

Environ Sci Technol. Author manuscript; available in PMC 2010 April 15.

Published in final edited form as:

Environ Sci Technol. 2009 April 15; 43(8): 2806-2811.

Enantiomeric Signatures of Organochlorine Pesticides in Asian, Trans-Pacific and Western U.S. Air Masses

Susan A. Genualdi 1 , Staci L. Massey Simonich 1,2,* , Toby K. Primbs 1 , Terry F. Bidleman 3 , Liisa M. Jantunen 3 , Keon-Sang Ryoo 4 , and Tong Zhu 5

- 1 Department of Chemistry, Oregon State University, Corvallis, Oregon
- 2 Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon
- 3 Science and Technology Branch, Environment Canada, Center for Atmospheric Research Egbert, ON
- 4 Andong National University, Andong, South Korea
- 5 College of Environmental Science, Peking University, Beijing, China

Abstract

The enantiomeric signatures of organochlorine pesticides were measured in air masses from Okinawa, Japan and three remote locations in the Pacific Northwestern U.S.: Cheeka Peak Observatory (CPO), a marine boundary layer site on the Olympic Peninsula of Washington at 500 meters above sea level (m.a.s.l); Mary's Peak Observatory (MPO), a site at 1250 m.a.s.l in Oregon's Coast range; and Mt. Bachelor Observatory (MBO), a site at 2763 m.a.s.l in Oregon's Cascade range. The enantiomeric signatures of composite soil samples, collected from China, South Korea, and the western U.S. were also measured. The data from chiral analysis was expressed as the enantiomeric fraction (1), defined as (+) enantiomer/(sum of the (+) and (-) enantiomers), where a racemic composition has EF = 0.5. Racemic α -hexachlorocyclohexane (α -HCH) was measured in Asian air masses at Okinawa and in Chinese and South Korean soils. Non-racemic α -HCH (EF = 0.528 \pm 0.0048) was measured in regional air masses at CPO, and may reflect volatilization from the Pacific Ocean and regional soils. However, during trans-Pacific transport events at CPO, the α -HCH EFs were significantly more racemic (EF = 0.513 ± 0.0003 , p < 0.001). Racemic α -HCH was consistently measured at MPO and MBO in trans-Pacific air masses that had spent considerable time in the free troposphere. The α -HCH EFs in CPO, MPO, and MBO air masses were negatively correlated (p = 0.0017) with the amount of time the air mass spent above the boundary layer, along the 10-day back air mass trajectory, prior to being sampled. This suggests that, on the West coast of the U.S., the α -HCH in the free troposphere is racemic. Racemic signatures of cis- and trans-chlordane were measured in air masses at all four air sampling sites, suggesting that Asian and U.S. urban areas continue to be sources of chlordane that has not yet been biotransformed.

Introduction

Organochlorine pesticides (OCPs) are semi-volatile, undergo long-range atmospheric transport and are persistent in the environment (1,2). Although most OCPs have been banned in the U.S. for many years, they continue to be detected in ambient air (3,4). In addition, several OCPs are classified as Persistent Organic Pollutants (POPs), and are being phased out by the United

^{*}Corresponding Author, E-mail: staci.simonich@orst.edu, v: (541)737-9194, f: (541)737-0497.

Supporting Information Available Additional details on the sampling locations, EF data, SRIFs, and PCA analysis are given. This information is available free of charge via the Internet at http://pubs.acs.org.

Nations Environmental Program (UNEP) (2). Re-volatilization of OCPs from contaminated soils is considered to be a significant source of OCPs to the atmosphere (2,3,5). In order to understand the sources of OCPs to the atmosphere, the geographic origins of the emissions need to be identified (2).

Some chiral OCPs are composed of two enantiomers that have the same physical and chemical properties. Therefore, abiotic (hydrolysis, photolysis, etc.) and transport processes (volatilization, deposition, etc.) affect the enantiomers equally (6). OCPs are manufactured and used in racemic form. However, microorganisms in soil and water can selectively degrade one enantiomer over the other, resulting in non-racemic signatures that are retained during transport processes, i.e. volatilized to the overlying air (2). The enantiomeric signatures of chiral OCPs in air masses can provide information about whether a pesticide has been transported from an area where it is currently being used or has not yet been biotransformed (a racemic signature) or has been transported from an area after historic use and biotransformation (a non-racemic signature).

The trans-Pacific and regional atmospheric transport of OCPs has been reported at sites in Asia and in the Pacific Northwestern U.S. (1,7–11). The objectives of this research were to use the enantiomeric signatures of OCPs to distinguish between air masses influenced by trans-Pacific and regional atmospheric transport and to determine if the sources of OCPs to the Pacific Northwestern U.S. were from current or historic use.

Experimental

Air Sampling

The air sampling sites included Hedo Station Observatory (HSO) on Okinawa, Japan (26.8° N, 128.2°E, 60 m.a.s.l) (9), Cheeka Peak Observatory (CPO) in Washington State (48.3°N, 124.6°W, 500 m.a.s.l) (10), Mary's Peak Observatory (MPO) in Oregon's Coast Range (44.5° N, 123.6°W, 1249 m.a.s.l) (10), and Mt. Bachelor Observatory (MBO) in Oregon's Cascade Range (43.9°N, 121.7°W, 2763 m.a.s.l) (7,8) (Figure SI.1). The distance from HSO to the East China Sea is 0.2 km, while the distance of CPO, MPO, and MBO to the Pacific Ocean is approximately 3 km, 26 km, and 120 km, respectively. HSO, CPO, MPO, and MBO have been previously used to study the atmospheric transport of semi-volatile organic compounds (SOCs), including OCPs (1,7–10).

High-volume air samples were collected at HSO during the spring of 2004 (18 samples) (9), at CPO during 2003 (12 samples) (10), at MPO during 2003 (14 samples) (10), and at MBO during 2004, 2005, and the spring of 2006 (69 samples) (7,8) (Table SI.2). Detailed information on the sample collection, OCP extraction procedures and analysis, including solvents and standards used, has been previously reported (7–10,12)

Soil Sampling

Soil samples were collected from four rice paddy fields in China (Nanjing, Tianjin, Guangzhou, and Tangdian) in the summer of 2006 (Figure SI.1). The sampling sites were chosen based on their proximity to intense agricultural regions, including the Yangtze and Pearl River Deltas. Rice paddies were chosen because of the large amount of technical HCH historically used in these areas. In 1980, approximately 50% of the HCH applied to agricultural fields in China was applied to rice paddies (13). Technical HCH was banned in China in 1983 and in South Korea in 1985. A previous study estimated the historical usage of technical HCH in China to be extremely high (usage density > 40 t/kha) and in South Korea to be very high (usage density is 10–40 t/kha) (14). Soil samples were collected from 7 agricultural fields containing beans and hot peppers in provinces in South Korea (Kyeongbuk, Gangwon, Chungnam, Jeonbuk,

Jeonnam, Kyeongnam, Ulsan City) in the spring of 2007. The latitude, longitude, and elevation of each of the soil sampling locations can be found in Table SI.1.

Twenty composite soil samples were collected in China, while twenty-one samples were collected from South Korea. Each composite soil sample was collected from $100~\text{m}^2 \times 100~\text{m}^2$ agricultural plots and consisted of 5 random surface (0-20~cm) samples combined and mixed thoroughly. The samples collected were representative of $200,000~\text{m}^2$ (China) and $210,000~\text{m}^2$ (South Korea) of land. Composite soil samples were also collected from CPO, MPO, and agricultural fields in the Willamette Valley, Oregon. A composite soil sample was not collected from MBO due to snow cover and volcanic rock present at the site location. Additional information on the soil extraction and OCP analysis is given in the Supporting Information.

Chiral Analysis

Chiral analysis was performed using an Agilent 6890 GC and 5973N MSD (GC/MS) in electron capture negative ionization mode (ECNI). A DB-5MS (28m, 0.25 mm id., 0.25 μ m film thickness, J&W Scientific, USA) column connected to a BGB 172 chiral column (10 m, 0.25 mm id, 0.25 μ m film thickness, BGB Analytik, Germany) was used for the enantiomer separation of α -HCH, heptachlor *exo*-epoxide (HEPX), oxychlordane (OXY), *cis*-chlordane (CC) *trans*-chlordane (TC), and *o,p'*-DDT. The DB-5 column minimized interferences during the chiral separation on the BGB 172 column. Extracts were injected (2 μ L) using splitless injection with an initial oven temperature of 90°C. Following a 1 minute hold, the following temperature program was used; 15°C/min to 140 °C, 55 min hold, 2°C/min to 180 °C, 40 min hold, 15°C/min to 240°C, 10 min hold resulting in a total run time of 133 minutes. The temperatures of the ion source and quadrupole were both 150°C and the methane gas was 60% of 5 mL/min.

The following ions were monitored in selective ion monitoring (SIM) mode: α -HCH (m/z 253, 255, 257), HEPX (m/z 316, 318), OXY (m/z 350, 352) CC and TC (m/z 408, 410, 412), and o,p'-DDT (m/z 246, 248). The enantiomer elution order was determined for α -HCH, CC and TC using enantiomer (+) pure standards (Dr. Ehrenstorfer, D-86199 Augsburg, Germany). The elution order on the DB-5 column in tandem with the BGB column was (–) α -HCH, (+) α -HCH, (+)TC, (–)TC, (+)CC, (–)CC, (+)HEPX, (–)HEPX, (+)OXY, (–)OXY, (–) α - α -PDT (15). The concentration of OCPs in field and lab blanks were below the detection limit for chiral analysis (S/N < 3:1). Enantiomer fractions (EFs) are calculated using the following:

$$EF = \frac{\text{area of the (+) enantiomer}}{\text{area of the (+) enantiomer} + \text{area of the (-) enantiomer}}$$

A macro was used to smooth the chromatograms in MSD ChemStation (G1701DA) before manual integration was performed. Seven replicate injections of racemic standards (25 pg/ μ L) were used to determine the racemic ranges (95% confidence intervals) for α -HCH (0.499 \pm 0.0095), TC (0.499 \pm 0.0052), and CC (0.497 \pm 0.0059). Because the EF precision of the standards was four decimal places, all EFs are reported to 3 decimal places. To ensure there were no interferences, ion ratios were monitored and required to fall within 20% of the standards. The detection limit for chiral analysis was defined as a S:N ratio > 3:1. Although all samples were analyzed for oxychlordane, heptachlor epoxide, and o,p'-DDT, their concentrations were below the detection limit for chiral analysis.

Air mass back trajectories and source region impact factors (SRIFs)

4-day (HSO) and 10-day (CPO, MPO, MBO) air mass back trajectories were calculated for each of the sampling dates using NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) (7–10,16). Source region impact factors (SRIFs) were calculated to assess the impact of Asia, Siberia, and agriculturally intense areas in Eastern Washington, the Willamette Valley in Oregon, and the Central Valley in California on sampled air masses. SRIFs were calculated by determining the percentage of time an air mass spent in a given source region (Asia, Siberia, California, W. Oregon, E. Washington) during the total 10-day (or 4-day in the case of HSO) trajectory time. Details of the calculation of SRIFs have been previously reported and the SRIFs for all air masses are given in Table SI.2 (7–10). The air mass back trajectories were also used to assess the influence of boundary layer (<1000 m) and free tropospheric (>1000 m) air on air masses sampled at MBO and have been previously reported for the air masses sampled at MPO and CPO (Table SI.2) (10).

Results

Enantiomeric Signatures of α-HCH

Asia—Six of the eighteen HSO air masses sampled during the spring of 2004 had α-HCH concentrations above the chiral analysis detection limit (S/N > 3:1). In addition, all of these samples had racemic α-HCH signatures, which is defined as EFs falling within the 95% CI of the racemic standard, EF = 0.500 (Table SI.2). Source region impact factors (SRIFs) were previously calculated for each HSO air mass in order to identify their source regions, including China, Korea, Japan, Russia, and ocean/local (9). The concentrations of α-HCH ranged from 5.94 to 36.2 pg/m³, and elevated concentrations were measured in air masses associated with China (9). Of the six HSO air masses with α-HCH concentrations above the detection limit for chiral analysis, three were primarily from China (Apr 1–2, Apr 2–3, Apr 3–4, 2004) and the other three were primarily from Ocean/local (Mar 30–31, Apr 26–27, Apr 27–28) (Table SI. 2). All of these HSO air masses had racemic α-HCH signatures, suggesting that the α-HCH outflow from China and Japan is racemic.

Racemic α -HCH signatures were also measured in all of the Chinese and South Korean soil samples that had concentrations above the detection limit for chiral analysis, including 10 of 20 composite soil samples collected from rice paddies in China and in 4 of 21 composite soil samples from agricultural fields in South Korea (Table SI.1). The α -HCH concentrations ranged from <DL to 474 pg/g dry weight (dw), with a median value of 156 pg/g dw, in the Chinese soils and 30 pg/g dw to 934 pg/g dw, with a median value of 150 pg/g dw, in the Korean soils. The α -HCH soil concentration range in southern China has been reported to be <DL to 3480 pg/g dw in cultivated soil (with a median concentration of 800 pg/g dw), <DL to 2760 pg/g dw in rice paddies (with a median concentration of 780 pg/g dw) (and <DL to 1460 pg/g dw in uncultivated soils (with a median concentration of 170 pg/g dw) (17). In this previous study, the rice paddy soils typically had racemic α -HCH signatures, while the cultivated and uncultivated soils typically had non-racemic α -HCH signatures, indicating preferential degradation of the (–) enantiomer (EFs > 0.5) (17).

Technical HCH was banned in China in 1983, in Korea in 1979, and in Japan in 1971. (13) The composition of technical HCH includes 60–70% α -HCH and 10–12% γ -HCH (18). Although technical HCH has been banned in most Asian countries, γ -HCH (lindane) is still registered for use (19). Technical HCH has an α/γ -ratio ranging from 4 to 10 and this ratio can be used to identify HCH sources (4). At HSO, the air masses with China as the source region had an average α/γ -ratio of 2.3 \pm 0.3 (9). In HSO air masses with Japan/Korea/Russia as the source region, the α/γ -ratio was significantly higher, with a maximum value of 5.9 (9). Previous studies in urban and rural areas of China measured α/γ -ratios between 1.6 and 2.9 in air,

indicating current use of lindane (19). However, the ratios measured in urban air in Japan and Korea ranged from 3.5 to 6, indicating a technical HCH composition with little contribution from lindane (19).

Racemic α -HCH was measured in all HSO air masses and in all Chinese and South Korean soil samples with concentrations above the detection limit for chiral analysis (Figure SI.3). This suggests that the primary source of α -HCH to Asian air masses is due to relatively fresh sources of α -HCH and/or limited biotransformation of α -HCH since it was discontinued from use in Asia. A previous study has shown that enantio-selective degradation of OCPs can be limited in environments with high microbial populations and nutrient-rich soils due to the preference of microbes for carbon sources other than the OCP (20).

Pacific Northwestern United States

Due to their respective elevations and relatively close proximity to each other, the three air sampling locations in the U.S.; CPO at 500 m.a.s.l, MPO at 1249 m.a.s.l, and MBO at 2700 m.a.s.l, are influenced by boundary layer and free troposheric air masses to varying degrees. Figure 1A shows a significant negative correlation (p-value = 0.002) between the percentage of time the 10-day air mass back trajectories spent above the boundary layer (>1000 m) and the α -HCH EFs measured in the CPO, MPO, and MBO air masses. This negative correlation suggests that, in the Pacific Northwestern U.S., there is a gradient of non-racemic α -HCH in the boundary layer to racemic α -HCH in the free troposphere. A previous study suggested that the racemic α -HCH in rain collected over Lake Ontario was due to racemic α -HCH scavenged from air masses above the boundary layer that had not yet reached equilibrium with the non-racemic α -HCH below the boundary layer (21).

Each of the CPO, MPO, and MBO air masses have been previously characterized for the relative influence of regional and trans-Pacific source regions and their composition of ~83 SOCs, including polycyclic aromatic hydrocarbons (PAHs), current and historical use pesticides, and polychlorinated biphenyls (PCBs) (7–10). The concentration of α -HCH ranged from <DL to 29.8 pg/m³ at CPO, 3.84 pg/m³ to 53.1 pg/m³ at MPO, and 2.03 pg/m³ to 42.7 pg/m³ at MBO.

Representative α -HCH EFs and the 10-day air mass back trajectories of the associated air masses for regional and trans-Pacific transport are given in Figure 2 for CPO, MPO, and MBO. Trans-Pacific air masses typically spent higher percentages of time above the boundary layer than regional air masses (Table SI.2) (10). Racemic α -HCH was measured in trans-Pacific air masses at MPO and MBO (Table SI.2). At CPO (the lowest elevation site), the trans-Pacific air masses contained non-racemic α -HCH (0.513 \pm 0.0027) (Table SI.2). However, the α -HCH EF in trans-Pacific CPO air masses was significantly lower (p-value < 0.001) than the α -HCH EF in regional CPO air masses (0.528 \pm 0.0048). The observation that trans-Pacific air masses at CPO spent larger percentages of time above the boundary layer, and had a more racemic α -HCH EF than regional CPO air masses, is consistent with our conclusion that the free troposphere may be a significant source of racemic α -HCH.

A principal component analysis (PCA) biplot was created using the SRIFs (Table SI.2) of the Pacific Northwestern U.S. air masses (CPO, MPO, and MBO) and whether the α -HCH measured in the air masses was racemic (R) or non-racemic (NR) (Figure SI.2A). The first two principal components retained 97.5% of the original variation. Based on all of the CPO, MPO, and MBO samples, air masses with strong source contributions from Siberia and Asia contained racemic α -HCH. This observation, in addition to the racemic α -HCH measured in Asian air masses at HSO, provides strong evidence that Asian and trans-Pacific air masses (which also spent considerable time in the free troposphere) contain relatively fresh sources of α -HCH and/

or the sources have undergone limited biotransformation of α -HCH since it was discontinued from use in Asia.

All CPO air masses contained non-racemic α -HCH, with selective degradation of the (–) enantiomer (EF > 0.5) (Figure 1A). Non-racemic signatures of α -HCH, also with selective degradation of the (–) enantiomer (EF > 0.5), have been previously measured in air at other low elevation marine influenced sites on the West coast of Canada, in British Columbia (22). These Canadian sites were far from agricultural source regions and the authors suggested that the sources of non-racemic α -HCH to these sites were volatilization of non-racemic α -HCH from the Pacific Ocean and/or trans-Pacific transport (22). In contrast, our data suggests that trans-Pacific air masses contain racemic α -HCH.

At CPO, the Clausius-Clapeyron equation indicated a statistically significant correlation ($r^2 = 0.81$, p-value = 0.0004) between the α -HCH concentration (ln α -HCH) and inverse site temperature (1/T), suggesting that volatilization from a local source influenced α -HCH concentrations in air. The CPO air sampler was located ~3 m above ground level, in an open clearing approximately ~ 3 km from the Pacific Ocean. A composite soil sample was taken near the air sampler and in the nearby forest. The α -HCH EF of the soil collected from the clearing, near the air sampler, was non-racemic (0.544) and the α -HCH concentration in the forest soil was below the detection limit for chiral analysis (Table SI.1). A previous study measured the α -HCH EF in soils, and in air at four different heights (5, 35, 75, and 140 cm) above the soil, in the Fraser Valley, British Columbia (23). Both the air (EF at 5 cm height above soil = 0.574) and soil (EF = 0.579) samples were preferentially depleted in the (-) enantiomer (23). However, at greater heights above the soil (75 and 140 cm), the air EFs decreased (EF = 0.552 and 0.543, respectively) (23).

The α -HCH EF of the Pacific Ocean is not well characterized. Previous studies have measured the α -HCH EFs in the Bering, Chukchi, and Greenland Seas (24), and in the North Pacific (25). Because the Pacific Ocean flows into the Bering and Chukchi Seas, the Pacific Ocean and the Bering and Chukchi Seas likely have similar α -HCH EFs (22). The average α -HCH EF of the Bering and Chukchi Seas was non-racemic (0.521 \pm 0.0058) and similar to the average α -HCH EF measured in CPO air masses (0.525 \pm 0.007) (24). This suggests that the Pacific Ocean likely has a non-racemic α -HCH signature and that sources of α -HCH to CPO air and soil likely include volatilization of non-racemic α -HCH from the Pacific Ocean. However, a study in the North Pacific measured non-racemic α -HCH EFs below 0.5 (24). This indicates that the enantioselective degradation patterns of α -HCH in the Pacific Ocean are not well characterized and that additional research is needed to investigate these patterns.

In two CPO air masses (June 2, 2003 and August 4, 2003), the α -HCH EF was significantly lower than the CPO average (p-value < 0.001) (Table SI.2). These two air masses have been previously identified as being influenced by trans-Pacific transport from Siberian biomass burning emissions (10). Trans-Pacific transport usually involves mid-latitude cyclones lifting Asian boundary layer air into the free troposphere (26). During these two trans-Pacific events at CPO, the observed decrease in the α -HCH EF may be due to greater influence of racemic α -HCH from the free troposphere and the Asian boundary layer.

Four of the ten MPO air masses had racemic α -HCH signatures, while six of the ten MPO air masses had non-racemic α -HCH signatures that were depleted in the (–) enantiomer (EF >0.5) (Table SI.2). During the concurrent sampling of trans-Pacific air masses at CPO and MPO (June 2 and August 4, 2003), α -HCH was racemic at both sites. In addition, the Clausius-Clapeyron equation indicated no statistically significant correlation between α -HCH concentration and inverse site temperature at MPO. This suggests that the α -HCH measured at MPO was likely due to long-range transport and not local volatilization. The α -HCH EF

could not be measured in the MPO composite soil sample because the concentration was below the detection limit for chiral analysis (Table SI.1).

Sixteen of twenty MBO air masses had racemic α -HCH signatures (Table SI.2). However, four of twenty MBO air masses had non-racemic α -HCH signatures that were depleted in the (-) enantiomer (Table SI.2). The Clausius-Clapeyron equation revealed a correlation between α -HCH concentration and inverse site temperature ($r^2 = 0.42$, p-value = 0.003). MBO air mass back trajectories with a high percentage of air from the free troposphere (>80%) had racemic α -HCH signatures, suggesting that the free troposphere was a source of racemic α -HCH (Figure 1). Non-racemic α -HCH signatures in MBO air masses were only measured during the winter months (Table SI.2). Volatilization of non-racemic α -HCH from surrounding site soil during the winter is unlikely due to snow cover. However, volatilization of α -HCH from the surrounding snowpack is possible. Previous studies have shown the influence of α -HCH volatilization from snowpack on boundary layer air concentrations (27).

The ratio of α/γ -HCH in MBO air masses has been previously used to distinguish between trans-Pacific and regional air masses (2.9 \pm 0.3) and Pacific Ocean and Siberian air masses (5.2 \pm 0.8). Out of the four MBO air masses with non-racemic α -HCH signatures, three had α/γ -ratios of 5.3, 5.4, and 4.5, providing additional evidence that the Pacific Ocean is a likely source of these non-racemic signatures. Regional air masses at MBO typically had racemic signatures. Combined, our data suggest that Asia, the free troposphere, and regional U.S. sources have racemic α -HCH signatures, while the Pacific Ocean has a non-racemic α -HCH signature (Figure SI.3).

Enantiomeric Signatures of Chlordanes

Asia—Technical chlordane is composed of two major isomers (*cis*- and *trans*-), as well as other chlorine containing compounds (28). Chlordane has been previously used in China and Japan as an agricultural pesticide. The use of chlordane was banned in Japan in 1986 and China in 1999 (29,30) However, both countries currently hold exemptions for the use of chlordane as a termiticide around buildings (31). Chlordane is also banned in all other central and northeast Asian countries, including South Korea (31).

Racemic TC and CC were measured in all of the HSO air masses above the detection limit for chiral analysis (Table SI.2 and Figure SI.3). The chlordane concentrations at HSO ranged from <DL to 5.40 pg/m^3 for CC and 0.448 pg/m^3 to 8.16 pg/m^3 for TC. The TC/CC ratio in HSO air masses (1.2 ± 0.3) did not vary based on source region influences and reflected the TC/CC ratio of the technical mixture (1-1.26) (9). The racemic chlordane signatures and TC/CC ratio suggest that Asian air masses are influenced by relatively fresh sources of chlordane and/or limited biotransformation of chlordane has occurred since it was discontinued from use in Asia.

The sum of *cis*- and *trans*-chlordane concentrations ranged from 16.9 pg/g dw to 197 pg/g dw in the South Korean soil and < DL to 2.00 pg/g dw in the Chinese soil. Previous studies measured chlordane concentrations ranging from <DL to 1370 pg/g in crop, paddy, and uncultivated soils from the Pearl River Delta region of China (17). Non-racemic signatures of CC and TC were measured in all of the South Korean agricultural soils (Table SI.1); however the chlordane concentrations in the Chinese agricultural soils were below the detection limit for chiral analysis. In the Korean soil samples, TC was typically depleted in the (+) enantiomer, while CC was depleted in the (-) enantiomer (Figure SI.3). The same chlordane enantioselectivity has been measured in agricultural soils from Alabama, the Midwestern U.S., Connecticut, Hawaii, and the U.K. (3). This suggests that re-volatilization of chlordane from agricultural soil is not a significant source to HSO.

Pacific Northwestern United States

Chlordane was used as an agricultural pesticide and termiticide in the U.S. until 1983 and for the control of subterranean termites until 1988 (32). The TC concentration in air masses ranged from <DL to 0.38 pg/m³ at CPO, <DL to 2.45 pg/m³ at MPO, and <DL to 4.94 pg/m³ at MBO. The CC concentrations in airsesses were below the detection limit at CPO and MPO, and ranged from <DL to 3.31 pg/m³ at MBO. The TC EFs were above the detection limit for chiral analysis in 36% of the CPO, 69% of the MPO, and 57% of the MBO air masses. The CC EFs were above the detection limit for chiral analysis in 27% of the CPO, 31% of the MPO, and 33% of the MBO air masses. Of the air masses with EFs above the detection limit, 50% at CPO, 89% at MPO, and 92% at MBO had racemic CC and TC signatures (Table SI.2). However, unlike α -HCH, a statistically significant correlation was not observed between the TC or CC EFs and the percentage of time the CPO, MPO, and MBO air mass spent above the boundary layer (Figure 1). Like α -HCH, when the air mass spent > 80% of time above the boundary layer prior to being sampled, TC was usually racemic (Figure 1B). This suggests that the free troposphere may also be a source of racemic TC.

While the α -HCH concentration was elevated during trans-Pacific transport events at CPO, MPO, and MBO, the TC and CC concentrations were not elevated at CPO or MPO during trans-Pacific transport events. This suggests that Asia is not a major source of TC or CC to CPO and MPO. However, during a strong trans-Pacific event at MBO on April 25–26, 2004, elevated racemic chlordane concentrations were measured (Figure SI.3) (7).

The Clausius-Clapeyron equation indicated that the chlordane concentrations were significantly correlated with inverse site temperature at a MBO ($r^2 = 0.14$, p-value = 0.005), but only slightly correlated at MPO ($r^2 = 0.26$, p-value = 0.076). At CPO, there were too few samples above the TC and CC detection limit for chiral analysis to test the Clausius-Clapeyron relationship.

Composite soil samples, taken from agricultural soils in the Willamette Valley of Oregon and at MPO, contained non-racemic TC and CC (Table SI.2). However, urban air and house foundation soils are dominated by racemic chlordanes (3) and generally have higher chlordane concentrations than rural areas due to house foundations being treated with chlordane for termites (11,33,34). In addition, racemic TC and CC have been measured in the Bering and Chukchi Seas (35). It is possible that racemic chlordane volatilizes from the Pacific Ocean and urban soils and may be a source of racemic chlordanes to these sites, including HSO.

At MBO, elevated TC and CC concentrations were measured in air masses associated with urban California source regions (May 7–8, 12–13, 27–29, 2005 and Apr 4–6, 13–14, 2006) (7). A PCA biplot was created using the SRIFs of the CPO, MPO, and MBO air masses and whether the TC measured in the air masses was racemic or non-racemic (Figure SI.2B). This biplot indicates that air masses with significant Asian influence had racemic chlordane signatures (Figure SI.2B). This suggests that U.S. urban areas and Asia (and/or the Pacific Ocean) are sources of racemic chlordanes to MBO.

Combined, our data suggest that Asian and U.S. air masses that pass over urban areas in the Western U.S. contain racemic chlordane due to volatilization from urban soils and house foundations. These soils have been treated with chlordane and have undergone limited biotransformation. In contrast, agricultural soils in South Korea, as well as the Western U.S., contain non-racemic chlordane signatures (with TC depleted in the (+) enantiomer and CC depleted in the (-) enantiomer). Finally, the Pacific Ocean may be a source of racemic chlordane.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was made possible by funding from the National Science Foundation CAREER (ATM-0239823), NSF EAPSI China 2006, and also the National Institutes of Health (P30ES00210). The authors thank Dr. Wang Feng, Dr. Wang Xinming, Haibo Zhang, Jen Krenz, Gao Dong, and Xie Hang for their assistance with soil sampling in China.

References

- 1. Killin RK, Simonich SL, Jaffe DA, DeForest CL, Wilson GR. Transpacific and regional atmospheric transport of anthropogenic semivolatile organic compounds to Cheeka Peak Observatory during the spring of 2002. JGR-Atmos 2004;109(D23)
- 2. Kurt-Karakus PB, Bidleman TF, Jones KC. Chiral organochlorine pesticide signatures in global background soils. Environ Sci Technol 2005;39(22):8671–8677. [PubMed: 16323761]
- 3. Bidleman TF, Leone AD, Falconer RL, Harner T, Jantunen LM, Wiberg K, Helm PA, Diamond ML, Loo B. Chiral Pesticides in Soil and Water and Exchange with the Atmosphere. The Scientific World 2002;2:357–373.
- 4. Regionally Based Assessment of Persistent Toxic Substances; Global Environmtal Facility: December 2002. http://www.chem.unep.ch/pts/regreports/C&NE%20Asia%20full%20report.pdf.
- Bidleman T, Leone AD, Falconer RL, Harner T, Jantunen L, Wiberg K, Helm PA, Diamond ML, Loo B. Air-water and air-soil exchange of chiral organochlorine pesticides. Environmental Fate and Effects of Pesticides Book Series: ACS SYMPOSIUM SERIES 2003;853:196–225.
- Bidleman TF, Falconer RL. Using enantiomers to trace pesticide emissions. Environ Sci Technol 1999;33(9):206A–209A.
- Primbs T, Wilson G, Schmedding D, Higginbotham C. Simonich, Staci Massey, Influence of Asian and Western United States Agricultural Areas and Fires on the Atmospheric Transport of Pesticides in the Western United States. Environ Sci Technol 2008;42:6519–6525. [PubMed: 18800524]
- Primbs T, Piekarz A, Wilson G, Schmedding D, Higginbotham C, Field J, Simonich SM. Influence of Asian and Western United States Urban Areas and Fires on the Atmospheric Transport of Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, and Fluorotelomer Alcohols in the Western United States. Environ Sci Technol 2008;42:6385–6391. [PubMed: 18800505]
- 9. Primbs T, Simonich S, Schmedding D, Wilson G, Jaffe D, Takami A, Kato S, Hatakeyama S, Kajii Y. Atmospheric Outflow of Anthropogenic Semivolatile Organic Compounds from East Asia in Spring 2004. Environ Sci Technol 2007;41(10):3551–3558. [PubMed: 17547177]
- 10. Genualdi S, Primbs T, Killin R, Woods J, Wilson G, Schmedding D, Simonich S. Trans-Pacific and Regional U.S. Atmospheric Transport of PAHs and Pesticides in Biomass Burning Emissions. Environ Sci Technol. 2009ASAP online
- 11. Harner T, Shoeib M, Kozma M, Gobas FAPC, Li SM. Hexachlorocyclohexanes and endosulfans in urban, rural, and high altitude air samples in the Fraser Valley, British Columbia: Evidence for trans-Pacific transport. Environ Sci Technol 2005;(3):39. 724–731.
- 12. Primbs T, Genualdi S, Simonich S. Solvent Selection for Pressurized Liquid Extraction of Polymeric Sorbents Used in Air Sampling. Environ Toxicol Chem 2008;27:1267–1272. [PubMed: 18220448]
- 13. Li YF, Cai DJ, Singh A. Technical hexachlorocyclohexane use trends in China and their impact on the environment. Arch Environ Contam Toxicol 1998;35(4):688–697. [PubMed: 9776788]
- 14. Li YF. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. Sci Tot Environ 1999;232(3):121–158.
- Falconer RL, Bidleman TF, Szeto SY. Chiral pesticides in soils of the Fraser Valley, British Columbia.
 J Ag Food Chem 1997;45(5):1946–1951.
- Draxler, RR.; Rolph, GD. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model. NOAA Air Resources Laboratory Silver Spring; MD: 2003. http://www.arl.noaa.gov/ready/hysplit4.html

17. Li J, Zhang G, Qi SH, Li XD, Peng XZ. Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China. Sci Tot Environ 2006;372 (1):215–224.

- 18. Willett KL, Ulrich EM, Hites RA. Differential Toxicity and Environmental Fates of Hexachlorocyclohexane Isomers. Environ Sci Technol 1998;32(15):2197–2207.
- 19. Lammel G, Ghim YS, Grados A, Gao HW, Huhnerfuss H, Lohmann R. Levels of persistent organic pollutants in air in China and over the Yellow Sea. Atmos Environ 2007;41(3):452–464.
- Law S, Diamond ML, Helm PA, Jantunen L, Alaee M. Factors Affecting the Occurence and Enantiomeric Degradation of Hexachlorocyclohexane Isomers in Northern and Temperate Aquatic Systems. Environ Toxicol Chem 2001;20(12):2690–2698. [PubMed: 11764150]
- Ridal JJ, Bidleman TF, Kerman BR, Fox ME, Strachan WMJ. Enantiomers of alphahexachlorocyclohexane as tracers of air-water gas exchange in Lake Ontario. Environ Sci Technol 1997;31(7):1940–1945.
- 22. Shen L, Wania F, Lei YD, Teixeira C, Muir DCG, Bidleman TF. Hexachlorocyclohexanes in the north American atmosphere. Environ Sci Technol 2004;38(4):965–975. [PubMed: 14998006]
- 23. Finizio A, Bidleman TF, Szeto SY. Emission of chiral pesticides from an agricultural soil in the Fraser Valley, British Columbia. Chemosphere 1998;36(2):345–355.
- 24. Jantunen LM, Bidleman T. Air-water gas exchange of hexachlorocyclohexanes (HCHs) and the enantiomers of alpha-HCH in arctic regions. JGR-Atmos 1996;101D22:28837–28846.
- 25. Ding X, Wang XM, Xie ZQ, Xiang CH, Mai BX, Sun LG, Zheng M, Sheng GY, Fu JM. Atmospheric Hexachlorocyclohexanes in the North Pacific Ocean and the Adjacent Arctic Region: Spatial Patterns, Chiral Signatures, and Sea-Air Exchanges. Environ Sci Technol 2007;41:5204–5209. [PubMed: 17822080]
- Liang Q, Jaegle L, Wallace JM. Meteorological indices for Asian outflow and transpacific transport on daily to interannual timescales. JGR-Atmos 2005;110(D18)
- 27. Hansen KM, Halsall CJ, Christensen JH, Brandt J, Frohn LM, Geels C, Skjoth CA. The Role of the Snowpack on the Fate of alpha-HCH in an Atmospheric Chemistry-Transport Model. Environ Sci Technol 2008;42(8):2943–2948. [PubMed: 18497148]
- 28. Dearth MA, Hites RA. Complete Analysis of Technical Chlordane Using Negative Ionization Mass-Spectrometry. Environ Sci Technol 1991;25(2):245–254.
- 29. Hirai Y, Tomokuni K. Levels of Chlordane, Oxychlordane, and Nonachlor In Human Adipose Tissues. Bull Environ Contam Toxicol 1991;47(2):173–176. [PubMed: 1912692]
- 30. Li, A. Persistent Organic Pollutants in Asia: Sources, Distributions, Transport and Fate. Elsevier; 2007. p. 825
- 31. Regionally Based Assessment of Persistent Toxic Substances; Global Environmental Facility: 2002 http://www.chem.unep.ch/pts/regreports/C&NE%20Asia%20full%20report.pdf.
- 32. Leone AD, Ulrich EM, Bodnar CE, Falconer RL, Hites RA. Organochlorine pesticide concentrations and enantiomer fractions for chlordane in indoor air from the US cornbelt. Atmos Environ 2000;34 (24):4131–4138.
- 33. Gouin T, Jantunen L, Harner T, Blanchard P, Bidleman T. Spatial and temporal trends of chiral organochlorine signatures in great lakes air using passive air samplers. Environ Sci Technol 2007;41 (11):3877–3883. [PubMed: 17612163]
- 34. Shen L, Wania F, Lei YD, Teixeira C, Muir DCG, Bidleman TF. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in north America. Environ Sci Technol 2005;39 (2):409–420. 22. [PubMed: 15707039]
- 35. Jantunen LMM, Bidleman TF. Organochlorine pesticides and enantiomers of chiral pesticides in Arctic Ocean water. Arch Environ Contam Toxicol 1998;35(2):218–228. [PubMed: 9680514]

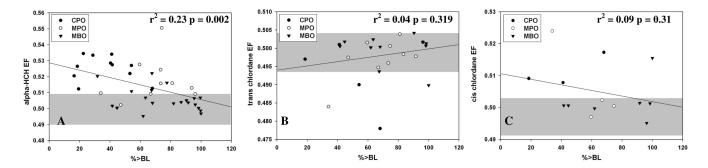
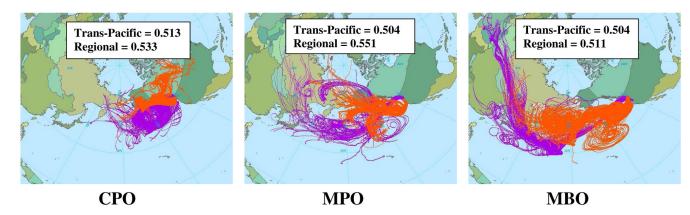


Figure 1.A) Alpha-HCH, B) *trans*-chlordane, and C) *cis*-chlordane EFs versus the percentage of time the 10-day air mass back trajectory spent above the boundary layer. The shaded regions represent the racemic range for alpha-HCH, *trans*-chlordane, and *cis*-chlordane.



- Trans-Pacific Event
- Regional Event

Figure 2.

Representative alpha-HCH EFs and 10-day air mass back trajectories for regional and trans-Pacific air masses at CPO, MPO, and MBO. Details of how the air mass back trajectories were calculated can be found in references 7,8, and 10. The sampling dates for the air masses displayed below are: CPO trans-Pacific – June 2–4, 2003; CPO regional – May 2–4, 2003; MPO trans-Pacific – Sept. 21–22, 2003; MPO regional – Aug 8–10, 2003; MBO trans-Pacific – April 25–26, 2004; and MBO regional – April 21–22, 2004.