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Sources and Fate of Chiral Organochlorine Pesticides in Western U.S. National Park Ecosystems

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Abstract

The enantiomer fractions (EFs) of alpha-hexachlorocyclohexane (α -HCH), *cis*-, *trans*-, and oxychlordanes, and heptachlor epoxide were measured in 73 snow, fish, and sediment samples collected from remote lake catchments, over a wide range of latitudes, in seven western U.S. National Parks/Preserves in order to investigate their sources, fate, accumulation and biotransformation in these ecosystems. The present study is novel because these lakes had no inflow or outflow and the measurement of chiral organochlorine pesticides (OCPs) EFs in snowpack from these lake catchments provided a better understanding of the OCP sources in the Western U.S., while their measurement in fish and sediment provided a better understanding of their biotic transformations within the lake catchments. Non-racemic α -HCH was measured in seasonal snowpack collected from continental U.S. National Parks, while racemic α -HCH was measured in seasonal snowpack collected from the Alaskan parks, suggesting the influence of regional sources to the continental U.S. parks and long-range sources to the Alaskan parks. The α -HCH EFs measured in trout collected from the lake catchments were similar to the α -HCH EFs measured in seasonal snowpack collected from the same lake catchments, suggesting that these fish did not biotransform α -HCH enantioselectively. Racemic *cis*-chlordanes was measured in seasonal snowpack and sediment collected from Sequoia, indicating that it had not undergone significant enantioselective biotransformation in urban soils since its use as a termiticide in the surrounding urban areas. However, non-racemic *cis*-chlordanes was measured in seasonal snowpack and sediments from Rocky Mountain, suggesting *cis*-chlordanes does undergo enantioselective biotransformation in agricultural soils. The trout from these lakes showed preferential biotransformation of the (+)-enantiomer of *cis*-chlordanes and the (–)-enantiomer of *trans*-chlordanes.

Keywords

Chiral Organochlorine Pesticides; Enantiomer Fraction

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Introduction

Organochlorine pesticides (OCPs) are persistent in the environment and have been shown to undergo long-range atmospheric transport and accumulation in remote high elevation and high latitude ecosystems [1–5]. Identifying OCP sources to these sensitive ecosystems is important because many of them are toxic and can potentially bioaccumulate in food webs [1]. A major objective of the Western Airborne Contaminants Assessment Project [WACAP, (http://www2.nature.nps.gov/air/Studies/air_toxics/wacap.htm)] was to determine the sources of semi-volatile organic contaminants in high-elevation and high-latitude ecosystems in Western U.S. National Parks [3, 6]. Organochlorine pesticides have been measured in seasonal snowpack, lake water, sediment, vegetation, and fish from these ecosystems [1–4, 7, 8]. Snow is a major route of OCP deposition to these ecosystems because it is an effective scavenger of both gas- and particulate-phase OCPs from the atmosphere [2, 7, 9, 10]. The melting of the seasonal snowpack results in the release of OCPs to the aquatic or terrestrial ecosystem and is a source of OCPs to the lake water, sediment, and fish [11].

The enantiomer fractions (EFs) of chiral OCPs have been used to identify their sources in ecosystems, as well as their accumulation and biotransformation in food webs [12–14]. Chiral pesticides are composed of two enantiomers and are typically manufactured in racemic (50:50) form. The enantiomers have the same physical and chemical properties and are affected by abiotic processes in the same way [15]. However, biotic processes, involving enzymatic activity, may result in enantioselective biotransformation [15]. Recent use of the pesticide and/or non-enantioselective biotransformation will result in a racemic EF, while enantioselective biotransformation will result in a non-racemic EF. As a result, EFs have been used to apportion chiral organic pollutant sources to water bodies [12], identify their emission source regions to the atmosphere [15], and track their fate and biotransformation in food webs [13].

The present study is novel because the WACAP lake catchments span a broad latitude range (36 to 68 decimal degrees N), from southern California to the northern point of Alaska. In addition, these lakes have no inflow or outflow through rivers or streams. Therefore, the OCP sources to the lakes include only atmospheric deposition processes and their removal includes abiotic and/or biotic transformation processes within the lake catchment. The measurement of chiral OCP EFs in snowpack from these lake catchments provides a better understanding of the OCP sources in the Western U.S., while their measurement in fish and sediment provides a better understanding of the biotic transformations within the lake catchments. In the present study, the EFs of alpha-hexachlorocyclohexane (α -HCH), *cis*-, *trans*-, and oxychlordane, and heptachlor epoxide B were measured in 73 snowpack, fish, and sediment samples collected from remote lake catchments in seven western U.S. National Parks. These data were used to identify the sources of these pesticides and assess their fate, accumulation, and biotransformation in these remote ecosystems.

Methods

Sampling sites

Seasonal snowpack, sediment cores, and fish: brook trout (*Salvelinus fontinalis*) and lake trout (*Salvelinus namaycush*), and on occasion cutthroat trout (*Oncorhynchus clarki*), rainbow trout (*Oncorhynchus mykiss*), and burbot (*Lota lota*) were collected from Emerald and Pear Lake catchments in Sequoia National Park, Lone Pine and Mills Lake catchments in Rocky Mountain National Park, LP19 and Golden Lake catchments in Mt. Rainier National Park, Oldman and Snyder Lake catchments in Glacier National Park, Wonder Lake catchment in Denali National Park, Burial Lake catchment in Noatak National Preserve, and Matcharak Lake catchment in Gates of the Arctic National Park and Preserve between 2003

and 2005 as part of the U.S. National Park Service's WACAP (Figure S1, Table S1) [1–4]. Seasonal snowpack samples were collected from 1 to 3 sites at each park at the end of the snow accumulation season in 2003, 2004, and 2005 [2, 7]. Sediment cores were collected from the deepest point in each lake, sectioned, and dated using ^{210}Pb and ^{137}Cs [4] and ten fish per lake were collected and analyzed [1]. Site and sampling procedure details have been previously reported [1–4].

Analysis of Chiral OCPs

The analytical methods for the extraction, cleanup, and instrumental analysis of OCPs in snow, fish, and sediment have been previously reported along with the chemicals, standards, and solvents used [1–4, 16]. The OCP concentrations in each of these matrices were determined using isotope dilution gas chromatographic mass spectrometry (GC/MS) and are reported elsewhere [1–4].

Enantioselective analysis of the OCPs and OCP degradation products was performed using GC/MS with electron capture negative ionization and a 30m DB-5 column (28m, 0.25 mm id., 0.25 μm film thickness, J&W Scientific, USA) connected to a 15m BGB Analytik chiral column (10 m, 0.25 mm id, 0.25 μm film thickness, BGB Analytik, Germany). The details of the GC temperature program, instrumental parameters, and ions monitored have been reported elsewhere [17]. The BGB column was used to separate the enantiomers of α -HCH, oxychlordan, *trans*-chlordan, *cis*-chlordan, heptachlor epoxide and *o,p'*-DDT. All of these chiral OCPs were measured above the detection limit for enantioselective analysis except for *o,p'*-DDT. Pure enantiomer standards were used to determine the elution order of α -HCH, *cis*-chlordan, and *trans*-chlordan (Dr. Ehrenstorfer, D-86199 Augsburg, Germany). The enantiomer fractions (EFs) of chiral OCPs were calculated using the following equation [18]:

$$\text{EF} = \frac{\text{area of the (+) enantiomer}}{\text{area of the (+) enantiomer} + \text{area of the (–) enantiomer}} \quad (1)$$

An EF of 0.5 indicates a racemic mixture. Pure enantiomer standards were not available for heptachlor epoxide and oxychlordan and the elution order of the enantiomers could not be determined. In these cases, the EFs were calculated using the following formula:

$$\text{EF} = \frac{\text{area of the (1) eluting enantiomer}}{\text{area of the (1) eluting enantiomer} + \text{area of the (2) eluting enantiomer}} \quad (2)$$

Manual integration of peak area was conducted using macro smoothed chromatograms in MSD ChemStation (G1701DA). The racemic ranges of the chiral OCPs were calculated from seven replicate injections of the racemic standard (25 $\text{pg}/\mu\text{L}$). The 95% confidence intervals for the racemic ranges were 0.499 ± 0.0095 for α -HCH, 0.499 ± 0.0052 for *trans*-chlordan, and 0.497 ± 0.0059 for *cis*-chlordan. Because the EF precision of the standards was four decimal places, all EFs are reported to three decimal places. Ion ratios were monitored in each sample to ensure there were no matrix interferences and the ratios were required to be within 20% of the ratios of the standards. Because of matrix interferences with the (+)-enantiomer, the EF of *trans*-chlordan was not determined in sediment extracts. As a result, we have limited our interpretation of the (+)-enantiomer of *trans*-chlordan to seasonal snowpack and fish.

Because of the relatively low OCP concentrations in the samples and the higher detection limit for enantioselective analysis, the measured OCP concentrations were used to prioritize

the samples for enantioselective analysis. All samples with OCP concentrations above the detection limit were analyzed [1, 2, 4, 7, 16]. Within a park, snowpack, sediment and fish samples with the highest OCP concentrations were analyzed first. If the concentrations were above the detection limit, additional samples from the park were analyzed. In all, 25 snowpack, 18 sediment sections, and 30 fish samples were analyzed.

The detection limit for enantioselective analysis was defined as a signal to noise ratio (S:N) of 3:1 [19] and these values can be found in Table S2. For α -HCH, this was approximately 0.05 ng/L in snow and 0.09 ng/g in fish. The S:N ratio for α -HCH was less than 3:1 in all of the sediment samples, resulting in a detection limit greater than 0.8 ng/g. For *trans*-chlordane, the detection limits were approximately 0.01 ng/L for snow, 0.07 ng/g for sediment, and 0.04 ng/g for fish. The detection limit for *cis*-chlordane was approximately 0.02 ng/g for fish, 0.2 ng/g for sediment, and 0.02 ng/L for snow. Oxy-chlordane and heptachlor epoxide were measured above the detection limit only in fish samples (detection limits of approximately 0.02 ng/g and 0.08 ng/g, respectively). All lab and field blanks had concentrations below the detection limit for enantioselective analysis.

Results and Discussion

Sources of Chiral Pesticides

Technical HCH, which is considered to be the primary source of α -HCH to the environment, was used in the United States until 1978 and in Canada until 1971. However, technical HCH was used in Asia until 2000 [20, 21]. With an atmospheric half-life of 115 d and physical-chemical properties that result in long-range atmospheric transport, α -HCH undergoes cold-condensation to remote regions [22]. The measurement of non-racemic α -HCH in snowpack indicates that its source to the lake catchment is re-volatilization from prior uses after biotic transformation, while racemic α -HCH in snowpack indicates a fresh source or a source that has only undergone abiotic transformation. Within a park, the seasonal snowpack was typically either consistently racemic or non-racemic for a given OCP year to year (Table S1(A)). However, the seasonal snowpack EF values varied somewhat among sites and years, within a park. For example, the seasonal snowpack α -HCH EFs in Mt. Rainier ranged from 0.520 to 0.562, but were consistently non-racemic and depleted in the (–)-enantiomer.

A t-test revealed a significant difference (p -value < 0.001) between the mean racemic α -HCH EFs (0.505 ± 0.0057) measured in seasonal snowpack in Alaska (Noatak, Gates of the Arctic, and Denali) and the mean non-racemic α -HCH EFs (0.529 ± 0.0131) measured in seasonal snowpack in all other parks (Sequoia, Glacier, Mt. Rainier, and Rocky Mountain) (Figure 1A, Table S1A). The seasonal snowpack historic-use pesticide (HUP) concentrations at WACAP sites in the continental U.S. (Sequoia, Olympic, Mt. Rainier, Glacier, and Rocky) result from their volatilization from regional agricultural soils, followed by regional atmospheric transport and deposition [2, 7]. However, the seasonal snowpack HUP concentrations in the Alaska parks (Denali and Gates of the Arctic/Noatak) result from long-range atmospheric transport and deposition [2, 7]. No statistically significant correlations were observed between the OCP concentrations and EF values.

The seasonal snowpack α -HCH EFs were negatively correlated with site latitude ($r^2 = 0.396$, p -value = 0.007) and positively correlated with mean site winter temperature ($r^2 = 0.455$, p -value = 0.003) (Figure S2). A positive correlation was also observed with site elevation (Figure S2). The correlations with site latitude and mean winter temperature confirm the observation that α -HCH EFs in seasonal snowpack were closer to racemic at higher latitude, lower temperature sites (the Alaskan parks) and that α -HCH undergoes cold condensation to the Alaskan parks. We measured non-racemic α -HCH (enhanced in the (+)-enantiomer) in seasonal snowpack at Sequoia, Glacier, Mt. Rainier and Rocky Mountain. Its likely source

was volatilization from areas where enantioselective biodegradation had occurred, such as regional agricultural soils and/or the Pacific Ocean, followed by transport and deposition to the site. Non-racemic α -HCH (also enhanced in the (+)-enantiomer) has been measured in air at a remote, marine site on the Pacific coast of the U.S. and was attributed to volatilization from background soils at the site and/or volatilization from the Pacific Ocean [17]. The racemic α -HCH in seasonal snowpack in the Alaska parks may be explained by long-range atmospheric transport. Racemic α -HCH has been measured in other matrices in the Arctic [23], as well as in free tropospheric air masses [17, 23].

Technical chlordane was banned in the U.S. for agricultural use in 1983 and from residential termiticide use in 1988. As a result, its presence in U.S. air is primarily from volatilization from agricultural soils in rural areas (showing a non-racemic EF) and soils surrounding the foundations of homes in urban areas (showing a racemic EF) [24, 25]. The non-racemic EFs in agricultural soils and racemic EFs in urban soils have been previously attributed to the higher chlordane concentrations in urban soils suppressing biotransformation [19]. Significant differences have also been measured between non-racemic chlordane EFs in tilled-planted and un-tilled soils, suggesting that tilling soils and growing crops can produce enantioselective changes [19]. We measured racemic *cis*- and *trans*- chlordane in seasonal snowpack from Sequoia and non-racemic *cis*- and *trans*-chlordane in Glacier, Noatak, and Gates of the Arctic (Figure 1B, 1C, Table S1(A)). The seasonal snowpack chlordane EFs were not correlated with site latitude, mean winter temperature, or elevation (Figure S2), indicating that chlordane did not undergo cold condensation to the Alaskan parks to the degree that α -HCH did. The Rocky and Mt. Rainier seasonal snowpack chlordane concentrations were below the detection limit for enantioselective analysis.

Of the WACAP parks, Sequoia has the highest population density within 300 km of the park (12,841,589 people) [3]. As part of a global passive air sampling study, some of the highest chlordane concentrations in the world were measured near Los Angeles, CA, a site approximately 250 km south of Sequoia National Park [26, 27]. Previous studies in the Western U.S. have also measured racemic *cis*- and *trans*-chlordane EFs in air masses influenced by California [17]. Because the chlordane concentration in urban soils is approximately 25 to 100 times higher than agricultural soils [19], re-volatilization of racemic chlordane from urban soils may be more significant than re-volatilization of non-racemic chlordane from agricultural soils at parks surrounded by high population densities.

In contrast, Glacier has a relatively low population density but a relatively high cropland intensity (including the surrounding agricultural land in Canada) [3]. Because both cropland intensity and population density were low surrounding the Alaskan parks [2, 3, 6], the non-racemic chlordane measured in Noatak and Gates of the Arctic seasonal snowpack was likely due to long-range transport from agricultural soils in Asia and North America. Together, our data suggests that the chlordane EF in seasonal snowpack at WACAP sites is influenced by regional transport from urban soils (racemic in Sequoia), regional transport from agricultural soils (non-racemic in Glacier), and long-range transport from agricultural soils (non-racemic in Noatak and Gates of the Arctic).

Fate, Accumulation, and Biotransformation of OCPs

Sediment—Only *cis*-chlordane was quantifiable in sediment samples because of matrix interferences in the measurement of *trans*-chlordane and α -HCH concentrations below the detection limit for enantioselective analysis. In Sequoia, racemic *cis*-chlordane was measured in seasonal snowpack and sediment from both Emerald and Pear lake catchments. This indicated that the sediment *cis*-chlordane EF reflected the EF of snow in both lake catchments (Figure 1C and Table S1(A,B)). Previous studies measured racemic *cis*-

chlordanes in Long Island Sound sediment and flooded soils, which suggested that the anaerobic conditions prevented enantioselective biodegradation [28, 29].

Racemic *cis*-chlordanes were also measured in sediment from Mt. Rainier (Figure 1C and S3). Of the national parks studied, Mt. Rainier has the second highest population density within 300 km of the park at 8,703,126 people [3]. Although the *cis*-chlordanes EF in the seasonal snowpack at Mt. Rainier was below the detection limit for enantioselective analysis, the sediment from Mt. Rainier suggests that, like Sequoia, this park receives racemic chlordanes from volatilization from surrounding urban soils.

A one-way analysis of variance (ANOVA) indicated that the mean *cis*-chlordanes EFs, measured in sediment from the different parks, were not equal. In addition, Scheffé confidence intervals showed that the non-racemic *cis*-chlordanes EFs (depleted in the (–)-enantiomer) in Mills Lake and Lone Pine Lake sediment in Rocky Mountain were not significantly different from each other (Figure S4). However, the non-racemic *cis*-chlordanes EFs in Rocky Mountain sediment were significantly different from the racemic *cis*-chlordanes EFs in Sequoia and Mt. Rainier sediment (Figure S4). A previous study has shown that *cis*-chlordanes are depleted in the (–)-enantiomer in agricultural soils from Alabama, the Midwestern U.S., Connecticut, Hawaii, and the United Kingdom. [30]. Our data suggests that the non-racemic *cis*-chlordanes in Rocky Mountain sediment is due to volatilization from regional agricultural soils, while the racemic *cis*-chlordanes in Sequoia and Mt. Rainier sediments is due to volatilization from surrounding urban areas, where chlordanes were commonly used as a termiticide.

Fish—Aquatic organisms are exposed to chiral pesticides through the water column, diet, and sediment [12]. For hydrophobic pesticides, such as chlordanes, with log octanol-water partition coefficients greater than five, pesticide uptake by fish through the food web is more significant than uptake through the water column [12]. In general, the EFs of chiral pesticides increase in their deviation from racemic in the following order: air < water < soil < biota because of increasing enantioselective biotransformation [13].

Alpha-hexachlorocyclohexane has a relatively low log octanol-water partition coefficient (~3.8) [31] but is the most abundant OCP in air and water in northern latitudes [32–35]. We measured α -HCH above the detection limit for enantioselective analysis in only 9 of the 30 fish samples (6 of the 9 were from Alaskan parks) and the EFs ranged from 0.309 to 0.507 (Figure 2B and Table S1(C)). The Wonder Lake fish in Denali had α -HCH EFs significantly (two-sided *p*-value < 0.0013) lower than all other fish in this present study (0.309 to 0.348). This may be due to increased enhanced biological activity (higher specific conductivity and suspended solids) in Wonder Lake compared to the other lakes [8]. Excluding the Denali fish, the α -HCH EFs in fish reflected the α -HCH EFs in seasonal snowpack from the same lake catchment (Figure 1A).

Cis- and *trans*-chlordanes were measured above the detection limit for enantioselective analysis in 15 of the 30 fish samples and 10 of the 30 fish samples, respectively. Non-racemic *cis*-chlordanes EFs ranged from 0.043 to 0.466 and were measured in all parks, except Sequoia. Non-racemic *trans*-chlordanes EFs ranged from 0.582 to 0.900 and were measured in all parks, except Glacier (Figure 2A and Table S1(C)). *Cis*-chlordanes were consistently depleted in the (+)-enantiomer in fish, while *trans*-chlordanes were consistently depleted in the (–)-enantiomer in fish (Figure 2A, S1C). Previous measurements made in rainbow trout and Arctic char found the same depletion patterns [36, 37]. The difference between the non-racemic chlordanes EFs in fish and the racemic chlordanes EFs in seasonal snowpack from the same lake catchments is likely due to enantioselective biotransformation in the fish or

biotransformation in the food web and bioaccumulation through trophic transfer (Figure 1B, 1C).

The results of the present study suggest that *cis*- and *trans*-chlordane are enantioselectively biotransformed in these trout species to a greater extent than α -HCH. A study by Wong et al. suggested that trout do not enantioselectively biotransform α -HCH and that non-racemic residues of α -HCH in rainbow trout are due to uptake of non-racemic α -HCH through the diet [37]. In this same study trout were also fed racemic chlordane and, after 13 d, the *cis*- and *trans*-chlordane EFs were significantly non-racemic. These laboratory studies support our hypothesis that fish from these national parks can enantioselectively biotransform *cis*- and *trans*-chlordane, but not α -HCH.

Oxy-chlordane (a metabolite of chlordane) was measured in 24 of the 30 fish samples and ranged in EF from 0.432 to 0.560 in fish from all parks (Figure 2A). A previous study with trout fed racemic chlordane measured *oxy*-chlordane a few days after measuring *trans*-chlordane in the fish [37]. However, the EF of *oxy*-chlordane was not measured [37]. Previous studies measured similar EF values of non-racemic *oxy*-chlordane in ringed seal and polar bears, indicating bioaccumulation of *oxy*-chlordane through the food web [14]. Non-racemic heptachlor epoxide (a metabolite of heptachlor) was measured in 5 out of the 30 fish samples (average of 0.619 ± 0.137) and was measured in fish from the Alaskan parks and Mt. Rainier (Figure 2B). Although heptachlor epoxide was below the detection limit for enantioselective analysis in seasonal snowpack, previous studies have measured its non-racemic EF in Lake Ontario air (0.65), and Lake Superior (0.67) and North Pole (0.62) surface water [13]. A previous study determined that fish are unable to biotransform heptachlor epoxide [38]. This suggests that the non-racemic heptachlor epoxide in WACAP fish may not be due to enantioselective biotransformation, but may be due to the deposition and accumulation of non-racemic heptachlor epoxide in the food web.

There were no significant correlations between the fish α -HCH, *oxy*-chlordane, *cis*-chlordane, and *trans*-chlordane EFs and fish age and weight. In addition, a t-test revealed that there was no significant difference between the α -HCH, *oxy*-chlordane, *cis*-chlordane, and *trans*-chlordane EFs due to fish sex or trout species. Previous studies have measured different EFs in different fish species. However, in this present study, it appears that the enantioselective biotransformation of *cis*- and *trans*-chlordane in trout was independent of fish age, weight, sex, and species. This may be an artifact of the relatively small sample size in this present study.

The measurement of OCP EFs in different parts of a high elevation or high latitude lake catchment is useful for identifying sources and tracking the fate of OCPs in the lake catchment, from deposition (snowpack) to accumulation (fish and sediment). In this present study, the EFs revealed that the OCP sources to these western U.S. lake catchments were dependent on the park's latitude, distance from populated regions, and proximity to agriculture. EFs were also used to gain a better understanding of which OCPs underwent biotic degradation once deposited to the lake catchment and which bioaccumulated in the food web.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Enantiomer Fractions (EFs) of **(A)** alpha-hexachlorocyclohexane (α -HCH), **(B)** *trans*-chlordane, and **(C)** *cis*-chlordane EFs in seasonal snowpack, sediment, and fish from lake catchments in Sequoia (SEKI), Rocky Mountain (ROMO), Mt. Rainier (MORA), Glacier (GLAC), Denali (DENA), Gates of the Arctic (GAAR), and Noatak (NOAT). The racemic range is shown by the solid lines on each graph. Matrices with no data points were below the detection limit.

Figure 2. Enantiomer Fractions (EFs) (A) *Oxy*-, *cis*-, and *trans*-chlordane and (B) alpha-hexachlorocyclohexane (α -HCH) and heptachlor epoxide EFs in fish collected from Sequoia, Rocky Mountain, Mt. Rainier, Glacier, Denali, and Gates of the Arctic. The black line represents a racemic EF of 0.5. The racemic ranges are different for each compound and are not displayed in the figure. Each symbol represents one measurement.