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ENVIRONMENTAL FACTORS AFFECTING THE LEVELS OF LEGACY PESTICIDES IN THE AIRSHED OF DELAWARE AND CHESAPEAKE BAYS, USA

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Abstract—Organochlorine insecticides and their degradation products contribute to toxicity in Chesapeake Bay, USA, sediments and affect the reproductive health of avian species in the region; however, little is known of atmospheric sources or temporal trends in concentrations of these chemicals. Weekly air ($n = 265$) and daily rain samples ($n = 494$) were collected over 2000 to 2003 from three locations in the Delmarva Peninsula, USA. Pesticides were consistently present in the gas phase with infrequent detection in the particle phase. Hexachlorocyclohexanes (HCHs) and *cis*- and *trans*-chlordane were detected most frequently (95–100%), and *cis*- and *trans*-nonachlor, oxychlordane, heptachlor, heptachlor epoxide, dieldrin, and 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene (4,4′-DDE) were also detected frequently. The highest mean air concentrations were for dieldrin (60–84 pg/m^3), γ-HCH (37–83 pg/m^3), and 4,4′-DDE (16–80 pg/m^3). Multiple regression analyses of air concentrations with temperature and wind conditions using modified Clausius-Clapeyron equations explained only 30 to 60% of the variability in concentration for most chemicals. Comparison of the air concentrations and enthalpy of air–surface exchange values at the three sites indicate sources of chlordanes and α-HCH sources are primarily from long-range transport. However, examination of chlordane isomer ratios indicates some local and regional contributions, and γ-HCH, 4,4′-DDE, dieldrin, heptachlor, heptachlor epoxide, and oxychlordane also have local or regional sources, possibly from contaminated soils. Median rain sample volumes of 1 to 3 L led to infrequent detections in rain; however, average measured concentrations were 2 to 10 times higher than in the Great Lakes. Dissipation half-lives in air were well below 10 years for all chemicals and below published values for the Great Lakes except dieldrin, which did not decline during the sample period. *Environ. Toxicol. Chem.* 2010;29:1893–1906. © 2010 SETAC

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INTRODUCTION

The Chesapeake Bay, located in the Mid-Atlantic region, is the largest estuary in the United States, supporting an abundant and diverse wildlife population. The increasing population in the Baltimore–Washington corridor exerts significant pressure on the health of this complex ecosystem. Sediments, nutrients, and other toxic chemicals enter the Chesapeake Bay via the atmosphere and the 150 major rivers and streams that feed the estuary, and studies have demonstrated that industrial and agricultural pollutants are entering the Chesapeake Bay through both riverine [1–3], and atmospheric sources [4–9].

Exposure to toxic chemicals alters both functional and structural aspects of the estuarine microbial food web, which could have serious implications for the higher trophic levels. In an agreement between the states within the Chesapeake Bay watershed, a commitment was made to achieve a Chesapeake Bay free of toxics from all controllable sources to levels that result in no toxic or bioaccumulative impact on living resources (http://www.chesapeakebay.net/content/publications/cbp_12081.pdf). A

recent report by Hartwell and Hameedi [10] (http://ccma.nos.noaa.gov/publications/NCCOSTM47.pdf), describes the level of contamination in sediments within the main stem of the Chesapeake Bay and some major tributaries. These data were examined along with measured toxicity, sediment characterization, benthic community analysis, and other key parameters such as dissolved oxygen. Their report indicates that concentrations of metals and organic pollutants such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), and the pesticides, 1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl) ethyl]benzene (4,4′-DDT) and chlordane, were positively correlated with toxicity response. Researchers working in the nearby Delaware River and Delaware Bay found that concentrations of the organic contaminants 4,4′-DDE, heptachlor epoxide, chlordanes, and total PCBs) were predictive of hatching success for osprey (*Pandion halieatus*) [11]. The recent Presidential Executive Order 13508 also requires that federal agencies make recommendations to expand environmental research, monitoring, and observation to strengthen scientific support for decision making on Chesapeake Bay restoration issues (http://www.whitehouse.gov/the_press_office/Executive-Order-Chesapeake-Bay-Protection-and-Restoration).

Previous studies on atmospheric concentrations and deposition of organic pollutants to the Chesapeake Bay region have primarily focused on PCBs, PAHs [7–9,12,13], and currently

used agricultural pesticides [4,14,15]. No long-term datasets of organochlorine insecticides and their degradation products in air and precipitation are available for the Chesapeake Bay area and Delmarva Peninsula. The closest available measurements of the legacy pesticides were carried out from six sites as part of the New Jersey Atmospheric Deposition Network project during 2000 and 2001 [16] and by Offenberg et al. [17] from three sites in the same network from 1997 to 1999.

The chlorinated insecticides were extensively used from the 1940s until as late as the mid-1980s, and nearly all have been banned in the United States due to their tendency for persistence, toxicity, and bioaccumulation in sensitive ecosystems [18]. The objectives of the present study were to determine the levels of banned organochlorine insecticides and selected degradation products in the atmosphere near the Chesapeake and Delaware Bays, and to compare these observations with measurements from Central America, the southern United

States (U.S.), and the Great Lakes region. Air and precipitation samples were collected over four years (2000–2003) at three locations in the upper Delmarva Peninsula. The data were assessed for spatial and temporal trends, and were analyzed to evaluate the processes that influence the levels of the organochlorine pesticides in the region. The Clausius-Clapeyron equation was used to examine the relationship of temperature and meteorological parameters (wind speed and direction) on gas phase concentrations and to discern the contribution of long-range transport versus possible local sources. In addition, the atmospheric half-lives of these chemicals were estimated.

MATERIALS AND METHODS

Weekly air samples were collected at three sites on the upper Delmarva Peninsula (Fig. 1) from April 2000 to September 2003 except during the winter months. The first site (HP) was

Fig. 1. Map of Chesapeake and Delaware Bays on the Atlantic Coast of the U.S. and the surrounding area indicating major cities and sample collection sites. Colors

located at University of Maryland Center for Environmental Studies, Horn Point Laboratory near the Choptank River in Cambridge, Maryland, USA (38.6011, −76.1297; population 10,911 in 2000) (http://www.census.gov/). In April 2001, a second site (LD) at University of Delaware (Lewes, DE, USA) (38.7739, −75.1389; (population 2,932) was added. The third site (DV) at the Delaware National Estuarine Research Reserve, St. Jones Component (Dover, DE, USA) (39.1581, −75.5239; population 32,135) was added in April 2002. Land use on the Delmarva Peninsula is mostly rural and agricultural with the nearest major urban and/or industrial centers being Washington, DC, Baltimore, Maryland, Philadelphia, Pennsylvania, and Wilmington, Delaware. Total air samples collected at HP, LD, and DV were 123, 95, and 47, respectively. Rainfall samplers were also deployed at each site and precipitation was collected on a daily basis; 245, 178, and 71 samples were collected at HP, LD, DV, respectively.

Meteorological data were collected near each site from the following sources. Meteorological towers were colocated at HP and DV. The meteorological center at University of Delaware at Georgetown, located 15 km southwest from Lewes, was used for LD. For the three sites, temperature, wind direction, and wind speed were averaged over each 24-h sampling period. Average wind direction was determined using vector averaging.

Sample collection procedures

Air samples (integrated over 24 h, 10 a.m. to 10 a.m. the next day) were collected simultaneously from all three sites) using a high-volume sampler (Model GPNY 1123, Grasby General Metal Works). The sampling assembly consisted of a filter (for particles) and a sorbent for the gaseous fraction. Air was pulled at a flow rate ranging from 0.29 to 0.64 m^3/min through a 20.3×25.4-cm rectangular glass fiber filter (Gelman A/E) followed by two 7.6×7.6 cm cylindrical polyurethane foam (PUF) plugs held within a glass sleeve. Concentration values were calculated from the sum of the analyte on both PUF plugs.

The effectiveness of the PUFs in collecting the air samples was evaluated by examining the back PUF:front PUF (BP:FP) ratio. The BP:FP ratio was <0.1 for most compounds. However, α- and γ-HCH, and heptachlor exhibited a BP:FP ratio of >0.20 in 59, 32, and 27% of samples, respectively. The greatest ratio values were observed during June, July, and August when temperature conditions were highest and the effective vapor pressure values are increased. The BP:FP ratio of of α-HCH, γ-HCH, and heptachlor exceeded 0.50 in 33, 8, and 10% of samples, indicating some loss during sample collection. Concentration values were not adjusted for breakthrough; therefore, concentration values presented for these three compounds are lower than actual values.

The PUF plugs were precleaned using tap water, distilled water, followed by Soxhlet extraction with acetone for 12 h and then with ethyl acetate for another 12 h. The PUF plugs were dried within a vacuum desiccator and kept sealed in individual, precleaned glass jars with Teflon®-lined lids. The glass jars and lids were cleaned using tap water, distilled water, and acetone; the jars were baked for 4 h at 400°C. Filters were wrapped individually in aluminum foil pocket and baked 400°C as described by McConnell et al. [19]. Sample PUFs and filters were returned to their individual containers after collection and were kept frozen at −20°C until processing.

Precipitation was collected on an event basis using a wet-only, commercially available MIC-B (Meteorological Instrument Center) sampler equipped with a $0.2\,m^2$ stainless steel funnel. Each event was any rain that fell during a 24-h period from 10 AM to 10 AM (±1 h) the following day. Rainwater was pumped through an in-line 45-mm glass fiber filter and then extracted using a solid-phase extraction (SPE) cartridge containing 200 mg of a hyper crosslined styrene–divinylbenzene copolymer (Isolute® ENV +, Biotage AB). A flow rate of approximately 20 to 50 ml/min was used to achieve extraction efficiencies of greater than 80% for most compounds (Z. Kuang. 2001. Master's thesis. University of Maryland College Park). After an event, the SPE cartridge was stored at 4°C and the filter was wrapped in aluminum foil and stored at −20°C. Rain samples were shipped weekly on ice packs in small Styrofoam coolers via overnight mail to the laboratory for processing and analysis. Field blanks for both air and precipitation samplers at the three sites were collected monthly.

Sample processing

The PUF plugs and glass fiber filters were fortified with diazinon-d_{10} and extracted separately in batches of 15 to 20 via Soxhlet extraction with ethyl acetate or dichloromethane, respectively, for 12 h. Extracts were reduced to 5 to 10 ml in vacuo, and reduced to 1.0 ml using a gentle stream of high purity (99.9%) nitrogen gas. A laboratory blank and a spike sample were processed with each batch of samples to observe any matrix interference or contamination and to determine extraction efficiency, respectively. Air filters were not analyzed for samples collected in 2000. For rain samples, SPE cartridges were dried upon receipt using clean nitrogen gas. Absorbed analytes were eluted from the cartridge with 6 ml dichloromethane followed by 9 ml 3:1 acetone:acetonitrile solvent mixture. The resulting extract was concentrated to a volume of about 1.0 ml under a gentle stream of high purity (99.9%) nitrogen gas. A second aliquot of 2 ml acetonitrile was added and the solution was blown down to 1.0 ml. The rain filters from 2000 did not contain appreciable amount of analytes (Z. Kuang. 2001. Master's thesis) and were not analyzed for subsequent years.

Analytical method

All samples and controls were analyzed for 15 legacy pesticides or degradation products (Table 1) except in 2000 when aldrin, heptachlor, heptachlor epoxide, oxychlordane, and 4,4′-DDD (1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]-benzene) were not part of the analyte suite. Details of the analytical methods for samples collected in 2000 can be found elsewhere and are similar to below [15]. Extracts for samples in 2001 to 2003 were analyzed using either a Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard 5989A mass spectrometer (GC-MS) or an Agilent Technologies 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer. Both were operated in selected-ion monitoring mode using electron capture negative ion mass spectrometry. The chromatographic conditions were as follows: column, J&W DB-17MS (Agilent Technologies), 30 m, 0.25-mm inner diameter (i.d.), 0.25-μm thickness; flow rate through the column, 1.4 ml/min; temperature program, 130°C, raised at 6°C/min to 205°C for 4.5 min and then at 6°C/min to 300°C for 5.5 min; interface, 300°C; quadrupole, 150°C; source, 200°C; injector, 290°C. The ionization gas was ultrahigh purity methane supplied at 60 kPa. Eighty nanograms of 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl were added to all extracts just before analysis and used as an internal standard.

The method detection limits (MDLs) for analytes in rainwater were determined by spiking 5 to 50 ng of each compound

Table 1. Target analytes with Chemical Abstracts Service (CAS) registry numbers, method detection limits, and average percent spike recovery values for sample matrices and selected physical–chemical properties

Common name	CAS No.	Method detection limit[a]			Average percent spike recovery			Molecular mass	Solubility[b]	Vapor pressure[b]	HLC[b]	log K_{OW}[b]
		Gas phase	Particle phase	Dissolved rain	Gas phase	Particle phase	Dissolved rain					
		(pg/m³)	(pg/m³)	(ng/L)	Avg. percent recovery (SD)			(g/mol)	(mol/m³)	(Pa)	(Pa m³/mol)	
Aldrin	309-00-2	1.2	2.4	0.33	90 (20)	90 (20)	40 (6)	364.9	0.0027	0.064	23	6.24
cis-chlordane	5103-71-9	1.8	1.2	0.76	86 (17)	100 (20)	62 (4)	409.8	0.0013	0.0073	5.7	6.20
trans-chlordane	5103-74-2	1.9	1.0 (1.3) c	0.64	82 (19)	100 (20)	55 (4)	409.8	0.0015	0.010	6.8	6.27
p,p'-DDD[d]	72-54-8	24	9.6	2.8	84 (19)	110 (30)	62 (3)	321	0.0023	0.0012	0.50	6.33
p,p'-DDE[e]	72-55-9	5.9	3.0	1.5	86 (19)	101 (18)	45 (4)	319	0.00079	0.0034	4.2	6.93
p,p'-DDT[f]	50-29-3	98	7.4	0.40	90 (60)	140 (60)	79 (12)	354.5	0.00042	0.00048	1.1	6.39
Dieldrin	60-57-1	1.4	1.2	0.24	120 (40)	90 (20)	70 (3)	380.9	0.013	0.014	1.1	5.48
Heptachlor[g]	76-44-8	0.8	1.1	0.80	90 (20)	100 (30)	63 (2)	373.4	0.0035	0.13	38	5.94
Heptachlor epoxide[g]	1024-57-3	1.5	1.2	0.80	90 (20)	100 (30)	75 (2)	389.2	0.013	0.022	1.7	5.42
α-HCH[h]	319-84-6	2.5	0.9	0.80	81 (18)	90 (30)	85 (7)	290.85	0.333	0.245	0.735	3.94
γ-HCH[i]	58-89-9	0.9	0.9	1.0 (5.6[c])	75 (17)	90 (30)	85 (8)	290.85	0.247	0.0757	0.306	3.83
cis-nonachlor	5103-73-1	1.0	1.0	0.61	80 (16)	100 (20)	63 (7)	444.22				
trans-nonachlor	5103-74-2	1.1	1.2	0.65	84 (19)	110 (20)	57 95)	444.22		0.00378[j]		7.10[j]
Mirex[g]	2385-85-5	1.5	1.1	0.20	77 (18)	100 (20)	30 (3)	545.59				
Oxychlordane	027304-13-8	1.8	1.0	0.85	84 (13)	100 (20)	58 (4)	423.76		0.0102[j]		4.95[j]

[a] Method detection limits provided assume an air volume of 720 m³ and a rain sample volume of 2 L.
[b] Values are designated as final adjusted values from Shen and Wania [21] or Ziao et al. [22].
[c] Values in parantheses are higher method detection limits used for Horn Point, unless otherwise noted.
[d] 1-Chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene.
[e] 1-Chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene.
[f] 1-Chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene.
[g] Method detection limit in rain was estimated from instrumental detection limits.
[h] (1α,2α,3β,4α,5β,6β)-1,2,3,4,5,6-hexachlorocyclohexane.
[i] (1α,2α,3β,4α,5α,6β)-1,2,3,4,5,6-hexachlorocyclohexane, also known as lindane.
[j] Estimated values from Paasivirta et al. [23].

(the equivalent to the lowest point of the calibration curve) into 4-L distilled water, which was poured into the funnel of the sampler, was extracted through the filter-SPE cartridge assembly, and was processed in the same manner as the samples. For the gaseous and particle-phase air samples, the MDLs were determined by spiking 5 to 50 ng of each compound onto precleaned PUFs or filters (8 replicates) and extracting and processing them in the same manner as samples. Standard deviations of measured replicate concentrations from these low-level spike experiments were used to calculate the MDL for each compound according to the U.S. Environmental Protection Agency standard methods ([20]; http://www.epa.gov/osw/hazard/ testmethods/sw846/index.htm). The pesticides were, in general, not detected in the field blanks. In a few cases when the levels were above the MDL, the MDL was modified accordingly. Method detection limits each chemical for air and rain sample extracts along with relevant physical chemical properties are provided in Table 1 [21–23].

Laboratory spike recoveries averaged greater than or equal to 75% for PUFs, greater than or equal to 90% for filters and greater than 60% for precipitation cartridges except for aldrin, 4,4'-DDE, *trans*-nonachlor, and mirex, which had recovery values of less than 60% (Table 1). Samples were not corrected for spike recoveries. Extraction surrogate recoveries averaged 76% for all PUF samples and averaged 104% for filter samples.

Statistical analysis

Multiple regression analyses were performed to determine heats of phase transition and half-life values using the general linear model procedure in SAS (SAS Institute). Box-plot analysis to assess temporal and spatial variability in analyte concentrations and one-way analysis of variance using a Kruskal-Wallis test were conducted using GraphPad Prism[®] (GraphPad Software).

RESULTS AND DISCUSSION

Legacy pesticides

The legacy pesticides included in the present study fall into several groups (Table 1). The first are related to chlordane, a product that was used initially on agricultural crops and lawn pests and then later restricted to use in the foundation of buildings for termite control and finally banned in 1988 (http://www.epa.gov/oppsrrd1/Rainbow/98rainbo.pdf). Technical chlordane is a mixture of approximately 120 compounds [24]. The primary chlordane-related compounds are *cis*- and *trans*-chlordane and *cis*- and *trans*-nonachlor. Heptachlor is also a major component of technical chlordane, but it was also used independently as an agricultural insecticide and was banned in 1988. Technical heptachlor contains approximately 72% heptachlor, 20 to 22% *trans*-chlordane, and 4 to 8% *trans*-nonachlor ([25]; http://www.who.int/ipcs/publications/ cicad/cicad70.pdf). Heptachlor epoxide and oxychlordane are persistent degradation products of heptachlor and chlordane, respectively.

The second group of legacy pesticides examined is the insecticide HCH. Technical HCH is a mixture of isomers made up of 55 to 80% α-HCH, 8 to 15% β-HCH, 2 to 16% γ-HCH, and lesser contributions from the δ- and ε-HCH isomers [26]; this product was banned in the U.S. in the late 1970s

(http://www.epa.gov/glindicators/air/airb.html). The γ-HCH isomer, also known as lindane, was still in limited use in the U.S. and Canada as a seed treatment for canola and other minor uses at the time of the present study, but it too was banned in Canada in 2004 [27] and in the U.S. in 2006 (http://www.epa.gov/fedrgstr/EPA-PEST/2006/December/Day-13/p21101.htm). The third group is the Diels-Alder products of cyclopentadiene and norbornadiene, aldrin, and dieldrin. Aldrin was used from 1950 to 1969 on many agricultural crops until uses were restricted to seed treatments in 1969. Dieldrin, also an oxidative degradation product of aldrin, was used during the same time period on cotton, corn, and citrus. Both products were limited to subterranean termite uses and other minor uses in 1974 before the registration of both were cancelled in 1986 (http://www.epa.gov/oppsrrd1/Rainbow/98rainbo.pdf).

The DDT-related compounds are the fourth group, consisting of the insecticide 4,4′-DDT and its degradation products 4,4′-DDD and 4,4′-DDE [28]. Originally used in the 1940s for control of mosquito-borne malaria and other vector-borne diseases, 4,4′-DDT was widely produced for agricultural and commercial applications (http://www.epa.gov/history/topics/ddt/02.htm). Total usage in the U.S. is estimated at over 600 kt. This product was cancelled in the U.S. for most uses in 1972. Finally, mirex, which was used both as an insecticide to control fire ants and as an industrial fire retardant, was banned in the U.S. in 1977.

Aldrin, dieldrin, chlordane, 4,4′-DDT, 4,4′-DDD, 4,4′-DDE, and mirex have all been identified by the U.S. Environmental Protection Agency as persistent, bioaccumulative, and toxic chemicals, and have been banned or severely limited in most countries (http://www.epa.gov/oppt/pbt/pubs/cheminfo.htm); however, continuing usage of DDT, chlordane, aldrin, and dieldrin has been reported in Mexico as recently as the late 1990s and early 2000s [29]. Because these compounds are persistent, residues remain in soils, surface waters, biota, and air. Furthermore, the atmosphere serves as a conduit, allowing movement and equilibration between environmental compartments. Heavy agricultural usage of some of these pesticides has left behind a reservoir of these materials in some U.S. soils. When the soils are tilled or when temperatures increase, the rate of pesticide volatilization can increase, which allows greater amounts of the chemicals to be transported. In the atmosphere, they partition with atmospheric aerosols or particles. These particles slowly settle from the atmosphere depositing residues onto terrestrial surfaces and into water bodies via dry deposition. The gas and particle-phase pesticides can also be scavenged from the air during rain events; however, this process may not be as important compared to other compounds because most legacy pesticides have low water solubilities (Table 1). Potential sources of the legacy pesticides to the Chesapeake and Delaware Bays and Delmarva Peninsula include a global background signal, transport from historically contaminated areas in the U.S., regional transport from surrounding urban areas, and local sources of contaminated agricultural and residential soils.

Legacy pesticides in air and precipitation

Three environmental compartments were investigated for legacy pesticide concentrations in this work: gas and particle-phase air and dissolved phase rain. Overall, target analytes were detected much more frequently in the gas phase compartment than in the particle or dissolved precipitation compartments (Table 2). This result is expected in view of the physical properties of the pesticides, the environmental conditions at the sites, and the methods utilized to collect the samples

(Table 1). The volume of the air samples collected was high at around 700 m^3, adequate for the detection of many persistent organic pollutants, but particle concentrations in these rural areas were likely low [30]; therefore, surface area for partitioning onto particles was limited. At least one target analyte was detected in the gas phase of every sample with an average of 10 compounds per sample at HP, 13 compounds at LD, and 11 compounds at DV.

Particle phase concentrations

Results of particle-phase air samples indicate that, especially in LD and DV, legacy pesticides reside almost completely in the gas phase (Table 2). Out of 95 filter samples collected at LD, only dieldrin was detected in one sample at levels above the limit of quantitation. At DV, only γ-HCH was detected in two samples at levels above the limit of quantitation. More legacy pesticides were detected in the particle phase at HP and the detections were more frequent. The compounds cis- and trans-chlordane were detected most often at 32 and 37%, respectively (Table 2) and were almost always detected together as would be expected from a technical chlordane source. However, the other major chlordane components (e.g., nonachlor and heptachlor) were rarely detected. Mirex was the third most frequently detected compound in the particle phase at HP (25%); however, mirex was only detected once in the gas phase at this site. Although cis- and trans-chlordane and mirex were detected much more frequently than the other legacy pesticides, their concentration levels averaged about 10% of that in the gas phase. The highest concentrations found in the particle phase were for γ-HCH, with a maximum concentration of 20 pg/m^3, but it was detected infrequently (7%) and was nearly an order magnitude less than the maximum observed in the gas phase.

The patterns of detection in air particle samples may provide some indication of the nature of particles present in the atmosphere at these three sites. The atmosphere at LD and DV is likely more strongly influenced by marine air from the Atlantic Ocean than at HP given their relative distances from the ocean (Fig. 1). In addition, the nature of particles at these sites is likely lower in organic carbon content than at HP. Dachs et al. [31] found that gas and particle-phase PAHs were readily transported with soot particles from Baltimore and deposited to the upper Chesapeake Bay, and that variability in concentrations was related to wind speed and direction. An examination of monthly wind direction frequency data at HP indicated that this site occasionally receives winds from the northwest direction (Baltimore–Washington metropolitan area) during the summer (5–10% of the time, data not shown) and more frequently during the fall and winter. The DV site also receives winds from the northwest in the winter from areas north of Baltimore, when concentrations are low; however, DV primarily receives winds from the southeast and southwest during the summer where no up-wind urban areas exist.

Gas phase concentrations

Patterns in gas phase concentrations at all three locations indicated that cis- and trans-chlordane and both HCH isomers are present continuously (95–100% detection) in the region at low levels averaging 20 to 50 pg/m^3. Trans-nonachlor was also continuously detected at LD and DV (96% at both locations), but was only detected in 61% of samples at HP. Concentrations of cis-nonachlor were up to an order of magnitude less than the concentration of the trans-nonachlor and were less frequently detected, ranging from 24% at HP to 88% at LD. Heptachlor and dieldrin were detected fairly frequently at all three locations,

Table 2. Summary of measured gas- and particle-phase air concentrations (pg/m³) and rain concentrations (ng/L)[a]

	Horn Point (HP)						Lewes (LD)						Dover (DV)					
	AVE	GM	MED	MIN	MAX	% Det	AVE	GM	MED	MIN	MAX	% Det	AVE	GM	MED	MIN	MAX	%Det
Gas phase (pg/m³)	(n = 123)						(n = 95)						(n = 47)					
Aldrin	4.3	4.3	3.9	2.5	6.1	2						0						0
cis-Chlordane	22	19	18	3.5	71	95	27	21	20	3.2	127	96	25	20	18	3.8	120	96
trans-Chlordane	24	20	20	4.0	97	93	31	24	22	1.6	155	99	25	23	19	3.2	90	98
4,4′-DDD[b]	37	33	35	25	54	2						0						0
4,4′-DDE[c]	16	12	14	7.0	52	29	27	19	20	4.5	109	83	80	74	56	7.9	230	89
4,4′-DDT[d]						0						0						0
Dieldrin	84	61	56	2.1	394	74	60	33	32	1.6	314	98	64	54	41	4.2	263	81
α-HCH[e]	31	22	25	4.6	142	99	23	19	19	2.0	61	100	24	23	22	5.5	53	100
γ-HCH[f]	37	27	28	4.0	150	97	52	28	28	2.2	382	100	83	54	49	1.2	343	81
Heptachlor	25	15	16	4.0	568	72	23	20	19	3.2	64	95	19	17	14	3.3	92	72
Heptachlor epoxide	7.7	5.6	5.8	1.7	31	47	5.6	4.6	4.9	1.4	14	60	11	8.7	8.8	1.7	28	57
Mirex	10	10	10	10	10	1	13	4.1	6.5	1.3	54	14	8.1	6.9	6.7	2.8	16	9
cis-Nonachlor	2.0	1.9	1.9	0.9	3.1	24	2.8	2.3	2.3	0.80	10	88	2.4	2.1	2.1	1.0	6.9	49
trans-Nonachlor	4.8	4.1	4.2	1.5	13	62	21	17	15	1.9	103	96	18	15	13	1.5	76	96
Oxychlordane	18	15	15	2.5	50	93	4.8	3.9	4.1	1.3	14	86	7.0	6.9	5.8	1.6	20	57
Particle phase (pg/m³)	(n = 91)[g]						(n = 95)						(n = 47)					
Aldrin						0						0						0
cis-Chlordane	2.3	2.2	2.2	0.7	4	32						0						0
trans-Chlordane	2.2	2.2	2.2	1.4	4	37						0						0
4,4′-DDD						0						0						0
4,4′-DDE						0						0						0
4,4′-DDT						0						0						0
Dieldrin						0				1.6	1.6	1						0
α-HCH				1.2	1.2	1						0						0
γ-HCH	7.0	4.7	4.7	1.3	20	7						0	17.1	13.9	17.1	7.1	27	2
Heptachlor						0						0						0
Heptachlor epoxide				4.8	4.8	1						0						0
Mirex	2.2	2.2	2.2	1.9	3.7	29						0						0
cis-Nonachlor				4.0	4.0	1						0						0
trans-Nonachlor	2.2	1.7	2.4	0.5	4	3						0						0
Oxychlordane						0						0						0
Dissolved rain (ng/L)	(n = 245)						(n = 178)						(n = 71)					
Aldrin						0				2.7	2.7	1						0
cis-Chlordane	1.4	1.1	1.3	0.4	3	2	0.9	0.8	0.6	0.4	2	3	1.5	1.2	1.0	0.5	6	23
trans-Chlordane	1.6	1.6	1.6	1.5	1.7	1				3.3	3.3	1	1.6	1.3	1.3	0.5	5.8	35
4,4′-DDD						0						0						0
4,4′-DDE	19	12	12	2.8	90	10	33	22	26	6.2	66	2	12	7.6	7.4	2.3	63	35
4,4′-DDT				14	14	0.4						0						0
Dieldrin	1.4	1.0	1.3	0.1	3	4	1.2	0.9	1.0	0.2	3	5	2.0	1.5	1.5	0.5	10	49
α-HCH	0.8	0.6	0.5	0.3	2	3	2.9	1.1	1.1	0.2	11	3	1.3	0.9	0.9	0.3	3.3	18
γ-HCH	2.9	2.0	1.8	0	22	20				35	35	1	5.0	2.7	2.7	0.5	35	61
Heptachlor	19	18	22	10	25	1.2	33	18	40	1.3	49	2						0
Heptachlor epoxide				56	56	0.4				18	18	1						0
Mirex						0	30	17	30	3.0	57	2						0
cis-Nonachlor						0						0	0.9	0.9	0.9	0.7	1.1	3
trans-Nonachlor						0						0	1.3	1.2	1.0	0.6	2.2	10
Oxychlordane				2.3	2.3	0.4						0	1.7	1.5	1.7	0.9	2.5	3

[a] AVE = average; GM = geometric mean; MED = median; MIN = minimum; MAX = maximum; % Det = percent detection.
[b] 1-Chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene.
[c] 1-Chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene.
[d] 1-Chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene.
[e] (1α,2α,3β,4α,5β,6β)-1,2,3,4,5,6-hexachlorocyclohexane.
[f] (1α,2α,3β,4α,5α,6β)-1,2,3,4,5,6-hexachlorocyclohexane, also known as lindane.
[g] Filter samples from the year 2000 at Horn Point were not analyzed.

ranging from 72 to 95% for heptachlor and 74 to 98% for dieldrin, with the highest number of detections observed at LD for both compounds. Heptachlor concentrations were similar to the chlordane components, averaging from 19 pg/m³ at DV to 25 pg/m³ at HP, whereas dieldrin concentrations were nearly twice as high, averaging from 60 pg/m³ at LD to 84 pg/m³ at HP.

The degradation products, heptachlor epoxide and oxychlordane, were observed somewhat less frequently than their parent compounds, heptachlor, and *cis*- and *trans*-chlordane, and at lower average concentrations of less than 11 pg/m³ and 18 pg/m³, respectively. The parent compound 4,4′-DDT was not detected above the limit of quantitation in any of the 265 air samples collected, and its degradation product 4,4′-DDD was detected in only two samples from HP. However, 4,4′-DDE, a more stable degradation product, was detected frequently at both LD (83%) and DV (89%), but much less frequently at HP (29%) and at average concentrations ranging from 16 pg/m³ at

HP to $80 \, pg/m^3$ at DV. Mirex was detected infrequently at all three sites at average concentration ranging from 8.1 to 13 pg/m^3, and aldrin was detected in only two samples from HP with a maximum concentration of $6.1 \, pg/m^3$.

Concentrations in precipitation

Observed dissolved pesticide concentrations in rain samples reflect the low aqueous solubility of the legacy pesticides included in the present study (Table 1). In 67% of all rain samples, concentrations of legacy pesticides were below their limits of quantitation. At the HP site, only one compound was detected in 32% of rain samples, at the LD site only 14%, but at the DV site, 82% of samples contained at least one compound. In addition, the three sites exhibited a slightly different profile with respect to the compounds most frequently detected. At HP, γ-HCH was detected most frequently at 20% followed by 4,4′-DDE at 10%, but the average γ-HCH concentrations were considerably lower (2.9 ng/L) than 4,4′-DDE concentrations (19 ng/L). Furthermore, the compound with the highest maximum concentration at HP was 4,4′-DDE (90 ng/L). All the remaining compounds were detected in less than 5% of samples (Table 2). The solubility of γ-HCH is $7.3 \, g/m^3$, the highest of any of the pesticides included in the present study; therefore, more frequent detection of this chemical in rain is reasonable.

At the LD site, all compounds were detected in less than 5% of samples and the most frequently detected compound was dieldrin. In contrast to HP, γ-HCH was only detected in one sample at the LD site and 4,4′-DDE was detected in only three samples. At the DV site, overall average concentrations were higher than at either the HP or LD sites, and the frequency of detections was much larger. Like HP, γ-HCH was detected most frequently (61% of samples); α-HCH was detected in 18% of samples; dieldrin in 49% of samples; and 4,4′-DDE and *trans*-chlordane in 35% of samples. This is somewhat unexpected as the solubility of 4,4′-DDE and *trans*-chlordane are an order of magnitude lower than the solubility of γ-HCH. *Cis*-chlordane and *trans*-nonachlor were also found in 23 and 10% of samples, respectively. For samples with concentrations above the detection limits, concentrations of α- and γ-HCH and 4,4′-DDE at DV were 2 to more than 10 times greater than average concentrations detected at the Integrated Atmospheric Deposition Network (IADN) in the Great Lakes [32].

Such drastic differences in the number of compounds detected between sites, especially for nearby sites LD and DV, was an unanticipated result. Rain sample volumes collected in the present study were minimal for the purpose of legacy pesticide concentration measurements. For example, in the present study, samples were collected over 24 h, whereas the IADN precipitation collection protocol uses the same type of collector as the present study but uses a 28-d composite rain sample [32]. The median rain sample volumes were significantly different ($p < 0.05$); the median volume at the DV site (2.3 L) was 43% greater than the HP site (1.3 L) and 61% greater than the LD site (0.9 L). A regression analysis of sample volume collected per rainfall amount indicated that no efficiency differences existed between the three samplers ($r^2 \geq 0.99$); the slopes for all three sites were virtually identical. Thus, the differences in the frequency of compound detection between the DV and LD sites is likely due to somewhat higher rainfall rates and therefore larger sample volumes at the DV site, leading to pesticide mass collection above the limit of quantitation in more samples. In the present study, a more in-depth analysis of gas phase air concentrations, where the dataset is more robust, is more likely to be useful for site comparisons and for evaluation of long-range versus local sources of legacy pesticides. The remaining discussion is limited to gas-phase air concentration results for the most frequently detected pollutants.

Spatial analysis of air concentrations

Local source strength of legacy pesticides is dependent upon the rate and duration of use, but these data for Maryland and Delaware are not available. The Delmarva Peninsula has a low population density, and historically land use has been primarily agriculture. Therefore, it is reasonable to expect that legacy pesticides were used in response to potential or actual pest pressures in the production of grain, vegetable, and fruit crops. Local source strength is also a function of soil half life. Soils on the Delmarva are generally sandy and lower in organic carbon than in other agricultural regions of the U.S., such as the Midwest; thus, release of these hydrophobic chemicals is expected to be greater as soils are disturbed.

Although no official definition of local, regional and long-range sources exists, the United Nations defines long-range transport of air pollutants as the ''atmospheric transport of air pollutants within a moving air mass for a distance of greater than 100 kilometers'' ([33]; http://unstats.un.org/unsd/environmentgl/). Therefore, for the purposes of this discussion, local sources are defined as between 0 and 10 km, regional sources are between 10 and 100 km, and long-range sources are >100 km. For all three sites, the 10 km local source area is limited to the Delmarva Peninsula or nearby surface waters. The HP site would include the city of Cambridge, Maryland, the LD site would include the city of Lewes, Delaware, and the DV site would include the city of Dover, Delaware, and the Dover Air Force Base, all relatively small cites as described above. Potential regional sources of <100 km would include Washington, DC, and Baltimore, Maryland, for the HP site, Baltimore and the Wilmington, Delaware, and Philadelphia, Pennsylvania areas would be included for the DV site, but only Wilmington would be included for LD.

Statistical analysis of all gas-phase air concentration observations at the three sites indicates that some compounds have long-range or regional sources, whereas others may have some contributions from local sources (Fig. 2). No significant differences were observed between sites for *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, or α-HCH, indicating long-range or distant regional sources provided significant contributions to the signals observed at each site and that no strong local sources existed. However, a comparison of the ratio of *trans*-chlordane:*cis*-chlordane (TC/CC) found that the median values of 1.06, 1.20, and 1.12 were significantly different from each other ($p \leq 0.01$) for HP, LD, and DV, respectively (Fig. 2). The median TC/CC values observed at our sites are similar to annual averages seen at urban centers in the Great Lakes, where ratios of 1.22 and 1.13 were found at Toronto, Canada, and Chicago, Illinois, USA, during the same time period as the present study [34]. Results suggest that nearby urban centers like Baltimore, Washington, Wilmington, and Philadelphia are probably regional sources of chlordanes to our sites.

The ratio of TC/CC in technical chlordane is 1.16, but the predicted ratio in air reflecting component vapor pressures is 1.63 to 1.85 at 20 or 25°C, respectively [17,35]. An examination of temporal trends in TC/CC ratio values (Fig. 3) reveals that, with the exception of one sample from HP, all ratios were well below that predicted from technical chlordane. This is to be expected, because global background chlordane profiles have become more depleted in TC since these products were banned [36]. The LD site did not go below a value of 1.0 in any sample,
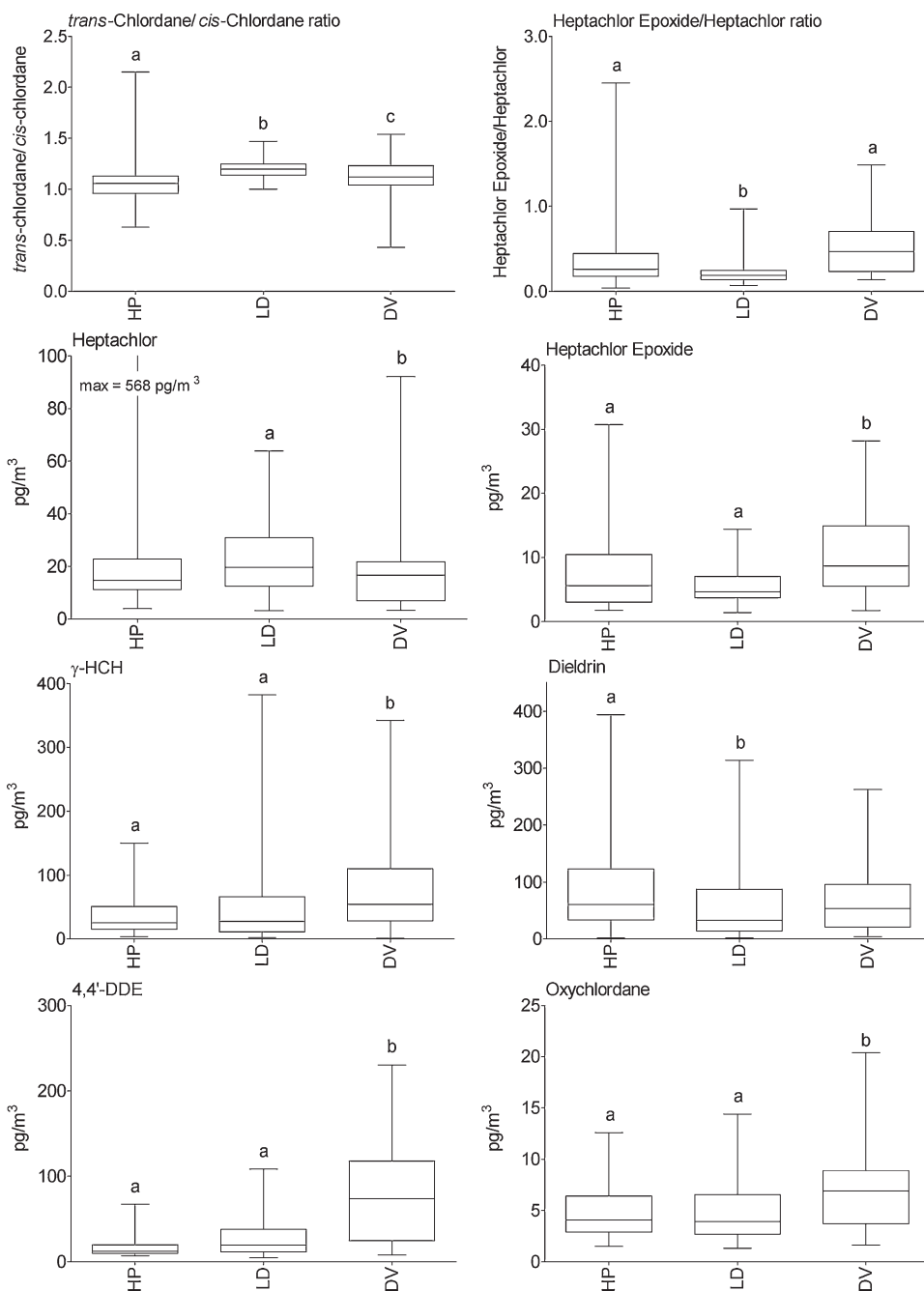
Fig. 2. Comparison of median (line), upper and lower quartile (box), minimum, and maximum (whiskers) gas phase air concentration (pg/m³) values for the three sample collection sites: Horn Point (HP), Lewes (LD), and Dover (DV). Use of the letters a, b, and c above the boxes indicates statistically significant differences between the median values ($p < 0.05$) using a one-way analysis of variance, Kruskal-Wallis test. The compound 4,4′-DDE is 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene, and HCH is hexachlorocyclohexane.

but the minimum TC/CC value for HP was 0.63 and for the DV site the minimum was 0.43, with the lowest values observed during the summer months. Gouin et al. [34] found that warmer temperatures enhanced local surface–air exchange influences, releasing chlordanes with low TC/CC ratios from rural soils in the Great Lakes area. Therefore, lower overall TC/CC ratios at the HP and DV sites may have been due to volatilization from nearby soils. Concentrations of oxychlordanes were also highest in the summer (data not shown) at all three sites with the highest maximum concentration found at DV (Fig. 2), and median oxychlordane concentration at the DV site was significantly higher than at the HP and LD sites ($p < 0.05$).

The median concentration of heptachlor was significantly higher at the LD site compared to the DV site, but not significantly different than the median concentration at the HP site where the highest heptachlor concentration was observed (Fig. 2). Because technical heptachlor contained around 20% *trans*-chlordane, contributions from technical heptachlor use may explain higher overall TC/CC ratio values at the LD site [25]. In contrast, the median concentration of the heptachlor degradation product, heptachlor epoxide was significantly greater at the DV site compared to the LD and HP sites ($p < 0.01$ and $p < 0.05$, respectively). This suggests that although more heptachlor may have been used at the LD site, perhaps as a termiticide in undisturbed locations where degra-
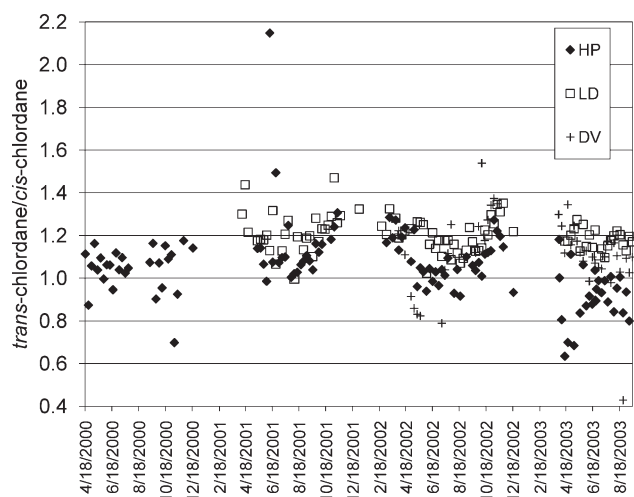
Fig. 3. Comparison of *trans*-chlordane:*cis*-chlordane ratio values in the gas phase for the sample collection sites: Horn Point (HP), Lewes (LD), and Dover (DV).

dation would be limited, heptachlor may have been applied as an insecticide to soils in the DV area where it more readily underwent microbial degradation to heptachlor epoxide. A comparsion of heptachlor epoxide:heptachlor ratios at the three sites reveals that the median values at both the HP and DV sites were significantly higher than at the LD site ($p < 0.01$ and $p < 0.001$, respectively).

The median concentrations of γ-HCH and 4,4′-DDE were also significantly higher at the DV site than at the other two sites ($p < 0.01$ and $p < 0.001$, respectively). From a spatial perspective, the Dover region appears to have stronger local sources of many of the legacy pesticides when compared to the other two sites. However, it is unclear if this is due to greater local sources or from more distant regional sources such as Wilmington or Philadelphia. One notable exception, was dieldrin, where the median concentration was significantly higher at the HP site ($p < 0.01$) compared to the LD site but not significantly different than the DV site, indicating the presence of local sources at the HP site. Dieldrin is both the degradation product of aldrin and was used directly on agricultural crops. Although information on specific use rates or overall usage is unavailable, the entire Delmarva Peninsula is a historically agricultural region dating back to the colonial period. Therefore, it is not surprising to discover that these legacy pesticides were used on soils near our sites.

Relating air concentration to temperature

A visual analysis of temporal trends in air concentrations at the three sites during the sample collection period indicated that air concentrations in the region do increase with average daily temperature (Supplemental Data, Fig. S1), as has been observed in numerous other studies. However, it is not possible to quantify the effect of local temperature changes on air concentration without a more detailed analysis. A common approach to evaluate the temperature

$$\ln P = -\frac{\Delta Hvap}{R}\left(\frac{1}{T}\right) + C \qquad (1)$$

dependence of atmospheric concentrations of organic compounds is to utilize the Clausius-Clapeyron equation (Eqn. 1), which describes the relationship between compound partial pressures, temperature, and the enthalpy of vaporization

[16,17,37–39]. If the atmospheric background concentration is low, and contamination in the local area is high, then the slope of ln P versus $1/T$ will reflect the thermodynamics of air–surface partitioning [40], where P is the vapor pressure of the compound (Pa), T is the temperature (K), the slope is equal to $-\Delta H_{vap}/R$ or the enthalpy of vaporization (kJ/mol) divided by the universal gas constant, and C is the intercept. When applied to ambient air concentration measurements, ΔH_{vap} is the enthalpy of phase change between air and the sorbed state, ΔH_{AS}. A shallow slope or a weak dependence on temperature indicates the influence of distant sources; whereas, a steep slope indicates that air concentrations are controlled by emissions from local sources [40].

The Clausius-Clapeyron equation can be modified (Eqn. 2) and used to perform a regression analysis of ln P versus $1/T$, where T is the average ambient temperature and t is the sample collection time (in Julian days relative to January 1, 2000). The coefficient α_1 ($-\Delta H_{vap}/R$) was used to determine the enthalpy of phase change, ΔH_{AS} (kJ/mol). The coefficient a_2, (d^{-1}) describes the rate of change of the partial pressures, that is, the observed concentrations, and is used to calculate dissipation half-life ($t_{1/2} = \ln 2/a_2$). For a compound whose concentration (i.e., partial pressure) is increasing with time, a_2 will be positive, and negative for a compound whose concentration is decreasing. Because the legacy pesticides are no longer in use in the U.S., the levels are expected to be on the decline and a_2 is expected to be negative. However, γ-HCH was still registered for limited uses in the U.S. and Canada during the sampling period of the present study; therefore, the rate of observed decline may be slower than some other pesticides.

$$\ln P = a_0 + a_1\left(\frac{1}{T}\right) + a_2 t \qquad (2)$$

The modified Clausius-Clapeyron equation (Eqn. 2) was moderately effective at describing the changes in the partial pressure of the legacy pesticides, indicating that temperature is an important factor governing air concentrations in this region (Supplemental Data, Table S1) [41,42]. At the HP site, the regression results for all compounds were highly significant ($p < 0.0001$) except for 4,4′-DDE ($p = 0.01$). At the LD site, all compounds were highly significant except for heptachlor epoxide ($p = 0.01$), and at the DV site, all compounds were highly significant ($p \leq 0.0006$) except for oxychlordane ($p = 0.04$) and γ-HCH, heptachlor, and *cis*-nonachlor, which were not significant. Although the regression results were significant for almost all chemicals, the coefficients of determination (r^2) values were generally less than 0.60 when using Equation 2. At HP, all r^2 values were less than or equal to 0.57 except for *cis*-nonachlor where r^2 was 0.70. At LD, all r^2 values were less than or equal to 0.51, and at the DV site, all r^2 values were less than or equal to 0.61. These results indicate that temperature does influence the observed concentrations, but that it can only explain some of the variability in observed concentrations for most of the legacy compounds at the three sites.

Inclusion of wind speed and direction

Using multiple linear regression analysis to evaluate the influence of parameters other than temperature on atmospheric levels of contaminants has been found to improve predictions for PCBs in Great Lakes [43] and organochlorines in Turkey [44]. The potential influence of local sources on levels of legacy pesticides was investigated by including wind speed, WS (m/s) and wind direction, WD (degrees) in the Clausius-Clapeyron

equation (Eqn. 3).

$$\ln P = a_0 + a_1 \left(\frac{1}{T}\right) + a_2 t + b_1 (\cos WD) + b_2 (\sin WD)$$

$$+ b_3 (LnWS) \tag{3}$$

Using the cosine and sine function of WD enables a clearer determination of the effect of wind direction, and the location of the sources can be identified with greater precision. If b_3 is positive and the values of the coefficients are significant ($p < 0.05$), then wind erosion from local sources (fields and fallow lands) is important, resulting in increased air concentrations with elevated wind speed. Inclusion of the wind speed and wind direction parameters in Equation 3 improved the r^2 values only slightly (5–9%) for most chemicals at the three locations. At the HP location, only 4,4′-DDE r^2 values were noticeably improved (18%). Overall, *cis*-nonachlor also had the largest r^2 value of any chemical in the present study (0.81) for Equation 3. At the LD site, the r^2 value for heptachlor epoxide was improved by 18%. At the DV site, using Equation 3 improved the r^2 value (26%) for oxychlordane only. The 24-h length of the air samples collected in the present study likely

reduces the usefulness of wind-related data as wind conditions can vary widely throughout the day at all three sites. Additional studies with shorter sample collection periods or wind-direction-triggered sampling would likely be necessary to discern more detailed information concerning local and regional sources.

Long-range transport versus local sources

An examination of the enthalpy of phase change (ΔH_{AS}) values calculated from the two modified Clausius-Clapeyron equations in comparison with ΔH_{vap} further supports the conclusion that most of the legacy pesticides observed in air in Delmarva region originate from long-range transport sources (Fig. 4). As described by Wania et al. [40], the low values of ΔH_{AS} compared with ΔH_{vap} for most of the compounds represent a shallow slope condition or distant sources. At the HP site, α-HCH has a slightly negative ΔH_{AS} value using Equation 2 and only 1.4 kJ/mol using Equation 3, indicating that levels of this compound are governed by background air concentrations with no significant local or regional sources. Although the ΔH_{AS} values of α-HCH at the LD and DV sites are positive, they are the lowest values for all the analytes where regression analysis
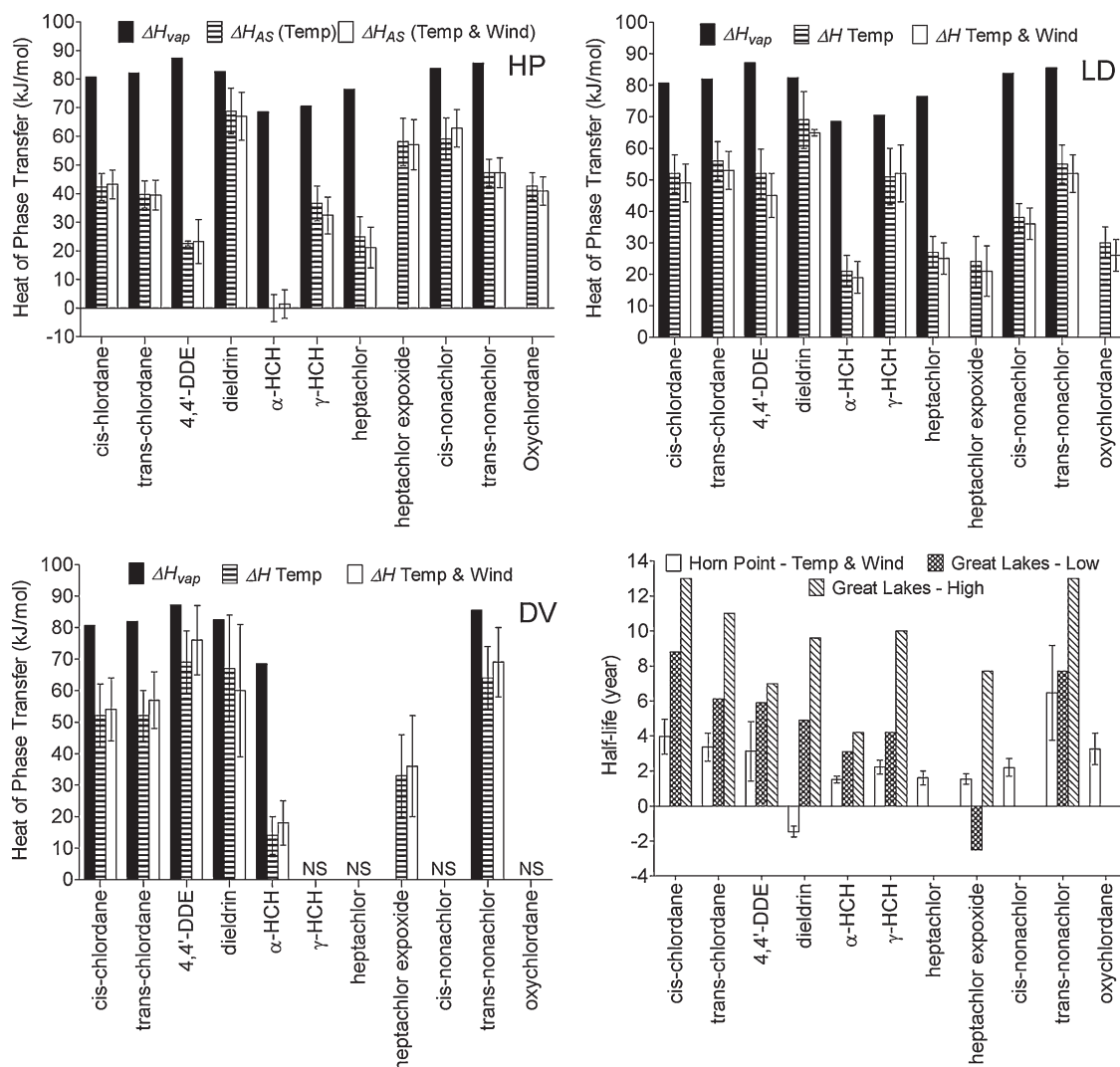

Fig. 4. Comparison of published enthalpy of vaporization (ΔH_{vap} kJ/mol) [15,45,46] with enthalpy of phase change (ΔH_{AS}, kJ/mol) for three sampling sites: Horn Point (HP), Lewes (LD), and Dover (DV). Also presented are calculated half-life ($t_{1/2}$, year) values for Horn Point compared with range of published half-life values observed at seven Great Lakes sites [32]. The compound 4,4′-DDE is 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene, and HCH is hexachlorocyclohexane.

results were significant. However, results for α-HCH may have been influenced by sampling losses under high temperature conditions, thereby lowering the slope values for this chemical. Other pesticides with low ΔH_{AS} values are heptachlor at both the HP and LD sites and 4,4'-DDE at the HP site.

The ΔH_{AS} for dieldrin, especially at the HP and LD sites, is similar to the published ΔH_{vap}, indicating that volatilization

from local sources is a likely contributor to the observed air concentrations and that dieldrin was used in the region in the past. At the DV site, the ΔH_{AS} for 4,4'-DDE is also close to the ΔH_{vap}, which strongly suggests that a local source is a major contributor to the observed concentrations. This local source may be contaminated soils where presumably DDT was used for mosquito control in the region. The ΔH_{AS} values for the
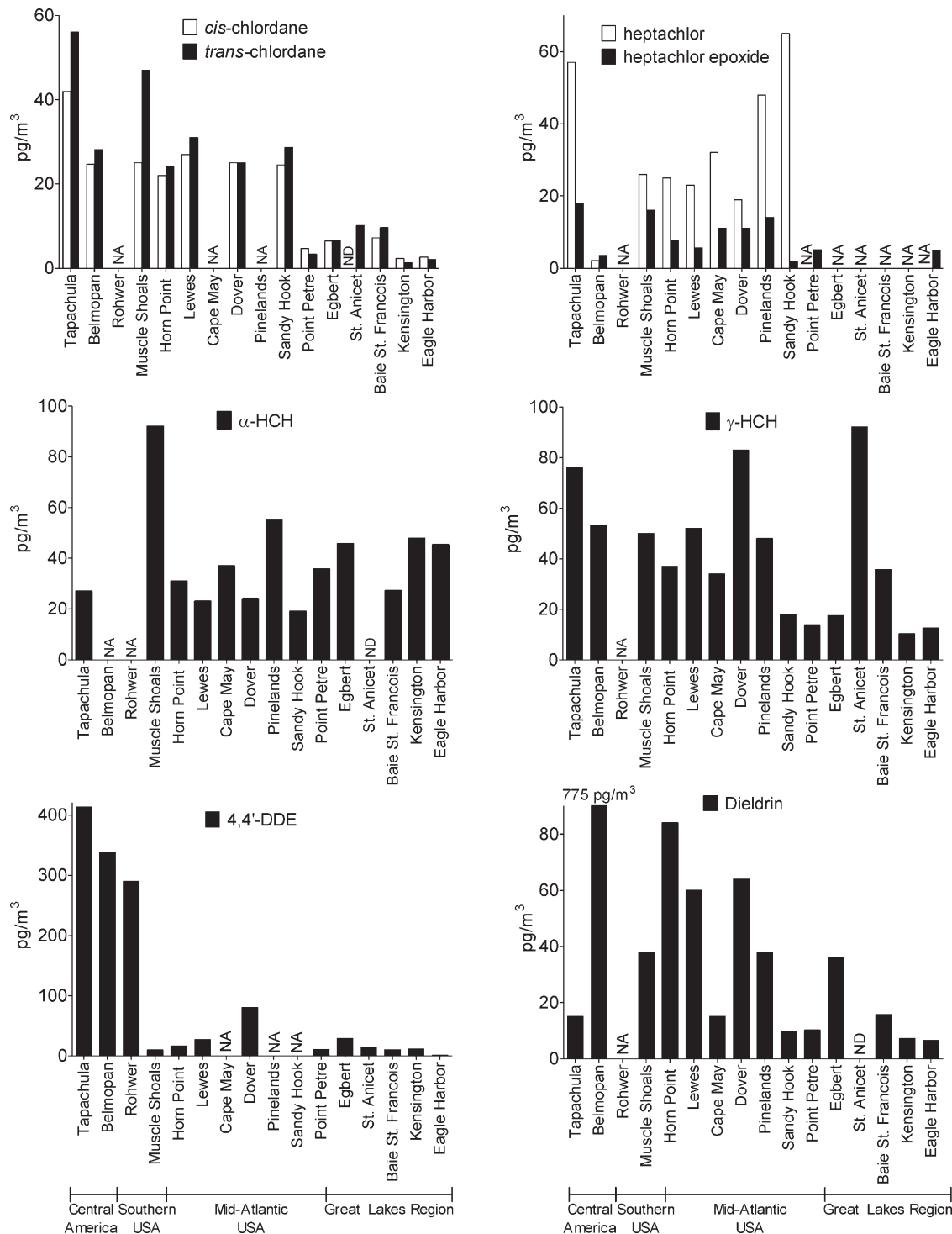
Fig. 5. Comparison of average gas-phase air concentrations from the present work (Horn Point, Lewes, Dover) with others collected in North and Central America during the same time period or few years just prior the present study. Data from Tapachula, Chiapas (Mexico) [29], Belmopan, Belize [45], Rohwer, Arkansas [39], Muscle Shoals, Alabama [46] are from a variety of sources. Data from Cape May, New Jersey (listed as Delaware Bay in the source), Pinelands, New Jersey, and Sandy Hook, New Jersey, are from Gioia et al. [16], except values for *trans-* and *cis*-chlordane for Sandy Hook, New Jersey, are from Offenberg et al. [17] and represent the geometric mean of gas plus particle phase concentrations. Data from Point Petre, Ontario (Canada), and Eagle Harbor, Michigan, are from the Integrated Atmospheric Deposition Network (http://www.epa.gov/glnpo/monitoring/air2/iadn/reports/IADN_Toxics_Deposition_Thru_2005.pdf). The remaining Canadian sites and Egbert, Ontario (Canada) are from Yao et al. [27]. NA = not available, and ND = not detected.

remaining legacy pesticides were approximately 50 to 75% of the ΔH_{vap} values. The ΔH_{AS} values from the present study are similar to what has been observed at a rural location at the mouth of Delaware Bay [16] and also in the Great Lakes [37], indicating that similar processes control atmospheric transport and occurrence at these sites and the current sites of interest.

Dissipation half-life estimates

Statistically significant ($p < 0.05$) rates were used to determine a theoretical half-life value, $t_{1/2}$ (year), using the formula ($t_{1/2} = [\ln2/a_2]/365$) for each compound at the HP site where sample collection was carried out for the longest period, four years. These half-life values are an indication of atmospheric concentration decline as opposed to a specific chemical reaction or process. Half-life values calculated from Equation 3 at the HP site ranged from 1.5 to 1.6 year for α-HCH, heptachlor, and heptachlor epoxide (Fig. 4). Values were slightly higher for γ-HCH and *cis*-nonachlor at 2.2 years. Half-life values for *cis*- and *trans*-chlordane, 4,4′-DDE, and oxychlordane ranged from 3.1 to 4.0 years. The greatest half-life calculated was for *trans*-nonachlor at 6.5 years. These half life values indicate that concentrations of these legacy pesticides were decreasing over time in the Delmarva Peninsula. In contrast, dieldrin concentrations did not decrease during the sampling period, and the calculated half life was negative, suggesting that a strong local source or sources exist. Clearly, additional investigations of dieldrin-contaminated soils on the upper Delmarva Peninsula are needed to clarify this issue.

The half-life values estimated from the measurements near the Chesapeake and Delaware Bays were in general two to three times lower than a range of half-life values measured in the Great Lakes region (Fig. 4) [37]. However, the half-life value for *trans*-nonachlor at HP was similar to the lower end of the range found in the Great Lakes. Dieldrin in the Great Lakes did not have a negative half-life but ranged from 4.9 to 9.6 years. These results indicate that for most legacy pesticides, concentrations should continue to diminish in the region more quickly than in the Great Lakes region. Furthermore, this may indicate that the sandier soils and warmer temperatures of the Delmarva Peninsula/Chesapeake Bay region facilitate both degradation and volatilization of legacy pesticides to a greater degree than in the colder Great Lakes region. Additional measurements over a longer period of time would increase the confidence in these dissipation half-life values.

Comparison with other studies

Results of the spatial comparison of concentrations at the three Delmarva sites and the enthalpy of phase transfer indicated that the sources of chlordanes, HCHs, and heptachlor are primarily long range transport and that 4,4′-DDE and dieldrin have substantial local sources at some sites. A further analysis comparing results of the present study with measurements from other locations in the U.S., Canada, and Central America may provide further insights as to the latitudinal gradient profile of these pesticides.

A number of other published studies of legacy pesticides and other pollutants were carried out during the same time period as this work or a few years just prior to this project (Fig. 5) (http://www.epa.gov/glnpo/monitoring/air2/iadn/reports/IADN_Toxics_Deposition_Thru_2005.pdf; [17,27,29,39,45,46]). Sites were chosen that were more rural and/or near coastal waters. A general decrease in concentration with increasing latitude was seen for *cis*- and *trans*-chlordane, indicating the Southern U.S. and areas of Central America remain source areas. This conclusion is supported by results from a 2000 to 2001 survey using passive air samplers across North America that found higher chlordane concentrations in the southeastern U.S. [47]. Observed concentrations in the present study were intermediate in range compared with observed concentrations in areas in the southern U.S. and Central America, but were similar to those found just north of the Delmarva Peninsula in New Jersey. The profile for 4,4′-DDE was similar to the chlordanes in that the highest levels were found in the south, but the decline was more pronounced. Concentrations of 4,4′-DDE in the Delmarva Peninsula area were similar to those found in the Great Lakes region and Canadian agricultural sites, but the average concentration at the DV site exceeded all the other selected data except for Mexico, Belize, and Arkansas, again suggesting a local source in the region.

Results for α-HCH were generally low at all sites with no clear trend, but the highest concentrations were found at an agricultural site in Alabama where high chlorinated insecticide use has occurred [46]. For γ-HCH, a general trend of decreasing concentration with latitude was overridden by apparent local sources at the DV site and at an agricultural site in Canada (St. Anicet, QC) [27]. The highest concentrations of dieldrin were found near an agricultural site in Belize [45]. However, the profile for dieldrin further supports the earlier discussion that local sources exist on the Delmarva Peninsula. Average concentrations from the present study were higher than in the southern U.S., New Jersey, and sites north. In contrast, the profile for heptachlor and heptachlor epoxide indicate source regions exist both south of the U.S. in Mexico and north of the Delmarva Peninsula in New Jersey.

CONCLUSION

Results of this work provide much needed data on the concentrations, the spatial and temporal trends, and the potential sources of organochlorine insecticides and their degradation products in the Chesapeake Bay and Delaware Bay region. Further research including paired air–water concentration measurements are needed to estimate air–water gas exchange fluxes of pesticides to surface waters; however, it is likely that gas exchange is a source of legacy pesticides to these water bodies as has been found for other pollutants [8,31]. Results from particle-phase sampling indicate that the Washington–Baltimore metropolitan area is a source of some legacy pesticides such as *cis*- and *trans*-chlordane. Shorter duration air sampling campaigns or wind direction-triggered sampling may be needed to examine further the potential regional and local sources and transport to sensitive areas in the watersheds.

Although soils in the southern U.S. have been identified as a source of many organochlorine pesticides, results of this work indicate that soils on the Delmarva Peninsula are contaminated with dieldrin, γ-HCH, and persistent pesticide degradation products (4,4′-DDE, oxychlordane, and heptachlor epoxide). Additional studies to investigate the extent of soil contamination in the region will be useful for determining volatilization especially in the summer or after tilling and for discerning residue availability to indigenous flora and fauna and bioconcentration in higher order organisms. Expanded wet deposition measurements with larger sample volumes is also needed to quantify further the monthly or annual wet deposition flux values to the region. Although detection frequencies were low in the present study using a daily sample regime, comparisons with Great Lakes rain concentrations and the large quantity of rainfall received in this area suggests that wet

deposition could also be an important source of legacy pesticides to the larger watershed. Dissipation half-life values based on temporal trends in gas phase concentrations at Horn Point are encouraging as most are less than 10 years except for dieldrin, which did not decline during the collection period. If global usage of these compounds continues to decline as expected, then concentrations of most legacy pesticides are likely to decrease to below 10% of today's values over the next 30 to 40 years.

SUPPLEMENTAL DATA

Table S1. Enthalpy of phase change (ΔH_{AS}, kJ/mol) ± stan-standard deviation and half-life ($t_{1/2}$, year) standard deviation calculated from two modified Clausius-Clapyeron equations compared with literature values of enthalpies of vaporization and octanol–air partitioning and with ΔH_{AS} values from Cape May, NJ, and the Great Lakes.

Figure S1. Air temperature (°C) and air concentrations (pg/m^3) of γ-hexachlorocyclohexane (γ-HCH), dieldrin, 4,4′-DDE (1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene), and *trans*-chlordane measured during the study period for all three sites. Dieldrin was not measured in 2000 and 4,4′-DDE was only detected once in 2000 at Horn Point (HP). Sample collections began in Lewes (LD) in 2001 and at Dover (DV) in 2002. (409.7 KB PDF).

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