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DISTRIBUTION OF DDT, CHLORDANE, AND TOTAL PCB'S IN BED SEDIMENTS IN THE HUDSON RIVER BASIN

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Abstract

Data from streambed-sediment samples collected from 45 sites in the Hudson River Basin and analyzed for organochlorine compounds indicate that residues of DDT, chlordane, and PCB's can be detected even though use of these compounds has been banned for 10 or more years. Previous studies indicate that DDT and chlordane were widely used in a variety of land use settings in the basin, whereas PCB's were introduced into Hudson and Mohawk Rivers mostly as point discharges at a few locations. Detection limits for DDT and chlordane residues in this study were generally 1 μg/kg, and that for total PCB's was 50 μg/kg. Some form of DDT was detected in more than 60 percent of the samples, and some form of chlordane was found in about 30 percent; PCB's were found in about 33 percent of the samples. Median concentrations for p,p'-DDE (the DDT residue with the highest concentration) were highest in samples from sites representing urban areas (median concentration 5.3 μg/kg) and lower in samples from sites in large watersheds (1.25 μg/kg) and at sites in nonurban watersheds. (Urban watershed were defined as those with a population density of more than 60/km2; nonurban watersheds as those with a population density of less than 60/km2, and large watersheds as those encompassing more than 1,300 km2. The median concentration of trans-nonachlor in samples from urban-watershed sites (2.3 μg/kg) is significantly higher than the median for both large and nonurban-watershed sites (less than 1 μg/kg). Median PCB concentrations in samples from large-watershed sites (80 μg/kg) and urban-watershed sites (56 μg/kg) were significantly higher than those for nonurban-watershed sites (less than 50 μg/kg). The highest PCB concentrations (greater than 800 μg/kg) were in samples from the upper Hudson River, near the largest documented source of PCB's in the basin, and from the Mohawk River near Utica, near a suspected source of PCB's. These results indicate that urban watersheds continue to be an important source of organochlorine residues in the Hudson River Basin, but that major sources of PCB's are few.

Introduction

In 1991, the U. S. Geological Survey (USGS) implemented the National Water Quality Assessment (NAWQA) Program to investigate water quality throughout the United States. This effort has included describing water quality conditions and trends in the Hudson River Basin, and identifying, describing, and explaining, to the extent possible, the major factors that affect these conditions and trends. The Hudson River Basin encompasses about 34,500 km2 (square kilometers) and lies in parts of eastern New York and adjacent states (Figure 1); 9.0 percent of the of the watershed is classified as urban, industrial, or residential lands, 24 percent as agricultural, and 62 percent as forested. Urban areas are concentrated within a few km (kilometers) of the Mohawk and Hudson Rivers, and agricultural areas are most prominent in the Mohawk River Basin. The occurrence and distribution of the toxic organochlorine compounds DDT (dichlorodiphenyltrichloroethane), chlordane, and PCB's (polychlorinated biphenyls) in the Hudson River Basin are of wide interest because they can persist in the environment and can accumulate in the tissues of fish, other wildlife, and humans.

This report presents results of analyses of the organochlorine compounds in bed sediment collected from streams and rivers in the Hudson River Basin during 1993-94 by the Hudson River Basin NAWQA project. It (1) identifies the predominant organochlorine compounds detected in bed sediments, (2) relates the occurrence of selected compounds to land use, (3) compares the concentrations of the compounds in streambed sediment with proposed New York State human health and wildlife bioaccumulation guidelines, and (4) discusses spatial patterns of PCB concentrations in parts of the Hudson and Mohawk Rivers.

Patterns of DDT, chlordane, and PCB use or application in the Hudson River Basin varied through time and according to land use. Whereas DDT and chlordane are largely associated with nonpoint applications, PCB's are largely associated with point sources. DDT was applied in a wide variety of settings, including urban, agricultural, and forested areas (Rod, 1989); its use peaked in 1957 and subsequently decreased until the compound was banned in the early 1970's. DDT use in the Hudson River Basin during the 1950's and 1960's was highest in the Mohawk River watershed and the northernmost parts of the Hudson River Basin. By 1970, nearly all the DDT use in the Hudson River Basin was confined to urban and residential settings; in 1972, DDT use was banned throughout the United States. In contrast, chlordane was used largely for the control of termites and other insects in suburban and urban settings, and its use in agricultural and forested areas was negligible (Rod, 1989). Most PCB's in the Hudson River sediment are associated with direct discharges into the Hudson River from manufacturing plants near Fort Edward before 1976

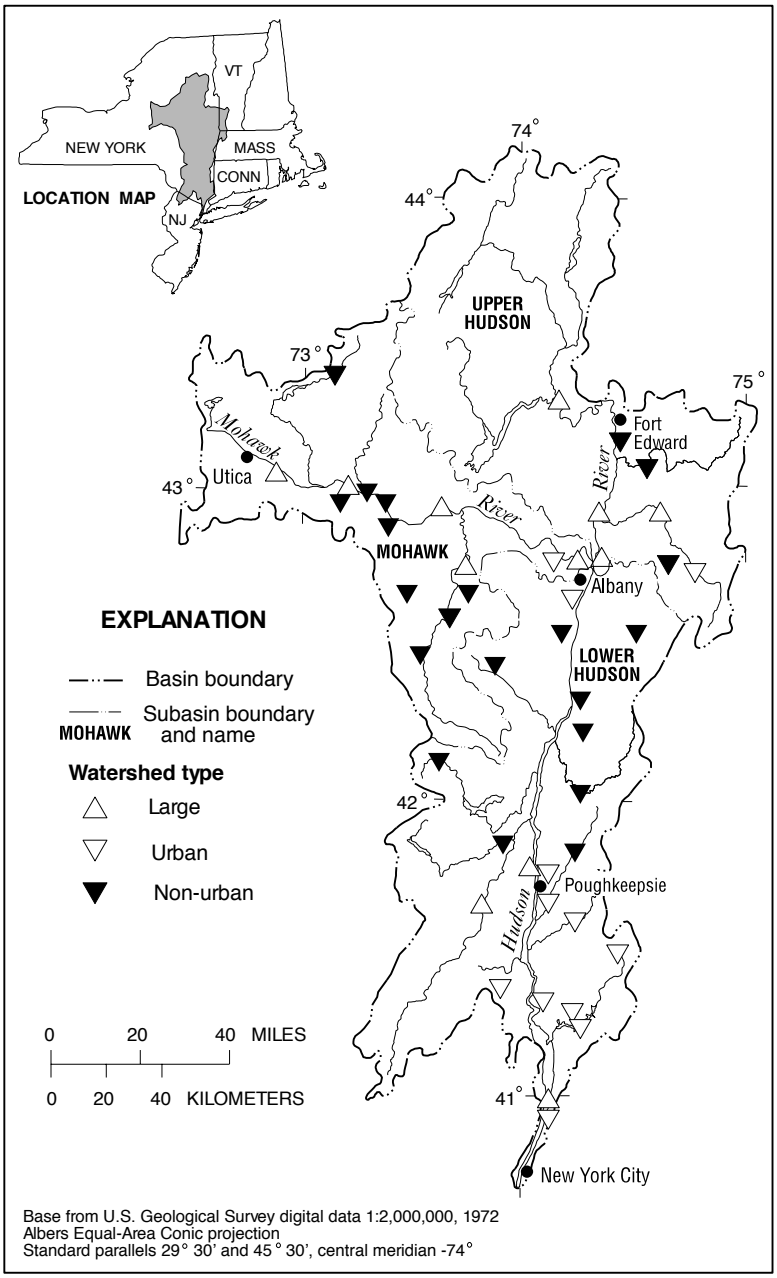

Figure 1. Locations and types of watersheds represented by sites with data on organochlorine-compound concentrations in riverbed sedment in the Hudson River Basin of New York and adjacent states.

(Bopp and others, 1981; Limburg, 1986). Recent studies have suggested another smaller, although significant, point source on the Mohawk River upstream of Utica that discharged before 1993, but the exact location this PCB discharge is unknown (Preddice and others, 1996).

Methods

Streambed sediment was sampled at 45 sites within the Hudson River Basin. Sites were chosen to represent a broad range of land-use conditions and watershed sizes. Each site was categorized in terms of the predominant watershed land use or size (Figure 1; table 1). Land use classification was based in part on population density, which was estimated by overlaying the digitized basin boundaries on digitized coverages of the 1990 U. S. Census tracts; the population of a basin was the sum of populations of all census tracts with centers within the watershed boundary. Land-use classification also was based on digitized land-use maps made from high-altitude photography and satellite imagery obtained in the mid-1970s (US Geological Survey, 1979a,b,c,d;1980a,b). This land-use information was updated through US Bureau of Census data (Hitt, 1994) to provide an indication of urbanization that occurred between the 1970 and 1990 censuses, because many areas, especially those near urban areas, have probably undergone significant land-use changes in this period.

Watersheds above each site were classified into three categories on the basis of size or population density. Watersheds with a population density of more than 60/km2 and a drainage area of less than 1,300 km2 were classified as urban (12 sites); some of these watersheds are highly urbanized (more than 80 percent of watershed area) and include industrial areas, whereas others are mainly residential. Watersheds with a population density of less than 60/km2 and drainage areas of less than 1,300 km2 were classified as nonurban (21 sites); only two of the nonurban are more than 90 percent forested. Watersheds greater than 1,300 km2 were classified as large watersheds (12 sites); many of the sites in these watersheds represent a mixture of urban and agricultural land use.

Samples were collected during late summer low flow conditions in 1993 and 1994 from depositional areas within 100-m (meter) stream reaches by methods described by Shelton and Capel (1994). Samples were collected from the upper 2 to 3 cm (centimeter) of the sediment surface with a Teflon spoon. (Use of trade, product or firm names in this publication if for descriptive purposes only and does not imply endorsement by the U.S. Government). Sediments collected from different parts of the reach were composited and sieved through a 2-mm (millimeter) stainless-steel sieve. Samples were frozen and sent to the USGS

Table 1. Location, and type of watershed represented by sites with data on organochlorine compounds in streambed sediment in the Hudson River Basin, 1993-94. [Site locations are shown shown in fig 1].

Site Name	Watershed Type
Hudson River south of Lake Luzerne NY	Large
Moses Kill near Fort Miller NY	Nonurban
Batten Kill at Battenville NY	Nonurban
Hudson River at Stillwater NY	Large
Hoosic River below Williamstown MA	Urban
Little Hoosic River at Petersburg NY	Nonurban
Hoosic River near Eagle Bridge NY	Large
Hudson River near Waterford NY	Large
Mohawk River near Utica NY	Large
West Canada Creek near Nobleboro NY	Nonurban
Nowadaga Creek at Newville NY	Non urban
Mohawk River near Little Falls NY	Large
Crum Creek at East Creek NY	Nonurban
Caroga Creek at Palatine Church NY	Nonurban
Canajohaire Creek near Canajoharie NY	Nonurban
Mohawk River at Fonda NY	Large
West Kill northwest of North Blenheim NY	Nonurban
Little Schoharie Creek at Middleburgh NY	Nonurban
Fox Creek near Schoharie NY	Nonurban
West Creek at Warnersville NY	Nonurban
Schoharie Creek at Esperance NY	Large
Lisha Kill northwest of Niskayuna NY	Urban
Mohawk River at Cohoes NY	Large
Patroon Creek at Albany NY	Urban
Coeymans Creek near South Bethlehem NY	Nonurban
Kinderhook Creek at East Nassau NY	Nonurban
Kinderhook Creek at Rossman NY	Nonurban
Clavarack Creek at Claverack NY	Nonurban
Tenmile Creek at Medusa NY	Nonurban
Roeliff Jansen Kill at Jackson Corners NY	Nonurban
Esopus Creek at Allaben NY	Nonurban
Rondout Creek at Rosendale NY	Nonurban
Wallkill River at Gardiner NY	Large
Hudson River near Poughkeepsie NY	Large
Fall Kill at Poughkeepsie NY	Urban
Wappinger Creek near Clinton Corners NY	Nonurban
Wappinger Creek near Wappingers Falls NY	Urban
Fishkill Creek near Hopewell Junction NY	Urban
Woodbury Creek near Highland Mills NY	Urban
Peekskill Hollow Cr at Van Cortlandtville NY	Urban
Haviland Hollow Brook near Putnam Lake NY	Urban
Hallocks Mill Brook at Yorktown Heights NY	Urban
Kisco River below Mount Kisco NY	Urban
Hudson River so. of Hastings-on-Hudson NY	Large
Saw Mill River at Yonkers NY	Urban

National Water Quality Laboratory (NWQL), where they were analyzed according to methods described by Foreman and others (1995). In general, organochlorine compounds and PCB's in the samples were analyzed by dual capillary-column gas chromatography with electron capture detection. Dual fused silica capillary columns, 30 m in length with an inner diameter of 0.25 mm, were used for analysis. Total PCB concentration was calculated as the sum of Aroclors 1042, 1254 and 1260. The NWQL also analyzed all samples for organic carbon (OC) content. A complete list of all compounds analyzed for is given in Firda and others (1993, 1994).

Detection limits for these compounds were generally 1 μg/kg (micrograms per kilogram of dry sediment), although the detection limits for p,p'-DDT was 2 μg/kg, and for total PCB was 50 μg/kg. The detection limits for some samples were higher because substances in the matrix caused interference. Detection limits for the compounds detected in bed sediments are given in table 2. Total DDT was defined as the sum of reported DDT residues because the NWQL reported DDT isomers and derivatives, and not total DDT. Total DDT was defined as the sum of all isomers of DDT, DDD, plus DDE. Similarly, total chlordane was defined as the sum of chlordane residues trans-chlordane, cis-chlordane, oxychlordane, trans-nonachlor, and cis-nonachlor. Computations of total DDT and total chlordane included only the actual measured concentrations; if a concentration for any component was reported as less than the detection limit, the concentration was treated as a zero in the total DDT and total chlordane computations. Total DDT or total chlordane was considered detected in a sample if any component was measured above the reporting limit.

Quality-control data provided by the NWQL indicate that, in general, the laboratory methods provided results of acceptable quality, but in a few analyses, substances in the matrix interfered with the ability of the analytical method to accurately detect and quantify compounds. The quality assurance data indicated that the analytical method performed acceptably; method blank samples showed no detections, spike recoveries ranged from 40 to 96 percent, and replicate differences were between 0 and 36 percent. Interference among organic compounds in the sample collected at the Sawmill River site was great enough that the sample was analyzed using negative chemical ionization/mass spectrometry rather than gas chromatography with electron-capture detection. Retention-time shifts and matrix interferences in the sample from the site at Mohawk River near Utica required analysis for trans-chlordane and p,p'-DDE by gas chromatography with mass spectrometry

Because the data were not normally distributed, significance of trends with respect to land use was tested through the nonparametric Mann-Whitney, or

Kruskall-Wallace and Tukey tests. Statistical significance is reported at the 5-percent level.

Table 2. Organochlorine compounds detected in stream-bed sediments in the Hudson River basin, their detection limits and percentage of sites, by land use category, in which each compund was detected.

Compound	Detection limit (ug/kg, dry weight)	Percentage of Sites with detection in specified watershed			
		Total	Urban	Non-Urban	Large
Total DDT	NA	62.2	100	43	58
p,p'-DDE	1	62.2	100	43	58
p,p'-DDT	2	*36.4	*91	14	25
p,p'-DDD	1	33.3	58	14	42
o,p'-DDD	1	4.4	0.0	4.8	8.3
PCB	50	33	50	4.8	67
Total Chlordane	NA	29	75	4.8	33
Trans-chlordane	1	22	50	0	33
cis-chlordane	1	20	58	0	17
Oxychlordane	1	2.2	8.3	0	0
trans-nonachlor	1	24	75	4.8	17
cis-nonachlor	1	4.4	12	0	0

*No from Saw Mill River; thus, these values are based on 11 urban sites rather than 12, and a total of 44 total sites rather than 45.

Results and Discussion

Samples from more than half of the sites sampled had detectable concentrations of some type of organochlorine compound. The most commonly detected organochlorine compounds are the forms of DDT or its isomers and derivatives - p,p'-DDE (dichlorodiphenyldichlorethylene), p,p'-DDT, p,p'-DDD (dichlorodiphenyldichlorethane), and o,p'-DDD - at least one of which was detected in more than 60 percent of the samples (Figure 2). PCB's were detected in a third of the samples, and some form of chlordane (trans-chlordane, cis-chlordane, oxychlordane, trans-nonachlor, or cis-nonachlor) was detected in almost 30 percent of the samples. The frequency of detection of total DDT, PCB, and chlordane varied with land use; total DDT and chlordane were most frequently detected in samples from urban-watershed sites, and PCB most frequently in samples from large-watershed sites.

DDT

DDT was detected in samples from all of the 12 sites in urban watersheds (100 percent), at 7 of the 12 sites in large watersheds (58 percent), and at 8 of the 21 sites in nonurban watersheds (38 percent) (Figure 2); the difference in percent frequency of detections between urban and nonurban watersheds was statistically significant. Two possible explanations for the greater prevalence of DDT residues in urban watersheds than nonurban watersheds are that: (1) DDT was used more extensively in urban watersheds than nonurban watersheds in the last decade that DDT use was allowed, and (2) DDT residues sorb to organic carbon in bottom sediments, and the organic content of stream sediments in urban watersheds is greater than in nonurban watersheds. Concentrations of DDT residues were highest in samples with a high organic carbon content.

Nearly all of the total DDT in samples collected in this study consisted of p,p'-DDE, p,p'-DDD, or p,p'-DDT. Among all samples, about 50 percent of total DDT consisted of p,p'-DDE, about 25 percent consisted of p,p'-DDT, and 20 percent consisted of p,p'-DDD (Figure 3a). However, the proportion of total DDT occurring as p,p'-DDE varied significantly with land use, and ranged from 41 percent in samples from urban watershed sites to 82 percent in samples from nonurban-watershed sites. The proportion of total DDT occurring as p,p'-DDT was highest (40 percent) in samples from urban-watershed sites, and the proportion of total DDT occurring as p,p'-DDD was highest (35 percent) in samples from large-watershed sites.

The proportions of total DDT occurring as p,p'-DDD and p,p'-DDE could indicate site-to-site differences in the patterns of DDT breakdown. Bopp's (1982) results, like those in the present study, showed that ratios of p,p'-DDD

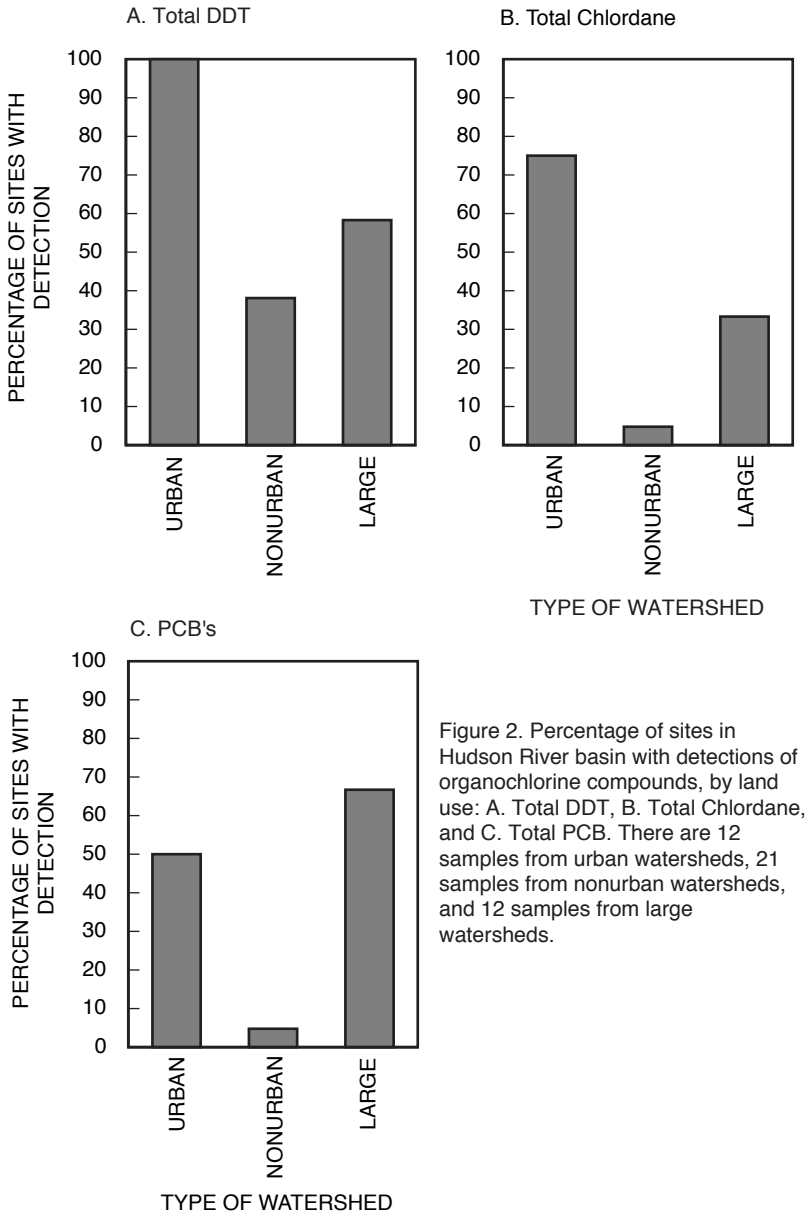

Figure 2. Percentage of sites in Hudson River basin with detections of organochlorine compounds, by land use: A. Total DDT, B. Total Chlordane, and C. Total PCB. There are 12 samples from urban watersheds, 21 samples from nonurban watersheds, and 12 samples from large watersheds.

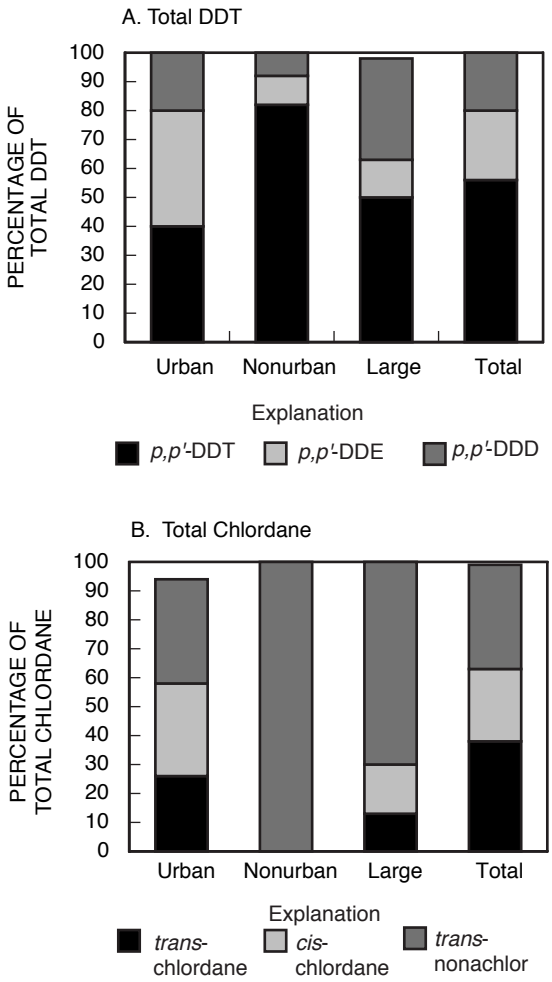

Figure 3. Percentage, by watershed land use for streambed sediment samples in the Hudson River basin, of: A. total DDT as *p,p'*-DDD, *p,p'*-DDT, *p,p'*-DDE (total for large watersheds is less than 100 percent because total DDT also includes *o,p'*-DDD), and B. total chlordane as *trans*-nonachlor, *cis*-chlordane, and *trans*-chlordane (total for uban watershed is less than 100 percent because chlordane also includes oxychlordane).

to p,p'-DDT in bed-sediment cores collected from the mainstem Hudson River before 1980 were generally high. Bopp attributed this pattern to anaerobic conditions, which favor conversion of p,p'-DDT to p,p'-DDE. In contrast, the high ratios of p,p'-DDE to p,p'-DDT in samples from nonurban-watershed sites likely reflect aerobic conditions in the sediments of these watersheds, because aerobic conditions favor the conversion of p,p'-DDT to p,p'-DDE. The high proportion of total DDT occurring as p,p'-DDT in samples from urban watersheds could indicate that the DDT in these watersheds was more recently deposited, or that some unknown factor is slowing the breakdown of DDT to its metabolites.

Median concentrations of p,p'-DDE were highest (5.3 μg/kg) in samples from urban-watershed sites and lower at large-watershed sites (1.25 μg/kg) and nonurban-watershed sites (less than 1 μg/kg) (Figure 4a), even though the smallest ratio of p,p'-DDE to total DDT was at the urban-watershed sites. Relations between watershed type and p,p'-DDT and p,p'-DDD are similar to those between watershed type and p,p'-DDE; the median p,p'-DDD and p,p'-DDT concentration was significantly higher in samples from urban-watershed sites than in samples from the other types of watersheds. The highest concentration of p,p'-DDE (56.6 μg/kg) was collected at the Wallkill River sites, which represents a large watershed with a high population density (105/km2) and a substantial amount of agricultural land use (53 percent). Because this sample also had the highest organic carbon concentration (110 mg/kg), the high p,p'-DDE concentrations at this site cannot be easily attributed to any one factor. These results indicate that, in general, concentrations of DDT residues are highest at urban watershed sites, and that because p,p'-DDE concentrations at large-watershed sites are intermediate between the concentrations at urban watershed sites and those at nonurban watershed sites, urban watersheds could represent the largest current source of DDT inputs into large rivers.

Results from the 1993-94 data differ from results of studies based on data collected before 1990, suggesting that the relation between land use and concentrations of DDT residues could have changed since 1990. Phillips and Hanchar (1996) found that the frequency of total DDT detection, and median total DDT concentrations, for 21 samples collected in the Hudson River Basin during 1970-90 did not differ between urban and nonurban watersheds. Rod (1989) concluded from data collected by Bopp and others (1982), that DDT residues would persist in nonurban watersheds in the Hudson River Basin well into the 1980s, but the 1993-94 data indicate that DDT residues have persisted longer in urban watersheds than in nonurban watersheds. The current pattern of DDT residues in the Hudson River Basin may largely reflect the greater DDT use in urban settings in the 1970's than elsewhere in the basin (Rod, 1989); the changes in frequency of DDT detections between the current and past study could also be related to differences in analytical methods.

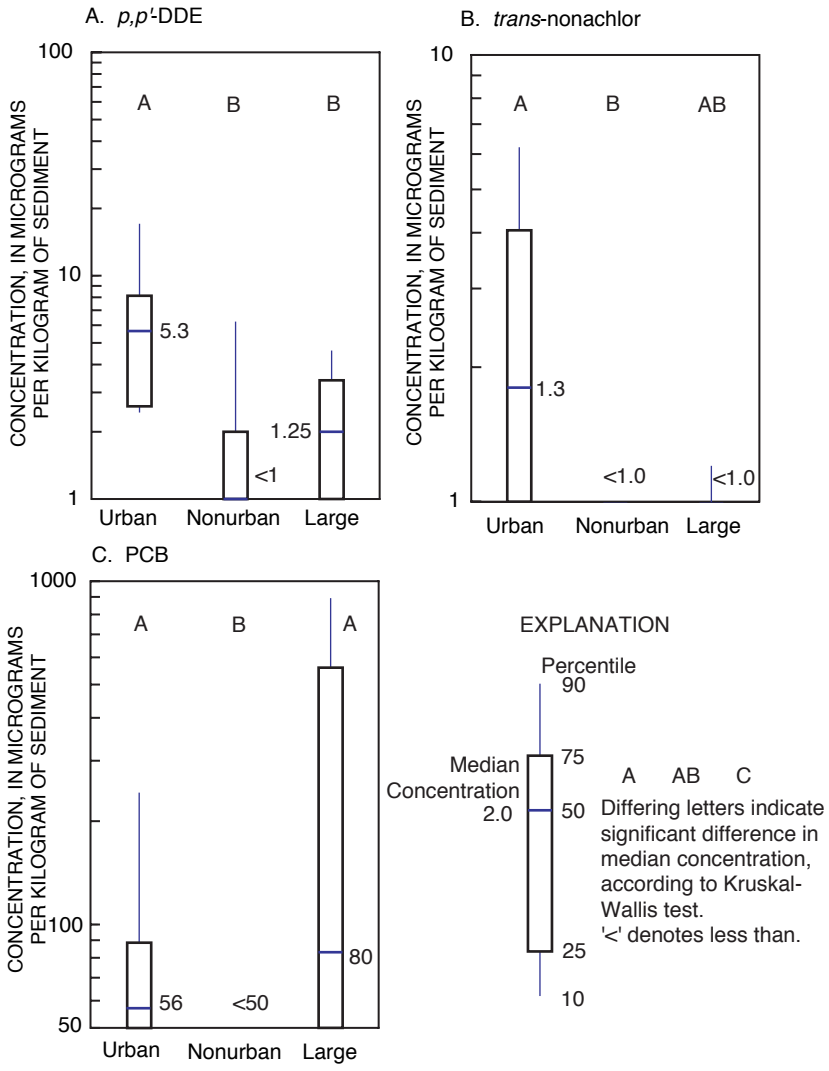

Figure 4. Concentration of A. *p,p'*-DDE, B. *trans*-nonachlor, and C. PCB, in streambed sediment of Hudson River basin, by land use category.

Comparison of carbon-normalized concentrations of total DDT in this study with proposed New York State sediment screening guidelines (New York State Department of Environmental Conservation, 1994) indicate that DDT concentrations at all sites with detectable total DDT concentrations exceed human health bioaccumulation sediment guidelines but do not exceed any other proposed guidelines (table 3). Carbon-normalized p,p'-DDE concentrations for all samples with detectable p,p'-DDE exceed the proposed human health bioaccumulation sediment guideline of 0.01 μg/g OC (micrograms per gram of organic carbon) (Table 3). No samples had carbon-normalized DDT residue concentrations greater than or equal to the proposed guidelines for wildlife bioaccumulation, benthic aquatic life chronic toxicity, or benthic aquatic life acute toxicity.

Chlordane

Total chlordane was detected at 9 of 12 sites (75 percent) in urban watersheds, at 4 of 12 sites (about 30 percent) in large watersheds, and at only 1 of the 21 sites (less than 5 percent) in nonurban watersheds (Figure 2); the difference in frequency of detection between the urban and nonurban watersheds was significant, as expected, because chlordane was mostly used in urban settings (Rod, 1989). The highest concentrations of chlordane residues were in samples with a high organic-carbon concentration.

Nearly all of the total chlordane in the samples collected in this study consisted of trans-nonachlor, cis-chlordane, or trans-chlordane. Of the total chlordane concentrations, about 37 percent was trans- nonachlor, about 36 percent was trans-chlordane, and 21 percent was of cis-chlordane (fig. 3b). Technical chlordane contains more than 40 compounds; trans-nonachlor represents about 7 percent of total chlordane, trans-chlordane 24 percent, and cis-chlordane 19 percent (Eisler, 1990). In the current study, trans-nonachlor constituted from 100 percent at the one site in nonurban watersheds with detectable total chlordane to only 13 percent at sites in large watersheds. cis-chlordane ranged from 32 percent of total chlordane at sites in urban watersheds to 18 percent in sites in nonurban watersheds, and trans-chlordane ranged from 57 percent of the total chlordane at sites in large watersheds to 25 percent at sites in urban watersheds. None of the differences in composition of total chlordane among the watersheds was statistically significant. cis-nonachlor was detected at only two sites - Peekskill Hollow, and Saw Mill River, which are in urban watersheds in the southernmost part of the study area. Oxychlordane, a metabolite of chlordane, was detected only at the Saw Mill River site, which represents the highest population density of any site.

Median concentrations of trans-nonachlor were highest in samples from urban watersheds. The median trans-nonachlor concentrations for all urban

Table 3. Proposed New York State bed sediment criteria for select organochlorine compounds from New York State Department of Environmental Conservation, 1994.
[Concentrations in micrograms per gram of organic carbon].

Compound	Guideline				
	Human health bioac-cumulation	Benthic		Wildlife bioaccumulation	
		Acute toxicity	Chronic toxicity		
DDT, DDD, and DDE*	0.01	1100	1.0	1.0	
Chlordane	0.001	1.4	0.03	0.006	
PCB	0.0008	2760.8	19.3	1.4	

*Criteria for acute and chronic benthic toxicity apply to DDT only.

watershed sites (1.8 μg/kg) is significantly higher than the median for nonurban and large-watershed sites (both less than 1 μg/kg) (Figure 4b), and the highest trans-nonachlor concentration (14 μg/kg) was in the sample from the Sawmill River site. Statistical comparisons of median trans-chlordane and cis-chlordane concentrations among sites with differing land uses yield similar results, indicating that concentrations of total chlordane components are highest in urban watersheds and that urban watersheds, therefore, probably represent the largest current source of total chlordane inputs into large rivers.

Results from the current study are similar to those of previous studies based on bed-sediment data collected before 1990; this similarity suggests that the relation of chlordane residues to land use has not changed since 1990. Phillips and Hanchar (1996) found that detection of total chlordane, and median total chlordane concentrations in 22 samples collected throughout the Hudson River Basin during 1970-90, were significantly higher at sites in urban watersheds than at sites in nonurban watersheds. Rod (1989) concluded, from data collected by Bopp and others (1982), that chlordane residues would not persist as long as total DDT residues in the Hudson River Basin. The current distribution of chlordane residues in Hudson River Basin stream sediments largely reflects the use of chlordane mainly in urban settings (Rod, 1989).

Comparison of carbon-normalized concentrations of total chlordane in this study with proposed New York State sediment screening guidelines (New York State Department of Environmental Conservation, 1994) indicate that concentrations of most sites with detectable total chlordane exceed the human-health bioaccumulation guidelines as well as other proposed guidelines (table 3). Carbon-normalized chlordane concentrations in all but one sample with detectable total chlordane exceed 0.03 μg/g OC and, thus, exceed the proposed human-health bioaccumulation, wildlife bioaccumulation, and benthic aquatic-life chronic-toxicity guidelines. No carbon-normalized total chlordane concentrations exceeded the proposed benthic-aquatic-life acute toxicity guidelines (1.4 μg/g OC), however.

PCB's

PCB's were detected at 8 of 12 sites (67 percent) in large watersheds, at 6 of 12 sites (50 percent) in urban watersheds, and at only one of the 21 sites (less than 5 percent) in nonurban watersheds Figure 2); the difference in frequency of detection between the sites in the urban and nonurban watersheds was significant. This pattern generally corresponds to the locations of known PCB sources. The two major PCB point sources in the Hudson River Basin are on the Hudson and Mohawk Rivers (Bopp and others, 1981; Limburg, 1986; Preddice and others, 1996), which drain 9 of the 12 large-watershed sites.

Median PCB concentrations were highest in samples from large-watershed sites (80 µg/kg) and urban-watershed sites (56 µg/kg); both medians are significantly higher than the median for samples from nonurban-watershed sites (less than 50 µg/kg) (Figure 4c). The highest PCB concentration (1,700 µg/kg) was collected at the Hudson River at Waterford, a large-watershed site located just above the confluence of the Hudson and Mohawk Rivers. All five sites with PCB concentrations above 300 µg/kg are in large watersheds - four on the Hudson River and one on the Mohawk River. These indications that PCB concentrations are highest in large watersheds suggest that, even though urban watersheds also have a high frequency of PCB detections, they are in general unlikely to be a major source of PCB's to large rivers.

Results from the 1993-94 bed-sediment samples are similar to those obtained by previous studies documenting major point sources of PCB's in the Hudson River Basin. PCB contamination of sediment in the Hudson River is largely associated with discharges from a manufacturing plant in Fort Edward before 1976 (Bopp and others, 1981; Limburg, 1986), and PCB concentrations in bed sediments at some locations near Fort Edward exceeded 50,000 µg/kg in 1978 (Tofflemire and Quinn, 1979). Bopp and others (1981) found that during the late 1970s, PCB concentrations in Hudson River bed sediment decreased between Waterford and New York City and concluded that, before 1980, 75 percent of the PCB's in New York Harbor sediment were from the Hudson River above Waterford. These conclusions are consistent with the southward decrease in PCB concentration from the upper Hudson to New York City observed in this study, as would be expected, given that the principal source is in the Upper Hudson basin.

The spatial distribution of PCB concentrations in samples collected during 1993-94 along the Hudson River is consistent with results from many studies that have documented the major PCB source in the upper Hudson River. The original source was an outfall from two facilities for capacitor production near Ft. Edward (Limburg, 1986). In 1973, a dam downstream from the releases was removed, and subsequent stormflows helped transport large amounts of PCB-contaminated sediments downstream over the length of the river (Bopp and others, 1982). Several studies have documented that the vast majority of the PCB's in the Hudson are from these sources (Bopp and others, 1981; Bopp and others, 1982; Turk and Troutman, 1981; Limburg, 1986). No PCB's were detected in the sediment sample collected upstream from Ft. Edward during the present study (at Lake Luzerne), but each of the next two sites, which are below Ft. Edward (Stillwater and Waterford) had PCB concentrations greater than 300 µg/kg (Figure 5a). Sediment samples collected in this study indicated that PCB concentration were highest at Waterford (1,700 µg/kg) and declined steadily downstream (to 790 µg/kg and 390 µg/kg at Poughkeepsie and Hastings-on-Hudson). This pattern is consistent with the conclusions of Bopp and others

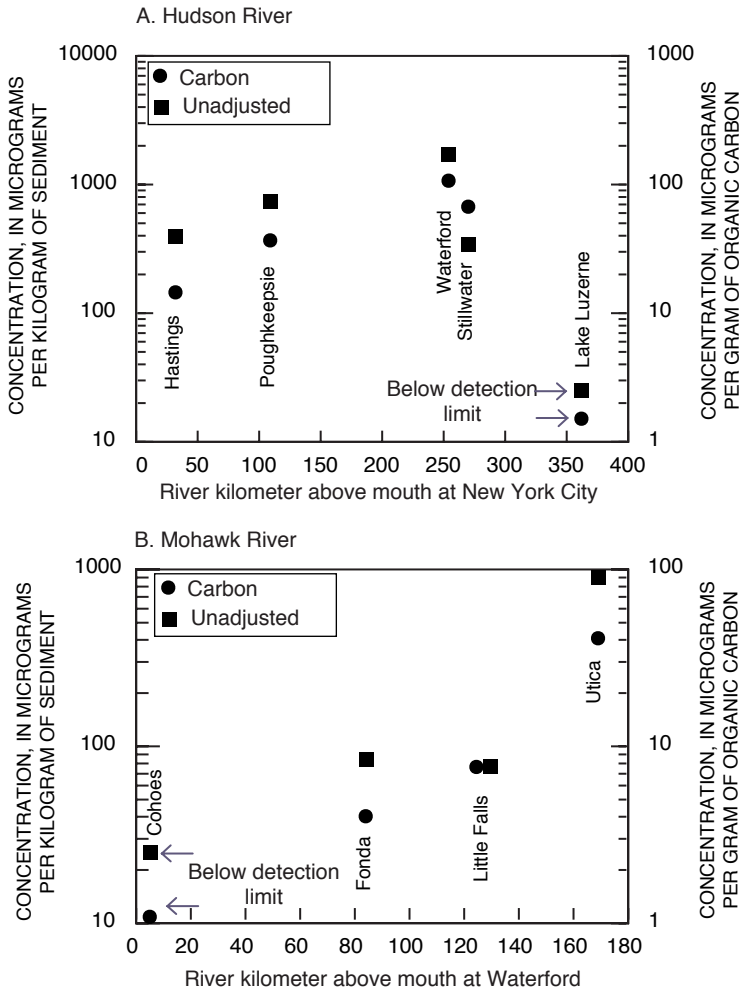

Figure 5. Concentration of PCB's in streambed sediments of Hudson River basin, by river kilometer: A. Hudson River, B. Mohawk River.

(1981) that PCB concentrations above the tidal reach of the Hudson River (which extends north to just below Waterford) are generally higher than those within tidal reaches of the river. Carbon-normalized concentrations of PCB's from the current data indicate a general pattern similar to that of the non-normalized data, although the difference between the carbon-normalized PCB concentrations at Waterford (110 μg/g OC) and Stillwater (67 μg/g OC) are less than the differences in noncarbon normalized PCB concentrations.

The spatial patterns of PCB concentrations in Mohawk River sediments are also consistent with a NYSDEC study that indicates a single major source of PCB's in the Mohawk River. Preddice and others (1996) concluded that the largest source of PCB's in the Mohawk River was near Utica. Similarly, the current USGS study found that the PCB concentrations were highest at Utica (890 μg/kg), and decreased downriver to between 70 and 90 μg/kg at the Little Falls and Fonda sites, and to less than 50 μg/kg at the Cohoes site, the mouth of the Mohawk River. This decreasing trend is even more striking in the carbon-normalized PCB concentrations, which decrease downstream from 41 μg/g OC near Utica to 7.6 μg/g and 4 μg/g OC at the Little Falls and Fonda Sites, and, finally, to less than 2 μg/g OC at the mouth of the Mohawk River. Together these data support previous evidence of a major source of PCB's near Utica and dilution downstream. The low PCB concentration (less than the detection limit) in bed sediment at the mouth of the Mohawk River indicates that the Mohawk River probably contributes little PCB's to the Hudson River.

Comparison of carbon-normalized concentrations of PCB with proposed New York State sediment screening guidelines (New York State Department of Environmental Conservation, 1994) indicates that concentrations of PCB's at some sites exceed some of the proposed guidelines. All the carbon-adjusted concentrations of 15 samples with detectable PCB concentrations exceeded the human-health bioaccumulation guideline of 0.0008 μg/g OC (Table 3), and all but two of the 15 samples with detectable concentrations of PCB exceeded the wildlife bioaccumulation sediment guideline of 1.4 μg/g OC. Four samples exceeded the benthic aquatic-life chronic-toxicity guideline of 19.3 μg/g OC.

Conclusions

Analyses of river-bed sediment samples at 45 sites representing a variety of watershed sizes and land uses in the Hudson River Basin indicate that residues of DDT, PCB's, and chlordane are detectable in many of the watersheds, even though use of these compounds has been banned for 10 years or more. Detection limits for most constituents were 1 μg/kg, although total PCB's had a detection limit of 50 μg/kg. The most frequently detected compounds (detected at 20 percent or more of the sites) included p,p'-DDE, p,p'-DDT, p,p'-DDD,

PCB, trans-nonachlor, trans-chlordane, and cis-chlordane. Some form of DDT residue was detected at about 60 percent of the sites, and some chlordane residue was detected at about 30 percent of the sites. All samples with detectable residues of DDT, or chlordane, or detectable PCB concentrations exceed the proposed New York State human health bioaccumulation sediment guideline for streambed sediment, and all samples with detectable chlordane residuals, and 13 of the 15 samples with detectable PCB concentrations, exceed the proposed New York State wildlife bioaccumulation guideline.

Results from this study indicate that frequency of detection of total DDT and chlordane, and concentrations of p,p'-DDE and trans-nonachlor in bed sediments of the Hudson River Basin, are greater in urban watersheds than in nonurban watersheds. Thus, although DDT was used in a variety of settings in the Hudson River Basin before it was banned in the 1970s, the residues are found mostly in urban settings. The current distribution of DDT residues in the Hudson River Basin seems to reflect the fact that most of the DDT use after 1960 in the basin was in urban settings (Rod, 1989). Chlordane, which was used primarily in urban and residential settings (Rod, 1989) was found primarily in urban settings. The high detection of DDT residues and chlordane residues at urban-watershed sites may also indicate that such watersheds constitute the major source of DDT and chlordane residues that enter large rivers.

In contrast to DDT and chlordane, patterns of PCB detection and concentration in bed sediments of the Hudson and Mohawk Rivers appear to be related to a few point sources in each river basin, and PCB concentrations in these rivers generally decrease downstream of these sources. In the Hudson River, PCB concentrations are highest in bed sediments below Ft. Edward, and in the Mohawk River, PCB concentrations in bed sediments are highest near Utica. These findings are consistent with previous studies on PCB's in the Hudson and Mohawk Rivers (Bopp and others, 1981; Bopp and others, 1982; Turk and Troutman, 1981; Limburg, 1986).

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