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Enantiomer fractions of chlordane components in sediment from U.S. Geological Survey sites in lakes and rivers

Elin M. Ulrich [a,1], William T. Foreman [a,*], Peter C. Van Metre [b], Jennifer T. Wilson [b], Stewart A. Rounds [c]

[a] U.S. Geological Survey, National Water Quality Laboratory, PO Box 25585, Lakewood, CO 80225-0585, United States
[b] U.S. Geological Survey, 8027 Exchange Dr., Austin, TX 78754, United States
[c] U.S. Geological Survey, 2130 S.W. 5th Ave., Portland, OR 97201, United States

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ABSTRACT

Spatial, temporal, and sediment-type trends in enantiomer signatures were evaluated for *cis*- and *trans*-chlordane (CC, TC) in archived core, suspended, and surficial-sediment samples from six lake, reservoir, and river sites across the United States. The enantiomer fractions (EFs) measured in these samples are in good agreement with those reported for sediment, soil, and air samples in previous studies. The chlordane EFs were generally close to the racemic value of 0.5, with CC values ranging from 0.493 to 0.527 (usually >0.5) and TC values from 0.463 to 0.53 (usually <0.5). EF changes with core depth were detected for TC and CC in some cores, with the most non-racemic values near the top of the core. Surficial and suspended sediments generally have EF values similar to the top core layers but are often more non-racemic, indicating that enantioselective degradation is occurring before soils are eroded and deposited into bottom sediments. We hypothesize that rapid losses (desorption or degradation) from suspended sediments of the more bioavailable chlordane fraction during transport and initial deposition could explain the apparent shift to more racemic EF values in surficial and top core sediments. Near racemic CC and TC in the core profiles suggest minimal alteration of chlordane from biotic degradation, unless it is via non-enantioselective processes. EF values for the heptachlor degradate, heptachlor epoxide (HEPX), determined in surficial sediments from one location only were always non-racemic (EF≈0.66), were indicative of substantial biotic processing, and followed reported EF trends.

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1. Introduction

Technical chlordane is a persistent organochlorine pesticide that consists of more than 140 compounds, with *cis*- and *trans*-chlordane being the most abundant and representing about 30% of the mixture (Dearth and Hites, 1991). Until it was banned in 1988 in the United States, chlordane was used as an agricultural insecticide and as a termiticide in the foundation of houses (Dearth and Hites, 1991). Chlordane residues and degradates such as heptachlor epoxide can be found across the globe, including remote areas such as the Arctic (Bidleman et al., 2004). Some chlordane components and degradates are acutely toxic, are suspected carcinogens, or possibly have estrogenic effects (Dearth and Hites, 1991; Smith, 1991; Colborn et al., 1993). Several major components are chiral, with each enantiomer having different biological properties and environmental fate. For example, the chlordane LD_{50} for *Tetramorium caespitum* (pavement ants) differs by isomer and enantiomer [*trans*-chlordane: (+) TC = 85 μg/g; (−) TC = 12 μg/g; *cis*-chlordane: (+) CC >50 μg/g; (−) CC = 25 μg/g] (White et al., 2002).

The behavior of chlordane enantiomers in the environment has been the topic of much research since the first chiral separations on cyclodextrin gas chromatography (GC) columns (König et al., 1991). When chlordane is manufactured, enantiomers of the primary components TC and CC are in a racemic mixture (Buser and Müller, 1993). As the compounds move through the environment, physical processes such as volatilization and photolysis are unlikely to change the enantiomer signature (Müller et al., 1997; Jantunen and Bidleman, 1998). However, contact with biota, including uptake, depuration, and metabolism, often is mediated by chiral biomolecules such as lipids and enzymes, which can result in changes to chlordane's enantiomer signature (Jantunen and Bidleman, 1998).

Enantiomer signatures of chlordane have been reported in biota (Wiberg et al., 2000; Fisk et al., 2001; Incorvia Mattina et al., 2007), soil (Falconer et al., 1997; Bidleman et al., 1998; Eitzer et al., 2001; Wiberg et al., 2001; Kurt-Karakus et al., 2007), water (Jantunen and Bidleman, 1998), and air (Ulrich and Hites, 1998; Jantunen et al., 2000; Leone et al., 2000; Hung et al., 2005). Enantiomer signatures have been used to trace chlordane sources from soil in the Midwest

* Corresponding author. Tel.: +1 303 236 3942; fax: +1 303 236 3499.
E-mail address: wforeman@usgs.gov (W.T. Foreman).
[1] Current address: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Maildrop D205-05, Research Triangle Park, NC 27711, United States.

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(Bidleman et al., 1998), to air above the soil (Leone et al., 2001), and to air near the Great Lakes (Falconer et al., 1998). Additionally, evidence of biological degradation has been shown through enantiomer signatures (Wiberg et al., 2000; Fisk et al., 2001). To date there have been few reports of chlordane enantiomer trends in sediments (Bidleman et al., 2004; Stern et al., 2005; Li et al., 2007).

Contaminant concentration profiles from lake-sediment cores have been used as a historical record of contaminant deposition and an indicator of increasing urbanization (Van Metre and Mahler, 2004, 2005). However, interpretation of core profiles can be confounded by physical processes (e.g., sediment mixing) and by analyte degradation over time. In this study, chiral analysis of *cis*- and *trans*-chlordane and heptachlor epoxide was employed to help assess concentration profile accuracy and biotic degradation. In addition, chlordane enantiomer signatures in surficial- and suspended-sediment samples were measured to compare with cored sediments. From these results, we suggest a likely source of EF signature and contamination to sediment. Sample extracts examined previously were collected as part of the U.S. Geological Survey's National Water-Quality Assessment Program and represent a range of spatial coverage. Trends with sediment type (core, surficial, suspended), location, deposition date, and concentration for several chlordane compounds are presented.

2. Experimental

Samples were collected as part of the U.S. Geological Survey's National Water Quality Assessment (NAWQA) program (U.S. Geological Survey, 2009) and NAWQA's Contaminant Trends in Lake Sediments Project. Details of sample collection, extraction, cleanup, and prior analysis for total technical or component-specific chlordane concentrations are published elsewhere (Ebbert et al., 2000; Noriega et al., 2004; Van Metre et al., 2004). Total chlordane in cored sediments was quantified versus a technical chlordane standard based on response of CC, TC, and *trans*-nonachlor. Sample extracts were stored (up to 10 years) at ≤−5 °C until they were chosen for enantiomeric analysis. Enantiomeric changes are not expected to occur in archived sample extracts because the storage environment (solvent) is achiral and microbial activity is unlikely due to storage conditions. This hypothesis was confirmed by analyzing extracts of reagent spike samples which showed racemic CC and TC after identical storage periods. Available extracts were analyzed for enantiomer composition only without additional treatment.

Several types of sediment samples were collected from sites in or near the major urban cities of Los Angeles, CA; Seattle, WA; Fort Worth, TX; Boston, MA; Atlanta, GA; and Portland, OR. Sediment cores were collected at five lake or reservoir sites (none at Portland) and were divided into 1- to 5-cm sections representing a record over time of sediment deposition. Core section ages were estimated using ^{137}Cs and total DDT concentration (Van Metre et al., 2004). Surficial bed sediments (top 1–2 cm) were collected from four rivers near to core locations (none at Fort Worth), and five additional surficial samples were collected at the Portland site. Eleven suspended-sediment samples were collected at the influent streams of two of the lake/reservoir sites (Boston and Fort Worth). Further details on the samples are presented in the supplemental information and in previously published reports (Bonn, 1999; Van Metre et al., 2004).

A Hewlett Packard 5890 series II GC connected to an HP 5989A mass spectrometer (MS) (Agilent Technologies, Palo Alto, CA) was used for enantiomer analysis. A γ-cyclodextrin 120 enantioselective column (Supelco, Bellefonte, PA; length 30 m, i.d. 250 μm, film thickness 0.25 μm) was used for enantiomer separations. The GC oven temperature program was a 1-min hold at 50 °C, ramped to 150 °C at 20 °C/min, ramped to 185 °C at 0.5 °C/min, and ramped to 230 °C at 20 °C/min and held for 2 min. Splitless (1 min) 2-μL injections of the extracts were made at 230 °C, with helium carrier at constant flow starting at 172 kPa at 50 °C.

The MS was operated in electron-capture negative-ionization mode with methane to increase selectivity, and in selected-ion monitoring mode to increase sensitivity. Other MS conditions were: transfer line at 230 °C ion source at 125 °C, and quadrupole mass analyzer at 100 °C. Ions (*m/z*) monitored were 318, 388, 390, and 392 for heptachlor epoxide (HEPX) and 374, 376, 408, 410, and 412 for *cis*-and *trans*-chlordane. Heptachlor and oxychlordane [a primary metabolite of CC and TC (Buser and Müller, 1993)] were either not detected or were at insufficient concentration for EF determination and, thus, were not considered further. Heptachlor epoxide was not detected or was at insufficient quantity for EF determination in the sediment cores at all locations.

Enantiomer-enriched standards of CC and TC (EQ Laboratories, Atlanta, GA) were analyzed to determine elution order. The HEPX elution order was compared to separations reported in the literature under similar conditions (Ulrich and Hites, 1998). The elution order using the GC conditions above was HEPX (−) then (+), TC (+) then (−), followed by CC (−) then (+). Racemic standards of varying concentration were analyzed along with samples to check for good separation and to provide data for statistical comparison.

Peak fitting with Peak Fit version 4.06 software (SPSS, Chicago, IL) was used to accurately determine the enantiomer fraction [EF = peak area of (+) enantiomer ÷ sum of peak areas of (+) and (−) enantiomers] (Harner et al., 2000). Details on this method are published elsewhere (Ulrich and Hites, 1998). Peak fitting is especially useful for close eluting peaks, such as enantiomers, and provides an estimate of the error (Asher et al., 2009).

Quality-control criteria were applied in the calculation of the sample EF values. Because each ion was peak fit separately, there were three to five calculations of EF for each compound per chromatographic analysis. The difference between the EF for ions was required to be within 5% of the average EF for that sample run. If one ion fell outside this range (usually due to low signal-to-noise ratio), it was removed and the criteria were applied again to the remaining ion EFs. To ensure that no coeluting compounds interfered with the analysis, ion ratios were examined for both enantiomer peaks for each analyte (*m/z* 408:410 for TC and CC; 388:390 for HEPX). The relative percent difference of this ratio between the first and second eluting enantiomer peaks was required to be less than 10% or the data were not considered reliable and not used. Reliable ion EFs were combined for replicate chromatographic runs before statistical analysis.

Statistical analysis was performed in Microsoft Excel by using a *t*-test assuming unequal variance with $\alpha = 0.05$. Enantiomer fractions of samples, using the average of all valid ions and replicate analyses, were compared to the EFs calculated for racemic standards (usually not equal to the presumed value of 0.5) by using the average of all concentrations, valid ions, and replicate analyses. Sample EFs were considered significantly different than racemic when probability values from the two-tailed test were <0.05.

3. Results

3.1. Enantiomeric sediment profiles

Figs. 1–5 show total technical chlordane concentration profiles (top, A) in sediment samples from five locations, along with enantiomer fraction profiles for *cis*-chlordane (middle, B) and *trans*-chlordane (bottom, C). Error bars on EF measurements correspond to the standard error of the replicate ion measurements. Core depth values less than zero are used to plot surficial sediments, suspended sediments, and racemic standards, with the most recent collection date having the largest negative depth value. Because EFs of the racemic standards were never exactly equal to the theoretical racemic value of 0.5, the experimental values for the standards (all locations) and a reagent-sand spike sample (West Street Basin; TC only) are shown with a triangle for reference. The racemic standard plotted at depth 0 cm was analyzed with core and surficial samples; additional