

Spatial and temporal trends of gas and particle phase atmospheric DDT and metabolites in Michigan: Evidence of long-term persistence and atmospheric emission in a high-DDT-use fruit orchard

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[1] Michigan was among the top three apple producing states in the United States from the 1940s to 1969 when DDT was heavily used on its fruit orchards. More than 2 decades after Michigan banned DDT use in 1969, we collected air samples from four sites around the state to measure concentrations of six DDT-related compounds in the atmosphere. At South Haven, an apple producing area, average gas phase concentrations of DDT and DDE compounds were at least 10 times greater than the other sites including Pellston in the north, Deckerville in the east, and Dexter in south-central.

Concentrations at South Haven showed a very strong seasonal cycle, an effect of higher air temperatures on moving these residues into the gas phase from a local source. We calculated ΔH values for all six compounds from the South Haven data which showed that *p,p'*-DDE was the highest at 108 kJ mol⁻¹. The ΔH values for all compounds at South Haven had a high correlation with Henry's Law Constant (HLC) ($r = 0.7$), verifying that HLC is a good indicator of tendency for compound conversion to the gas phase. South Haven was the only site with significant atmospheric particle-associated DDT.

Particle/gas ratios there for *p,p'*-DDT and *p,p'*-DDE also had a predictable seasonal variation. Overall, these results show that agricultural sites with similar DDT use history will be continuous sources of atmospheric DDT for decades after application.

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1. Introduction

[2] Dichlorodiphenyltrichloroethane, or DDT, has been part of the human ecology of the globe since its first synthesis in the late 19th century. The discovery of its pesticidal properties in 1939 led to rapid development of its use in the United States on cotton plants, apples and other tree fruits [Harris *et al.*, 2000]. Orchards are now considered to be the most likely environmental sink for DDT group compounds because of their persistence, historic heavy use and lack of soil disruption by tillage [Harris *et al.*, 2000].

[3] Early research on orchard soils in the 1970s suggested that DDT had a persistence of up to about 4 years, with losses caused by metabolism to DDE and DDD, vaporization or erosion [Hiltbold, 1974; Stringer *et al.*, 1974, 1975; Voerman and Besemer, 1975]. Later investigations have

shown that soil DDT and related residues, including the metabolites, remain much longer, on the order of decades, and are lost by metabolism and vaporization [Diamond and Owen, 1996; Harris *et al.*, 2000; Szeto and Price, 1991]. These findings concerning vaporization losses have encouraged us to investigate air samples from four sites in Michigan from the 1990s for spatial and temporal trends of atmospheric DDT-group compounds in gas and particle phases. One of our sampling sites was in an apple orchard, although it was not known to us at the time the project started if DDT had ever been used there.

[4] During the DDT era in the US (~1945–1972), Michigan was always among the top three apple producing states nationwide [U.S. Bureau of the Census, 1977]. Eight counties in western Michigan produced ~70% of the state's apples between 1965 and 1967, near the peak of DDT use (Figure 1) [Jackman *et al.*, 1976; U.S. Department of Agriculture, 1966]. Berrien County, in far southwestern Michigan, was the largest single producer with 19% of the state's apple acreage during that time. On the basis of documented DDT uses there, we have estimated that about 181 metric tons of DDT were used in those eight counties from 1965 to 1967. DDT was also used in urban areas throughout Michigan from the early 1950s to combat the spread of Dutch Elm disease, but that ended in 1960 because of bird deaths [Wallace *et al.*, 1961], a typical

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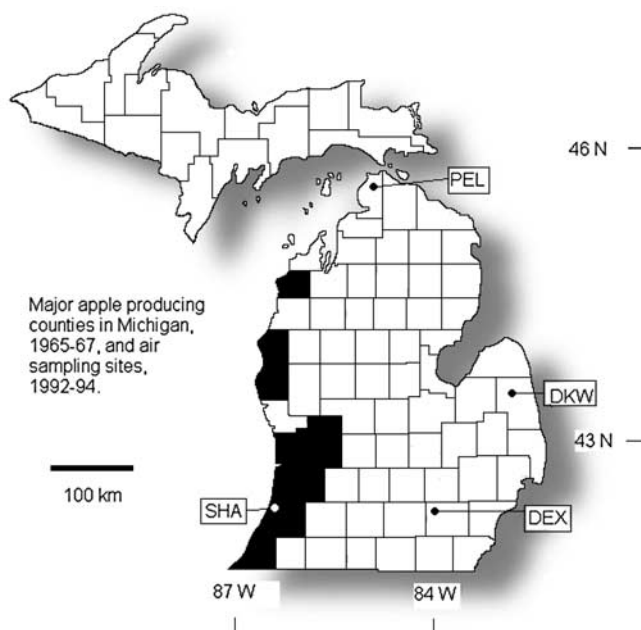


Figure 1. Map of Michigan noting eight western major apple producing counties (1965–1967) and air sampling sites (1992–1994).

problem elsewhere in the United States [DeWitt, 1955]. DDT was banned throughout Michigan in April 1969 (Michigan Environmental Council, 2002; <http://www.mecprotects.org/lewbatts.html>). DDT remains a significant issue in Michigan as recently as 2004 because of fish advisories in tributaries to southern Lake Michigan and to Lake Huron (http://www.michigan.gov/documents/FishAdvisory03_67354_7.pdf; <http://www.deq.state.mi.us/documents/deq-ogl-lhi-2002ha.pdf>). DDT is considered to be a possible public health issue in Michigan because of its historic heavy use, persistence and suspected toxic effects in humans [Downes *et al.*, 2003]. Toxic effects can be influenced by inhalation of gas phase DDT which deposits in lung tissues making atmospheric analysis particularly important [Volckens and Leith, 2003].

[5] Our objective is to identify if residues of DDT and its metabolites were still found in atmospheric gases and particles around Michigan more than 2 decades after the end of application in apple producing counties. This will help to corroborate the results of some investigators showing that DDT residues linger in orchards much longer than believed in the 1970s. Our results include quantifying gas and particle phase DDT-group atmospheric concentrations. These data are used to identify relationships to local air temperature for both gases and particles and the relationship between them. Our results are applicable to many other areas where DDT was or is still used and remains in soils for decades [Aigner *et al.*, 1998; Dimond and Owen, 1996; Vandervoort, 1999], and particularly to the several countries where it was still used in 2000 [Curtis and Lines, 2000].

2. Experimental Methods

2.1. Field Sampling and Sample Analysis

[6] Atmospheric gas and particle samples were collected on a 6-day cycle from four sites between May 1992 and

February 1994 as part of a large-scale multicontaminant study intended to give broad spatial coverage over Michigan (Figure 1). A total of 446 samples were collected each in the gas and particle phases. The Pellston (PEL) site was located at the University of Michigan Biological Station; Deckerville (DKW) was located about 5 km from Lake Huron; Dexter (DEX) was 15 km northwest from Ann Arbor on a University of Michigan site. South Haven (SHA) was approximately 8 km from Lake Michigan in an orchard. None of the sites was located in an area known to be contaminated at the time.

[7] Air temperature measurements were made at local meteorological stations. The station used for Deckerville data closed at the end of 1992, so we estimated air temperature using the HYSPLIT model with surface temperatures for 1993 and 1994 extracted from the National Centers for Environmental Prediction's Nested Grid Model (NGM) (<http://www.arl.noaa.gov/ready.html> and <ftp://www.arl.noaa.gov/pub/archives/ngm>). The results of Bland-Altman analysis for comparing measured temperatures during 1992 and modeled data showed that the mean bias was 0.08°C, with all modeled data within two standard deviations of the measured data [Bland and Altman, 1986].

[8] We analyzed all samples collected from South Haven on a continuous 6 day cycle during the entire sampling period because early data for various organochlorine compounds were showing it to be a periodically contaminated site [Hermanson *et al.*, 1997]. At the other sites we analyzed samples collected on the same cycle during nonwinter seasons. Several winter samples were collected at these sites simultaneously with South Haven to identify background concentrations during periods when there would be less vaporization of DDT-group compounds into the atmosphere from frozen or snow covered surfaces.

[9] Samples were collected by pumping a target volume of 250 m³ of air through a glass fiber filter (GFF) which collected particles >0.1 μm diameter, followed by a 6 cm diameter glass cylinder consisting of XAD-2 held between two layers of precleaned polyurethane foam (PUF) which collected the gas phase. All sampling materials were pre-cleaned: GFF were sterilized by heating at 450°C for 4 hours before sampling, then weighed. The glass cylinder was washed and muffled at 450°C for 4 hours. The PUF was pre-cleaned in two 24 hour Soxhlet extractions in dichloromethane (DCM) followed by 1/1 (v/v) acetone/hexane. PUF was dried in a vacuum desiccator before it was used. The XAD-2 was pre-cleaned in a series of 24 hour extractions in methanol, DCM, acetone, hexane, DCM and 1/1 (v/v) acetone/hexane. Glass cylinders with PUF and XAD were assembled in lab and shipped to the sampling sites. Blanks were collected by loading GFF and PUF/XAD cylinders onto a sampler and removing without pumping any air. Collected samples were stored and shipped frozen except when GFF were allowed to dry in a desiccator. Some vaporization losses of our analytes from GFF may have been possible, so our reported particle concentrations are minima.

[10] Sample extraction methods for this project were discussed previously [Hermanson *et al.*, 1997]. All samples were extracted in 1/1 (v/v) acetone/hexane using a Soxhlet extractor. Four surrogate standards were added before extraction began (PCB 14, PCB 65, PCB 166, δ-HCH).

Table 1. Quality Control Data for Analysis of *p,p'*- and *o,p'*-DDD, DDE and DDT^a

	Blank, ng	Limit of Detection, pg/m ³	Matrix Recovery, ^b %	Column Recovery, ^c %
Gases^d				
<i>p,p'</i> -DDD	0.03	0.4	79.9	88.9
<i>o,p'</i> -DDD	0.03	0.3	108.4	110.5
<i>p,p'</i> -DDE	0.04	0.6	86.5	88.3
<i>o,p'</i> -DDE	0.05	0.6	91.4	104.1
<i>p,p'</i> -DDT	0.05	0.9	94.8	103.8
<i>o,p'</i> -DDT	0.08	1	105.3	94.4
Particles^e				
<i>p,p'</i> -DDD	ND	0.4	90.6	88.9
<i>o,p'</i> -DDD	ND	0.4	80.8	110.5
<i>p,p'</i> -DDE	0.01	0.3	107.3	88.3
<i>o,p'</i> -DDE	ND	0.3	79.5	104.1
<i>p,p'</i> -DDT	0.04	0.8	109.7	103.8
<i>o,p'</i> -DDT	ND	0.8	88.4	94.4

^aND, not detected. Detection limit is estimated as instrumental detection.

^bTotal recovery from all sample fractions of matrix of column spikes.

^cTotal recovery of all sample fractions from silica-gel columns, used for both gases and particles.

^dSurrogate recoveries (recovery of surrogate spikes added to samples, average %) are δ -HCH = 89.7, n = 383, and PCB-65 = 79.6, n = 383.

^eSurrogate recoveries are δ -HCH = 94%, n = 396, and PCB-65 = 77.1%, n = 396.

Extracts were volume-reduced by rotary evaporation and were separated into 2 fractions using elutions of hexane and 40/60 (v/v) DCM/hexane through silica-gel deactivated 3.5% with purified H₂O [Hermanson *et al.*, 1997; Monosmith and Hermanson, 1996]. Both fractions were analyzed for all 6 DDT-group compounds by gas chromatography with electron capture detection (GC-ECD) using a 60-m DB-5 column, and quantified using PCB 204 as an internal standard. QC data, including column recoveries and surrogate recoveries and limits of detection appear in Table 1. Between May 1992 and February 1994 *p,p'*-DDT, DDE and DDD were quantified. During the last 12 months of that period the *o,p'*-isomers of these compounds were also included in the analysis. This analytical scheme resulted in quantification of contaminant mass in a volume of collected air sample in pg m⁻³ for both gases and particles.

2.2. Data Analysis: Clausius-Clapeyron Equation

[11] We used the Clausius-Clapeyron (CC) equation to measure the heat of vaporization (ΔH) from the condensed phase to a gas as a way of identifying if DDT sources were local and how those sources respond to seasonal temperature changes. A steep trend in the CC slope (high ΔH) is a characteristic indication of a local contaminant source [Wania *et al.*, 1998]. Since there are a variety of matrices (leaves, bark, soils) where DDT group compounds can be dissolved in lipids or water, or perhaps condensed on inert surfaces, the value of ΔH from the CC equation is a measure of the relationship between changes in air temperature and emission of contaminant into the gas phase. DDT residues dissolved in lipids, water or bound by organic carbon may not be affected by air temperature changes.

[12] The CC equation has been widely used for comparing energy requirements for moving compounds into the gas phase. In addition to identifying local contamination sources, its results contribute to predicting regional or long-distance transport in the atmosphere [Buehler *et al.*, 2001; Glassmeyer *et al.*, 1999; Hermanson *et al.*, 2003; Hillery *et al.*, 1997; Panshin and Hites, 1994]. Traditionally the CC equation was used for measurement of vapor pressures in closed systems [Atkins, 2001].

[13] Using the CC equation with our DDT-group data expressed in pg m⁻³ requires conversion of the pesticide concentration values to C , in moles L⁻¹, then to partial pressures (P) using a version of the ideal gas law:

$$P = CRT \quad (1)$$

where T = average air temperature during sampling (K), R = gas constant. As traditionally written, the CC equation assumes that P is the unknown, appearing on the left of the equation:

$$\ln P = (-\Delta H/RT) + c, \quad (2)$$

where c is a constant representing the $\ln P$ intercept and $-\Delta H/R$ is the slope of the CC line. To solve for ΔH , we used

$$-\Delta H = RT \ln P - c. \quad (3)$$

[14] Since DDT was banned in Michigan 23 years before we collected our first sample we assume that pesticide spraying did not contribute to any of our observations and that all measured gas phase DDT-group compounds were emitted into the air by vaporization from local sources or were delivered to the sites by long-range atmospheric transport (LRAT). Previous research concerning orchards suggests that vaporization from soil or other surfaces is only one loss mechanism of DDT-group compounds. Other losses include leaching through soil or erosion, loss by vaporization and then to lipids such as in tree bark or into fruits that are later harvested [Forsyth *et al.*, 1983; Harris *et al.*, 2000; Nash and Beall, 1970; Yule *et al.*, 1972]. Some DDT-group compounds can be lost by vaporization from organic carbon or other lipids: Results from Harner and Mackay [1995] show that the octanol-air partition coefficient (K_{oa}) for *p,p'*-DDT declines with higher air temperatures, suggesting that some losses are experienced from organic matter (with absorption properties similar to octanol) during warmer weather. The value of ΔH therefore

Table 2a. Maximum, Average, and Minimum Concentrations of All Analytes: Gas Phase^a

	Maximum	Average	Minimum
<i>South Haven</i>			
<i>p,p'</i> -DDD	113	7.83	0.4
<i>o,p'</i> -DDD	79.7	17.4	1.58
<i>p,p'</i> -DDE	5420	698	2.2
<i>o,p'</i> -DDE	2780	77.2	0.6
<i>p,p'</i> -DDT	1910	245	3.9
<i>o,p'</i> -DDT	687	104	2.92
<i>Pellston</i>			
<i>p,p'</i> -DDD	8.41	2.54	0.4
<i>o,p'</i> -DDD	7.93	2.85	0.532
<i>p,p'</i> -DDE	30.2	6.98	0.806
<i>o,p'</i> -DDE	12.1	2.7	0.336
<i>p,p'</i> -DDT	36	7.34	0.9
<i>o,p'</i> -DDT	16.4	4.7	1
<i>Dexter</i>			
<i>p,p'</i> -DDD	22.6	4.01	0.481
<i>o,p'</i> -DDD	16.8	3.98	0.625
<i>p,p'</i> -DDE	222	27.3	0.6
<i>o,p'</i> -DDE	38.2	6.9	0.6
<i>p,p'</i> -DDT	62.4	16.2	1.89
<i>o,p'</i> -DDT	26.9	8	1
<i>Deckerville</i>			
<i>p,p'</i> -DDD*	14.5	3	0.4
<i>o,p'</i> -DDD	35.8	5.35	0.494
<i>p,p'</i> -DDE*	206	12.6	0.715
<i>o,p'</i> -DDE*	24.9	4.33	0.6
<i>p,p'</i> -DDT*	98.7	8.79	0.9
<i>o,p'</i> -DDT	22.2	5.26	1

^aUnit is pg m^{-3} . Bold values are detection limit.

only represents the average amount of energy required for vaporization losses to the atmosphere from a number of possible matrices.

2.3. Particle/Gas Measurements

[15] Seasonal fluctuations of gas phase concentrations of semivolatile compounds with high concentrations in summer suggests that vaporization may occur from atmospheric particles or local soils. A theoretical relationship between compounds associated with particles and in the gas phase is calculated using a particle/gas coefficient based on vapor pressures of a given compound [Finizio *et al.*, 1997; Kaupp and McLachlan, 1999; Pankow, 1999] called K_p and defined by

$$K_p = (F/TSP)/A \quad (4)$$

where F = concentration of contaminant on (filtered) particles, pg g^{-1} , TSP = density of total suspended particulate matter in air, pg m^{-3} , A = gas phase (absorbed) contaminant concentration, pg m^{-3} . If the particle concentration, F , is measured as pg m^{-3} as in our analysis, then the equation simplifies to

$$K_p = F/A \quad (5)$$

According to Pankow [1991], $\log K_p$ will depend on temperature for any given compound, any type of particulate matter and in any atmospheric condition. A

similar coefficient measured from actual field data is designated as a gas/particle ratio, or $A/(F/TSP)$ and has been used in the literature [Bidleman *et al.*, 1986; Cotham and Bidleman, 1992; Pankow and Bidleman, 1992; Sanusi *et al.*, 1999]. For our purposes, we calculated a particle/gas ratio (F/A) and $\log (F/A)$ to be consistent with K_p . We plotted $-\log (F/A)$ against 1000 T^{-1} in order to identify the comparative temperature-related trends of particle/gas distribution. We also compare our measured results with the theoretical vapor-pressure based calculations of Finizio *et al.* [1997]. We have sufficient data from this project for comparison of *p,p'*-DDT and *p,p'*-DDE at South Haven.

3. Results and Discussion

3.1. DDT-Group Atmospheric Concentrations

[16] Results for gas phase *p,p'*- and *o,p'*-isomers of DDT, DDE and DDD show that concentrations of all but *o,p'*-DDD are at least one order of magnitude greater in the orchard at South Haven than at the other sites (Tables 2a and 2b and Figures 2–4). The highest concentrations are for the *p,p'*-isomers with maximum levels of 1,910 (DDT), 5,420 (DDE) and 113 (DDD) pg m^{-3} , all of which are reached during warmer summer periods (Figure 2). The maximum concentrations for *o,p'*-DDT, DDE and DDD at South Haven are 687, 313 and 80 pg m^{-3} . Since the *o,p'*-group compounds were a small component of a typical lot of commercial DDT (not $> \sim 15\%$ of the total DDT product), the magnitude of these numbers again reveals the signifi-

Table 2b. Maximum, Average, and Minimum Concentrations of All Analytes: Particle Phase^a

	Maximum	Average	Minimum
<i>South Haven</i>			
<i>p,p'</i> -DDD	5.99	1.22	0.4
<i>o,p'</i> -DDD	5.74	1.24	0.433
<i>p,p'</i> -DDE	70.8	6.79	0.3
<i>o,p'</i> -DDE	53.3	3.96	0.3
<i>p,p'</i> -DDT	148	14.9	0.8
<i>o,p'</i> -DDT	20.6	2.4	0.8
<i>Pellston</i>			
<i>p,p'</i> -DDD	8.41	2.54	0.4
<i>o,p'</i> -DDD	2.49	1.51	0.538
<i>p,p'</i> -DDE	6.46	0.75	0.3
<i>o,p'</i> -DDE	1.19	0.9	0.336
<i>p,p'</i> -DDT	23.7	4.48	0.8
<i>o,p'</i> -DDT	ND	ND	ND
<i>Dexter</i>			
<i>p,p'</i> -DDD	17.2	4.67	0.653
<i>o,p'</i> -DDD	ND	ND	ND
<i>p,p'</i> -DDE	4.42	0.989	0.3
<i>o,p'</i> -DDE	1.48	1	0.3
<i>p,p'</i> -DDT	56.2	4.12	0.8
<i>o,p'</i> -DDT	2.54	0.9	0.8
<i>Deckerville</i>			
<i>p,p'</i> -DDD	1.64	3	0.4
<i>o,p'</i> -DDD	2.94	1.92	0.889
<i>p,p'</i> -DDE	3.44	0.94	0.3
<i>o,p'</i> -DDE	ND	ND	ND
<i>p,p'</i> -DDT	55.3	4.23	0.8
<i>o,p'</i> -DDT	2.62	0.8	0.8

^aUnit is pg m^{-3} . Bold values are detection limit. ND, not detected.

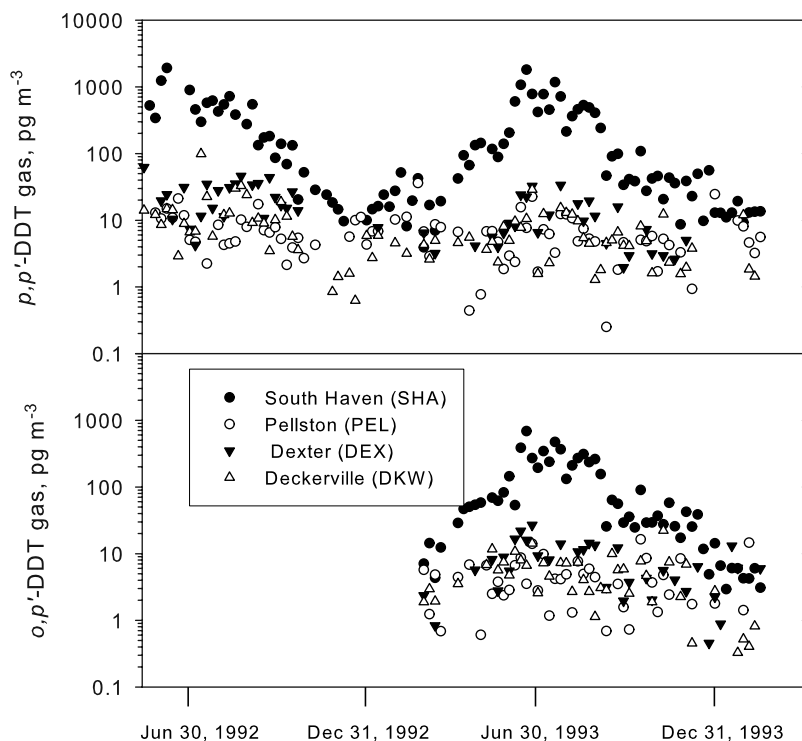


Figure 2. Time trends of atmospheric gas concentrations of p,p' -DDT and o,p' -DDT at four Michigan air sampling sites.

cance of the local sources of these compounds at South Haven.

[17] The peak concentration at South Haven of all 6 compounds combined (Σ DDT) on a given date ($8,122 \text{ pg m}^{-3}$)

is about 20 times greater than observations at any other Great Lakes or upper Midwest site reported since 1990 [Buehler *et al.*, 2001; Hawthorne *et al.*, 1996; Hoff *et al.*, 1992, 1996; McConnell *et al.*, 1998; Monosmith and

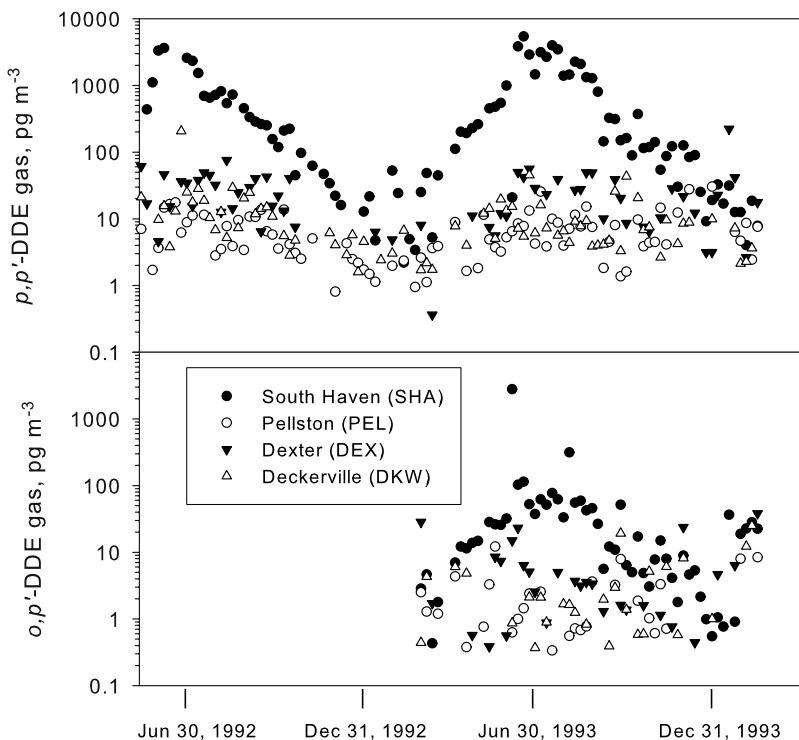


Figure 3. Time trends of atmospheric gas concentrations of p,p' -DDE and o,p' -DDE at four Michigan air sampling sites.

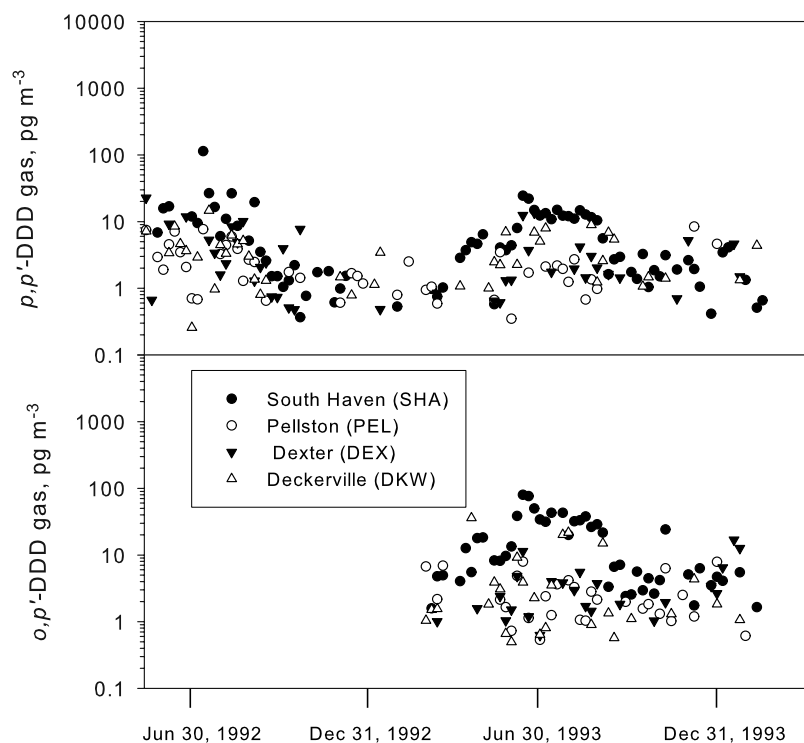


Figure 4. Time trends of atmospheric gas concentrations of p,p' -DDD and o,p' -DDD at four Michigan air sampling sites.

Hermanson, 1996] which show a maximum Σ DDT (sum of p,p' -DDT and p,p' -DDE) concentration of about 417 pg m^{-3} over Lake St. Clair [McConnell *et al.*, 1998]. This peak concentration of Σ DDT is also about 8 times greater than average concentration in Belmopan, Belize in the mid-1990s (992 pg m^{-3}), where a regional current DDT use was suspected [Alegria *et al.*, 2000], perhaps in Mexico at the time [Lopez-Carrillo *et al.*, 1996], and in Zimbabwe in 1994 (1050 pg m^{-3}) where it was used as late as 1988 [Larsson *et al.*, 1995]. It is consistent with off-season gas phase Σ DDT concentrations in a Mississippi cotton field in the early 1970s ($10,800 \text{ pg m}^{-3}$ in December) where DDT was used during summer [Arthur *et al.*, 1976]. During South Haven sampling there apparently was a significant local source of DDT-group compounds, likely a residue of its use on fruit trees in the 1950s and 1960s. Soil analysis in the area by Vandervoort [1999] in 1998 suggests that the source of these compounds is likely to be local soils. Results show that surface soils contain a maximum of $22,180 \text{ } \mu\text{g g}^{-1}$ p,p' -DDT and $11,700 \text{ } \mu\text{g g}^{-1}$ p,p' -DDE. At “middle” depths in the same soil column, the p,p' -DDT concentration exceeded $232,000 \text{ } \mu\text{g g}^{-1}$ and p,p' -DDE was $1,411 \text{ } \mu\text{g g}^{-1}$. These concentrations of p,p' -DDT are extremely high: In Maine forest soils where DDT was applied in the 1960s, the maximum concentration was $4.5 \text{ } \mu\text{g g}^{-1}$ [Dimond and Owen, 1996]. Stringer *et al.* [1974] show a maximum DDT concentration in a British orchard of $14.8 \text{ } \mu\text{g g}^{-1}$ in 1964 during active spraying. Another British orchard contained a maximum of $3.75 \text{ } \mu\text{g g}^{-1}$ Σ DDT (p,p' -isomers only) in 1968, the final year of DDT application [Cooke and Stringer, 1982]. In Brazil, at a site where DDT was sprayed, soils contained up to $351 \text{ } \mu\text{g g}^{-1}$ Σ DDT [Vieira *et al.*, 2001]. The extremely high soil Σ DDT concentrations at

South Haven show that its persistence is on the order of decades. The high concentrations of DDT relative to DDE show that metabolic processes there are slow.

[18] In contrast to South Haven, the lowest atmospheric concentrations of any DDT-group compound for a given date usually occurred at Pellston or Deckerville, with Dexter between these extremes. The lowest maximum and average values for all six compounds are at Pellston (Tables 2a and 2b). The concentrations at sites other than South Haven are more characteristic of other observations in the Great Lakes region.

3.2. Clausius-Clapeyron Results

[19] The Clausius-Clapeyron equation was applied to all 6 compounds at all 4 sites. Statistical results, including correlation coefficient (r) and significance of the CC relationship (ρ) are shown in Table 3. The results show that the relationships for all six DDT-group compounds are strong at South Haven ($r = 0.638$ or higher) and significant ($\rho < 0.0001$ for each compound). At Pellston, the CC relationship is significant only for p,p' -DDE although the correlation is weak ($r = 0.433$). At Dexter, p,p' -DDE, p,p' -DDT and o,p' -DDT are significant, but again the correlations are not strong ($r = 0.467, 0.472, 0.517$ respectively). At Deckerville, the p,p' -DDD relationship is significant but not strong, as are p,p' -DDE, p,p' -DDT ($r = 0.350, 0.559, 0.338$ respectively). Deckerville has a significant relationship for o,p' -DDE which is also the strongest of any site for this compound ($r = 0.769$). However, this relationship is based on only 20 observations, while at South Haven it is based on 55. The general weakness of CC results or low numbers of observations or lack of evidence of a local DDT-group compound source for sites other than South Haven has led us to exclude them from analysis of ΔH using the CC equation.

Table 3. Statistical Results for the Clausius-Clapeyron Equation^a

	n	r	ρ
<i>South Haven</i>			
<i>p,p'</i> -DDD ^b	76	0.705	<0.0001
<i>o,p'</i> -DDD ^b	46	0.708	<0.0001
<i>p,p'</i> -DDE ^b	94	0.866	<0.0001
<i>o,p'</i> -DDE ^b	55	0.638	<0.0001
<i>p,p'</i> -DDT ^b	96	0.848	<0.0001
<i>o,p'</i> -DDT ^b	57	0.904	<0.0001
<i>Pellston</i>			
<i>p,p'</i> -DDD	35	0.315	0.065
<i>o,p'</i> -DDD	24	0.052	0.809
<i>p,p'</i> -DDE ^b	76	0.433	<0.0001
<i>o,p'</i> -DDE	20	0.198	0.404
<i>p,p'</i> -DDT	70	0.014	0.911
<i>o,p'</i> -DDT	33	0.2	0.264
<i>Dexter</i>			
<i>p,p'</i> -DDD	41	0.276	0.081
<i>o,p'</i> -DDD	24	0.264	0.213
<i>p,p'</i> -DDE ^b	62	0.467	0.00013
<i>o,p'</i> -DDE	25	0.014	0.948
<i>p,p'</i> -DDT ^b	60	0.472	0.00014
<i>o,p'</i> -DDT ^b	31	0.517	0.0029
<i>Deckerville</i>			
<i>p,p'</i> -DDD ^b	35	0.35	0.0392
<i>o,p'</i> -DDD	22	0.184	0.413
<i>p,p'</i> -DDE ^b	69	0.559	<0.0001
<i>o,p'</i> -DDE ^b	20	0.769	<0.0001
<i>p,p'</i> -DDT ^b	65	0.338	0.0058
<i>o,p'</i> -DDT	32	0.072	0.695

^an, number of observations; r, correlation coefficient.

^bSignificant at 0.05 level.

[20] The plots of CC results for all six DDT-group compounds from South Haven appear in Figure 5. The slopes of the regression lines in these plots (Table 4) suggest that the ΔH values for DDT and DDD isomers are quite similar, but that DDE isomers are very different. For DDT, the *p,p'*-DDT value is 84.8 kJ mol⁻¹ and *o,p'*-DDT is similar, 80.6 kJ mol⁻¹. The ΔH value for *p,p'*-DDE is 108 kJ mol⁻¹, the highest of the entire group and nearly double that for *o,p'*-DDE, 60.7 kJ mol⁻¹. For DDD isomers, the ΔH values are 60.5 for *p,p'*-DDD and 53.2 kJ mol⁻¹ for *o,p'*-DDD and are similar. The suggestion of these data is that *p,p'*-DDE will require the greatest input of energy to enter the gas phase. The slopes of all six compounds suggest that there is a local source.

[21] It is often considered that Henry's Law Constant (HLC), a ratio of vapor pressure to water solubility, is associated with transfer of a compound into the gas phase because it accounts for possible dissolution in water as well as air [Unsworth *et al.*, 1999]. Values of HLC are shown in Table 4. A correlation of ΔH and HLC from Table 4 is 0.70 and indicates that the trends in these data sets are similar, again supporting the observation by other investigators that HLC is a good indicator of pesticide transfer into the gas phase.

3.3. Particle-Associated DDT-Group Concentrations and Particle/Gas Distribution

[22] Our results for particle-associated *p,p'*-DDT and *p,p'*-DDE (Figure 6) show that South Haven concentrations are the highest among all sampling sites. The highest concentrations of these compounds occurred during both summers,

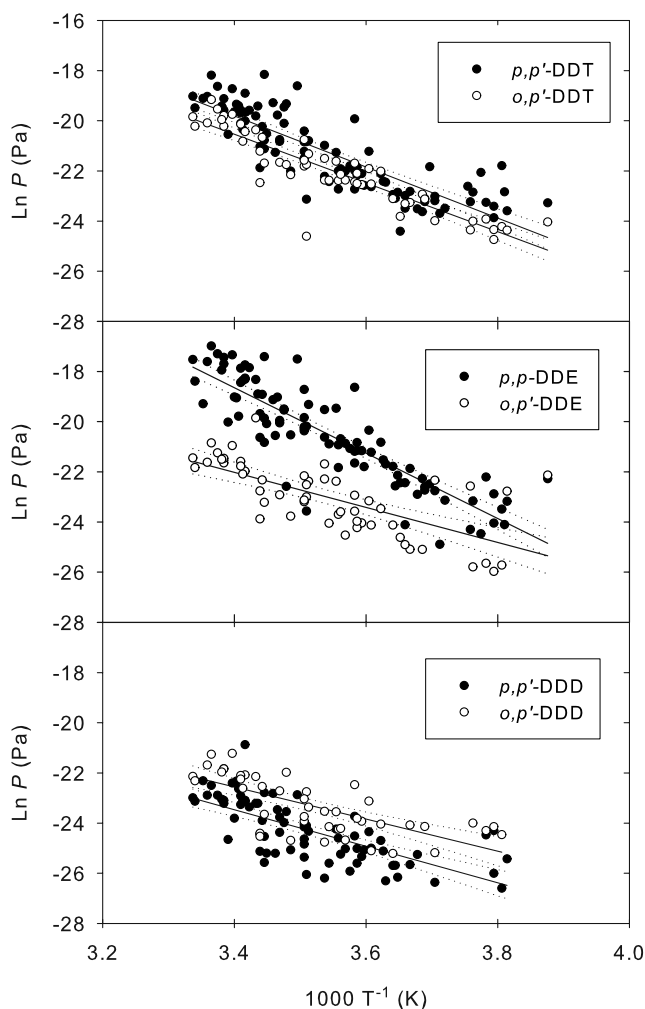


Figure 5. Clausius-Clapeyron plots of six DDT group compounds from South Haven. See Table 3 for statistical results for all sites and Table 4 for ΔH values.

although with less predictable variance with changing air temperature than gases (Figures 2 and 3). Our gas phase results show that these compounds are apparently vaporizing from local soils at higher temperatures, and it would be expected that particle concentrations would be lower in summer for the same reason. The fact that they change very little or are sometimes higher in late June and early July suggests that some airborne local soils are part of the particle sample and that vaporization is not occurring.

[23] Our calculated values of $-\log(F/A)$ are regressed with inverse temperature (Figure 7) to identify seasonal

Table 4. Calculated Values of ΔH and Henry's Law Constants (HLC)

	ΔH , kJ mol ⁻¹	HLC, ^a 25°C
<i>p,p'</i> -DDT	84.8	0.832
<i>o,p'</i> -DDT	80.6	0.741
<i>p,p'</i> -DDE	108	4.16
<i>o,p'</i> -DDE	60.7	1.85
<i>p,p'</i> -DDD	60.5	0.66
<i>o,p'</i> -DDD	53.2	0.817

^aUnits are 10⁻⁵ atm·m³ mol⁻¹, from <http://www.syrres.com/esc/physdemo.htm>.

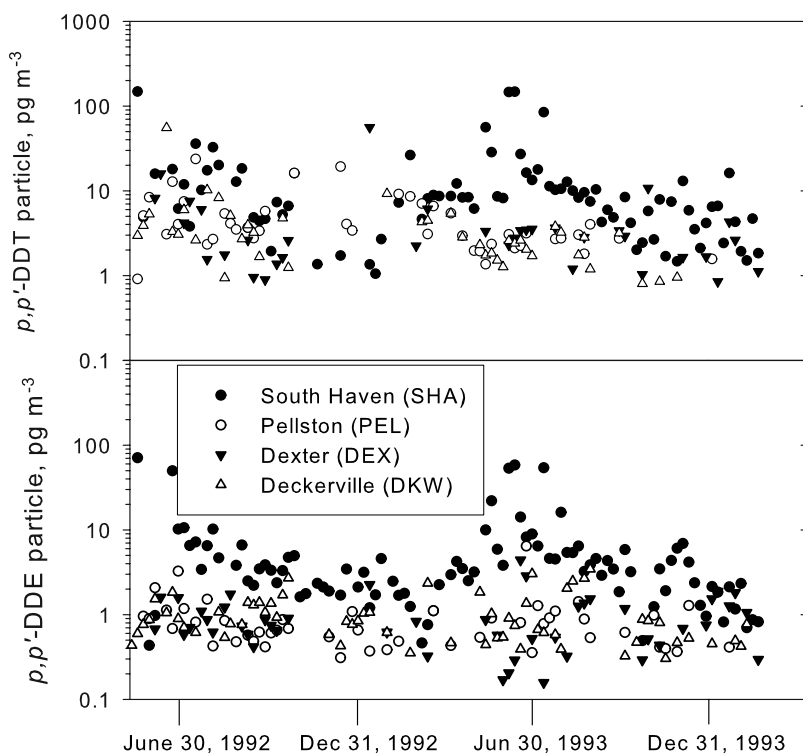


Figure 6. Time trends of atmospheric particle associated concentrations of p,p' -DDT, and p,p' -DDE at four Michigan air sampling sites.

trends. The regression slope for p,p' -DDE is greater than p,p' -DDT and predicted regression values for p,p' -DDE are higher for most temperatures, except for the coldest ($\sim -10^{\circ}\text{C}$) (Figure 7). Results from Bidleman *et al.* [1986] show combined data from four sites in a plot for p,p' -DDT ($n = 18$) and p,p' -DDE ($n = 20$). They show lower equivalent F/A values for p,p' -DDT for given 1000 T^{-1} values than p,p' -DDE, which is what we observe. The slope for p,p' -DDT, however, was steeper than for p,p' -DDE, unlike our result. Their F/A equivalent values are lower than ours for both compounds by roughly 1 order of magnitude. This difference may reflect the fact that none of the sites sampled by Bidleman *et al.* [1986] had high concentrations of gas phase or soil p,p' -DDT and p,p' -DDE.

[24] Calculated theoretical $-\log K_p$ values from Finizio *et al.* [1997] are shown on Figure 7 for p,p' -DDE and p,p' -DDT at 298 K (3.35 on the x axis). These values (3.22 and 2.73 , respectively) were calculated from subcooled liquid vapor pressure and are different than values predicted by our regression lines, which are 2.4 and 1.6 . Our South Haven results again suggest that the particle associated concentration of these compounds is greater than expected: On the basis of the $-\log(F/A)$ amounts, our results are about 6 times greater than predicted by Finizio *et al.* [1997] for p,p' -DDE and 14 times greater for p,p' -DDT. If using our highest F/A values instead of values predicted by the regression line, the comparisons are much closer: our p,p' -DDE values are about 1.7 times greater and p,p' -DDT is about 4 times greater than predicted by Finizio *et al.* [1997]. The source of these differences is not known but there is a possibility that highly contaminated soils at South Haven could have become airborne or particulate matter on the

GFFs is adsorbing some of the high gas phase concentrations during sampling [Cotham and Bidleman, 1992].

4. Conclusion

[25] Our results show that DDT residues can be found in the atmosphere at South Haven, Michigan, a high-use site,

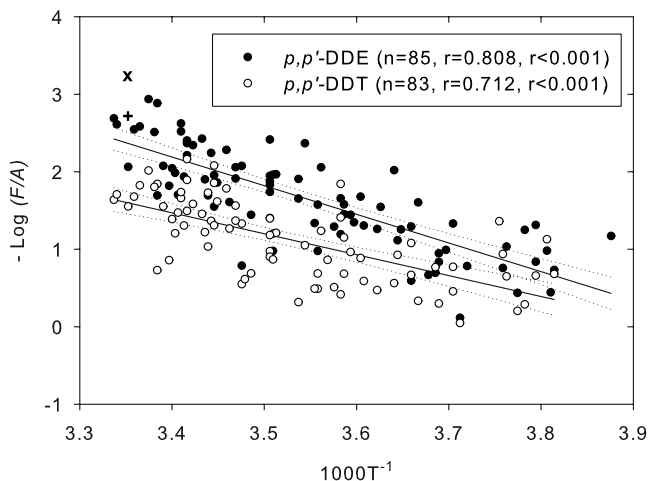


Figure 7. Calculated values for $-\log(F/A)$ (equivalent to $-\log K_p$) for p,p' -DDT and p,p' -DDE at South Haven. Dashed lines represent the 95% confidence interval. The “X” and “+” at a 1000 T^{-1} value of 3.35 (corresponding to 298 K) represent the vapor pressure based calculation of $\log K_p$ for p,p' -DDE and p,p' -DDT, respectively, from Finizio *et al.* [1997].

decades after its applications have ended. It appears that the source of these high atmospheric DDT-group compounds are from highly contaminated soils in the area and that concentrations are high enough to be influenced significantly by modern air temperature fluctuations. The values of ΔH are quite similar for the two isomers of DDT and DDD, but are very different for DDE isomers and very high for p,p' -DDE. Among these compounds, variation in values of ΔH are highly correlated with Henry's Law Constant as suggested by other investigations.

[26] Particle-associated p,p' -DDT and p,p' -DDE residues are also significant in the atmosphere at South Haven and also tend to vary positively with changes in air temperature, although less predictably than the gas phase. The difference between our $-\log(F/A)$ values and $-\log K_p$ predicted by Finizio et al. [1997] suggests that our observed particle/gas distribution is not a result of equilibrium partitioning. While the cause of this difference is unknown, it is likely related to the highly contaminated environment at South Haven.

[27] Our general results show that orchards can be large sinks for pesticides and that they can be major sources of atmospheric contamination. Countries still using DDT can expect to have experiences similar to what we have observed at South Haven for decades after ending application of this pesticide.

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