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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 (PCB)s, 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 Billinghurst, 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