



Composition, distribution, and potential toxicity of organochlorine mixtures in bed sediments of streams

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ABSTRACT

Mixtures of organochlorine compounds have the potential for additive or interactive toxicity to organisms exposed in the stream. This study uses a variety of methods to identify mixtures and a modified concentration-addition approach to estimate their potential toxicity at 845 stream sites across the United States sampled between 1992 and 2001 for organochlorine pesticides and polychlorinated biphenyls (PCBs) in bed sediment. Principal-component (PC) analysis identified five PCs that account for 77% of the total variance in 14 organochlorine compounds in the original dataset. The five PCs represent: (1) chlordane-related compounds and dieldrin; (2) *p,p'*-DDT and its degradates; (3) *o,p'*-DDT and its degradates; (4) the pesticide degradates oxychlordane and heptachlor epoxide; and (5) PCBs. The PC analysis grouped compounds that have similar chemical structure (such as parent compound and degradate), common origin (in the same technical pesticide mixture), and/or similar relation of concentrations to land use. For example, the highest concentrations of chlordane compounds and dieldrin occurred at urban sites, reflecting past use of parent pesticides for termite control. Two approaches to characterizing mixtures—PC-based mixtures and unique mixtures—were applied to all 299 samples with a detection of two or more organochlorine compounds. PC-based mixtures are defined by the presence (in the sample) of one or more compounds associated with that PC. Unique mixtures are defined as a specific combination of two or more compounds detected in a sample, regardless of how many other compounds were also detected in that sample. The simplest PC-based mixtures (containing compounds from 1 or 2 PCs) commonly occurred in a variety of land use settings. Complex mixtures (containing compounds from 3 or more PCs) were most common in samples from urban and mixed/urban sites, especially in the Northeast, reflecting high concentrations of multiple chlordane, dieldrin, DDT-related compounds, and/or PCBs. The most commonly occurring unique mixture (*p,p'*-DDE, *p,p'*-DDD) occurred in both simple and complex PC-based mixtures, and at both urban and agricultural sites. Mean Probable Effect Concentration Quotients (PEC-Q) values, which estimate the potential toxicity of organochlorine contaminant mixtures, were highest for complex mixtures. Mean PEC-Q values were highest for urban sites in the Northeast, followed by mixed/urban sites in the Northeast and agricultural sites in cotton growing areas. These results demonstrate that the PEC-Q approach can be used in combination with PC-based and unique mixture analyses to relate potential aquatic toxicity of contaminant mixtures to mixture complexity, land use, and other surrogates for contaminant sources.

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1. Introduction

Organochlorine pesticides and related compounds, including degradation products, manufacturing by-products, and polychlorinated biphenyls (PCBs), have entered streams in many parts of the world for more than a half century and have been found to accumulate and persist in bed sediments (Cesar et al., 2007; Gilliom et al., 2006; Kim et al., 2008; Vigano et al., 2003; Vighi et al., 2003). Although no longer used in the U.S., these compounds still occur frequently in streams as

mixtures of multiple contaminants that may pose a threat to aquatic life (Gilliom et al., 2006). Organochlorine compounds such as DDE and DDT have been identified as hormonally active, and may have additive or interactive effects by eliciting both androgenic and estrogenic responses in vertebrates (Foster, 1995; Li et al., 2008). Even for invertebrates, which are organisms of particular concern in bed sediments, organochlorine compounds such as DDT, chlordane, dieldrin, and PCBs have been implicated in causing endocrine disruption (Depledge and Billingham, 1999; Oetken et al., 2004) and/or immunotoxicity (Galloway and Depledge, 2001). Because of their continued occurrence at levels of potential concern, the composition, geographic distribution, and potential environmental significance of such mixtures are important to characterize and understand.

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Traditionally, preliminary risk assessment is performed by comparing concentrations of individual chemicals with water-quality benchmarks, or other measures of toxicity, that are specific to an individual chemical. One limitation of this approach is that it does not address potential additive or interactive effects of multiple contaminants that co-occur. To more fully evaluate the biological significance of contaminant mixtures in stream sediment, it is important to characterize the composition of environmental mixtures in relation to their potential toxicity, frequency of occurrence, and geographic distribution. Assessment of mixtures is hampered, however, by the large potential number of possible unique mixtures. Squillace et al. (2002) defined a unique mixture as a specific combination of two or more given compounds detected in a sample, regardless of how many other compounds were also detected in that sample. For example, a hypothetical mixture of 20 organic compounds contains 190 unique pairs of compounds and more than one million possible combinations in terms of pairs, triplets, etc. (Lydy et al., 2004). Gilliom et al. (2006) reported that the most common unique mixtures of organochlorine pesticides in fish were dominated by relatively few pesticides and their degradates—DDE, DDD, various chlordane compounds, and dieldrin—all of which accumulate in bed sediment as well as in fish. Fish from streams in urban areas had a greater number and increased frequency of complex unique mixtures compared to fish collected from other land use settings.

The vast number of possible combinations has led some researchers to restrict the number of compounds included in mixture assessment. One approach consists of prioritizing compounds within a mixture on the basis of toxicity, such as by excluding the least toxic compounds present (Belden et al., 2007a). Other approaches entail identifying mixtures associated with specific crops or land uses, such as corn and soybeans in the United States (Belden et al., 2007b) or maize in Europe (Finizio et al., 2005), or limiting the target compounds within a complex mixture to those with the highest concentrations (Feron et al., 1998; Tierney et al., 2008). One drawback to limiting the compounds included in a mixture analysis on the basis of either concentration or toxicity is that both factors are relevant to potential hazard; low concentrations of a chemical may be important if that chemical is highly toxic, and chemicals with low-to-moderate toxicity may be important if they are widely detected or present at high enough concentrations.

Another approach to mixture characterization is to use multivariate regression techniques, which decrease complexity in the dataset without resorting to arbitrary exclusion of compounds. Principal-component (PC) analysis, the approach applied in the present study, uses a correlation matrix to define a smaller set of computed values that reflect underlying shared variance in variables present in the original data set (Davis, 1986). Previous studies have used PC analysis to understand mixtures of hydrophobic contaminants in a variety of environmental media at the local or regional scale. For example, PC analysis was used to describe mixtures of organochlorine pesticides, PCBs, and polybrominated diphenyl ethers in maternal adipose tissue in Singapore (Tan et al., 2008); metals, PCBs, and polynuclear aromatic hydrocarbons (PAH) in bottom sediment in Spain and Brazil (Cesar et al., 2007) and in bottom sediment in the Po River in Italy (Vigano et al., 2003); organochlorine pesticides in bottom sediment in Gwangyang Bay, South Korea (Kim et al., 2008); and in source apportionment of PAHs in suspended sediment in Ontario, Canada streams (Sofowote et al., 2008). The particular value of PC analysis is its ability to group contaminants by common source, or associated environmental parameters or effects.

1.1. Estimating toxicity of mixtures

Many studies have measured the toxicity of particular mixtures in water, sediment, or other media (for example, see reviews by Deneer, 2000; Altenburger et al., 2003; Belden et al., 2007a; Cedergreen et al., 2008). The Agency for Toxic Substances and Disease Registry (ATSDR) is developing “Interaction Profiles” for chemical mixtures of concern to public health, such as persistent chemicals found in fish (chlorinated

dibenzo-*p*-dioxins, PCBs, *p,p'*-DDE, methyl mercury, hexachlorobenzene; Agency for Toxic Substances and Disease Registry, 2004). Despite the growing body of literature on chemical mixtures, toxicity data on most of the mixtures that occur in the environment are not available. In the absence of toxicity data on a particular mixture, combining toxicity data for individual compounds to estimate the toxicity of the mixture may provide a partial solution (Teuschler, 2007).

One approach to preliminary risk assessment that has been used is the concentration-addition (CA) model, in which the effect of co-occurring compounds is assumed to be additive, without interaction, such that the effect of the mixture is represented by the sum of the toxicity-weighted concentrations of each compound in the mixture. Although the assumptions of CA may theoretically be invalid for mixtures of chemicals with dissimilar modes of action (Deneer, 2000), several studies indicate that CA provides a reasonable approximation of the total effect (within a factor of two or three), even for complex mixtures of compounds with multiple modes of action (Deneer 2000; Belden et al., 2007a; Cedergreen et al., 2008). A modified CA approach for assessment of contaminant-mixture toxicity in bed sediment is the mean Probable Effect Concentration Quotient (PEC-Q) method developed by MacDonald et al. (2000). One commonly used method for assessing mixtures in bed sediment is a modified CA approach—this is the mean Probable Effect Concentration Quotient (PEC-Q) method developed by MacDonald et al. (2000). This method (used in the present study) weights the concentrations of individual contaminants in sediment by their respective Probable Effect Concentrations (PEC), which are consensus-based sediment benchmarks for individual contaminants. PECs are empirically based benchmarks designed to predict the presence of toxicity in field-collected sediments; they are defined as threshold concentrations above which adverse effects are likely to frequently occur (MacDonald et al., 2000). The mean PEC-Q method calls for summing the PEC-weighted concentrations for all contaminants (or contaminant groups) in a sample, and then calculating the mean to indicate the potential toxicity of the sample. The mean PEC-Q method is like a CA method in that concentrations are weighted by relative measures of toxicity and then summed, thus assuming that the contaminants exert some form of joint toxic action (Ingersoll et al., 2001). The PEC-Q method is unlike a CA method in that the sum of toxicity-weighted concentrations is then divided by the number of contaminants measured. Thus, it indicates average toxicity of contaminants in the mixture, rather than summed toxicity—however, this feature of the method permits comparison of sites or samples with different numbers of contaminants measured. The authors conducted validation tests of the mean PEC-Q method, in which mean PEC-Q values greater than 0.5 were associated with a high incidence of toxicity (MacDonald et al., 2000; Ingersoll et al., 2001). The mean PEC-Q approach, which is used in the present study, is discussed further in Section 2.5.

2. Methods

2.1. Purpose and approach

The present study applies two different approaches to identify and characterize the composition of mixtures of organochlorine pesticides and PCBs in bed sediment sampled from streams throughout the United States. Mixtures, which are defined only for samples with two or more organochlorine compounds detected, are evaluated for potential toxicity using the mean PEC-Q approach. The focus of this paper is on organochlorine compounds to provide a manageable prototype of procedures for characterizing mixtures in sediment, and also to correspond with previous analysis of unique mixtures of organochlorine pesticides in fish (Gilliom et al., 2006). In ongoing work, procedures from the present analysis are being applied to a more extensive set of sediment contaminants.

The objectives of this paper are (1) to use PC analysis to evaluate co-occurring organochlorine compounds in bed-sediment samples and their patterns of occurrence in relation to land use and contaminant

sources; (2) to evaluate the occurrence of unique mixtures of organochlorine compounds in relation to mixtures characterized by the PC analysis; and (3) to evaluate the potential toxicity of these mixtures to aquatic organisms through a PEC-Q analysis.

2.2. Sediment sampling and analysis

Bed-sediment samples were initially collected from 967 stream sites during 1992–2001 using methods described by Shelton and Capel (1994). These stream sites were selected to represent specific land-use and environmental settings, so were located either in watersheds with specific, relatively homogenous land use and physiographic features, or in large, mixed land-use watersheds (see Appendix A in the online Supplementary material). At each site, fine-grained surficial bed sediment (sieved to <2 mm) was collected from multiple depositional areas within a stream reach on a single date, usually during low-flow conditions, and combined into a single composite sample for chemical analyses for organochlorine pesticides and total PCBs using analytical methods described by Foreman et al. (1995). Some sediment samples were eliminated from analysis in the present study because they had data missing (not analyzed) for one or more of the target analytes, or if the reporting level of an analyte was raised by more than three times the normal level (shown in Table 1) due to analytical interference (raised reporting levels occurred in less than 4% of samples). Of the 967 sites initially sampled, 845 met the criteria listed above and were included in the results presented in this paper.

The 14 organochlorine compounds included in the analysis are shown in Table 1, with their minimum reporting levels and detection frequencies. (A complete list of analytes measured in sediment and a detailed description of individual stream sampling sites can be found online—see Appendices 1 and 5, respectively, at US Geological Survey, 2006). These 14 compounds are the most frequently detected organochlorine compounds in the national data set, as well as select compounds (*o,p'*-DDT, *o,p'*-DDE, oxychlordane, and heptachlor epoxide) that were less frequently detected but are chemically related to frequently detected compounds. Except for total PCBs, every other compound listed in Table 1 is either a pesticide, a pesticide degradate, or a component of a technical pesticide mixture (such as technical chlordane or DDT). PCBs are determined as Aroclor equivalents (the sum of Aroclors 1242, 1254, and 1260; Foreman et al., 1995). PCBs were used primarily as an insulating fluid in electrical equipment such as transformers and capacitors (U.S. Environmental Protection Agency, 1979), although they had other uses (such as a component of waste oil applied to dust control on roads). Reagent wet

spikes indicated that average recoveries for the target analytes were within control limits for the study period (1992–2001), as were recoveries for certified reference materials. Surrogate recoveries ranged from 71 to 80%, and mean relative percent differences for field replicates ranged from 46 to 146%. Further details on sediment sampling and analysis are given in the online Supplementary material, Appendix B.

2.3. Statistical analysis

The present study used nonparametric statistical methods because the contaminant concentration data had non-normal distributions. Differences in organochlorine concentrations and other attributes among sites representing different land uses were tested using nonparametric tests of association, including Kruskal–Wallis and Tukey tests. For most computational tests, concentrations reported as not detected (ND) were set to a value of 0.1 µg/kg, which is below the lowest reported concentration for all target analytes. (Some of the concentrations reported as detections were below the reporting levels given in Table 1.) Because the statistical analysis uses ranked data, the use of a value below all detected values (0.1 µg/kg) for all NDs had no effect on the analysis results; they are treated as tied values at the lowest level. All statistical analyses were performed using SAS version 9.1 for Windows.

A PC analysis was used to transform the original data set into a smaller set of principal components. Each component represents a new set of orthogonal variables that are a linear combination of the original variables, and each successive component includes a decreasing amount of variability in the original data set. The PC analysis was performed on a correlation matrix, and ranked variables were substituted for concentrations due to the skewed concentration data. A varimax rotation of the principal components was used to highlight the differences among the resulting components, and is frequently used in PC analysis to aid in interpretation of the resulting variables (Davis, 1986; Sofowote et al., 2008). Each of the original 14 variables has a loading for each component, such that loadings reflect the correlation (or shared variance) of the compound with that component. Loadings of 0.71 or more indicate that half of the variance in a variable ($0.71^2 = 0.50$) is associated with that component, and this value was used to indicate high loadings of variables on a PC. Loadings of 0.4 to 0.7 were considered moderate.

2.4. Classification of sample sites by land use and other variables

Each site was initially classified into one of four land-use classes—agricultural, urban, undeveloped, and mixed—based on the percentage

Table 1
Compounds included in statistical analysis of bed-sediment concentrations, with CAS number, minimum reporting level, and percentage of total samples ($n = 845$) in which each compound was detected.

Compound	Type of compound	CAS number	Minimum reporting level (µg/kg)	Percentage of samples with a detection
<i>Chlordane compounds</i>				
<i>cis</i> -Chlordane	Insecticide	5103-71-9	1	15.3
<i>trans</i> -Chlordane	Insecticide	5103-74-2	1	16.4
<i>cis</i> -Nonachlor	By-product in technical chlordane	5103-73-1	1	7.9
<i>trans</i> -Nonachlor	By-product in technical chlordane	39765-80-5	1	16.4
Oxychlordane	Degradate (chlordane)	27304-13-8	1	1.2
<i>DDT compounds</i>				
<i>o,p'</i> -DDD	Degradate of <i>o,p'</i> -DDT	53-19-0	1	7.5
<i>p,p'</i> -DDD	Insecticide, degradate of <i>p,p'</i> -DDT	72-45-8	1	26.0
<i>o,p'</i> -DDE	Degradate of <i>o,p'</i> -DDT	3424-82-6	1	1.5
<i>p,p'</i> -DDE	Degradate of <i>p,p'</i> -DDT	72-45-8	1	40.6
<i>o,p'</i> -DDT	By-product in technical DDT	789-02-6	2	3.2
<i>p,p'</i> -DDT	Insecticide	50-29-3	2	18.5
<i>Other compounds</i>				
Dieldrin	Insecticide; degradate of insecticide aldrin	60-57-1	1	15.4
Heptachlor epoxide	Degradate of insecticide heptachlor	1024-57-3	1	1.9
PCB	Industrial compound	1336-36-3	50	9.5

[CAS, Chemical Abstracts Service Registry number for compound. µg/kg, micrograms per kilogram (dry weight). All samples were collected during 1992–2001].

of watershed area that consisted of agricultural, urban, and undeveloped land (Table 2). Details on the classification methods are given in Appendix A in the Supplementary material. The “mixed” land-use category was further divided into two subcategories—mixed/urban and mixed/agricultural—according to the percentage of urban land within the watershed (Table 2).

Four additional factors were used to evaluate PC scores and pesticide-occurrence data: these are geographic region, major crop type, termite-urban score, and population density. The derivation of these factors is described in Appendix A in the Supplementary material. The termite-urban score was computed for urban sites as a surrogate variable to represent past pesticide use in termite control (Nowell et al., 2006), based on the assumption that termiticide use corresponded to termite occurrence in urban areas. This score is derived from (a) urban land use in the USGS's 1970s land-use and land-cover data set (which is in Geographic Information Retrieval and Analysis System format and is based on aerial photography taken from the 1970s through the mid-1980s; U.S. Geological Survey, 1998, as enhanced by Price et al., 2007), and (b) the national distribution of subterranean termite density (Beal et al., 1994). Regional analysis was based on U.S. Department of Agriculture (USDA) farm production regions (Eichers et al., 1970). The ten USDA regions were aggregated into four regions (Northeast, Southeast, West Coast, and Other) because relatively few sampling sites were located in each of the mid-continent regions.

2.5. Characterization of mixtures

All of the samples with detections of two or more organochlorine compounds were classified in two different ways, as PC-based mixtures and as unique mixtures. PC-based mixtures are defined as combinations of one to five PC descriptors (CDI, PPD, OPD, OXH and PCB). Each PC descriptor denotes the presence (in the sample) of one or more compounds associated with that PC, as summarized in Table 3 and described further in Section 3.1. For example, a sample whose mixture name includes CDI contains one or more of the five compounds associated with the PC descriptor CDI (*cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, and dieldrin; see Table 3). A PC-based mixture name can consist of a single descriptor (such as CDI), which indicates the presence of two or more compounds associated with that PC descriptor, or the name can contain multiple descriptors (such as CDI/PPD), each indicating the presence of one or more compounds associated with each specified PC descriptor. A single PC-based mixture name can reflect various combinations of detected compounds. For example, both sample A, containing *cis*-chlordane and dieldrin (compounds included in the CDI descriptor) and *p,p'*-DDD (a compound included in the PPD descriptor), and sample B, containing *cis*-chlordane, *trans*-nonachlor, and dieldrin (compounds in the CDI descriptor) and *p,p'*-DDE (a compound in the PPD descriptor) would be classified as CDI/PPD mixtures.

Samples with two or more organochlorine compounds detected were also classified as containing one or more *unique* mixtures—defined as a specific combination of two or more compounds detected in a sample, regardless of how many other compounds were also

Table 2

Criteria for sampling-site classification according to dominant land uses within a drainage basin.

Land-use classification	Watershed land-use criteria
Agricultural	>50% agricultural land, <5% urban land
Urban	>25% urban land, ≤25% agricultural land
Undeveloped	<5% urban land, ≤25% agricultural land
Mixed/urban	Watersheds not classified as agricultural, urban, or undeveloped, but with ≥5% urban land
Mixed/agricultural	Watersheds not classified as agricultural, urban, or undeveloped, but with <5% urban land

[Modified from Gilliom et al., 2006].

Table 3

Organochlorine compounds represented by principal-component (PC) descriptors determined from PC analysis.

PC descriptor	Mixture constituents
CDI	<i>cis</i> -Chlordane, <i>trans</i> -chlordane, <i>cis</i> -nonachlor, <i>trans</i> -nonachlor, dieldrin
PPD	<i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT
OPD	<i>o,p'</i> -DDD, <i>o,p'</i> -DDE, <i>o,p'</i> -DDT
OXH	Oxychlordane, heptachlor epoxide
PCB	Total PCB

detected in that sample (Squillace et al., 2002; Gilliom et al., 2006). This approach focuses on the occurrence of specific combinations of individual contaminants within a sample, rather than on the total number of target contaminants within that sample. A single sample can contain many unique mixtures; for example, a sample containing compounds A, B, and C contains four unique mixtures—AB, AC, BC, and ABC, whereas a sample with five compounds contains 26 unique mixtures. Unique mixtures are important to evaluate because some specific combinations of contaminants may have greater effects when occurring together.

2.6. Calculation of PEC-Q values

Potential toxicity of organochlorine mixtures to aquatic organisms was assessed using a modified CA approach that utilizes consensus-based sediment-quality guidelines developed by MacDonald et al. (2000)—specifically, the PEC, which defines a concentration of sediment-associated contaminants above which adverse effects on aquatic organisms are expected to occur more often than not. The contaminants used in the MacDonald et al. (2000) study were individual organochlorine pesticides, PAHs, metals, and total PCBs. Although PECs apply to individual constituents, they can be combined to indicate the potential toxicity of mixtures in a sample, expressed as the mean PEC-Q. For each compound with a PEC value, the PEC-Q equals the ratio of the measured concentration of that compound to its PEC. The mean PEC-Q for a sample is equal to the mean of the PEC-Q values for all compounds in the sample. The mean PEC-Q procedure first weights the concentration of each compound detected by its PEC; sums PEC values for all compounds in the mixture, assuming additive joint toxic action; then takes the mean so that samples with different numbers of compounds analyzed can be compared. In a variation of the method, Ingersoll et al. (2001) computed a mean PEC-Q that equally weights the contribution of the major classes of contaminants being studied (metals, PCBs, and PAHs), by first computing the PEC-Q (or mean PEC-Q) for each class, then averaging the three quotients. The mean PEC-Q is a measure of potential toxicity for the whole mixture. PEC-Qs are calculated values, and do not represent measured toxicity, although mean PEC-Q values greater than 0.5 were associated with a high likelihood of measured toxicity in published studies evaluated by the authors (MacDonald et al., 2000; Ingersoll et al., 2001).

The present analysis corresponds to the PEC-Q procedure described by MacDonald et al. (2000), except for three modifications that were made to fit the scope and methods of the present study:

- (1) *Target compounds*: MacDonald and colleagues computed the mean PEC-Q for metals, PAHs, PCBs, and sometimes DDE (MacDonald et al., 2000; Ingersoll et al., 2001). The present study, however, computes the mean PEC-Q for PCBs, DDE, dieldrin, and total chlordane. With DDE to represent the DDT family, these four compounds represent the organochlorine contaminants most frequently detected in the bed-sediment samples in the NAWQA Program. Total chlordane was defined as the sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane concentrations, and DDE as the sum of *o,p'*- and *p,p'*-DDE concentrations.

Table 4
Component loadings for compounds included in PC analysis of streambed-sediment data.

Compound	Principal component					Percentage of total variance included in five components
	CDI	PPD	OPD	OXH	PCB	
<i>cis</i> -Chlordane	0.90	0.21	0.061	0.095	0.21	91
<i>trans</i> -Chlordane	0.88	0.22	0.058	0.084	0.16	87
<i>cis</i> -Nonachlor	0.79	0.084	0.15	0.27	-0.058	74
<i>trans</i> -Nonachlor	0.88	0.23	0.045	0.085	0.21	88
<i>p,p'</i> -DDD	0.25	0.84	0.15	0.070	0.15	81
<i>p,p'</i> -DDE	0.19	0.85	0.087	0.035	0.12	79
<i>p,p'</i> -DDT	0.23	0.77	0.25	0.12	0.049	73
<i>o,p'</i> -DDD	0.26	0.45	0.60	0.10	-0.083	65
<i>o,p'</i> -DDE	0.089	0.010	0.82	0.077	0.32	80
<i>o,p'</i> -DDT	0.032	0.33	0.73	0.056	-0.25	71
Dieldrin	0.55	0.28	0.16	0.30	-0.093	51
Oxychlordane	0.12	0.13	-0.038	0.86	0.17	80
Heptachlor epoxide	0.27	0.017	0.10	0.83	0.0055	77
Polychlorinated biphenyls (total)	0.25	0.23	0.026	0.16	0.83	83
Percentage of total variance included in component	27	19	12	12	7.5	-

[Abbreviations for principal components are described in Table 3. Dark shading denotes loadings >0.7 (high loadings), light shading denotes moderate loadings (0.4–0.7)]. Compounds with high or moderate loadings are considered to be associated with this PC.

- (2) *Restrictions on PEC predictive ability*: In summing PEC-Q values, MacDonald et al. (2000) included only those contaminants with “reliable” PECs (defined as correctly predicting toxicity in more than 75% of sediment samples in a validation data set that contained a minimum of 20 samples). Of the compounds addressed in the present study, only DDE and total PCB meet MacDonald’s criteria for a “reliable” PEC. Total chlordane and dieldrin also were included in the present study because (1) they were frequently detected in stream sediment samples and (2) their PECs came close to meeting MacDonald’s criteria for reliability. In MacDonald’s evaluation, the total chlordane PEC correctly predicted toxicity in 73% of 37 samples, and the dieldrin PEC correctly predicted toxicity in 100% of only 10 samples. Chlordane and/or dieldrin also were included in PEC-Q calculations for other studies in which chlordane (Van Metre and Mahler, 2004) or chlordane and dieldrin (Tao et al., submitted for publication) were considered major contaminants.
- (3) *Threshold of likely toxicity*: MacDonald et al. (2000) determined an empirical threshold (mean PEC-Q > 0.5) above which toxicity is likely by comparing observed toxicity for metals, PAHs, PCBs, and DDE in field studies with the mean PEC-Q values computed for these compounds. This 0.5 threshold was used in the present study as an indicator of likely toxicity despite the different contaminants incorporated in our mean PEC-Q (PCBs, DDE, chlordane, and dieldrin) because other studies have confirmed an increased incidence of toxicity at mean PEC-Q values greater than 0.5 for various combinations of metals, PAHs, and PCBs (Ingersoll et al., 2001) and for organochlorine pesticides (DDE, chlordane, dieldrin) alone and in combination with metals, PAHs, and PCBs (Tao et al., submitted for publication). In the Tao study, organochlorine pesticides appeared to contribute substantially to the toxicity of stream sediments (which were sampled in Kansas and Missouri in 2003) measured in 28-day sediment toxicity tests with *Hyalella azteca*. Toxicity was observed in a third of samples (4 of 12) that had a mean PEC-Q for organochlorine pesticides (chlordane, dieldrin, DDE) greater than 1.0, and in half the samples (4 of 8) with an overall mean PEC-Q for metals, PAHs, PCBs, and organochlorine pesticides greater than 1.0. The Tao study suggests that it is reasonable to apply the mean PEC-Q method to organochlorine pesticides, both alone and in combination with other contaminants such as PCBs.

3. Results

3.1. Results of principal-component analysis

The PC analysis yielded five components with eigenvalues greater than 1.0, indicating that each of these components accounts for a greater proportion of the variance than any one of the 14 individual compounds in the original dataset. For the five PCs, each of which is assigned a three-character abbreviation that denotes its constituents (Table 3), component loadings are summarized in Table 4. These five components accounted for a total of 77% of the total variance in the 14 compounds, and the percentage of total variance included in the five components was generally over 79% and ranged from 51% for dieldrin to 91% for *cis*-chlordane (Table 4). The results of the PC analysis used in this paper were similar to other PC analyses conducted as part of this study, including ones that (1) used log-transformed concentration data in place of rank transformation, (2) used organochlorine concentrations normalized by organic carbon content, and (3) determined six instead of five components, indicating that the results presented below are robust. Specific details on these three additional PC analyses are given in Appendix C in the Supplementary materials.

The two most important principal components (in terms of variance explained) were CDI and PPD (Table 4), which account for 27% and 19% of the variance, respectively. The CDI component has high loadings (>0.7) for the four major compounds in technical chlordane (*cis*-nonachlor, *trans*-nonachlor, *cis*-chlordane, and *trans*-chlordane), and a moderate loading (0.55) for dieldrin (Table 4). The PPD component has high loadings for *p,p'*-DDT and its degradates, *p,p'*-DDE and *p,p'*-DDD, and a moderate loading (0.45) for *o,p'*-DDD (Table 4). The components identified by the PC analysis reflect differing sources of these compounds, as indicated by their similar chemical structure (such as parent compound and degradate), common origin (in the same technical pesticide mixture), and similar relation of concentrations to land use.

The highest concentrations of CDI compounds occurred at urban sites followed by mixed urban sites (Fig. 1). The relation of *cis*-chlordane to land use and other factors discussed below is similar to those for *trans*-chlordane, *cis*-nonachlor, and *trans*-nonachlor (see Supplemental Figs. 1–3 in Appendix D), so concentrations of *cis*-chlordane are used to illustrate general trends for the CDI compounds. Chlordane, aldrin (the parent pesticide of dieldrin), and dieldrin were used for termite control until the late 1980s (U.S. Environmental Protection Agency, 1983, 1990,

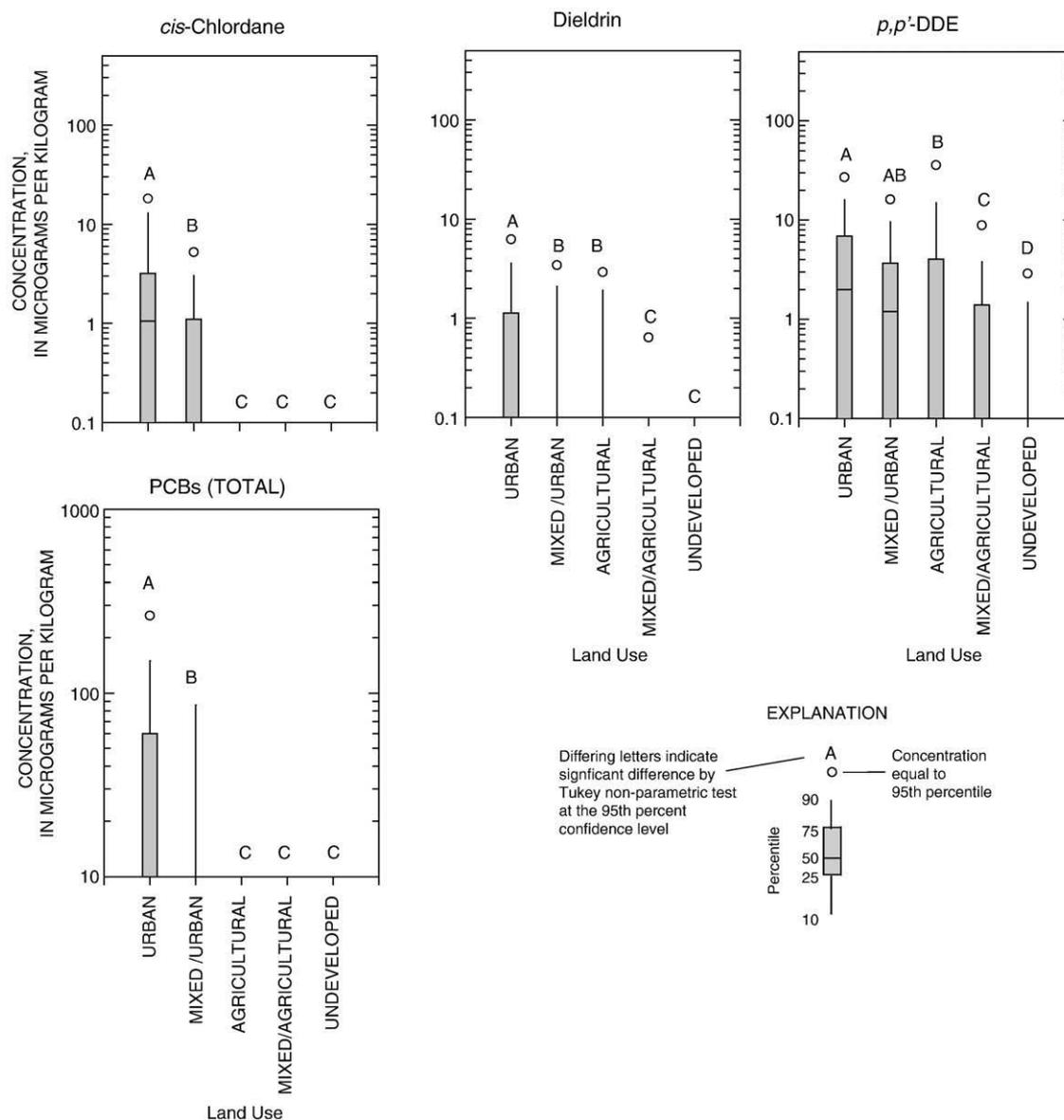


Fig. 1. Concentrations of selected organochlorine compounds in relation to the dominant land uses in the watershed of the bed-sediment sampling site. Non-detections are plotted at 0.1 $\mu\text{g}/\text{kg}$, except for PCBs (10 $\mu\text{g}/\text{kg}$). For categories with no boxplot or dot, more than 95% of concentrations are non-detected.

1992, 2000). Although direct estimates of termiticide use are unavailable (Nowell et al., 2006), the positive rank correlation between *cis*-chlordane concentrations for samples from urban sites and the termite-urban score ($r = 0.49$, $p < 0.0001$; see Supplemental Fig. 4, in Appendix E of the Supplementary materials), indicates that chlordane concentrations are correlated with urbanization and density of subterranean termite distribution. Concentrations of *cis*-chlordane were highest in the Northeast region (Fig. 2), which is a highly urbanized area with moderate to heavy termite distribution. By contrast, sites in the South and West Coast regions that have heavy termite distribution had lower median *cis*-chlordane concentrations. Elevated *cis*-chlordane concentrations also were observed at some urban sites located outside these three regions.

The moderate loading of dieldrin on the CDI component reflects 1) the co-occurrence of dieldrin with chlordane compounds in urban areas, and 2) the occurrence of dieldrin without chlordane compounds in agricultural areas. Concentrations of dieldrin are correlated with chlordane compounds in urban areas (where both were used for termite control); more than 80% of the urban and mixed/urban samples in which dieldrin was detected also had a detection for at least one chlordane

compound (57 of 69 samples). By contrast, dieldrin occurrence in agricultural areas is independent of chlordane occurrence, with only 16% of the agricultural samples containing dieldrin (7 of 43 samples) having one or more chlordane compounds also detected. Dieldrin occurrence in agricultural areas is largely associated with corn-crop sites (Fig. 3), which is due to historical use of aldrin and dieldrin on corn. Over 90% of the aldrin and dieldrin used on crops during 1964–1976 was applied to corn (Eichers et al., 1968, 1970, 1978; Andrienas, 1974). Although chlordane also was applied to corn until its use was discontinued in 1978, agricultural use of chlordane was less than 15% of that of aldrin and dieldrin (Eichers et al., 1968, 1970, 1978; Andrienas, 1974).

The highest concentrations of PPD compounds occurred at urban sites, followed by mixed urban sites (Fig. 1). The relation of *p,p'*-DDE to land use and other factors discussed below is similar to those for *p,p'*-DDD and *p,p'*-DDT (see Supplemental Figs. 1–3 in Appendix D), so concentrations of *p,p'*-DDE are used to illustrate general trends for the PPD compounds. Concentrations of *p,p'*-DDE were higher in samples from urban sites in the Northeast than from urban sites in the Southeast and West Coast regions (Fig. 2), which suggests that the use of DDT in urban areas was substantially greater in the Northeast than elsewhere.

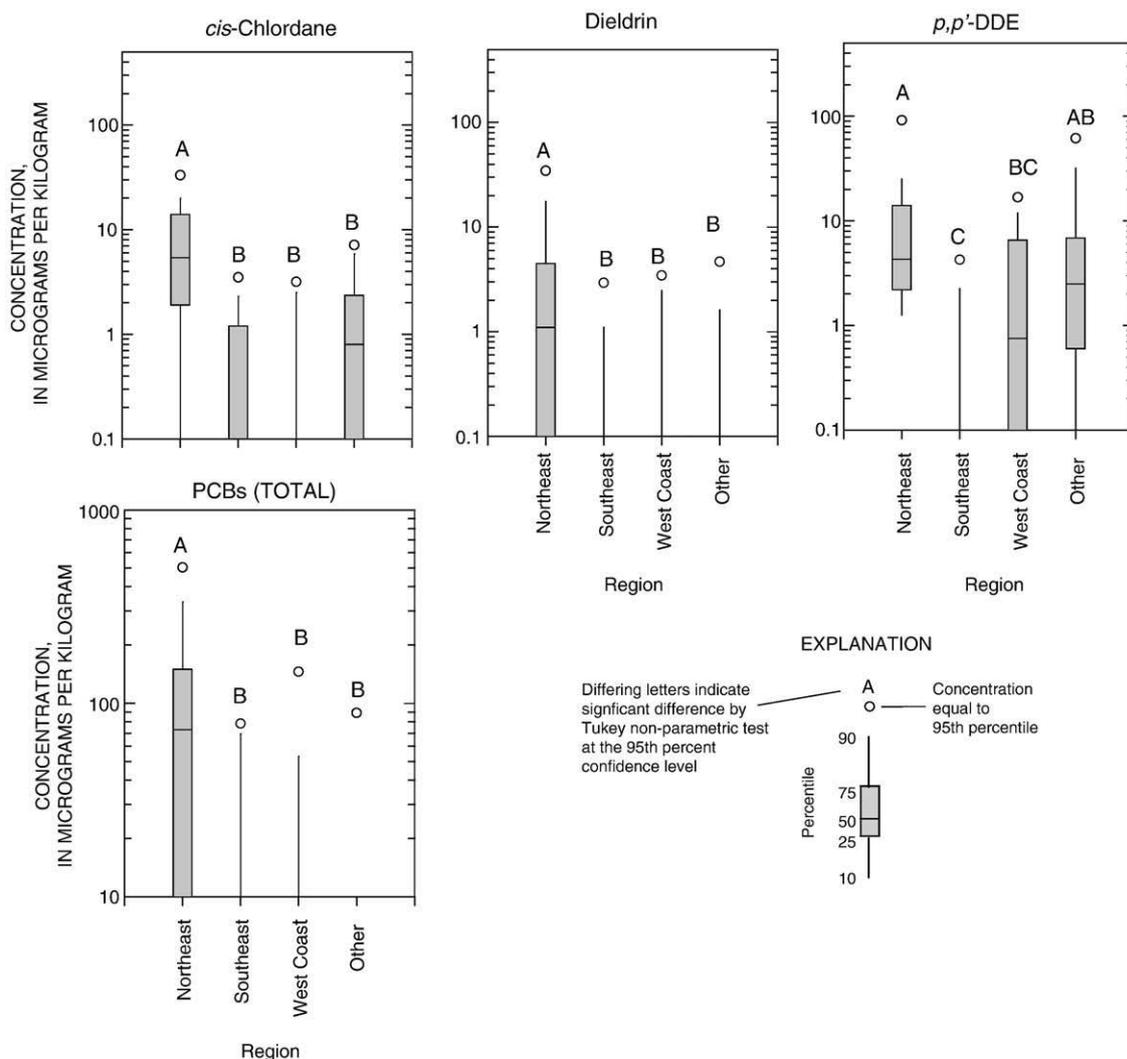


Fig. 2. Concentrations of selected organochlorine compounds in bed-sediment samples from urban sites in relation to major geographic regions. Northeast region includes 35 sites located in CT, MA, NH, NJ, NY, and PA; Southeast includes 23 sites located in FL, GA, and SC; West Coast includes 20 sites in CA, OR, and WA; and Other includes 21 sites located in AZ, CO, IL, IA, LA, MI, MN, NM, NC, TN, TX, and UT. Non-detections are plotted at 0.1 $\mu\text{g}/\text{kg}$, except for PCBs (10 $\mu\text{g}/\text{kg}$). For categories with no boxplot or dot, more than 95% of concentrations are non-detected.

Concentrations of *p,p'*-DDE were also high in some urban sites located outside these three regions (Fig. 2). Unlike *cis*-chlordane, *p,p'*-DDE concentrations in urban samples were not significantly related to the termite-urban score (see Supplemental Fig. 4, Appendix E, Supplementary materials). This is consistent with past use of DDT in urban settings, which was applied for control of public health and nuisance vectors (such as mosquitoes). Concentrations of *p,p'*-DDE in agricultural settings were significantly higher for samples collected from cotton-crop sites than for samples from either corn or 'other crop' sites (Fig. 3), with many of the highest concentrations occurring in the southeastern states (not shown). These patterns reflect the historical agricultural use of DDT on cotton, which accounted for 80% of the total nationwide DDT use on crops (U.S. Environmental Protection Agency, 1975).

The remaining three components (OPD, OXH and PCB) accounted for between 12 and 7.5% of the total variance (Table 4). The OPD component had high or moderate loadings for the three *o,p'*-DDX compounds (*o,p'*-DDE, *o,p'*-DDT, and *o,p'*-DDD), the OXH component had high loadings for oxychlordane (a degradate of chlordane) and heptachlor epoxide (a degradate of heptachlor), and the PCB component had high loadings for total PCB only. Nearly all (97%) of the samples with detections for the *o,p'*-DDX compounds also had detections for one or more of the *p,p'*-DDX isomers (*p,p'* isomers of DDT, DDD, and DDE), reflecting their common origin (application of

technical DDT). Because the *o,p'*-DDX isomers were detected far less frequently than the *p,p'*-DDX isomers, these compounds loaded on separate components. All of the 19 samples with a detection for oxychlordane or heptachlor epoxide also had a detection for one or more of the chlordane compounds, attributable to the fact that the parent compounds chlordane and heptachlor are both components of technical chlordane (U.S. Environmental Protection Agency, 1992). The PC analysis classified oxychlordane and heptachlor epoxide separately from the other chlordane compounds because of their lower frequency of detection. The highest PCB concentrations were in samples from urban sites (Fig. 1), and in particular those in the Northeast region (Fig. 2). Most of the 80 samples with a detection for PCB also have a detection for one or more of the *p,p'*-DDX compounds (66 samples, or 83%), and most also have a detection for one or more of the chlordane compounds (52 samples, or 65%).

3.2. PC-based mixture characterization

PC-based mixtures can be considered simple (that is, containing one or two PC descriptors, such as CDI or CDI/PPD) or complex (containing three or more PC descriptors, such as CDI/PPD/OPD/PCB), where each PC descriptor denotes the presence of one or more compounds associated with that PC. In the national data set, 299

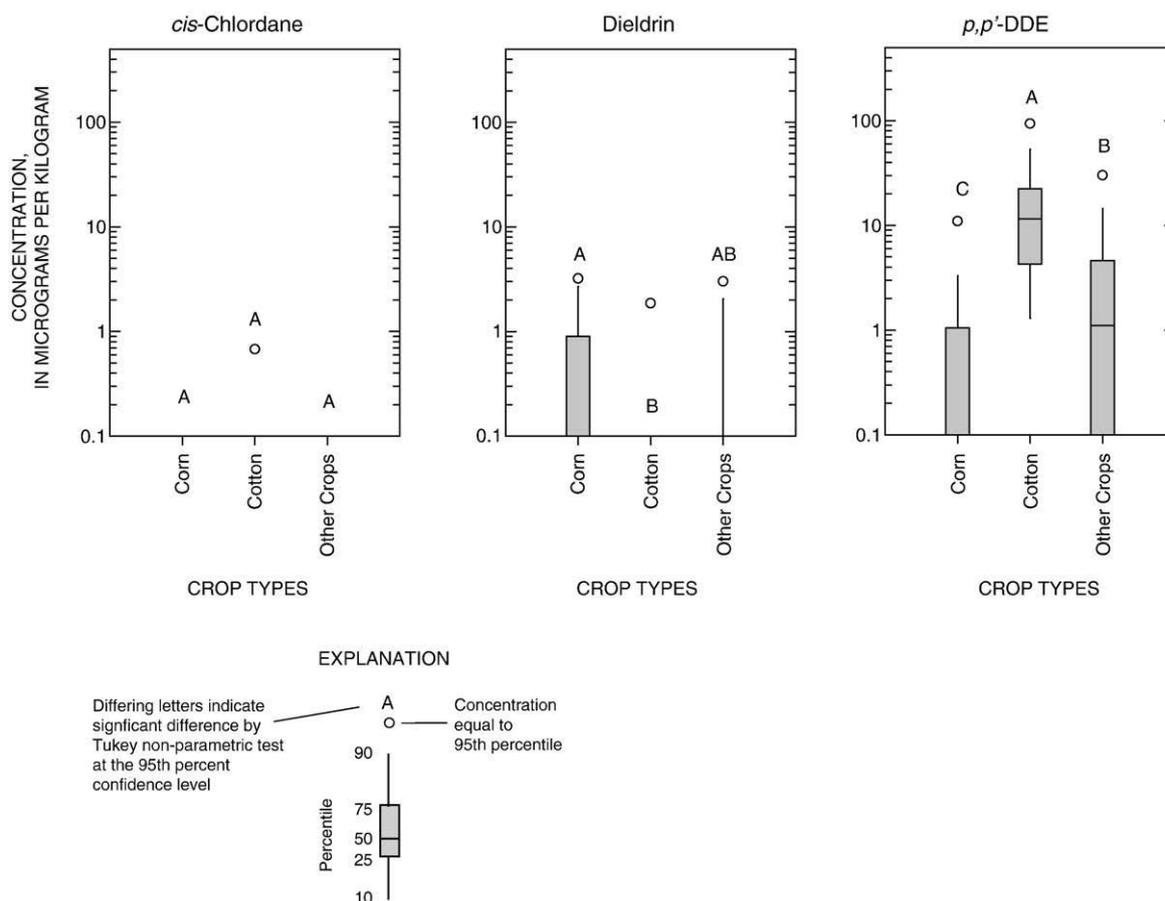


Fig. 3. Concentrations of selected organochlorine compounds in bed-sediment samples from agricultural sites in relation to major crop types. Corn crop includes 120 sites, Cotton crop 34 sites and Other crops 54 sites. Non-detections are plotted at 0.1 µg/kg. For categories with no boxplot or dot, more than 95% of concentrations are non-detected. PCB concentrations are not included due to low frequency of detection at agricultural sites.

samples contained two or more compounds, and 94% of these samples were classified as one of the nine most commonly occurring PC-based mixtures. These nine PC-based mixtures include five simple mixtures (CDI, PPD, PPD/PCB, PPD/OPD, and CDI/PPD), and four complex mixtures (CDI/PPD/OPD, CDI/PPD/PCB, CDI/PPD/OPD/PCB, and CDI/PPD/OPD/OXH/PCB). Most (86%) samples classified as simple PC-based mixtures had detections for fewer than five compounds, whereas most (70%) samples classified as complex PC-based mixtures had detections for seven or more compounds.

The five simple PC-based mixtures were associated with a variety of land-use settings, whereas the complex mixtures were associated mostly with urban sites (Fig. 4A). The complex PC-based mixtures tended to be most common in urban samples from the Northeast; they were found at 74% of urban sites in the Northeast, but in only 14% to 22% of urban sites in other regions (Fig. 4B). This is consistent with the significantly higher concentrations of CDI and PPD compounds at urban sites in the Northeast than in other regions (Fig. 2). Mixed/urban samples with complex mixtures also were more common among sites in the Northeast (37%) than elsewhere (9%).

3.3. Unique mixtures

The five most frequently detected unique mixtures at each complexity level (number of compounds in the unique mixture) are dominated by various combinations of compounds derived from technical DDT and technical chlordane (Tables 5a and 5b). The most commonly occurring unique mixtures are compared to simple PC-based mixtures in Table 5a, and to complex PC-based mixtures in Table 5b. Dieldrin does not appear in the top five unique mixtures

until the six-compound complexity level (Tables 5a and 5b), and PCB does not appear in the top five until the seven-compound complexity level (not shown).

The single most commonly detected unique mixture was *p,p'*-DDD, *p,p'*-DDE, which was present in 70% of all samples containing two or more compounds. (The two compounds *p,p'*-DDE and *p,p'*-DDD have the two highest detection frequencies of individual organochlorine compounds—41 and 26%, respectively, see Table 1—and they tend to co-occur because they are degradates of the same parent compound.) The second most frequently occurring unique mixture (*p,p'*-DDE, *p,p'*-DDT) was present in far fewer samples (49% of samples with two or more compounds). Except for the top unique mixture *p,p'*-DDD, *p,p'*-DDE, the five most frequently detected unique mixtures at each complexity level had similar frequencies to each other, generally ranging from 40 to 50% (of samples with two or more compounds) for two-compound unique mixtures, to 32–41% for three-compound unique mixtures, 27–31% for four-compound unique mixtures, 20–27% for five-compound unique mixtures, and 13–19% for six-compound unique mixtures (Tables 5a and 5b). The most common unique mixtures shown in Tables 5a and 5b serve as examples, rather than as a comprehensive compilation of all mixtures, because other mixtures occurred almost as frequently.

3.4. Comparison of approaches

The PC-based mixture characterization results in classification of 94% of the 299 samples containing 2 or more compounds into one of nine PC-based mixtures on the basis of which PCs are represented by the compounds in that sample, whereas the unique mixture approach identifies

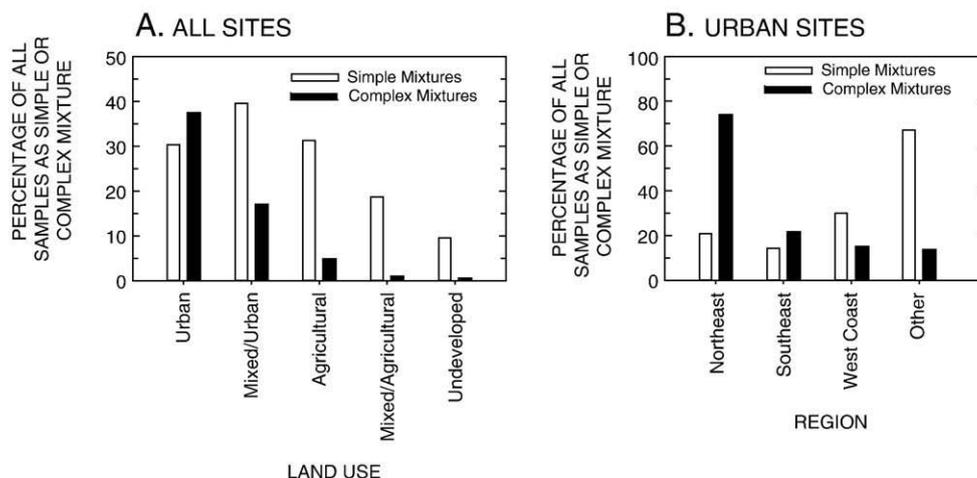


Fig. 4. Distribution of simple and complex mixtures A) for all samples by land use setting and B) for urban sites by major geographic regions. PC-based mixtures associated with simple and complex mixtures are given in Fig. 5. For Urban sites, Northeast region includes 35 sites located in CT, MA, NH, NJ, NY, and PA; Southeast includes 23 sites located in FL, GA, and SC; West Coast includes 20 sites in CA, OR, and WA; and Other includes 21 sites located in AZ, CO, IL, IA, LA, MI, MN, NM, NC, TN, TX, and UT.

one or more (frequently many more) unique mixtures present in each sample, of which only the most common are listed in Tables 5a and 5b. Tables 5a and 5b also list, for each of the most commonly detected unique mixtures, the percent of mixture samples classified as both the PC-based mixture and the indicated unique mixture.

The most complex unique mixtures were generally associated with the most complex PC-based mixtures (Tables 5a and 5b). The two-compound unique mixtures were most commonly associated with two simple PC-based mixtures—PPD and CDI/PPD. By contrast, over 60% of the five- or six-compound unique mixtures were classified as one of the four complex PC-based mixtures (CDI/PPD/OPD, CDI/PPD/PCB, CDI/PPD/OPD/PCB or CDI/PPD/OPD/OXH/PCB) (Table 5b). The simple PC-based mixture CDI/PPD was associated with a wider range of unique mixtures than the other simple PC-based mixtures (Table 5a), reflecting the fact that most four, five and six-compound unique mixtures all include some combination of chlordane and *p,p'*-DDX compounds.

An advantage of the PC-based mixture approach is that it reduces complexity, classifying samples into a smaller number of categories, and supports characterization of patterns in mixture occurrence in relation to land use and other factors. By contrast, the unique mixture approach identifies specific combinations of contaminants that most frequently occur and provides detailed information on a limited number of these combinations. Analysis of unique mixtures complements findings of PC-based mixtures by focusing attention on specific combinations of compounds that occur most often in relation to the broad patterns in the distribution of PC-based mixtures. This has implications for toxicity, as discussed in Section 3.5.

Many of the most common unique mixtures found in bed sediment are similar to those detected in fish from a similar set of stream sites (Gilliom et al., 2006). A notable exception is that dieldrin appears in unique mixtures in fish tissue more commonly than in unique mixtures in sediment. For example, dieldrin and *p,p'*-DDE were present together in fish from 53% of urban and 59% of agricultural streams (Gilliom et al., 2006), but in sediment from only 29% of urban and 12% of agricultural streams in the present study. This indicates that dieldrin may be more stable in fish tissue than in sediment, which is consistent with the hypothesis by Van Metre and Mahler (2004) that dieldrin is probably not preserved in lake-sediment cores. Conversely, *p,p'*-DDT is present in several common unique mixtures in bed sediment, but rarely in fish. The inference that *p,p'*-DDT may be more stable in sediment than in fish is consistent with the observation that fish metabolize *p,p'*-DDT to *p,p'*-DDE and *p,p'*-DDD (Addison and Willis, 1978), although *p,p'*-DDT (like dieldrin) does not appear to be

stable over time in aquatic sediment (Agee, 1986; Van Metre and Mahler, 2004).

3.5. Potential toxicity of mixtures

In general, mean PEC-Q values for the four complex PC-based mixtures (CDI/PPD/OPD, CDI/PPD/PCB, CDI/PPD/OPD/PCB, and CDI/PPD/OPD/OXH/PCB) were higher than those for the five simple mixtures (CDI, PPD, PPD/PCB, PPD/OPD, and CDI/PPD) (Fig. 5). More than half of samples classified as CDI/PPD/OPD/PCB or CDI/PPD/OPD/OXH/PCB had mean PEC-Q values greater than 0.5 and thus a high probability of being toxic to aquatic organisms (Fig. 5). The mean PEC-Q value for the PPD/OPD mixture is more similar to the mean value for the complex PC-based mixtures than the mean value of other simple mixtures (Fig. 5), reflecting the high concentrations of *p,p'*-DDE that typically occur when *o,p'*-DDX isomers are present at high enough concentrations to be detected. This occurs most often at agricultural sites in cotton-crop settings.

Mean PEC-Q values for organochlorine contaminants in sediment were highest for urban sites in the Northeast, followed by mixed/urban sites in the Northeast and agricultural sites in cotton growing areas (Fig. 6). Mean PEC-Q values were lowest for agricultural sites in corn-growing areas, mixed/agricultural sites, and undeveloped sites (Fig. 6). This pattern is consistent with concentrations of chlordane, DDX, and PCB compounds, which were highest in samples from urban and mixed/urban sites (Fig. 1). Urban and mixed/urban sites (especially those located in the Northeastern states) also typically have a higher frequency of complex PC-based mixtures (Fig. 4) and complex unique mixtures (not shown) than samples from other land use settings.

About 30% of urban sites in the Northeast had mean PEC-Q values greater than the threshold of 0.5, which indicates a high probability of toxicity, compared to 1.6% of urban sites elsewhere (Fig. 6). For mixed/urban sites, the mean PEC-Q values are significantly different in the Northeast than elsewhere, although there is little difference in the frequency of mean PEC-Q values above 0.5 (Fig. 6). These results for stream sediment are consistent with the common co-occurrence of DDT and chlordane compounds in urban lake sediments across the United States, and with the correspondingly higher mean PEC-Q values in sediments from urban lakes than in those from reference lakes (Van Metre and Mahler, 2004).

The PEC-Q data presented here indicate that bed sediments with the highest potential for toxicity are associated with complex organochlorine mixtures, which occur more frequently in urban and mixed/urban settings than elsewhere, especially at urban sites in the

Table 5a
Relations among unique mixtures and simple PC-based mixtures for the most commonly occurring unique mixtures of 2 to 6 compounds.

Most commonly occurring two-through six-compound unique mixtures	Percent of mixtures classified as indicated unique mixture (n = 299)	Percent of mixture samples classified as both the indicated PC-based mixture and the indicated unique mixture				
		CDI	PPD	PPD/PCB	PPD/OPD	CDI/PPD
<i>Two-compound unique mixtures</i>						
<i>p,p'</i> -DDD, <i>p,p'</i> -DDE	70	–	21	3.0	5.7	15
<i>p,p'</i> -DDE, <i>p,p'</i> -DDT	49	–	12	0.7	5.0	11
<i>p,p'</i> -DDD, <i>p,p'</i> -DDT	42	–	7.4	0.7	4.7	9.0
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane	40	3.3	–	–	–	12
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane	40	4.3	–	–	–	12
<i>Three-compound unique mixtures</i>						
<i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	41	–	7.4	0.67	4.7	8.7
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane	37	3.0	–	–	–	11
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>p,p'</i> -DDE	33	–	–	–	–	12
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE	32	–	–	–	–	12
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE	32	–	–	–	–	12
<i>Four-compound unique mixtures</i>						
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE	31	–	–	–	–	11.0
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	28	–	–	–	–	8.0
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	28	–	–	–	–	8.4
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD	27	–	–	–	–	7.7
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	27	–	–	–	–	7.7
<i>Five-compound unique mixtures</i>						
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	27	–	–	–	–	7.7
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	–	–	–	–	3.7
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	–	–	–	–	4.0
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	–	–	–	–	3.3
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	–	–	–	–	3.3
<i>Six-compound unique mixtures</i>						
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	19	–	–	–	–	3.3
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, dieldrin	16	–	–	–	–	3.0
<i>c</i> -Nonachlor, <i>tr</i> -nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	14	–	–	–	–	3.0
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT, dieldrin	14	–	–	–	–	2.0
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT, dieldrin	13	–	–	–	–	1.3

The number given in each cell below the PC-based mixture heading denotes the percentage of all samples classified as both the indicated unique mixture and the indicated PC-based mixture. For example, 21% of the 299 samples that are mixtures (defined as samples containing two or more organochlorine detections) are classified as both the unique mixture *p,p'*-DDD, *p,p'*-DDE and as the PC-based mixture PPD. [*c*, *cis*; *tr*, *trans*; PC, principal components; %, percent; – denotes no occurrence].

Table 5b
Relations among unique mixtures and complex PC-based mixtures for the most commonly occurring unique mixtures of 2 to 6 compounds.

Most commonly occurring two- through six-compound unique mixtures	Percent of mixtures classified as indicated unique mixture (n = 299)	Percent of mixture samples classified as both the indicated PC-based mixture and the indicated unique mixture				
		CDI/PPD/OPD	CDI/PCB	CDI/PPD/OPD/PCB	CDI/PPD/OPD/OXH/PCB	
<i>Two-compound unique mixtures</i>						
<i>p,p'</i> -DDD, <i>p,p'</i> -DDE	70	8.4	7.4	4.0	2.0	
<i>p,p'</i> -DDE, <i>p,p'</i> -DDT	49	7.7	5.0	3.3	2.0	
<i>p,p'</i> -DDD, <i>p,p'</i> -DDT	42	7.7	4.3	3.3	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane	40	6.4	7.7	4.0	2.0	
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane	40	6.4	7.0	4.0	2.0	
<i>Three-compound unique mixtures</i>						
<i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	41	7.4	4.3	3.3	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane	37	6.0	7.0	4.0	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>p,p'</i> -DDE	33	5.7	7.0	4.0	2.0	
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE	32	5.7	6.7	4.0	2.0	
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE	32	6.0	6.3	4.0	2.0	
<i>Four-compound unique mixtures</i>						
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE	31	5.7	6.4	4.0	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	28	5.0	6.0	4.0	2.0	
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	28	5.0	6.0	4.0	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD	27	5.0	6.0	4.0	2.0	
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	27	5.4	5.7	4.0	2.0	
<i>Five-compound unique mixtures</i>						
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	27	5.0	5.7	4.0	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	4.7	4.3	3.3	2.0	
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	4.3	4.3	3.3	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	4.3	4.3	3.3	2.0	
<i>c</i> -Chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	20	4.7	4.3	3.3	2.0	
<i>Six-compound unique mixtures</i>						
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	19	4.3	4.3	3.3	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, dieldrin	16	3.0	2.3	3.3	2.0	
<i>c</i> -Nonachlor, <i>tr</i> -nonachlor, <i>c</i> -chlordanane, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE	14	3.0	1.7	2.3	2.0	
<i>tr</i> -Nonachlor, <i>tr</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT, dieldrin	14	3.0	2.0	2.7	2.0	
<i>tr</i> -Nonachlor, <i>c</i> -chlordanane, <i>p,p'</i> -DDD, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT, dieldrin	13	3.0	2.0	2.7	2.0	

The number given in each cell below the PC-based mixture heading denotes the percentage of all samples classified as both the indicated unique mixture and the indicated PC-based mixture. For example, 8.4% of the 299 samples that are mixtures (defined as samples containing two or more organochlorine detections) are classified as both the unique mixture *p,p'*-DDD, *p,p'*-DDE and as the PC-based mixture CDI/PPD/OPD. [*c*, *cis*; *tr*, *trans*; PC, principal components; %, percent].

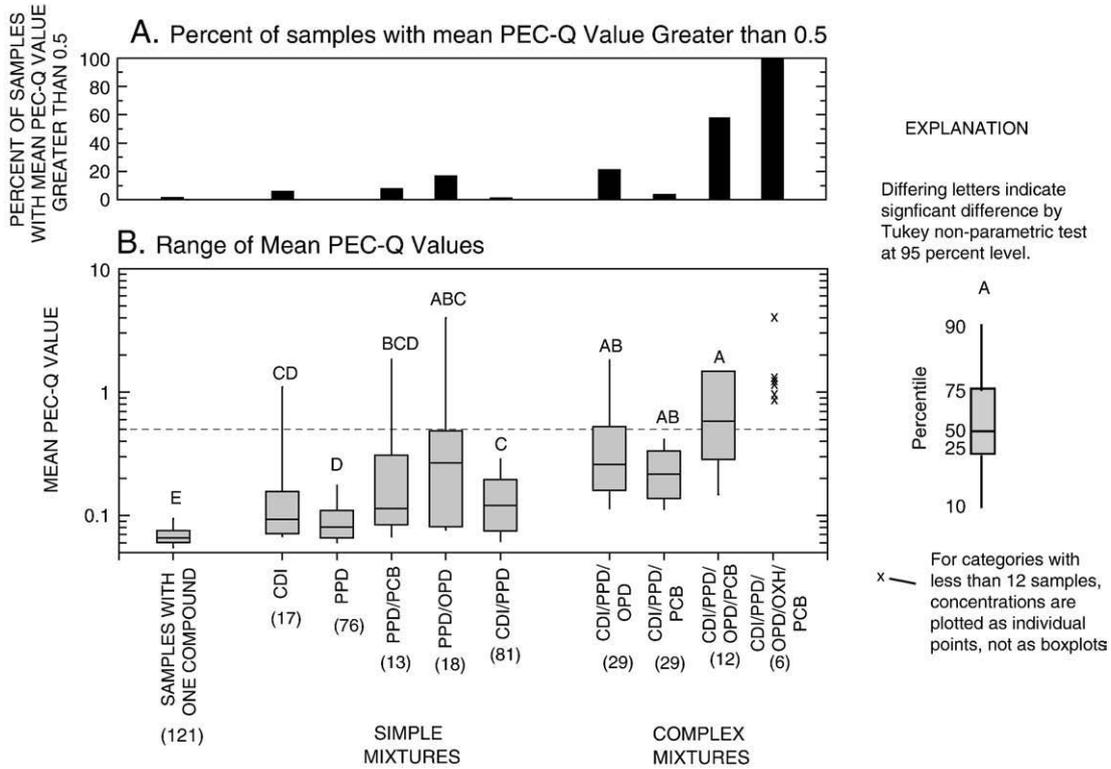


Fig. 5. Predicted organochlorine toxicity (PEC-Q) in relation to simple and complex PC-based mixtures. A) Percent of samples with mean PEC-Q values greater than the 0.5 threshold of likely toxicity and (B) range of mean PEC-Q values, for samples with one compound detected and for simple and complex PC-based mixtures. In (B), statistical comparison was not made for mixtures with fewer than 12 occurrences, which are plotted as individual points and not as boxplots. Dashed line indicates mean PEC-Q value of 0.5. Number in parentheses below each group name indicates number of samples in that group.

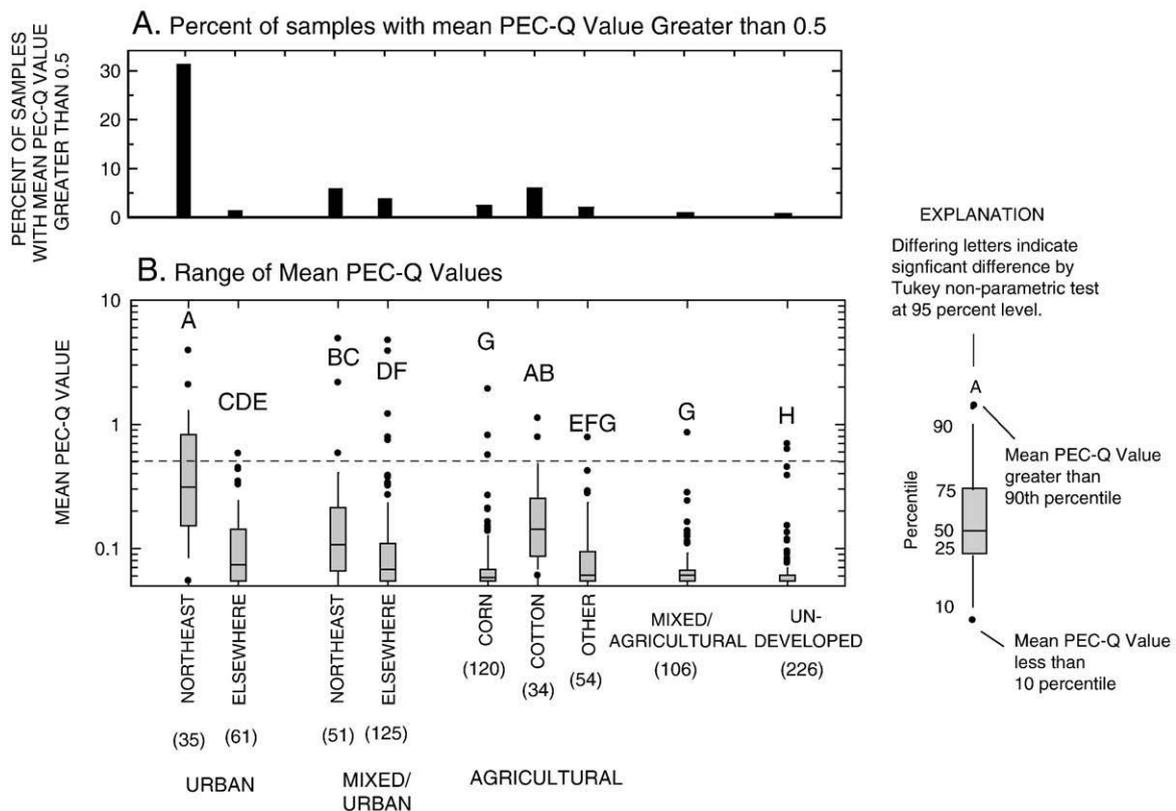


Fig. 6. Predicted organochlorine toxicity (PEC-Q) in relation to land use, region, and crop type. (A) Percent of samples with mean PEC-Q values greater than the 0.5 threshold of likely toxicity and (B) range of mean PEC-Q values, by land use and location or crop type. Dashed line indicates mean PEC-Q value of 0.5. Number in parentheses below each land use type indicates number of samples for that combination of land use and location or crop type.

Northeast. The primary contributors to potential toxicity at urban sites are DDX and chlordane compounds, and the primary contributors at agricultural sites are DDX compounds, especially in cotton growing areas. PCB generally contributes less than 10% of the mean PEC-Q at all sites.

Each contaminant mixture may have a specific toxicity and significance in terms of water quality; thus, the evaluation of frequently occurring mixtures is useful in prioritizing specific combinations of contaminants for investigation of potential adverse effects (such as was done for human-health effects of persistent chemical mixtures in fish by the Agency for Toxic Substances and Disease Registry, 2004). Toxicity tests may be conducted with unique mixtures of contaminants (that is, combinations of specific compounds) or with PC-based mixtures (that is, groups of related compounds that share a common source or land use setting).

4. Conclusions

The co-occurrence of organochlorine pesticide compounds and PCBs in sediment samples collected across the United States during 1992–2001 was evaluated in relation to land use, using a principal-component (PC) analysis. Five PCs accounted for 77% of the total variance in 14 organochlorine compounds detected in sediment. Chlordane compounds and dieldrin had high and moderate loadings (respectively) on the first component (CDI; explained 27% of variance); concentrations of these compounds were highest in samples collected from urban sites, which is consistent with historical use of chlordane, aldrin, and/or dieldrin for termite control. Concentrations at urban sites were especially high in the Northeast. The *p,p'* isomers of DDT, DDE, and DDD had high loadings on the PPD component (which explained 19% of variance); concentrations of *p,p'*-DDX compounds were also higher in urban areas than other sites, especially in the Northeast. At agricultural sites, *p,p'*-DDX compounds had the highest concentrations, especially in cotton growing areas. These patterns reflect the historical use of DDT on cotton and in urban settings for control of public health and nuisance vectors such as mosquitoes.

Two types of mixtures—PC-based mixtures and unique mixtures—are defined for all 299 samples with two or more organochlorine compounds detected. Nine PC-based mixtures—defined as combinations of one to five PC descriptors (CDI, PPD, OPD, OXH and PCB)—were identified, with each PC descriptor denoting the presence (in the sample) of one or more compounds associated with that PC. The simplest PC-based mixtures (containing compounds from 1 or 2 PCs) commonly occurred in a variety of land use settings, whereas complex mixtures (containing compounds from 3 or more PCs) were most common in samples from urban and mixed/urban sites. The most commonly occurring unique mixture was *p,p'*-DDE, *p,p'*-DDD (both persistent degradates of *p,p'*-DDT); this occurred in both simple and complex PC-based mixtures, and at both urban and agricultural sites. Unique mixtures containing four or more compounds were associated more often with complex PC-based mixtures than simple ones.

Mean PEC-Q values for the four complex PC-based mixtures (which have three or more PC descriptors) were higher than those for the five simple mixtures. More than half of the two most complex PC-based mixtures (CDI/PPD/OPD/PCB and CDI/PPD/OPD/OXH/PCB) had mean PEC-Q values greater than 0.5 and thus a high probability of being toxic to aquatic organisms. Mean PEC-Q values for organochlorine contaminants in sediment were highest for urban sites in the Northeast, followed by mixed/urban sites in the Northeast and agricultural sites in cotton growing areas.

Organochlorine compounds generally were found more often in mixtures than as individual compounds in bed-sediment samples. These results also demonstrate how the PEC-Q approach can be used in combination with PC-based mixture analysis to relate potential aquatic toxicity of contaminant mixtures to mixture complexity and land use and other surrogates for contaminant sources.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2009.09.052.

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