures 3 and 4; Table 1) (see Supporting Information for trend results for all constituents by site). ΣDDT and p,p'-DDE decrease in about one-half of the lakes and increase in none; p,p'-DDD decreases in about one-half of those lakes with sufficient detections to test and increases in one lake. ΣPCB decreases in about one-quarter of the lakes and increases in none. DDT use in the United States peaked in the early 1960s and was canceled in 1972; PCB use peaked about 1970, was restricted in 1971, and was canceled in 1976 (*26*). These restrictions have resulted in widely reported decreases in the environment (*3, 4, 7*), although detections in soils, aquatic sediments, and aquatic biota remain very common (*27, 28*). About one-half of the lakes sampled showed no trend. This may be in part because of large variability in concentrations and small sample sizes at some lakes, which reduces the power of statistical tests to identify trends. For many reference lakes, a lack of a statistically significant decreasing trend in the DDTs may result from relatively small or no direct inputs during use and continuing diffuse inputs from atmospheric transport. For PCBs, all of the reference lakes either had no trend (29%) or insufficient detections to test (71%).
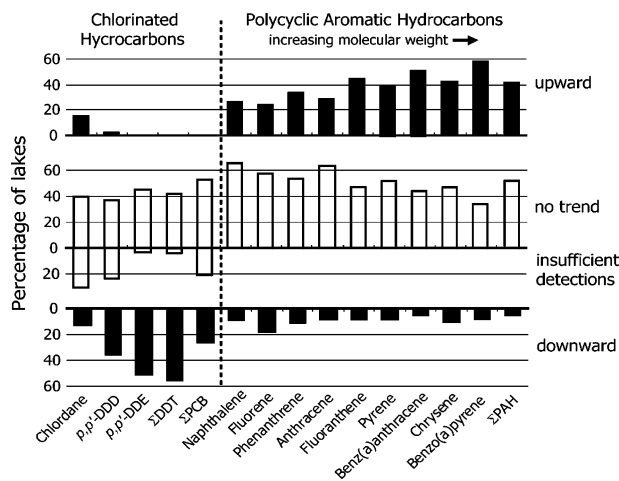
FIGURE 4. Percentage of 38 lakes with indicated trend for 1970–2001.

For chlordane, in contrast, there are roughly equal numbers of increasing and decreasing trends, and the most common result is no trend (Figure 4; Table 1). Chlordane was routinely detected in urban lakes, but the reference lakes had either no trend (29%) or insufficient detections to test (71%). As with ΣDDT and ΣPCB, the results for chlordane generally are consistent with historical use and regulation. Chlordane use in agriculture was primarily on corn, and agricultural applications were canceled in 1978, but use in urban areas, primarily for subterranean termite control, continued until 1988 (29). Substantial urban use by home-owners, permitted after cancellation of most other uses in 1988, was reported in 1990 (30). Thus, the lack of significant decreasing trends from 1970 to present is not surprising considering the test is for monotonic trend. Another factor that could result in incorrect indication of lack of trend or increasing trend is the degradation of chlordane in older aquatic sediment, which has been suggested for a few settings (14).

While concentrations of chlorinated hydrocarbons are relatively stable or decreasing, concentrations of PAHs are increasing. Increasing trends in ΣPAHs occur in 42% of the 38 lakes sampled, and decreasing trends occur in only 5%. Increasing trends in PAHs are almost exclusively in lakes with urbanized watersheds (Table 1). Although a few reference lakes had trends in an individual PAH, no reference lake had a trend in ΣPAH. Other researchers have reported decreasing trends in PAHs in remote and urban lakes in recent decades (e.g., 31–33) and attributed the decreases to reduced use of coal for home heating, industrial emissions controls, and increased efficiency of power plants (31, 34, 35). Van Metre et al. (6), however, investigated PAH trends in 10 urban lakes, all of which are included in this study, and concluded most were increasing coincident with urbanization and increases in vehicle traffic in the watersheds. Here, we see increasing PAH trends in urban settings across the country.

Changes in PAH assemblages indicate combustion sources are responsible for increasing trends in the urban lakes. Increasing trends are more common as molecular weight increases (Figure 4); 26% of lakes have increasing trends for naphthalene (2 rings), 34% for phenanthrene (3 rings), 45% for fluoranthene (4 rings), and 58% for benzo[a]pyrene (5 rings). Combustion of hydrocarbons produces mostly higher molecular weight (4- to 7-ringed) parent PAH, whereas uncombusted fuels and organic matter contain more lower molecular weight PAH and their alkylated homologues. Combustion sources of PAHs are further indicated by changes in the ratio of 2- and 3-ringed PAH plus homologues to 4- and 5-ringed parent PAH, a value that decreases as combustion sources of PAH become more dominant (6). The median

TABLE 1. Summary of Trend Results and Decadal-Mean Concentrations for Selected Compounds [nd, Not Detected; PEC, Probable Effect Concentration (25)]

| parameter | land-use setting | percentage of lakes with trend of indicated type | | | | median of decadal mean concentrations (µg/kg) | | median percent change among lakes |
		increasing	decreasing	no trend	insuff det	1965–1975	1990–top of core	
ΣPAH	all lakes	42	5	53		1100	3400	41
PEC = 22 800	dense urban	50	7	43		9000	8900	74
	light urban	53	6	41		620	1300	76
	reference	0	0	100		200	320	0
phenanthrene	all lakes	34	11	55		140	240	27
PEC = 1170	dense urban	36	14	50		760	750	48
	light urban	47	6	47		56	150	49
	reference	0	14	86		26	40	21
fluoranthene	all lakes	45	8	47		270	790	61
PEC = 2230	dense urban	43	0	57		1500	2200	38
	light urban	59	6	35		120	240	93
	reference	14	29	57		35	83	−7
benzo[a]pyrene	all lakes	58	8	34		81	350	78
PEC = 1450	dense urban	57	0	43		580	1500	84
	light urban	76	6	18		50	120	105
	reference	14	29	57		7	20	5
chlordane	all lakes	16	13	39	32	12	26	0
PEC = 17.6	dense urban	36	14	50		52	92	−20
	light urban	6	18	35	41	8	4	nd
	reference	0	0	29	71	nd	nd	nd
ΣDDT	all lakes	0	55	42	3	45	17	−69
PEC = 572	dense urban	0	43	57		107	29	−68
	light urban	0	71	29		27	9	−73
	reference	0	43	43	14	7	4	−53
ΣPCBs	all lakes	0	26	53	21	65	43	−47
PEC = 676	dense urban	0	29	71		275	108	−59
	light urban	0	35	47	18	51	15	−61
	reference	0	0	29	71	nd	nd	nd

of this ratio in the 38 lakes decreased from 1.05 in 1970 to 0.58 in the 1990s; among the lakes with an increasing trend in ΣPAH, the decrease was from 0.90 in 1970 to 0.39 in the 1990s.

Concentrations and Relations to Urban Land Use. In addition to the direction of trends, the magnitude of change in concentrations over time and the concentration in recent sediment in these lakes are important indicators of environmental condition. Median values of decadal-mean concentrations for 1965−75 and 1990 to top-of-core (Table 1) and percent change in concentrations for individual lakes show pronounced increases or decreases consistent with trends. The mean ΣDDT concentration in the 1990s was lower than the mean 1970 concentration in 34 of the 38 lakes (89%), and the median percent change was a decrease of 69%. For ΣPCB, 28 lakes (74%) had a decrease in mean concentration, and the median change was a decrease of 47%. Decadal-mean concentrations of chlordane are consistent with the general lack of trends, with 14 lakes increasing, 16 lakes decreasing, and a median change of 0%. In contrast, 28 of the 38 lakes had increases in decadal-mean concentrations of ΣPAH, and the median change was a 41% increase.

Urban land use exerts a strong influence on HOC concentrations, as indicated by differences in the decadal-mean concentrations by land-use setting (Table 1). Spearman's rank correlations between percent urban land use and concentration were significant for all compounds listed in Table 1 (all p-values < 0.003). Categorization of sites in groups by urban land use percentages for this study is based on the NLCD92 land use data for 1992 (*17*). To explore relations between land-use change and contamination in the 1970s and the 1990s, a land-use data set is needed for the 1970s. An earlier national land use data set is available for the 1970s (GIRAS (*36*)), but because of different classification schemes, the 1970s GIRAS and the NLCD92 data set are not sufficiently consistent for representation of land use change at the small urban watershed scale. Therefore, an alternative method for evaluating urban land-use change over the time period trend tested in the cores was used: the 1970s GIRAS data were compared to the 1970s GIRAS data updated with 2000 U.S. Census population data compiled at the block-group level to estimate new residential area (*37*). The GIRAS and the updated GIRAS were used in relation to mean decadal concentrations and mean decadal mass accumulation rates of contaminants (MAR_C; the product of sediment MAR and contaminant concentration) to evaluate relations to urbanization in more detail.

Decadal mean contaminant concentrations and MAR_C in the cores show strong relations to urban land use (Figure 5). Lines in Figure 5 are regression equations relating percentage of urban land use to the logarithm of concentration or of MAR_C (Table 2). In every case, the slope is significant at greater than 99.9% confidence (p-value < 0.001). The strengths of the relations were roughly similar using concentrations and MAR_C, although some differences are evident graphically (Figure 5). For all four contaminants, there is less scatter among the reference sites (urban land use at or near 0%) using MAR_C. Input of contaminants to the reference lakes is dominated by atmospheric deposition; thus concentrations will usually vary inversely with sediment MAR (more sedimentation causes more dilution). In these settings, a more representative measure of contaminant input is achieved using the MAR_C and less scatter about the regression lines results. In lakes with urban development in the watershed, in contrast, there is wider scatter about the regression lines using MAR_C than those using concentration (Figure 5). In urban settings, MAR_C scales to sediment MAR because most of the contaminant loading is via fluvial particulate loading from the watershed (*13, 14*). Higher sedimentation rates can
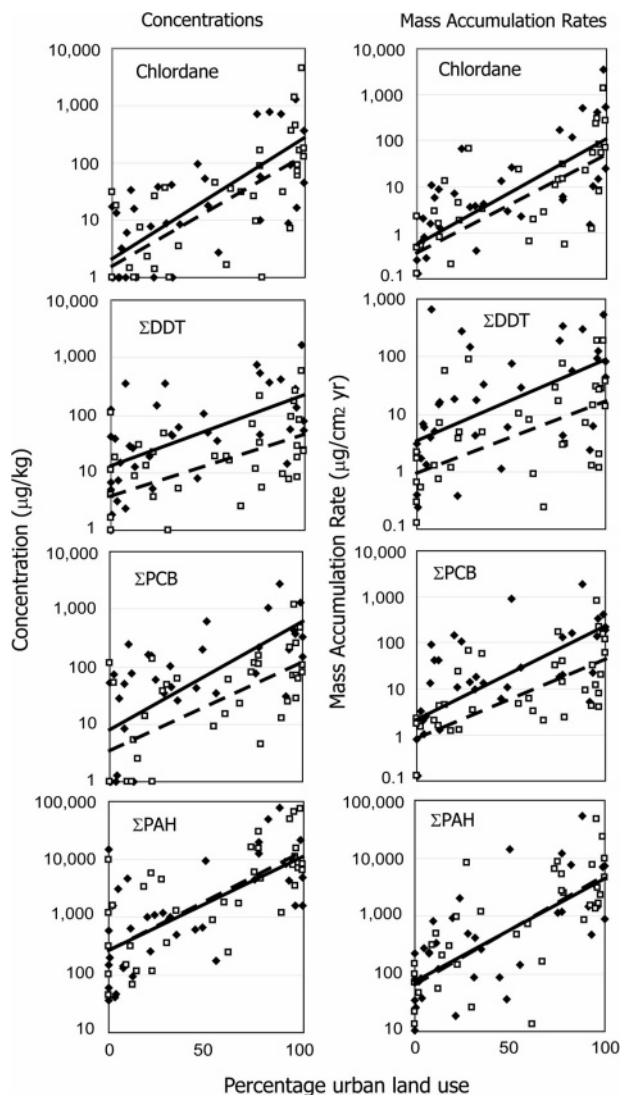

FIGURE 5. Mean concentration in lake cores in 1970 (1965−1975) (◆) and the 1990s (1990 to the top of the core) (□) as compared to percentage urban land use in the watershed. Lines on each graph are regressions fit to logarithms of concentrations or contaminant mass accumulation rates. Black line is fit to 1970 data; dashed line is fit to 1990s data.

result in higher MAR_C, even for similar anthropogenic source strength in the watershed (in effect, greater sediment focusing). In this case, concentrations might be more representative of historical changes in contaminant releases to the watershed than are MAR_C's.

On the basis of regression line slope, chlordane has the strongest relation to urban land use, followed by ΣPCB and ΣPAH. All three of these have (or had) many urban sources and limited rural sources, whereas ΣDDT, which here has a weaker relation to urban land use, was used heavily in agricultural areas and occasionally in forested and other more remote areas. The relative strength of the relation is also evident in the number of log cycles the lines cross, with about 2 cycles (factor of 100) for chlordane, about 1.5 for ΣPCB and ΣPAH, and about 1 cycle (factor of 10) for ΣDDT.

Chlordane, with about equal numbers of increasing and decreasing trends, has a small decrease in the regression lines between time periods (Figure 5). ΣDDT and ΣPCB decrease markedly, about one-half a log cycle. For ΣDDT, the decrease is uniform across the range in land use, but for ΣPCB narrows with less urban land use, with mostly nondetections in the reference settings in both time periods

TABLE 2. Regression Equations and Statistics Relating Logarithm of Concentrations and Logarithm of Contaminant Mass Accumulation Rates to Percent Urban Land Use [Land Use for the 1970s Is Based on the GIRAS Data (*36*), and Land Use for the 1990s Is GIRAS Updated Using the U.S. Census Data (*37*)]

parameter	equation	n	*p*-value slope	*p*-value intercept	*F*-statistic	r^2	standard error of the estimate
			1970s				
log(ΣPAH)	0.0161(lu) + 2.43	38	<0.001	<0.001	30.5	0.46	0.66
log(chlordane)	0.0211(lu) + 0.325	38	<0.001	0.068	44.4	0.55	0.72
log(ΣDDT)	0.0123(lu) + 1.12	38	<0.001	<0.001	19.7	0.35	0.63
log(ΣPCB)	0.0188(lu) + 0.898	38	<0.001	<0.001	36	0.5	0.71
log(ΣPAH MAR)	0.0179(lu) + 1.86	38	<0.001	<0.001	37.5	0.51	0.66
log(chlordane MAR)	0.0228(lu) − 0.249	38	<0.001	0.19	40.7	0.53	0.81
log(ΣDDT MAR)	0.0141(lu) + 0.547	38	<0.001	0.008	15.6	0.3	0.81
log(ΣPCB MAR)	0.0206(lu) + 0.325	38	<0.001	0.12	30.7	0.46	0.84
			1990s				
log(ΣPAH)	0.0170(lu) + 2.43	38	<0.001	<0.001	40.9	0.53	0.63
log(chlordane)	0.0193(lu) + 0.197	38	<0.001	0.3	44.6	0.55	0.69
log(ΣDDT)	0.0107(lu) + 0.591	38	<0.001	0.002	15.4	0.3	0.65
log(ΣPCB)	0.0154(lu) + 0.543	38	<0.001	0.004	31.3	0.47	0.65
log(ΣPAH MAR)	0.0190(lu) + 1.81	38	<0.001	<0.001	45.1	0.56	0.67
log(chlordane MAR)	0.0213(lu) − 0.425	38	<0.001	0.054	41.5	0.54	0.78
log(ΣDDT MAR)	0.0126(lu) − 0.031	38	<0.001	0.88	15.2	0.3	0.77
log(ΣPCB MAR)	0.0174(lu) − 0.080	38	<0.001	0.68	32.9	0.48	0.72

for ΣPCB (nondetections were entered in the plots and regressions at the method reporting level). Despite the strong relations to urban land use for these "legacy" pollutants, increases in urban land use in individual watersheds since the 1970s did not translate into increasing trends. The median percent change in urban land use for the light urban watersheds from the 1970s to 2000, based on the land-use data sets used here, is a 115% increase. Among the dense urban watersheds, the median is no change (1% increase), although some of these watersheds experienced growth. The lack of increasing trends, especially for ΣDDT and ΣPCB, which were banned in the 1970s, indicates that recently urbanized areas are not contributing significantly to contamination of legacy pollutants.

ΣPAH shows a relation similar to urban land use in both the 1970s and the 1990s; thus the strong relations to urban land use and frequent increasing trends suggest that increasing urbanization, rather than an increase in the relative strength of urban sources, is responsible for the increase in PAHs. Light urban lakes had the most urban growth (proportionally) and the most frequent increasing trends in PAH, with 76% having an increasing trend in benzo[*a*]pyrene, although benzo[*a*]pyrene also increased in over 50% of dense urban lakes (Table 1). Palmer Lake in Minneapolis, MN, illustrates the magnitude of PAH increase with urbanization: urban land used increased from 28% in the 1970s to 74% in 2000, and decadal mean ΣPAH concentrations increased from 1190 to 16 100 μg/kg from 1970 to the 1990s. In a general sense, increased urbanization can explain increasing concentrations in PAHs, but their specific sources in the urban landscape are not as clear. Van Metre et al. (*6*) showed that PAH increases exceeded the rate of growth in urban land use for 10 lakes (all included here) and suggested that rapid increases in vehicle traffic in urban areas could be a contributing factor. Another possible factor recently reported is the use of parking lot sealants, many of which contain high concentrations of coal tar (20−35 wt %) and could be the dominant source of PAHs in some urban watersheds (*38*).

Rate of Change of DDT and PCBs. Van Metre et al. (*4*) found that concentrations of ΣDDT and ΣPCB followed an exponential decline since about 1970 in cores from 11 U.S. reservoirs, suggesting a first-order process. Three of the lakes used in that study are used in this study. First-order regression

models fit to the concentration profiles yielded median half-lives of 12 and 9.6 yr for ΣDDT and ΣPCB, respectively. Decadal-mean concentrations for lakes presented here with detections in both time periods (36 lakes for ΣDDT and 30 for ΣPCB) were used to estimate half-lives, assuming a first-order process (exponential decrease). The median half-life for ΣDDT was 14.9 yr, and the median for ΣPCB was 19.7 y (interquartile ranges of 11.5−25 yr for ΣDDT and 14.4−47 yr for ΣPCB). The slightly longer half-lives (slower rate of decrease) than those found by (*4*) could result partly from using the mean value from 1965 to 1975 as the starting point instead of the peak concentration, and from inclusion here of reference lakes.

These half-lives can provide an estimate of expected changes in loading of persistent HOCs to aquatic systems following cessation of use. The lakes with detections of HOCs are mostly urban lakes, and most have relatively large DA:SA ratios. As a result, in these lakes the contaminant levels in surficial sediments are controlled primarily by recent loading from the watershed. Rates of change in concentrations of legacy pollutants in such systems are an indication of chemical processes in soils and erosion and transport of soil from the watershed, with historically contaminated soils gradually less available to erosion and transport to streams (*4, 14*). This is in contrast to large systems such as the Great Lakes, large estuaries, and the oceans, where contaminant occurrence in surficial bottom sediments can be influenced greatly by atmospheric processes and internal cycling (*39−41*).

Implications. PCBs, DDT, dieldrin, and chlordane are responsible for many of the fish-consumption advisories in the United States (*42*). Are the 15−20-year half-lives for DDT and PCBs in sediments an indication of trends in fish? The National Contaminant Biomonitoring Program sampled fish at approximately 100 sites across the country, mostly in rivers, on an annual or bi-annual basis during 1969−86 (*7, 43*). Regression equations fit to the natural logarithm of annual median fish concentrations yield half-lives of 7.0 (5.9−8.6, based on the standard error of the slope) and 5.5 (4.5−7.1) yr for ΣDDT and PCB Aroclor 1254 (the only PCB measure that spans the entire sampling period), respectively. These are approximately one-half to one-quarter the median half-lives in the sediment cores, indicating that concentrations, on average, decreased more than twice as fast in fish as in
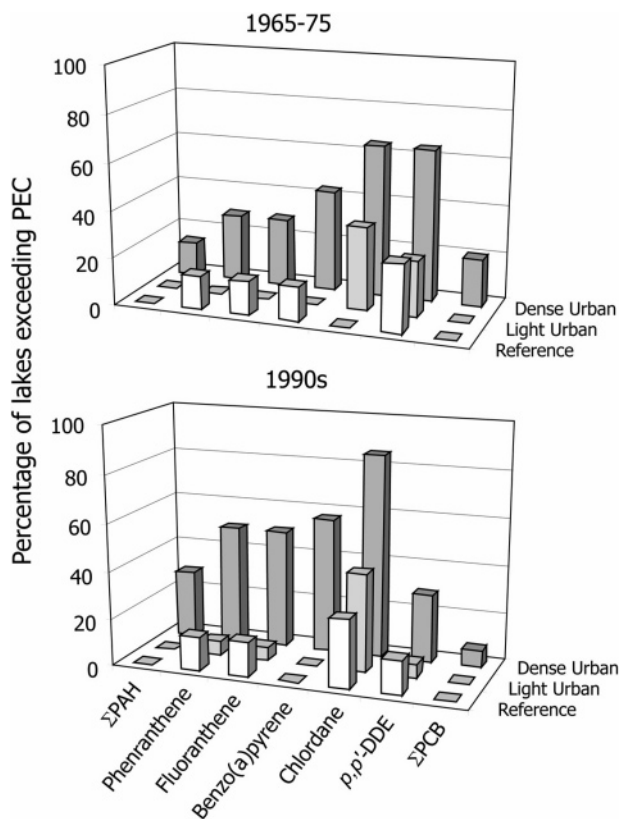
FIGURE 6. Percentage of lakes with a decadal-mean concentration exceeding the probable effect concentration (*25*).

cores. Although sediments are recognized as the primary reservoir of HOCs available to fish, the relations between fish and sediment are complex and not completely understood (*44*). Are concentrations decreasing more slowly in sediments than they are in fish? If so, could it be an indication of the effects of aging and sequestration on the bioavailability of HOCs in sediment (*45*)? Or does fish metabolism lead to more rapid reductions in fish than in sediment? These and other questions remain as to whether rates of contaminant decrease modeled in sediment cores can be extrapolated to other media and what factors control trends in each medium.

In addition to concerns for bioaccumulation, the HOCs presented here can be toxic to benthic biota, prompting the development of sediment quality guidelines (*25*). To assess the significance of trends in cores in relation to potential toxicity to aquatic biological communities, decadal-mean concentrations were compared to PECs, the concentration above which adverse effects on benthic biota are likely (*25*). Of the compounds examined, chlordane most frequently exceeds the PEC in the 1990s, followed by several individual PAHs and *p,p*′-DDE (Figure 6). The frequency with which both *p,p*′-DDE and ΣPCB exceed the PEC declined by more than one-half from 1970 to the 1990s, consistent with decreasing trends observed in both. Conversely, the frequency with which PAHs exceed the PEC approximately doubled during the same time period. Individual PAHs frequently exceed the PEC in the dense urban lakes but not in the other lakes.

The implications of the comparisons to PEC values and the concern for bioavailability extend to the streams flowing into these lakes and reservoirs. Van Metre and Mahler (*14*) showed that concentrations of HOCs in suspended sediment in urban streams are similar to or greater than concentrations in downstream reservoir sediments, often by a factor of 2 or more. This implies that reservoir sediment cores could underestimate the potential risk posed by HOCs to biota in

urban streams. The increasing trends in PAH concentrations, the strong association of PAHs with urban settings, and the rapid urbanization occurring in the United States suggest that PAHs could surpass chlorinated hydrocarbons in the threat posed to aquatic biota in urban streams and lakes. Also, while improvements brought about by regulation of chlorinated hydrocarbons are occurring, the continuing high levels of chlordane and the slow rate of decreasing trends for DDT and PCBs indicate that chlorinated hydrocarbons will remain a concern for many years to come.

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