

ORGANOCHLORINE PESTICIDES IN THE ATMOSPHERE: CURRENT USAGE OR GHOSTS OF THE PAST?

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Introduction

International conventions have called for reduction or elimination of priority substances which are persistent, bioaccumulating and toxic. The International Negotiating Committee of the United Nations Environmental Program Governing Council (INC-UNEP-GC) is proceeding towards ratification of a global ban for twelve persistent organic pollutants (POPs), eight of which are organochlorine (OC) pesticides (DDT, aldrin, dieldrin, heptachlor, chlordane, endrin, mirex and toxaphene). These pesticides have been banned for decades in Canada and the U.S., but are still found in air and precipitation from the Great Lakes region (1) and the Arctic (2,3).

What are the sources of OCs today, atmospheric transport from countries where they are still used, or "ghosts of the past" – recycled from contaminated soil and water? The "new" vs. "old" question is particularly relevant today, as countries work towards an agreement to eliminate OCs. Once an agreement is reached, there will be a need to monitor atmospheric levels to assess the effectiveness of the ban and to verify compliance. The contribution of old sources to the atmospheric background of OCs will have to be taken into account in such a program.

In this paper we compare atmospheric levels of OCs in regions where current usage is suspected (Central America) and in the Great Lakes region, where old sources may contribute to atmospheric burdens. We show how the distinctive chemical signatures of weathered OC residues in soil and water show promise for tracing their emission into air.

New Sources, Old Sources

Air samples were collected in Belize, Central America during 1995-96 (4), Alabama during 1996-97 (5) and South Carolina during 1994-95 (6). Sampling and analytical methods are described in these papers. Comparisons are made to levels of OCs measured at Integrated Atmospheric Deposition Network (IADN) stations on the Great Lakes (1).

DDT and dieldrin were particularly elevated in central Belize compared to levels found in Alabama and at IADN stations. Toxaphene in southern U.S. air was 10-30 times higher than in the Great Lakes region and 6 times higher than in Belize (Table 1). Chlordane in Belize fell between Great Lakes and southern U.S. values, while lindane was similar in all three locations (Table 1). Results suggest that Central America is a current source for DDT and dieldrin, but not a major emitter of chlordane, lindane, nor toxaphene. However, these conclusions are based on a limited study in Belize, which may not be representative of Central America as a whole. The southern U.S. appears to be a continuing source of toxaphene and chlordane, even though these pesticides were deregistered 10-15 years ago.

Soils containing OCs are capable of releasing them to the atmosphere. This is shown by higher-than-ambient levels of OCs in air sampled directly above soil at farms in California (7) and British Columbia (8). In this work, air samples were collected 40 cm above the soil at five farms in Alabama and Texas during June, 1999. Concentrations of toxaphene in ambient air in Alabama during 1996-97 averaged 0.28 ng/m³ in the summer months and 0.19 ng/m³ annually (5). Soils in Alabama contain toxaphene residues from previous agricultural use (9) and a soil-air exchange model predicted emissions of toxaphene that could account for observed ambient air concentrations (10).

Chemical Markers of Old Sources

Ratios of parent DDT to its DDE metabolite have been used to infer sources and age of residues. Total DDT residues in peat layers from the Great Lakes region and eastern Canada contained a high proportion of parent DDT, leading to the hypothesis that "new" DDT continued to be atmospherically transported from Mexico, Central America and the Caribbean after its 1972 ban in the U.S (11). Ratios of DDT/DDE in Belize air averaged 1.2 in winter and 6.3 in summer (4). By comparison, DDT/DDE ratios were 0.6-0.9 at IADN stations (1) and 0.3-0.4 in the Arctic (2). This suggests that both new and old sources are contributing to background DDT levels in the air of North America.

Certain toxaphene congeners are depleted in soils of the southern U.S. relative to technical toxaphene. Figure 1 shows the profiles of octachlorobornanes in soil and overlying air samples from Texas and Alabama. Note the depletion of Parlar congeners 39 and 42 in both sample types. Reduced proportions of Parlar 39 and 42 were also found in ambient air samples from Alabama (5). The signatures of individual chlorobornanes may provide a way to distinguish soil emissions of toxaphene from current usage.

A new technique for tracing emissions from soil makes use of the enantiomers of certain chiral pesticides. Most chiral pesticides are manufactured as a racemic (1:1) mixture of enantiomers, which is not changed by abiotic reactions nor physical processes (e.g., volatilization, deposition). However, one enantiomer is often preferentially broken down by microorganisms in soil and water. The distinctive non-racemic enantiomer signatures, expressed as enantiomer ratios (12-14) or fractions (15) can be employed to follow volatilization.

Chlordanes in ambient air may result from soil emissions, termiticide usage in homes and long-range transport from current usage. Non-racemic chlordanes have been reported in soils of the midwestern U.S. (16) and Alabama (17) and in ambient air of the Great Lakes region (13,18,19). Chlordanes in ambient air of the Alabama (5) and in the air of private homes in the southern (5) and midwestern (20) states were racemic. This suggests that soil emissions contribute to atmospheric chlordane in the Great Lakes region (13), but not in Alabama (5). Chlordane residues in Alabama soils are lower than those in the midwestern U.S. (9), and a volatilization model indicates that soil emissions cannot account for observed concentrations in Alabama air (10).

OCs in arctic air come from both new and old sources. The α -hexachlorocyclohexane (α -HCH) in air over ice-covered regions of the Arctic Ocean is racemic, as expected from long-range transport of technical HCH. One enantiomer is preferentially degraded in Arctic Ocean water, and volatilization can be traced by the appearance of non-racemic α -HCH in air above open water areas (21,22).

The ratio of trans-chlordane to cis-chlordane isomers (TC/CC) in arctic air follows a regular pattern of higher values in winter and lower ones in summer (2). Examination of TC/CC trends in arctic air over the last ten years indicates that the ratios have been declining in both winter and summer (12). Since TC is more labile in the environment, this suggests that old residues of chlordane are contributing to today's atmospheric levels. Support comes from chiral analysis of 1994-95 air samples from Canadian and Russian monitoring stations. Enantiomer ratios of TC averaged 0.87 ± 0.04 ($n=28$), significantly ($p<0.001$) different from the racemic value of 1.00. Chlordanes in Arctic Ocean surface water are racemic (23), so local volatilization cannot be responsible. Long-range transport of old chlordane residues is more likely, probably from soil emissions in temperate regions.

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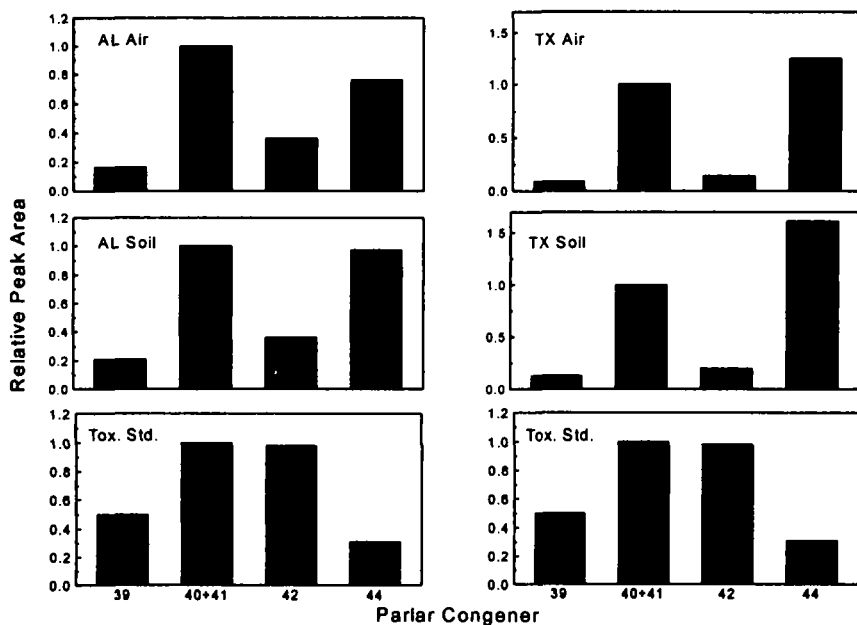


Figure 1. Relative peak areas of octachlorobornanes in soil and overlying air samples from Alabama and Texas.

Table 1. Organochlorine Pesticides in Ambient Air, $\mu\text{g}/\text{m}^3$

	$\Sigma\text{DDT}^{\text{a}}$	Dieldrin	$\Sigma\text{Chlordane}^{\text{b}}$	Lindane	Toxaphene	Ref.
Belize, 1995-96						
Inland	1036	775	67	53	35	4
Coastal	192	34	46	28	27	
Alabama, 1996-97	10	38	95	50	176	5
South Carolina, 1994-95 ^c			308		189	6
Great Lakes, 1996-97 ^d	1.6-34	2.4-22	3.3-31	6.4-25	6-40	1,24-26

a) p,p' -DDT + o,p' -DDT + p,p' -DDE + p,p' -DDD in Belize and the Great Lakes, p,p' -DDE in Alabama.

b) *cis*-chlordane + *trans*-chlordane + *trans*-nonachlor.

c) City of Columbia

d) Toxaphene from IADN stations and shipboard measurements on lakes Superior and Ontario; other OCs from IADN stations on lakes Superior and Erie.