

Chlordanes in the Mid-Atlantic Atmosphere: New Jersey 1997–1999

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To characterize the atmospheric dynamics and behavior of chlordane compounds in the mid-Atlantic region of the United States, atmospheric concentrations were measured in 1997–1999 at three New Jersey locations as part of the New Jersey Atmospheric Deposition Network (NJADN) project. Observed concentrations of Σ -chlordanes (*cis*-chlordane + *trans*-chlordane + *cis*-nonachlor + *trans*-nonachlor) are log-normally distributed, with a geometric mean concentration of 77.1 pg m⁻³ and range from 6.1 to 481 pg m⁻³. Gas-phase species comprised 83% ($\pm 23\%$) of the Σ -chlordanes species across all samples at all location. Gas-phase Σ -chlordane concentrations are inversely proportional to temperature, with higher concentrations during periods of warmer air temperatures. Observed concentrations do not correlate with wind direction or air mass history, which suggests that observed concentrations in the New Jersey atmosphere are due to volatilization from soils and surfaces on the regional scale.

Introduction

Long-range atmospheric transport and deposition of organochlorine pesticides is the major source of many of these chemicals to the remote regions of the Arctic and high northern latitudes (1–3). Atmospheric transport and deposition also accounts for much of the contaminant loadings to midlatitude ecosystems such as the Great Lakes and Chesapeake Bay (4–6). Airborne concentrations of organochlorines have been found to vary seasonally and to correlate with ambient atmospheric temperature (7–9). Additionally, Hoff et al. (7, 10) found that higher concentrations of select organochlorine compounds in air in southern Ontario were associated with transport of air masses from the southern U.S., while lower concentrations were associated with transport from northerly regions. Soil to air exchange can release organochlorine pesticides from soils and thus impact the concentration in the overlying air (11). Indeed, chiral

analysis of chlordanes and other organochlorine pesticides in soils and overlying air further supports the hypothesis that volatilization from agricultural soils is a significant source of these compounds to the air (12, 13).

Chlordane was first synthesized in 1944 and introduced as an agricultural pesticide in the U.S., gaining widespread use as a broad-spectrum pesticide from the 1940s through the 1960s. Chlordane use was regulated in 1979, restricting most above ground and agricultural uses. By 1983, the only remaining application of chlordane in the U.S. was as a termiticide, mainly in building construction. In 1988, the termiticide registration was cancelled (14), ending the sale and use of chlordane in the U.S. The major producer, Velsicol Chemical Co., Rosemont, IL, voluntarily halted global production in 1997 (15).

Technical chlordane is a mixture of more than 140 compounds with six to nine chlorine atoms attached (16). Major components of the technical chlordane mixture include *trans*-chlordane (TC; 13%), *cis*-chlordane (CC; 11%), *trans*-nonachlor (TN; 5%), and heptachlor (5%) as well as many less abundant chlordanes, chlordenes, and nonachlors (9, 16–18). Owing to the physiochemical properties of these compounds, they are distributed across the northern hemisphere, being found in both biotic and abiotic matrices from the Arctic to midlatitudes and equatorial regions (7, 8, 19–32). Strong evidence supports atmospheric long-range transport of these compounds from areas of known historical application to remote regions of the globe (9–11, 33–35). Further, chlordanes bioaccumulate in aquatic organisms and have been shown to biomagnify in animals of higher trophic levels such as whales, seals, polar bears, and humans (19, 21, 36, 37).

More locally, chlordane compounds have been quantified in several estuarine and coastal finfish and shellfish of New Jersey (38). The highest concentrations of chlordanes in these aquatic organisms are measured near metropolitan centers of New York, Newark, and Camden (38). Despite the high population density, heavy industry, and agriculture in the region, limited research has been conducted on persistent organic pollutants, including chlorinated pesticides, in the air of the mid-Atlantic region of the United States. To assess the transport and dynamics of chlordanes and other persistent organic pollutants (POPs) in the coastal, urban, suburban, and rural mid-Atlantic region, an air research and monitoring network in New Jersey was established in 1997 (39–44). This network of air samplers offers better understanding of local, regional, and long-range atmospheric transport and impacts of this highly industrial and populous region. Here, we present data for chlordane concentrations measured over 19 months at three sites that represent differing regional land use criteria. Back trajectory analyses have been used to explore concentrations that deviate substantially from values explained and predicted by temperature correlations. Elevated levels of chlordane compounds in the atmosphere of the mid-Atlantic region do not appear to relate to regions from which air masses are transported.

Materials and Methods

As part of the New Jersey Atmospheric Deposition Network (NJADN), atmospheric samples were collected at three sites in New Jersey: New Brunswick, (40.48° N, 74.43° W), Sandy Hook (40.46° N, 74.00° W), and Jersey City (40.71° N, 74.05° W; Figure 1). The New Brunswick site is located on the campus of Rutgers Gardens, a horticultural station situated in a suburban area. Located within 15 km of the site are major

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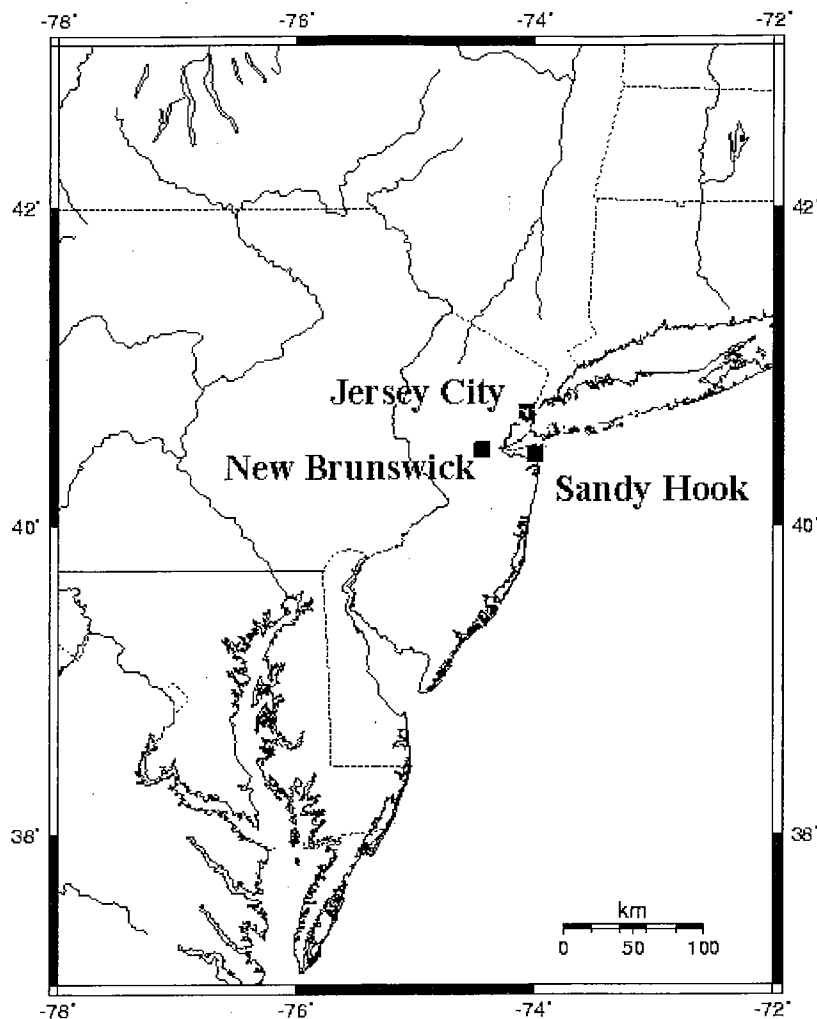


FIGURE 1. Location of sampling sites across New Jersey.

TABLE 1. Overview of NJADN Samples Collected for Chlordane Analysis as Described in the Text

site	latitude	longitude	start date	end date	n
New Brunswick	40.48° N	74.43° W	Jul 5, 1997	Mar 30, 1999	103
Sandy Hook	40.46° N	74.00° W	Feb 4, 1998	Feb 13, 1999	68
Jersey City	40.71° N	74.05° W	Oct 7, 1998	Mar 30, 1999	35

industries and several major transportation corridors. The Sandy Hook site is located on a sandy barrier reef peninsula separating Raritan Bay and the Atlantic Ocean and thus is surrounded by water. It is influenced by air/surface exchange with the surrounding waters, and urban/industrial source to the north and west, being 10 km south of New York City. The Jersey City site is located within 500 m of a major interstate highway and is situated on the grounds of Liberty State Park in the middle of a major urban/industrial setting 3 km west of lower Manhattan.

Samples were collected every 6 and then 9 days (after August 1998) from October 1997 to March 1999. Samples collection dates are outlined in Table 1. Additionally, an intensive sampling campaign was undertaken from July 5–11, 1998, which included air sampling over the Raritan Bay and lower Hudson River estuary as well as the land sites described previously. The air samples during this intensive period were collected over 12 h periods (changing at 0800 and 2000 h). For a detailed description of sampling, preparation, and workup, we refer the reader to Gigliotti et al. (39, 44) and Brunciak et al. (40).

At each site, integrated air samples were collected using a modified organics high-volume air sampler (General Metal Works, Village of Cleves, OH) at a calibrated flow rate of ~ 0.5 $\text{m}^3 \text{min}^{-1}$. Quartz fiber filters (8×11 rectangular; QFF), precombusted at 450 °C overnight, were used to capture the particles and particle bound species, and a cylindrical 3 inch diameter \times 4 inch thick polyurethane foam (PUF) adsorbant was used downstream to capture the gas-phase contaminants. Prior to use, the PUFs were cleaned in aqueous solution with Alconox detergent and rinsed with deionized water. After air-drying, the PUFs were further cleaned by two consecutive 24 h Soxhlet extractions with acetone followed by a single 24 h Soxhlet extraction with petroleum ether. After cleaning, the PUFs were desiccated under vacuum to remove excess solvent and stored frozen in precombusted glass jars with an aluminum foil liner.

After sample collection, QFFs and PUFs were sealed and stored frozen until analysis. Samples were Soxhlet extracted for 24 h with dichloromethane (QFFs) or petroleum ether (PUFs). Sample extracts were rotary evaporated to ~ 5 mL and transferred to hexane then further reduced to ~ 1 mL

TABLE 2. Operational, Media-Specific Blank Based Limits of Detection by Compound^a

	QFF (pg m ⁻³)	PUF (pg m ⁻³)
<i>trans</i> -chlordane	0.233	0.038
<i>cis</i> -chlordane	0.105	0.030
<i>trans</i> -nonachlor	0.063	0.019
<i>cis</i> -nonachlor	0.033	0.026
oxychlordane	0.146	0.093
MC5	0.063	0.069

^a LODs are expressed in concentrations (pg m⁻³) assuming an average sample volume of 584 m³. QFF represents quartz fiber filter media (particle-bound phase), and PUF denotes polyurethane foam plug sampling media (vapor phase).

under a gentle stream of clean, dry N₂. Samples were then fractionated on a column containing 4.0 g of 3% water-deactivated, precombusted alumina. The column was pre-conditioned with 5 mL of 2:1 dichloromethane/hexane followed by 15 mL of hexane. The columns were eluted with 12 mL of hexane followed by 15 mL of 2:1 dichloromethane/hexane. The compounds described in this paper eluted in the second fraction. The eluate was concentrated under a gentle stream of clean, dry N₂ to ~0.5 mL prior to analysis. After completion of sample preparation, both gas and particle-bound phases were separately analyzed for *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, oxychlordane, and MC5 by gas chromatography-negative chemical ionization mass spectrometry on a HP6890 Gas Chromatograph coupled to a HP 5973 Mass Spectrometer (Agilent, Palo Alto, CA) with methane as the reagent gas after the method of Jantunen et al. (9). Data were acquired with the system operating in selected ion monitoring mode. The gas chromatograph was equipped with a 30 m HP5-MS capillary column having 0.25 mm i.d. with 0.25 μm film thickness. Operating conditions were as follows: He carrier gas, constant pressure 29 psi, interface temperature 310 °C, injector temperature 310 °C, initial temperature 100 °C hold 1 min, then 100–180 °C at 10 °C/min to 180 °C, then 3.5 °C/min to 245 °C, followed by 25 °C/min to 310 °C with a 10 min final hold.

Quality Assurance. Identification of each compound was performed by matching the retention time and the major ion of each compound to authentic standards of known concentration. Surrogate compounds used to quantify analytical recovery of both polychlorinated biphenyls and polycyclic aromatic hydrocarbons and quantified in the same samples (39, 40) were applied. The reliable recovery of these other compounds of similar physicochemical properties from the same samples using the methodology described previously were such that measured concentrations of chlordane compounds were not adjusted for surrogate recoveries. Additionally, recovery of target analytes in matrix spike studies average 86% (*n* = 4). Periodically, PUFs were cut in half to evaluate breakthrough of analytes over the 24 h sampling period. Greater than 97% of each compound was present in the top half of the PUF (*n* = 2), indicating that the gas-phase species were efficiently captured by the PUF. Blank-based limits of detection (LOD) were defined for each sampling matrix (PUF and QFF) as the average contaminant mass of field blanks plus 3 standard deviations. LODs are outlined in Table 2. Contaminant mass was above LOD in all cases except for occasional instances of oxychlordane and *cis*-nonachlor in the airborne particle-bound phase.

Results and Discussion

Atmospheric Concentrations. Concentrations of Σ-chlordanes (presented here as *trans*-chlordane + *cis*-chlordane + *trans*-nonachlor + *cis*-nonachlor; TC + CC + TN + CN,

respectively) ranged from 6.1 pg m⁻³ at Sandy Hook on August 3, 1998, to 481 pg m⁻³ at New Brunswick on June 26, 1998 (Table 3). Atmospheric concentrations of each of the four species defined here as Σ-chlordanes are log-normally distributed as are oxychlordane (OXY), MC5, and Σ-chlordanes. Averages (±1 standard deviation) of the natural log transformed Σ-chlordanes concentrations (ln C expressed in pg m⁻³) were 4.52 ± 0.99 (New Brunswick, suburban; NB), 4.16 ± 0.83 (Sandy Hook, coastal; SH), and 4.31 ± 0.93 (Jersey City, urban; JC), showing that there are no significant differences in average concentrations among the three locations. These translate into geometric mean concentrations of approximately 92 pg m⁻³ (NB), 64 pg m⁻³ (SH), and 74 pg m⁻³ (JC), respectively. *trans*-Chlordane comprised the greatest fraction of the Σ-chlordanes (41%), followed by *cis*-chlordane (35%) and *trans*-nonachlor (22%), with the remaining ~2% occurring as *cis*-nonachlor. Across all samples at all locations, 83% (±23%) of the Σ-chlordanes species were found in the gas phase. Generally, higher concentrations occur in the summer, while lower concentrations are found in the winter (Figure 2). The concentrations measured in New Jersey are only slightly lower than the high levels measured in the southern United States (South Carolina in 1994–96 and/or Alabama 1996 and 1997; refs 9 and 34) and yet higher than the levels measured near the Laurentian Great Lakes (ref 8; Table 4). The concentrations reported here are at least an order of magnitude higher than measurements in Arctic, high Arctic, and Antarctic atmospheres (27, 33).

The average proportions of TC/CC/TN/CN in air samples, as calculated from the geometric mean concentrations, are as follows: 1.00:0.87:0.56:0.051 (New Brunswick), 1.00:0.86:0.54:0.061 (Sandy Hook), and 1.00:0.80:0.48:0.050 (Jersey City). These values exhibit an increased relative concentration for CC as compared to those measured in ambient air of Columbia, SC, in 1994–1995 where values for TC/CC/TN/CN were found to be 1.00:0.63:0.36:0.043. Likewise was for Alabama air in 1996–97, where the values for TC/CC/TN were found to be 1.00:0.56:0.52 (9). The relative ratios in New Jersey air are similar to those reported by Jantunen et al. (9) for two reference samples of technical chlordane (1.00:0.85:0.42 and 1.00:0.86:0.41; TC/CC/TN as measured by U.S. EPA and Radian Corp., respectively, as reported by Jantunen et al.). Earlier measurements by Buchart et al. (45) reported relative concentrations of these compounds to be 1.00:0.77:0.62:0.15 (TC/CC/TN/CN, respectively) in technical chlordane. Measurements of these compounds in soils from across the U.S. cornbelt showed ratios of geometric mean concentrations to be 1.00:0.878:1.04 (TC/CC/TN; ref 46). However, air samples collected in the U.S. cornbelt region (not directly above agricultural soils) exhibited ratios of geometric mean concentrations of 1.00:1.19:1.00 (12). The difference in concentration ratios between New Jersey air and Midwest cornbelt region air suggests a differing relative importance of source emissions of these compounds. It is likely that Leone et al. (12) observed a much stronger influence of soil volatilization from U.S. cornbelt region agricultural soils to the overlying air in the cornbelt region than is seen in the mid-Atlantic atmosphere of New Jersey.

The relative concentrations reported here for mid-Atlantic air exhibit greater concentrations of both CC and TN, relative to TC, than has been predicted (47) for ambient air at equilibrium with technical chlordane at 20 °C (1.00:0.54:0.34; TC/CC/TN; ref 34) and at 25 °C (1.00:0.61:0.23; ref 9). The measured values in New Jersey air are not as enriched in CC and TN relative to TC as Arctic air samples (27) but are enriched relative to Alabama and South Carolina atmospheres. This relative enrichment, especially in light of the lower observed concentrations of these compounds relative to the suspected source regions (9), suggests that weathering of TC may play a role in these observed concentration ratios.

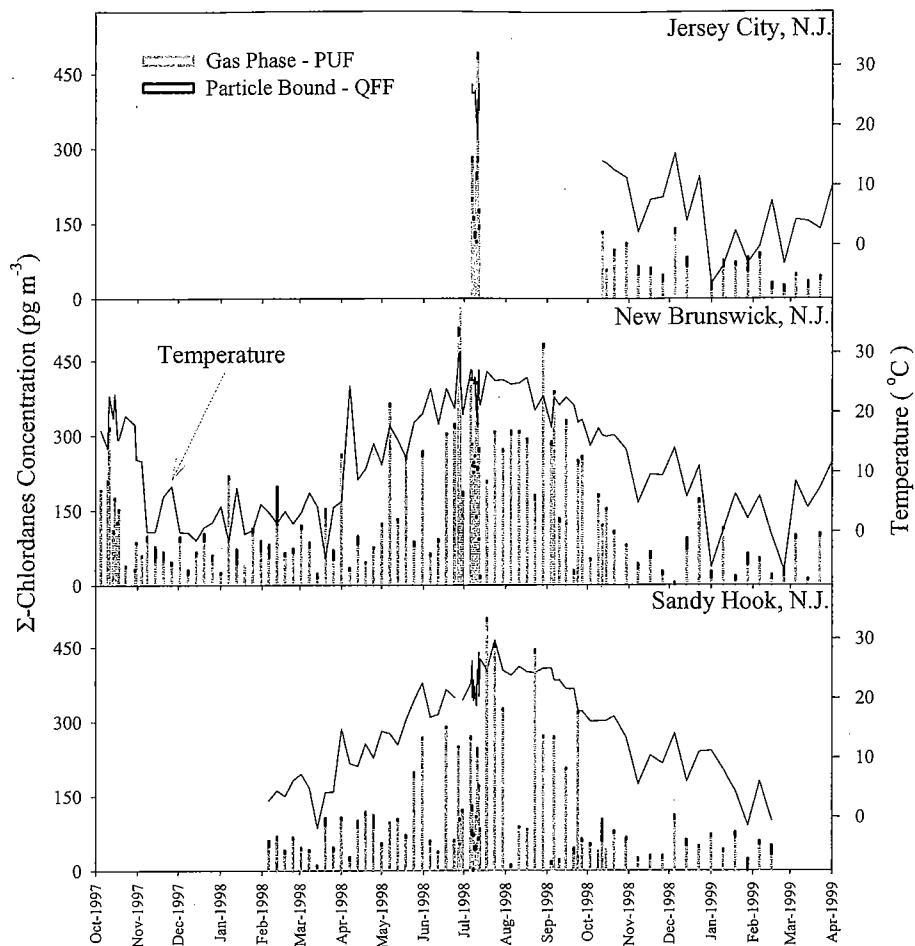


FIGURE 2. Concentrations of chlordane compounds (*trans*-chlordane + *cis*-chlordane + *trans*-nonachlor + *cis*-nonachlor) measured at each site. The line in each pane indicates the average ambient temperature at the respective site, during each sampling period.

TABLE 3. Summary Statistics of Total (Gas + Particle-Bound) Chlordane Concentrations ($\mu\text{g m}^{-3}$) and Concentration Ratios in Air, Given as Geometric Mean and Range (Minimum and Maximum)^a

	New Brunswick, NJ 10/5/1997–10/30/1999 <i>n</i> = 88	Sandy Hook, NJ 2/4/1998–2/13/1999 <i>n</i> = 60	Jersey City, NJ 7/5/1998–3/30/1999 <i>n</i> = 32
<i>trans</i> -chlordane	32.5 (3.0–173.2)	28.56 (1.35–196.3)	30.6 (5.9–176.9)
<i>cis</i> -chlordane	28.4 (2.33–148.8)	24.53 (1.89–153.7)	24.5 (3.59–150.9)
<i>trans</i> -nonachlor	18.3 (1.85–92.0)	15.45 (1.47–107.61)	14.8 (2.19–93.5)
<i>cis</i> -nonachlor	1.67 (0.2–16.8)	1.74 (0.16–11.3)	1.54 (0.34–7.76)
oxychlordane	7.24 (0.50–43.6)	3.08 (0.13–30.6)	3.40 (0.79–23.6)
MC5	5.11 (0.61–42.9)	5.08 (0.56–33.2)	4.67 (0.93–27.9)
tc:cc	1.16 ± 0.15 (0.73–1.64)	1.18 ± 0.18 (0.45–1.59)	1.26 ± 0.14 (1.00–1.64)
tn:cn	11.1 ± 2.80 (5.12–21.76)	9.64 ± 2.91 (3.69–20.17)	9.78 ± 1.69 (5.79–12.55)
tc:tn	1.81 ± 0.28 (1.26–2.56)	1.88 ± 0.33 (0.74–2.7)	2.08 ± 0.22 (1.68–2.69)
tc:oxy	4.13 (1.16–95.37)	7.69 (2.77–23.88)	8.73 (5.07–18.49)

^a Concentration ratios given as mean ± standard deviation with the exception of *trans*-chlordane/oxychlordane, which is log-normally distributed and as such is reported as geometric mean (minimum and maximum).

Transformations of TC, especially in relation to the observed concentrations of oxychlordane (OXY) and other species measured are discussed next.

Diurnal Changes. During the July 1998 sampling intensive, continuous 12 h integrated sampling was performed to measure day (0800–2000) and night (2000–0800 + 1)

TABLE 4. Σ -Chlordane Concentrations and *trans*-/*cis*-Chlordane Ratios in Air: Latitudinal Gradient Across North America^a

site	year of sampling	Σ -chlordane (pg m ⁻³)	TC/CC ^b	FTC ^b	ref
Alert, Canada	1997	1.54	0.61	0.38	61
Eagle Harbor, MI	1995-1997	11*	1.10	0.52	8 as reported by 9
Sturgeon Pt., NY	1995-1997	27.8*	0.91	0.48	8 as reported by 9
Jersey City, NJ	1998-1999	74.4	1.26	0.56	this paper
Sandy Hook, NJ	1998-1999	64.0	1.18	0.54	this paper
New Brunswick, NJ	1997-1999	91.8	1.16	0.54	this paper
Columbia, SC	1994-1995	280	1.95	0.66	29
NW Alabama	1996-1997	98.1	1.79	0.65	9
Midwest soils	1995/1996	1.43 ng/g*	1.23	0.55	46
NW Alabama soils	1996	0.17 ng/g*	1.21	0.55	35
technical chlordane			1.18	0.54	9
technical chlordane			1.30	0.56	45
predicted air in equilibrium with technical chlordane at 20 °C			1.63	0.61	9
predicted air at equilibrium with technical chlordane at 25 °C			1.85	0.65	29

^a Sum chlordane equals *trans*-chlordane + *cis*-chlordane + *trans*-nonachlor + *cis*-nonachlor except where denoted by *, which indicates that *cis*-nonachlor was not included. † indicates geometric mean instead of arithmetic mean. ^b Where TC/CC = R and FTC = TC/(TC + CC) = R/(1 + R).

conditions. The diurnal variation in atmospheric concentrations not explained by diurnal temperature variations suggests *trans*-chlordane oxidation evident in the ratios of both *trans*-chlordane to *cis*-chlordane and *trans*-chlordane to oxychlordane. *trans*-/*cis*-Chlordane ratios are 1.04 \times 0.07 during the daytime and 1.16 \pm 0.04 during nighttime in New Brunswick. Daytime and nighttime ratios at Sandy Hook (coastal) are 1.00 \pm 0.09 and 1.05 \pm 0.18, respectively, and exhibit no significant difference. However, changes between daytime and nighttime ratios at Jersey City (urban) are comparable to those observed at New Brunswick (suburban), with values of 1.08 \pm 0.05 and 1.20 \pm 0.02, respectively. The slight increase in *trans*-chlordane to *cis*-chlordane ratio during nighttime at the two urban locations is matched with an increase in *trans*-chlordane-to-oxychlordane ratios at night. *trans*-Chlordane-to-oxychlordane ratios (TC/OXY) are 2.05 \pm 0.89 during the daytime and 2.98 \pm 0.84 during nighttime in New Brunswick. Corresponding increases from daytime-to-nighttime ratios can also be seen in the samples collected at both Sandy Hook and Jersey City locations (Sandy Hook day 4.34 \pm 0.63 and night 5.63 \pm 1.75; Jersey City day 7.39 \pm 1.7 and night 9.75 \pm 1.3). This translates into *trans*-chlordane-to-oxychlordane ratios that are on average ~30% higher at night. This increased TC/OXY ratio indicates that relatively more oxychlordane is present during daytime hours.

Relationships to Temperature. Atmospheric concentrations of semivolatile compounds in air vary with temperature over long time scales of weeks to months (10, 48-50) and even diurnally (8, 34, 51, 52). This translates to atmospheric concentrations reaching a maximum in the warmer, summer months.

The Clausius-Clapeyron equation describes the relationship between ambient temperature and the gas-phase partial pressures of semivolatile organic compounds (10):

$$\ln P = (\Delta H/R)(1/T) + \text{constant} \quad (1)$$

where *P* is the partial pressure of the compound (Pa), ΔH is a characteristic environmental phase-transition energy of the compound (kJ mol⁻¹), *R* is the gas constant (8.31 Pa m³ mol⁻¹ = kJ mol⁻¹), and *T* is temperature (Kelvin). To apply this relationship, measured atmospheric concentrations must be expressed as partial pressures, which can be calculated through the use of the ideal gas law. As Cortez et al. (8) describe, conversion of concentrations in air to partial pressures involves a temperature correction, but this cor-

rection is not large as compared to the exponential function implied by eq 1.

The Clausius-Clapeyron relationship can be represented graphically as a plot of ln *P* versus 1/*T* (Figure 3). In these plots, a negative slope was found for all of the chlordane compounds, indicating that gas-phase concentrations increase with increasing temperature. The slope of a line fit to these data (*m* from Table S-1 in the Supporting Information) multiplied by the negative universal gas constant (-*R*; 8.314 Pa m³ mol⁻¹ K⁻¹) gives the compound specific phase-transition energy (ΔH ; J mol⁻¹). This is the energy necessary to overcome the chemical's own attractive forces to convert 1 mol from the dissolved or liquid phase to the gas phase. In a dynamic environment, an increase in temperature can affect other processes that will lead to an increase or decrease in atmospheric gas-phase concentrations of pesticides, such as transfer across the air/water interface and partitioning from terrestrial surfaces. Despite confounding effects, calculation of ΔH can give insight into environmental behavior; thus, ΔH was calculated for the chlordane compounds measured in this study. The resulting energies of environmental phase change are outlined for both the pooled data set and for site-specific data in Table 5. With one exception, the average ΔH determined in this study for each of the compounds does not differ by location.

The average ΔH determined for OXY is significantly greater at the Sandy Hook, NJ (sandy, barrier reef peninsula) location as compared with either of the land-surrounded urban or suburban locations. This suggests that inclusion of the 60 samples collected at Sandy Hook in the pooled dataset may be misleading, as oxychlordane in these samples (~35% of the pooled dataset; *n* = 169) appears to be undergoing reactions and/or air/surface exchange that differs from the other two sites. Exclusion of these sixty Sandy Hook samples from correlation of the combined New Brunswick plus Jersey City dataset, oxychlordane ln *P* versus 1/*T*, results in a slope of -7639.6 \pm 683.3 and an intercept of -12.70 \pm 2.41, respectively (*n* = 93; *r*² = 0.510; *p* < 0.001). This result is not largely different from the outcome of the same correlation with entire pooled dataset, due mainly to the surfeit of samples from the New Brunswick site.

The higher value for ΔH of OXY at Sandy Hook, NJ may be related to the influence of the proximate waters and thus the increased relative importance of air/water gas exchange. Interestingly, the lack of difference among the sites for the

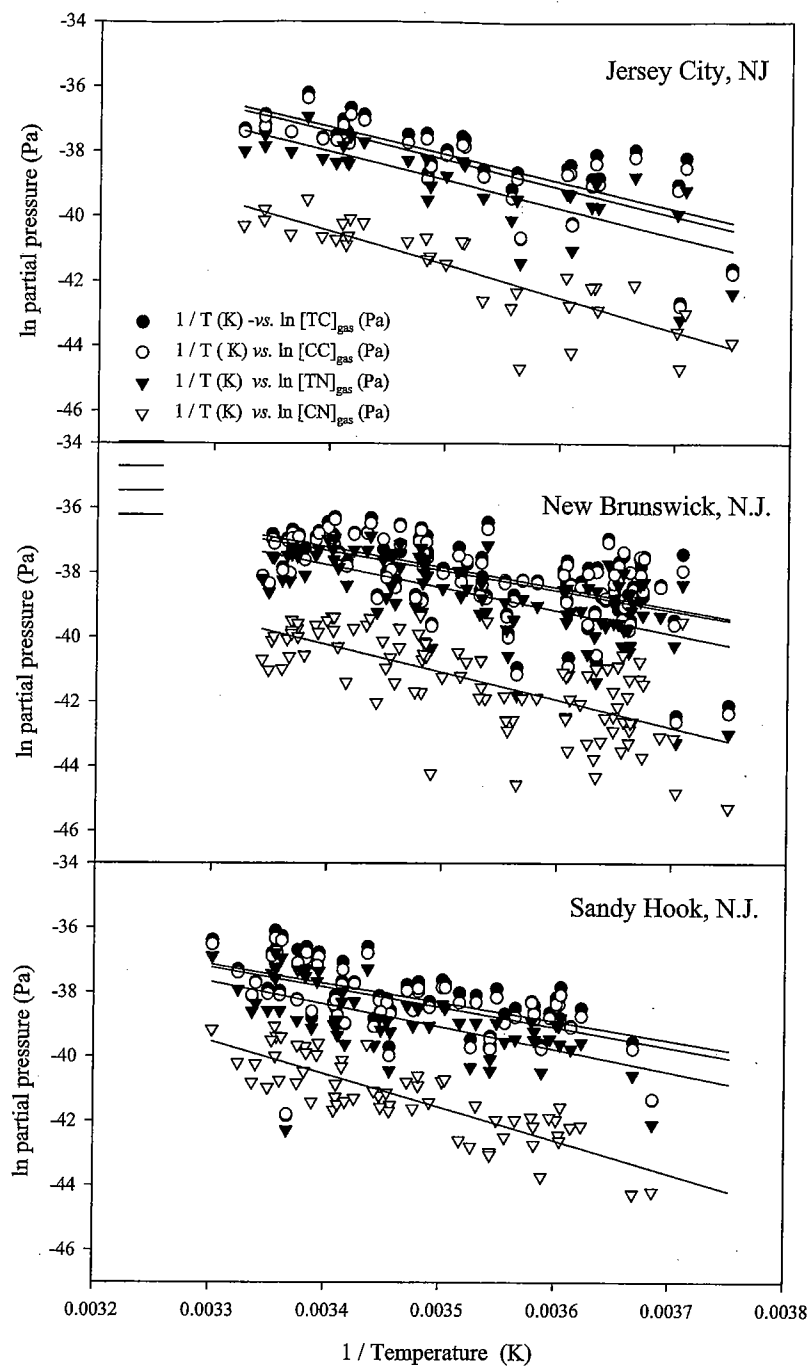


FIGURE 3. Correlations of concentration (as \ln partial pressure – Pa) vs $1/T$ (temperature (K)) for individual compounds at (a) New Brunswick, (b) Sandy Hook, and (c) Jersey City.

TABLE 5. Phase Transition Energies (ΔH , ± 1 SD) Determined by Linear Regression of $\ln P$ (Pa) vs $1/T$ (Ambient Temperature, K)^a

ΔH (kJ mol ⁻¹)	pooled data set all NJ sites	New Brunswick, NJ	Sandy Hook, NJ	Jersey City, NJ
<i>trans</i> -chlordane	50.4 \pm 4.9	49.2 \pm 7.1	55.8 \pm 8.1	59.1 \pm 9.9
<i>cis</i> -chlordane	51.3 \pm 4.7	48.0 \pm 7.1	58.4 \pm 7.3	61.5 \pm 9.4
<i>trans</i> -nonachlor	56.8 \pm 4.7	55.8 \pm 7.0	64.8 \pm 7.6	62.8 \pm 9.7
<i>cis</i> -nonachlor	75.4 \pm 5.0	69.6 \pm 8.1	86.0 \pm 7.4	80.9 \pm 9.3
oxychlordane	63.4 \pm 4.9	67.2 \pm 6.0	81.2 \pm 7.2	61.4 \pm 7.3
MC5	60.2 \pm 4.9	57.7 \pm 7.7	65.7 \pm 6.9	67.6 \pm 9.1

^a ΔH (J) = $-mR$ where $R = 8.31$ Pa m³ mol⁻¹ and m is slope from linear least squares fit to the equation: $\ln P = m/T + b$ (Pa).

other five compounds measured here indicates that this difference in the observed ΔH for oxychlordane at Sandy

Hook may be related to differing degradation at the coastal site, thereby generating OXY in a different manner than at

other locations, and will be discussed later. These calculated values for ΔH compare favorably to those found elsewhere. For example, ΔH values calculated from concentrations measured around the Great Lakes range from 32 to 51 kJ mol⁻¹ for *trans*-chlordane, from 42 to 51 kJ mol⁻¹ for *cis*-chlordane, and from 45 to 73 kJ mol⁻¹ for *trans*-nonachlor at the five IADN master station locations (8).

Air/Surface Exchange. If the compounds measured herein were still in widespread agricultural use, the observed temperature dependent, seasonal behavior might be related to application coinciding with the crop planting cycle. At the time these samples were collected, the use of these pesticides had been banned or use-restricted; therefore, other influences must also be considered. However, release from chlordane contaminated soils may still be related to the crop planting cycle, through volatilization from freshly tilled soils as suggested by Harner et al. (11), Jantunen et al. (9), Leone et al. (12), and Eitzer et al. (13).

Air/surface exchange, including air/water exchange, may also play a significant role in the dynamics of these compounds. It is challenging to assign relative importance of local versus historical (over the history of the air mass) interactions with the surface, to determine the relative roles of various air/surface exchange processes (13). In this light, the Sandy Hook sampling location is approximately 6 km from mainland on a 500 m wide sandy peninsula and thus is surrounded by water. As described previously, no significant difference in the ΔH values was found between SH and JC or NB. This is surprising, as ΔH values for air/water and air/land interactions typically differ by approximately 8 kJ mol⁻¹ (53). This indicates that local surface interactions (closer than ~10 km) do not appear to dominate the processes captured in ΔH expressed here, with the previously noted exception of oxychlordane at the Sandy Hook site. The processes described by these environmental phase transition energies likely relate to the regionally integrated interaction processes over a history of air mass transport of several to many hours.

Influence of Air Mass Transport. The correlation resulting from the plot of $\ln P$ (Pa) versus $1/T$ shows a significant relationship between the inverse temperature and the measured concentrations of individual compounds. The correlation with Σ -chlordanes is also significant ($p < 0.001$), with an r^2 of 0.31. This r^2 value is less than the 0.46 reported for the Great Lakes (10) and 0.59 from Columbia, SC (34). Days with residuals greater than one standard deviation from the $\ln P$ versus $1/T$ correlations described previously were checked against three-day back trajectories at the middle of the sampling period using the NOAA HYSPLIT model (54). While individual days with concentrations greater than 1 standard deviation from the linear least squares correlation were shown to come from the southern part of the U.S. (large positive residuals), this is not always the case (Figure S-1 in the Supporting Information). In fact, taken as a whole, there do not appear to be any air mass transport or wind direction associations with deviations from the $1/T$ relationships shown in Figure 3. This is also the case for negative deviations from the $1/T$ correlation. There are clearly days during which concentrations were lower than predicted from the relationships versus $1/T$, which were associated with air mass transport from central Canada/Great Lakes regions (large negative residuals), although this does not explain a majority of the cases. This indicates that, in addition to the influence of air temperature, air mass source region plays a role in the delivery of chlordanes to the mid-Atlantic region of the United States during a subset of days. The role of local air/surface exchange, and the importance of agricultural versus residential soils as suggested by Eitzer et al. (13), remains unclear in these datasets.

Relationships with Wind Direction. Air masses flowing across a source area can lead to emissions and subsequently higher atmospheric concentrations. The importance of wind direction on atmospheric concentrations of persistent organic pollutants has been observed in several studies (40, 55–58). For example, Simcik et al. (56) reported a 4-fold increase in atmospheric PCBs over southern Lake Michigan when winds were blowing from a vector between Evanston, IL, and Gary, IN. A similar 4-fold increase in atmospheric concentrations was observed for gas-phase phenanthrene over the northern Chesapeake Bay when winds blew from Baltimore (57).

A multiple linear regression of the form below may describe the effect of wind direction, while also accounting for the known influence of temperature on the observed concentrations:

$$\ln P = a + b/T + c \sin(\text{wd}) + d \cos(\text{wd}) \quad (2)$$

where P is again the gas-phase partial pressure (Pa), T is the temperature, and wd is the wind direction (8, 40).

For *trans*-chlordane at New Brunswick, the correlation described in eq 2 gave nonsignificant terms for $\sin(\text{wd})$ and $\cos(\text{wd})$ ($p > 0.25$ for each), indicating that the wind direction does not play a major role in determining the observed concentrations. Removal of these two terms results in the correlation analysis as described in eq 1. This lack of significant correlation with wind direction was consistent throughout all other chlordane compounds at each of the sites ($p > 0.20$ in all cases, except for $\cos(\text{wd})$ at Sandy Hook for *trans*-nonachlor where $p = 0.134$). Unlike atmospheric PCB contamination measured at the same three sites, which shows an increase in concentration winds blow from the New York Metropolitan area located to the northeast (40), there is no apparent influence of wind direction on the observed chlordane concentrations, which suggests a regional contamination signal for chlordanes in the mid-Atlantic atmosphere.

Evidence of Weathering. The *trans*-chlordane isomer can be oxidized to oxychlordane by both biotic, and possibly, abiotic processes (59). Thus, examination of both the *trans*-chlordane to *cis*-chlordane and the *trans*-chlordane-to-oxychlordane ratios can provide information into the relative weathering of the chlordane compounds measured. *trans*-/*cis*-Chlordane ratios across the three sites averaged 1.18 ± 0.16 and ranged from 0.45 (Sandy Hook, March 12, 1998) to 1.64; (Jersey City, February 13, 1999). When compared to results measured at other locations, the observed *trans*-/*cis*-chlordane ratios fit well the gradient of values reported in the literature for various latitudes (see Table 4).

Alternatively, it is possible to examine these relationships through the use of the fraction of *trans*-chlordane, where $F_{TC} = TC/(TC + CC)$. Thus, the relative ratios of TC:CC translate into a F_{TC} equaling 0.54 ± 0.04 across all samples of New Jersey air presented here. This average value compares favorably with values reported by Bidleman et al. (27) for Arctic air, and those computed from concentration ratios reported by Jantunen et al. (9). Confounding the interpretation of F_{TC} values (and TC/CC ratios) is the fact that technical heptachlor is contaminated with chlordane isomers, especially TC (60). This translates into the possibility that higher F_{TC} in soils or air could be associated with the source of heptachlor. Indeed, Hung et al. (61) identified occasional spikes of high F_{TC} in air samples during 1995, several of which also exhibited elevated heptachlor levels.

trans-Chlordane/oxychlordane ratios at the three New Jersey sites were log-normally distributed and exhibited a geometric mean value of 5.63. Both highest and lowest values for this ratio were found at New Brunswick, with values ranging from 1.16 to 95.37 (New Brunswick, June 4, 1998, and January 8, 1999, respectively). Ratios of *trans*-chlordane

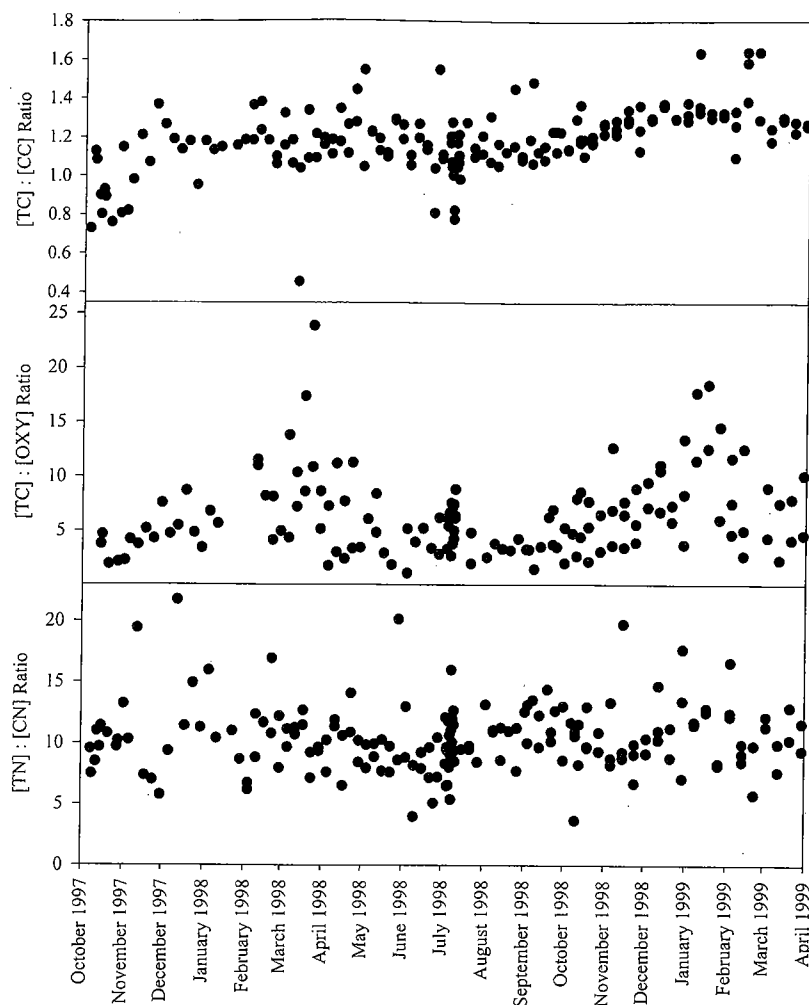


FIGURE 4. Species ratios vs date for (a) TC/CC, (b) TC/OXY, and (c) TN/CN. Note: one TC/OXY value of 95.37 on January 8, 1999 ($1/T = 0.003709$) was omitted from this figure for visual clarity.

to oxychlordanes were higher at both of the other locations, where the geometric mean values were 7.69 and 8.73 (Sandy Hook and Jersey City, respectively). However, these measured values at Jersey City and Sandy Hook were not significantly different either from one another nor from the value measured at New Brunswick. Furthermore, a seasonal pattern is apparent in the TC/OXY ratio (Figure 4), with higher TC/OXY ratios occurring during winter months (December through March). Both TC/CC and TN/CN ratios appear to not exhibit seasonal cycles and remain constant throughout the yearly cycle. When examined against temperature, the TC/OXY ratio exhibits a greater range of values during colder periods ($T < 12^\circ\text{C}$), with values ranging from 1.8 to 23.8 across all samples (Figure S-2). One extreme value of 95.4 on January 8, 1999 ($1/T = 0.003709$, $T = -4^\circ\text{C}$, Jersey City) was omitted from this figure for clarity, yet is a good example of the extreme values TC/OXY ratios can reach during cold weather. For comparison, TC/OXY ratios range from 1.2 to 9.5 during temperatures greater than 12°C . This seasonal cycle of TC/OXY ratio, along with increased variability during cold periods, suggests a process that is may be related to photochemical degradation as suggested elsewhere (12). Additionally, this degradation appears to occur seasonally, with greater rates of formation of OXY and/or greater degradation of TC during summer months. Interestingly, greater biologically mediated degradation is also expected during warmer months, which would also result in increases of OXY. As suggested previously, there is not enough information to draw definitive conclusions, although inter-

actions with photochemical species may play a noteworthy role in the reaction/transformation of *trans*-chlordanes.

Generally, chlordanes were found above detection limits in all air samples collected in New Jersey. Gas-phase concentrations and *trans*-/*cis*-chlordanes ratios can be well-explained by ambient temperature. Elevated concentrations are found during warmer air temperatures. Likewise, lower chlordanes concentrations are measured in colder air temperatures. There were no apparent relationships between wind direction or air mass source region and observed concentration, suggesting that the observed concentrations were due to volatilization from soils on local to regional scales. Although concentrations might be expected to decrease with a half-life of several years similar to the findings of Beuhler et al. (62) for the Great Lakes region, due to the limited (19 month) sampling time scale, no long-term time trend in atmospheric concentrations was observable. Additional data from the three sites will provide valuable information on the longer-term concentrations trends as well as additional information for use in elucidation of sources and sinks.

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Supporting Information Available

Plots of partial pressure vs 1 over temperature denoting the air mass source region, and species ratios vs 1 over temperature as well as a table detailing the relationships with temperature for each measured chlordane compound. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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