Similar Rates of Decrease of Persistent, Hydrophobic and Particle-Reactive Contaminants in Riverine Systems

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Although it is well-known that concentrations of anthropogenic radionuclides and organochlorine compounds in aquatic systems have decreased since their widespread release has stopped in the United States, the magnitude and variability of rates of decrease are not well-known. Paleolimnological studies of reservoirs provide a tool for evaluating these long-term trends in riverine systems. Rates of decrease from the 1960s to the 1990s of ^{137}Cs, PCBs, and total DDT in dated sediment cores from 11 reservoirs in the eastern and central United States were modeled using first-order rate models. Mean half-times of 10.0 ($\pm$2.5), 9.5 ($\pm$2.2), and 13 ($\pm$5.8) yr for decay-corrected ^{137}Cs, PCBs, and total DDT, respectively, are surprisingly similar. Similar rates of decrease in a few reservoirs are also demonstrated for chlordane and lead. Conceptual and simple mathematical models relating two soil distributions of ^{137}Cs to trends in the cores provide insight into differences in trends between watersheds with different land uses and suggest that trends are controlled by erosion, transport, mixing, and deposition of sediments. These results, supported by similar trends reported for other settings and environmental media, could provide an estimate of the decadal response time of riverine systems to changes in the regulation of other persistent hydrophobic or particle-reactive contaminants.

Introduction

Environmental regulations have reduced concentrations of some persistent organic [for example, polychlorinated biphenyls (PCBs) and DDT] (*1, 2*) and inorganic (for example, lead) (*3*) contaminants in aquatic systems since the early 1970s. Large amounts of these contaminants, however, remain mobile in the environment and continue to cause environmental concerns (*4*). Rates of decrease in PCBs and total DDT (sum of DDT, DDD, and DDE) in lake sediments and fish have been estimated in a number of studies (for example, refs *5*–*7*). Rapid decreases in concentrations, noted soon after restrictions on use were imposed, have slowed (*6, 8*), and disagreement on the long-term direction of trends remains (*7*). Similarities in trends from diverse riverine settings have not, to our knowledge, been reported. These trends can have important management implications as

indicated by controversy over the hypothesized "new equilibrium" for PCBs in the Great Lakes (*7*). Understanding rates of change also could benefit State and Federal agencies charged with managing fisheries where hydrophobic contaminants are of concern.

In this paper we present an analysis of rates of decrease of decay-corrected ^{137}Cs, PCBs, and total DDT following restrictions on their use or release. Rate models are developed from trends identified in dated reservoir-sediment cores from 11 reservoirs in the eastern and central United States (Figure 1). We discuss several factors that could contribute to the surprising similarity of rates of decrease of these three constituents. This study is part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program (*9*).

Methods

Sediment cores were collected from 11 reservoirs representing a wide range of environmental settings and scales (Figure 1; Table 1). Sampling and analytical methods used are presented elsewhere (*2, 10, 11*) and are only briefly described here. Cores were collected using a 3 m long, 6.3 cm diameter gravity corer, a piston corer of the same dimensions, or a 14 × 14 × 20 cm box corer. Cores were sectioned into vertically discrete subsamples that were analyzed for major and minor elements, ^{137}Cs, chlorinated organic pesticides, and PCBs. One site was sampled in each reservoir. The site was selected on the basis of sedimentation surveys and reconnaissance coring in each reservoir, with the objective of obtaining as thick a sequence of undisturbed lacustrine sediment as possible, yet still penetrating the prereservoir land surface. The prereservoir surface provides an unambiguous date marker and was identified on the basis of lithologic and chemical changes. The sampling site is in the middle or lower part of each reservoir, and several cores were obtained at each site.

Organochlorine compounds were determined in organic solvent extracts using a dual capillary-column gas chromatograph with dual electron-capture detectors (*12, 13*). Accuracy and precision were determined by analyzing spiked samples and monitoring recovery of surrogates and by analyzing duplicate samples from the field. Nine percent of samples were analyzed in duplicate. The median relative percent difference for duplicate analyses of PCBs and total DDT is 17%.

Sediment ^{137}Cs activities were measured by counting freeze-dried sediments (20–75 g) using a high-resolution, intrinsic germanium detector γ spectrometer. The method is similar to that used by Callender and Robbins (*14*). Replicate counts of samples agreed within $\pm$15% (*2*). Concentrations of lead were determined on concentrated-acid digests using graphite furnace atomic adsorption (*15*).

Results and Discussion

Median organic carbon concentrations range from 2.0 to 3.9 wt %. In cores in which lacustrine sediments are relatively homogeneous with respect to grain size and organic carbon content (standard deviation less than $\pm$25% of mean and no trend), concentrations of ^{137}Cs, PCBs, and total DDT were not normalized before interpretation of trends. In sediments from Lake Anne, organic carbon concentrations varied more, and organochlorine concentrations were normalized. Grain-size variations in sediments from Elephant Butte Reservoir led us to normalize ^{137}Cs concentrations for those sediments. Lead concentrations presented here are normalized with respect to aluminum.
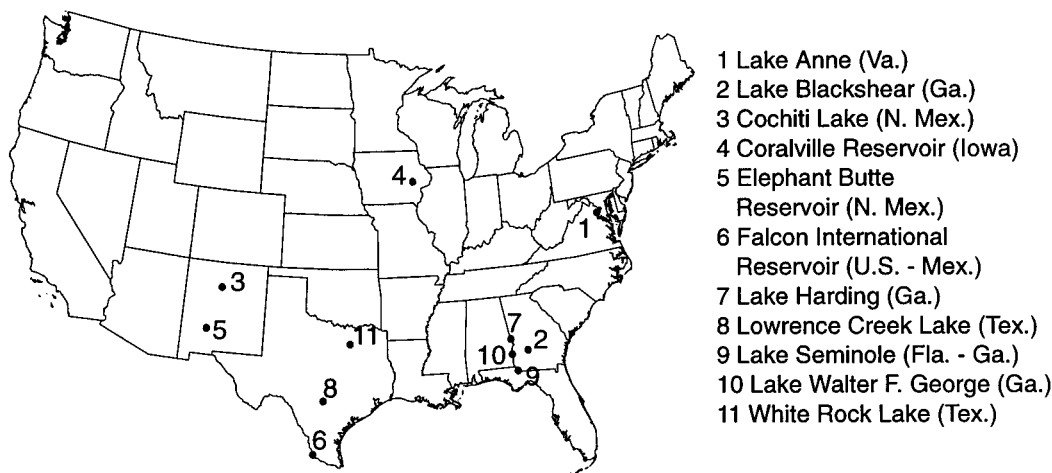
1 Lake Anne (Va.)
2 Lake Blackshear (Ga.)
3 Cochiti Lake (N. Mex.)
4 Coralville Reservoir (Iowa)
5 Elephant Butte
  Reservoir (N. Mex.)
6 Falcon International
  Reservoir (U.S. - Mex.)
7 Lake Harding (Ga.)
8 Lowrence Creek Lake (Tex.)
9 Lake Seminole (Fla. - Ga.)
10 Lake Walter F. George (Ga.)
11 White Rock Lake (Tex.)

FIGURE 1. Locations of reservoirs sampled from 1992 to 1996.

TABLE 1. Reservoirs Sampled

reservoir	drainage area (km^2)	reservoir surface area (km^2)	drainage area surface area ratio	av sedimentation rate since 1963 (g/cm^2 yr)	av linear sedimentation rate in core (cm/yr)	dominant land use in watershed
Lake Anne	1.85	0.13	14	0.30	0.5	suburban
Lake Blackshear	9 090	35	260	0.54	0.9	agriculture
Cochiti Lake	30 000	4.2	7 100	2.9	7.2	range
Coralville Reservoir	7 620	101	75	2.2	4.7	agriculture
Elephant Butte Reservoir	83 100	148	560	3.4	3.8	mixed
Falcon Int. Reservoir	525 000	350	1 500	1.0	2.2	mixed
Lake Harding	12 350	24	510	1.5	3.7	urban
Lowrence Creek Lake	5.2	0.05	100	0.52	0.7	suburban
Lake Seminole	44 200	163	270	1.0	2.2	agriculture
Lake Walter F. George	19 700	188	100	2.4	4.7	urban/mixed
White Rock Lake	259	4.4	59	0.76	1.7	urban

The analysis presented here involves the time period from approximately the ^{137}Cs peak (1963−1964) to the tops of cores (1993−1996). [137]Cs was detected in all samples deposited since the ^{137}Cs peak in the early 1960s. Sediment cores were age-dated based on core lithology and ^{137}Cs occurrence (initial occurrence dated as 1953.0 and peak as 1964.0) (2) and corroborated based on total DDT peaks [generally early 1960s (1, 2)] and lead peaks [mid-1970s (3)]. Dates were assigned to individual samples based on (assumed) constant mass accumulation rates between date-depth markers, thus accounting for the effects of compaction. Prior to interpretation of trends, ^{137}Cs concentrations were decay-corrected between the analysis date and the assigned date for the specific interval.

Two processes could lead to the occurrence of ^{137}Cs, PCBs, and total DDT in the upper parts of cores long after their use or release to the environment has ceased: postdepositional mixing and continued inputs from the watershed or the atmosphere. Pronounced ^{137}Cs, lead, and organochlorine peaks; relatively high sedimentation rates; and the presence of laminations in sediment cores indicate limited postdepositional mixing in these cores (2, 10). Continuing fluvial inputs of ^{137}Cs, PCBs, and total DDT can be inferred from (i) the occurrence of PCBs and DDT metabolites in streambed sediments in the streams draining to these reservoirs (16−18); (ii) the recent (post-1990) occurrence of [137]Cs (19) and PCBs in suspended sediments in streams (20); and (iii) the occurrence of ^{137}Cs, PCBs, and total DDT in sediment cores from reservoirs constructed after about 1970 (2, 11, 21). We conclude that postdepositional mixing has not appreciably altered profiles of particle-bound constituents in these reservoirs and that reservoir sediments predominantly are influenced by fluvial sediment inputs.

First-Order Rate Models. Trends in concentrations of ^{137}Cs, PCBs, and total DDT decrease exponentially since the 1960s in reservoir sediment cores (2, 10) suggesting a first-order rate process. We fitted first-order rate models to concentrations of ^{137}Cs, PCBs, and total DDT versus estimated deposition date (Figure 2). Samples dated as 1963 or after were included in the regression analysis. The range of individual sample dates for each parameter and lake are dependent on sampling interval in the core and core collection date and are identified as the "calibration period" in Table 2. [137]Cs concentrations were decay-corrected prior to model fitting. This empirical model is process-neutral in that it does not indicate a specific chemical, physical, or radioactive decay process. The model is of the form $C_t = C_0 e^{-kt}$, where C_t is the concentration at time t; C_0 is the initial concentration; k is the time constant; and t is time, in years. C_0 and k values were determined by least-squares fit to the natural logarithm of concentrations versus time in years.

The constituent concentrations in reservoir sediments are assumed to correlate to constituent concentrations in the influent streams at the time of deposition; therefore, the rates of change in sediment cores are interpreted as indicating rates of change in sediment contaminant concentrations in the influent streams. The models adequately represent changes in ^{137}Cs, PCB, and total DDT concentrations in the upper parts of most of these reservoir cores as indicated by r^2 values of about ≥ 0.5 and p values ≤ 0.12 (Table 2). In general, the greatest confidence is achieved for [137]Cs.

Rates of decrease are surprisingly similar among reservoirs and among constituents (Figure 2; Table 2). Mean half-times are 10 [±2.5 (1 SD)], 9.5 (±2.2), and 13 (±5.8) yr for decay-corrected ^{137}Cs, PCBs, and total DDT, respectively, excluding cases with excessive nondetections and the three cases that
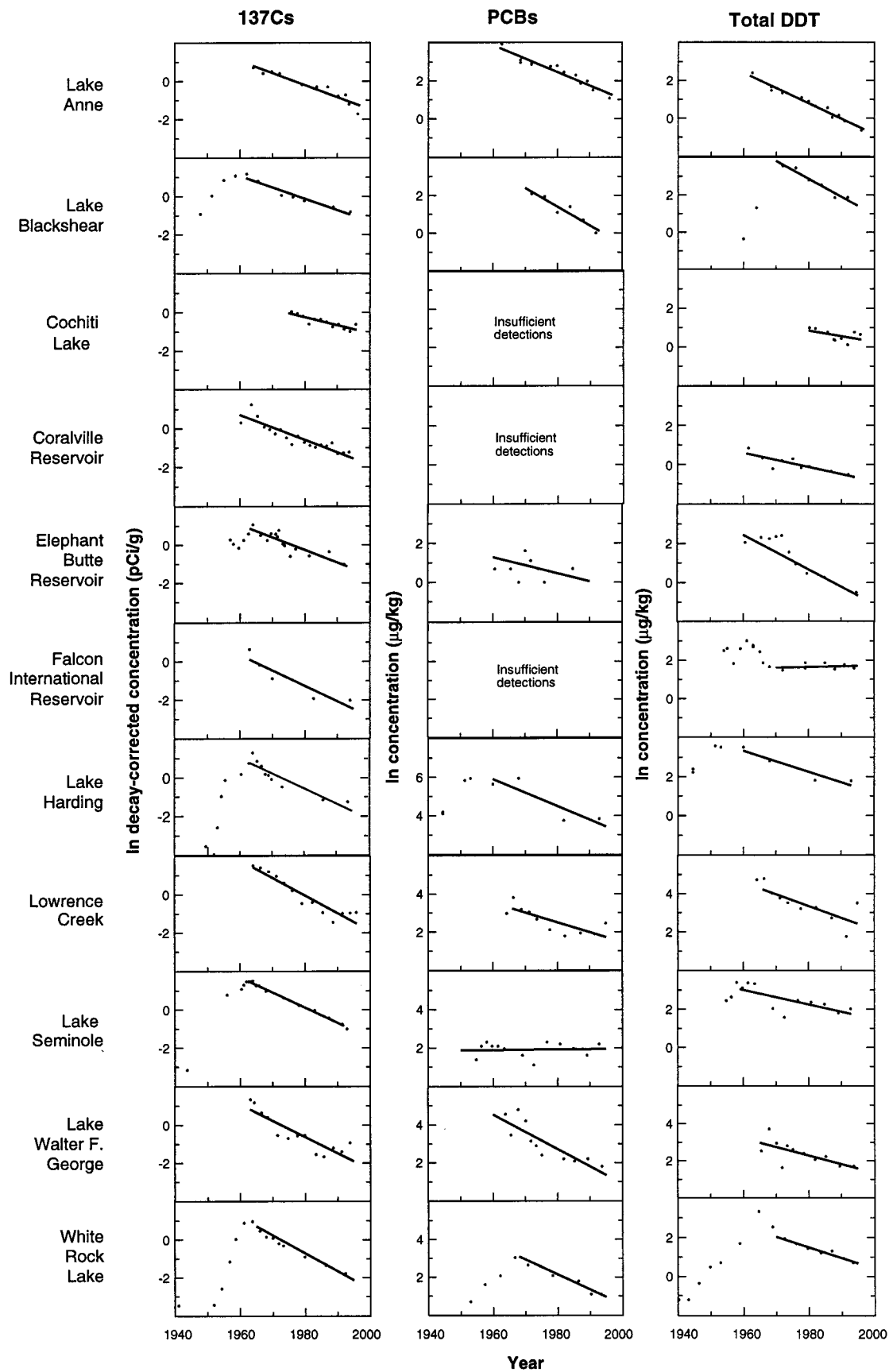
FIGURE 2. Time series and rate models of ^{137}Cs, PCBs, and total DDT in sediment cores.

had p values greater than 0.12. Median half-times for the same three constituents are 8.9, 9.6, and 12 yr. Median rates for the three constituents are not statistically different on the basis of the Kruskal–Wallis test (p value = 0.498). The

overall mean half-time is 11.3 (±4.3) yr, and the overall median is 9.8 yr (interquartile range = 5.0 yr).

The three cases without significant trends are PCBs in Elephant Butte Reservoir and Lake Seminole and total DDT

TABLE 2. First-Order Rate Model Statistics

reservoir	$T_{1/2}$ (90% confidence interval)[a] (yr)	p value	R^2 value	no. of cases	calibration period (yr)
137Cs					
Lake Anne	10.9 (9.2–13.6)	0.00001	0.91	11	1964–1997
Lake Blackshear	11.6 (9.5–15.0)	0.00029	0.94	7	1962–1994
Cochiti Lake	16.4 (12.4–24.2)	0.00023	0.76	12	1975–1996
Coralville Reservoir	10.7 (8.9–13.5)	<0.00001	0.82	18	1963–1994
Elephant Butte Reservoir	10.5 (8.1–15.1)	0.00007	0.74	14	1964–1992
Falcon International Reservoir	8.6 (5.4–20.6)	0.027	0.84	5	1963–1994
Lake Harding	8.9 (6.8–13.1)	0.00056	0.84	9	1964–1994
Lowrence Creek	7.5 (6.4–9.3)	<0.00001	0.89	13	1964–1996
Lake Seminole	8.7 (8.2–9.2)	<0.00001	0.99	10	1964–1993
Lake Walter F. George	8.1 (6.3–11.4)	0.00007	0.78	13	1963–1994
White Rock Lake	7.8 (6.9–8.8)	<0.00001	0.97	9	1963–1993
PCBs					
Lake Anne	9.8 (8.4–11.6)	<0.00001	0.92	13	1962–1996
Lake Blackshear	7.0 (5.1–11.0)	0.0043	0.89	6	1972–1992
Cochiti Lake	insuff. detections				
Coralville Reservoir	insuff. detections				
Elephant Butte Reservoir	15.1	0.30	0.49	4	1970–1985
Falcon International Reservoir	insuff. detections				
Lake Harding	9.8	0.11	0.78	4	1960–1993
Lowrence Creek	13.4 (8.3–33.6)	0.016	0.58	9	1966–1995
Lake Seminole	510	0.88	0.0023	13	1954–1993
Lake Walter F. George	7.6 (5.6–12.0)	0.00074	0.74	11	1964–1994
White Rock Lake	9.4 (8.0–11.3)	0.00007	0.97	7	1966–1993
Total DDT					
Lake Anne	8.6 (7.8–9.5)	<0.00001	0.96	13	1962–1996
Lake Blackshear	7.3 (5.8–9.6)	0.00091	0.95	6	1972–1992
Cochiti Lake	24.0	0.12	0.27	10	1980–1996
Coralville Reservoir	19.2 (14.1–29.8)	0.0008	0.77	10	1961–1994
Elephant Butte Reservoir	6.1 (4.9–8.0)	0.0001	0.90	9	1965–1995
Falcon International Reservoir	220	0.73	0.025	7	1972–1994
Lake Harding	12.8 (7.6–39.4)	0.049	0.90	4	1960–1993
Lowrence Creek	11.2 (6.9–30.2)	0.019	0.56	9	1966–1995
Lake Seminole	18.1 (10.9–54.6)	0.024	0.49	10	1959–1993
Lake Walter F. George	15.0 (9.0–46.6)	0.024	0.45	11	1964–1994
White Rock Lake	9.6 (7.6–13.0)	0.00031	0.90	8	1962–1993

[a] Not shown where β lacks significance.

in Falcon International Reservoir. PCB concentrations in Elephant Butte Reservoir are relatively small and highly variable, although they do appear to be decreasing (11). PCB concentrations in Lake Seminole range from 3 to 10 μg/kg and, unlike concentrations in the other reservoirs, do not have a distinct temporal trend (2). Falcon International Reservoir is on the Rio Grande about 440 km upstream from the Gulf of Mexico. Total DDT concentrations decreased rapidly following the ban on DDT use in the United States; however, concentrations stopped decreasing and have remained stable since the early 1970s, suggesting continuing use of DDT in the Falcon watershed, although at smaller levels than were found during the period of use in the United States (11).

Factors Contributing to Similarity and Variability in Rates of Change. Rates of change of decay-corrected 137Cs, PCBs, and total DDT are surprisingly similar among these 11 reservoirs. There is even some indication that similar rates of change for sediment-bound contaminants are occurring in such diverse media as fish in the Great Lakes (22) and suspended sediment in the Mississippi River (23). We fitted a first-order rate model to published logarithmic mean concentrations of PCBs and DDE in 4-year-old Lake Ontario lake trout over the period 1977–1988 (22) that yields half-times of between 9 and 10 yr for each. In a study of plutonium transported on suspended sediment in the Mississippi River, Scott and others (23) found that fallout ^{239,240}Pu concentrations in river suspended sediment decreased exponentially with time during 1977–1983 with a half-time of 4.3 yr. Scott and

others (23) attributed the exponential decrease in Pu to a complex function of the source term of fallout to the soil, the erosive processes delivering soil to the river, and the transport processes in the river and its flood plains.

Four factors could contribute to the similarity in trends in a given watershed. 137Cs, PCBs, and total DDT (i) are widely distributed in the environment, both directly (for example, DDT applications) and atmospherically; (ii) were released and then banned over a relatively similar time period; (iii) associate with sediment; and (iv) are resistant to chemical and biological transformation (when evaluating total DDT and when 137Cs is decay corrected). The similarity in trends suggests that other biogeochemical factors that could cause differences in the environmental behavior of these constituents are relatively unimportant in controlling trends in their occurrence in inland waters over decadal time periods. 137Cs, for example, is strongly adsorbed on clay minerals and is essentially nonexchangeable (24), although mobilization of 137Cs from sediments, attributed to ion-exchange displacement by competing ions, has been demonstrated in some higher ionic strength systems (25). In contrast, the sorption of nonionic organic compounds such as DDT and its metabolites and PCBs is characteristic of a partitioning process. Octonol–water partition coefficients determined for PCB congeners and total DDT compounds are high, ranging from about 4 to more than 6 ($\log_{10}$), indicating that these compounds have a strong tendency to partition into sediment organic matter (26). Decay processes also vary among these constituents. By decay-correcting 137Cs, it can

Chlordane
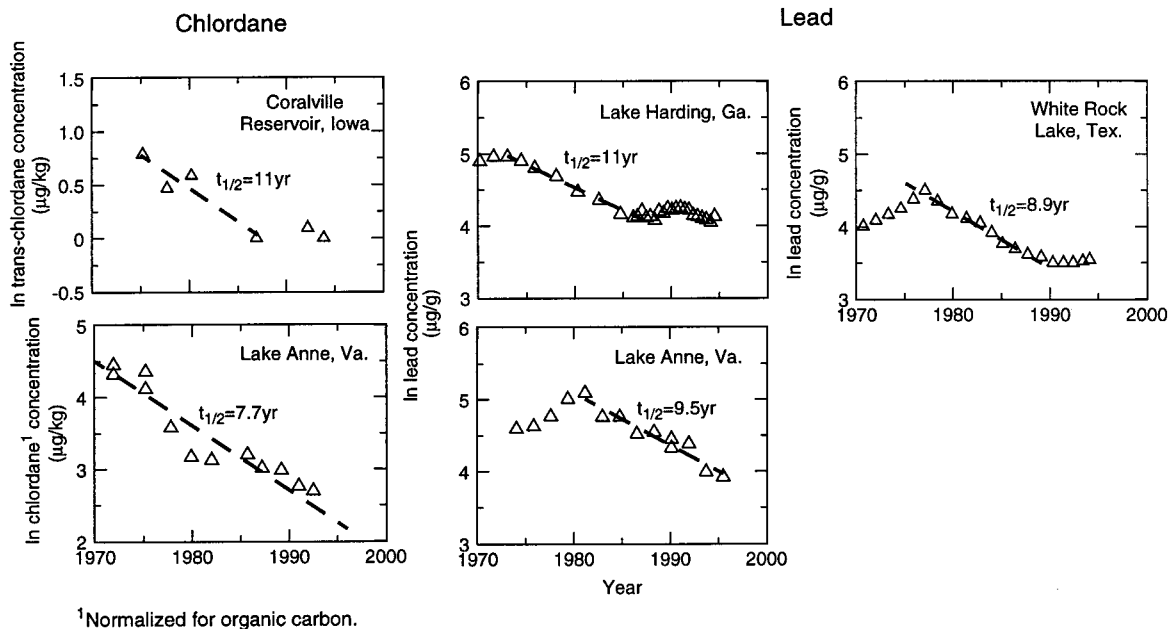

Lead

[1]Normalized for organic carbon.

FIGURE 3. Rates of decrease in chlordane and lead in selected sediment cores.

essentially be viewed as stable. Total DDT should be relatively stable over time because DDD and DDE are quite resistant to biodegradation. The biodegradability of PCBs varies among congeners with a general decrease with increased chlorination. Although they are generally resistant to degradation, PCBs are relatively volatile (26). These differences in properties appear to be outweighed by other processes controlling decadal trends in ^{137}Cs, PCBs, and total DDT, although it is possible that they contribute to the greater variability among sites for trends in PCBs and total DDT than for [137]Cs (Figure 2). Inputs from both local and atmospheric sources of PCBs and total DDT, in contrast to ^{137}Cs that is only from atmospheric sources, could also contribute to less consistent trends in the organic compounds.

Although the four factors identified above can help explain similarities in trends among constituents in a single watershed, they do not explain the similarities in trends among these 11 diverse watersheds. An explanation of why rates of change are similar among reservoirs presumably lies in an understanding of processes governing the erosion, transport, mixing, and deposition of sediments that these constituents are associated with. Two processes that will cause decreases in concentrations of sediment-borne contaminants in stream/reservoir systems over time are the depletion of the contaminant in source soils and a shift in the proportion of surficial soils versus deeper (clean) soils eroded. The possible importance of these processes in determining trends can be evaluated using simple conceptual and mass balance models.

[137]Cs profiles in undisturbed soils decrease exponentially (for example, refs 27 and 28). Erosion is therefore expected to remove particles with progressively smaller concentrations of [137]Cs. The average sediment yield from the watershed of White Rock Lake is 0.04 cm/yr^{-1}, based on sedimentation surveys of the lake (29). If an exponential ^{137}Cs profile in basin soils is assumed with an $h_{1/2}$ (depth to one-half the surface concentration) of 3 cm (matching the $h_{1/2}$ reported by ref 28), uniform erosion at the estimated yield will take 73 yr to reduce ^{137}Cs concentrations by one-half, an order of magnitude longer than the 8.6-yr half-time observed in the core since 1970. This model is supported by an evaluation of the ^{137}Cs inventory remaining in the watershed. The estimated ^{137}Cs fallout over White Rock Lake of 5.1 pCi/cm^2 (2) times the drainage area of 259 km^2 yields an estimated burden of 13×10^{12} pCi. Assuming that the 1994 core burden

of ^{137}Cs of 11.6 pCi/cm^2 (2) is representative of the lake area (4.4 km^2), an estimated 4% of the fallout ^{137}Cs has reached the lake. The large remaining inventory in the watershed is consistent with the slow rate of removal of ^{137}Cs by erosion indicated by the 73-yr half-time calculated above. Assuming the exponential decrease in ^{137}Cs concentrations continues, most of the ^{137}Cs in the watershed will never reach the lake, a conclusion consistent with Scott and others (23) for Pu in the Mississippi.

Because the relatively rapid decreasing trend observed cannot be explained by depletion from the watershed by mass transfer, a temporal change in soils subject to erosion must result in a decrease in the proportion of surficial sediments relative to older clean sediments. This conclusion is supported by ref 10. Extensive urban development of the White Rock Lake watershed has occurred since the 1950s. Changes in sedimentation rates, particle size, and major element chemistry have occurred that indicate a shift from erosion dominated by well-developed soils to erosion of more subsoils and parent material (10). The shift to proportionally more erosion of deeper material, including the contribution from streambank erosion, will cause more rapid decreasing trends in contaminants associated with surface soils than those predicted assuming uniform erosion of the entire watershed.

Agricultural settings lead to a different conceptual model of trends in soil-associated contaminants in streams. Profiles of ^{137}Cs in agricultural soils are characterized by relatively constant ^{137}Cs concentrations to the depth of plowing (28). One effect of homogenizing soils annually could be to cause a more rapid decrease in contaminant concentrations immediately after release stops, followed by a slowing of the rate of decrease during subsequent years. This pattern occurs for ^{137}Cs in Lake Blackshear in Georgia and Coralville Reservoir in Iowa, the two most agricultural watersheds sampled. The half-times for decay-corrected ^{137}Cs after 1970 in Lakes Blackshear and Coralville are 16.7 and 15.6 yr, respectively, considerably longer than half-times if data from the 1960s are included (Table 2; 11.6 and 10.7 yr, respectively). In contrast, half-times after 1970 in Lakes White Rock, Anne, and Lowrence Creek, the three watersheds extensively urbanized since the 1960s, are 8.6, 9.2, and 8.7 yr, respectively. Rapid and selective erosion does appear to lead to more rapid decreasing trends in sediment-bound contaminants

in the urbanizing settings as compared to the agricultural settings where soils are homogenized.

Both models presented above result in first-order decreases as observed in cores. Both models are consistent with temporal increases in the proportion of older sediments relative to surficial sediments. By these simple approaches, trends should be proportional to erosion rates; however, there is not a significant correlation between ^{137}Cs half-time and sedimentation rates in the reservoirs (Spearman's rank correlation = 0.24; p value = 0.48). This test assumes that erosion rates in watersheds correlate with sedimentation rates in reservoirs. Therefore, the proportion of the sediment that is eroded and transported to the reservoirs that is ^{137}Cs-free (older sediment) must be changing at comparable rates among these watersheds. The similarity in the magnitude of ^{137}Cs concentrations (Figure 2), independent of sedimentation rates, supports the contention that proportions of recent and older sediments are comparable among reservoirs. The similar concentrations, independent of sedimentation rates, also indicate that the ^{137}Cs is provided to the lakes by fluvial inputs and is not being delivered by direct atmospheric fallout on the lake surface.

One hypothesis that may account for the similarity in observed trends among watersheds is that the proportion of the watershed area that is actively eroding is proportional to the erosion rate. To illustrate, coring sites in Lake Anne and Coralville Reservoir have sedimentation rates of 0.30 and 2.2 g cm^{-2} yr^{-1}, respectively, yet concentrations and trends in ^{137}Cs are relatively similar (Figure 2; Table 2). If erosion in the watershed of Coralville Reservoir were occurring from the same percentage of the watershed as in Lake Anne, older ^{137}Cs-free sediment would be encountered more quickly and decreasing trends would be more rapid (assuming that erosion rates are correlated to the reservoir sedimentation rates). If, however, a proportionally larger part of the watershed of Coralville Reservoir is contributing sediment to streams, then similar ^{137}Cs trends in these two diverse settings could occur. This is not unreasonable considering that 90% of the watershed of Coralville Reservoir is plowed each year.

Implications for Other Constituents. If, as proposed, trends in ^{137}Cs, PCBs, and total DDT are similar because of similarities in their release and environmental behavior and are controlled largely by soil erosion, transport, and deposition, then trends in other constituents with similar characteristics also should be similar. This hypothesis can be tested, within the limitations of small sample size and the use of reservoir coring as an approach to defining trends, using chlordane and lead in selected reservoir cores. Chlordane use in agriculture was restricted in 1974, leading to decreasing trends in trans-chlordane concentrations in a Coralville Reservoir core (2) (Figure 3). Unlike urban sites in Texas and Georgia (2), decreasing trends in chlordane have occurred in urbanized Lake Anne since the 1970s (Figure 3). First-order rate models fit to the Coralville data yield half-times of 11−17 yr, depending on how recent nondetections are handled. Chlordane concentrations in the Lake Anne core are decreasing with a half-time of 7.7 yr. Both of these rates of decrease are in the range observed for ^{137}Cs, PCBs, and total DDT.

Lead concentrations decreased rapidly in the United States following the introduction of unleaded gasoline in the mid-1970s (3). First-order rate models fit to lead concentrations in cores from Lakes Anne, Harding, and White Rock had half-times of 9.5, 11, and 8.9 yr, respectively (Figure 3). These rates also are in agreement with rates of decrease observed for ^{137}Cs, PCBs, and total DDT. These three reservoirs were chosen because they had much more pronounced lead trends than the more rural reservoirs sampled (3). Although the test results described here are very limited, they do support the hypothesis that concentrations of widely distributed, hydrophobic, persistent constituents in riverine systems will decrease with a half-time of about 10 yr following elimination of releases to the environment.

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