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FIONA WONG,[†,⊥] HENRY A. ALEGRIA,[#]
TERRY F. BIDLEMAN,[†,*]
VÍCTOR ALVARADO,[▽] FELIPE ANGELES,[▽]
ALFREDO ÁVILA GALARZA,[○]
ERICK R. BANDALA,[◆]
IDOLINA DE LA CERDA HINOJOSA,[¶]
IGNACIO GALINDO ESTRADA,[$]
GUILLERMO GALINDO REYES,[%]
GERARDO GOLD-BOUCHOT,[&]
JOSÉ VINICIO MACÍAS ZAMORA,[‡]
JOAQUÍN MURGUÍA-GONZÁLEZ,[§] AND
ELIAS RAMIREZ ESPINOZA[||]

Centre for Atmospheric Research Experiments, Science and Technology Branch, Environment Canada, 6248 Eighth Line, Egbert, ON, L0L 1N0, Canada, Department of Chemistry, University of Toronto, 1265 Military Trail, Toronto, ON, M1C 1A4, Canada, Department of Environmental Science, Policy and Geography, University of South Florida St. Petersburg, 140 Seventh Avenue S., St. Petersburg, Florida 33701, Sustancias Tóxicas En Suelos y Residuos, Centro Nacional de Investigación y Capacitación Ambiental (CENICA), Av. San Rafael Atlixco 186, Col. Vicentina, Delegación Iztapalapa, C.P. 09340, México, D.F., México, Facultad de Ingeniería, Universidad Autónoma de San Luis Potosí, Av. Manuel Nava No. 8, Zona Universitaria, C.P. 78290, San Luis Potosí, México, Departamento de Ingeniería Civil y Ambiental, Universidad de Las Americas-Puebla. Sta. Catarina Mártir. Cholula, C.P. 82720, Puebla, México, Jefa del Sistema Integral de Monitoreo Ambiental Agencia de Protección al Medio Ambiente y Recursos Naturales Av. Alfonso Reyes No. 1000, Interior del Parque Niños Héroes, Col. Regina Monterrey, C.P. 64290, Nuevo León México, Centro Universitario de Investigaciones en Ciencias del Ambiente, Universidad de Colima, Revolución No. 427, Col. Centro, C.P. 28000, Colima, México, Laboratorio de Toxicología, Facultad de Ciencias del Mar, Univeridad Autónoma de Sinaloa, Paseo Claussen s/n, C.P. 82000, Mazatlán, Sinaloa, México, Cinvestav del IPN, Unidad Merida, Km 6 Antigua Carretera a Progreso, C.P. 97310, Mérida, Yucatán, México, Instituto de Investigaciones Oceanológicas, Universidad Autónoma de Baja California, Km. 107 Carretera Tijuana - Ensenada, C.P. 22880, Ensenada, Baja California, Mexico, Facultad de Ciencias Biológicas y Agropecuarias, Región Orizaba-Córdoba, Universidad Veracruzana, Km 1 Carretera Peñuela-Amatlan de Los Reyes, C.P. 94945, Veracruz, Mexico, and Centro de Investigación en Materiales Avanzados, S.C., Miguel de Cervantes 120, Complejo Industrial Chihuahua, C.P. 31109, Chihuahua, Chihuahua, México

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The spatial and temporal variation of organochlorine pesticides (OCs) in air across Mexico was investigated by deploying passive samplers at eleven stations across the country during 2005–2006. Integrated samples were taken over three-month periods and quantified for DDT compounds,endosulfans, toxaphenes, components of technical chlordane, hexachlorocyclohexanes (HCHs), and dieldrin. Enantiomers of chiral chlordanes and *o,p′*-DDT were determined on chiral stationary phase columns as an indicator of source and age. Results are discussed in combination with pumped air samples taken at four other stations in southern Mexico during 2002–2004. DDT and its metabolites, endosulfan and toxaphene were the most abundant OCs detected in all sampling sites. Atmospheric concentrations of ΣDDT (*p,p′*-DDT + *o,p′*-DDT + *p,p′*-DDE + *o,p′*-DDE + *p,p′*-DDD + *o,p′*-DDD) ranged from 15 to 2360 pg m^{-3} with the highest concentrations found in southern Mexico and the lowest found in northern and central Mexico. A fresher DDT residue was observed at sites with greater DDT use and in the southern part of the country, as shown from the higher F_{DDTe} = *p,p′*-DDT/(*p,p′*-DDT + *p,p′*-DDE) and nearly racemic *o,p′*-DDT. This agrees with the former heavy use of DDT in the endemic malarious area of the country. A local hotspot of endosulfan was identified at an agricultural area in Mazatlan, Sinaloa, with a annual mean concentration of ΣENDO (endosulfans I + II + endosulfan sulfate) = 26,800 pg m^{-3}. At this site, higher concentrations of ΣENDO were recorded during the winter (November to February) and spring (February to May) periods. From back trajectory analysis, this coincides with a shift in the air mass coming from the Pacific Ocean (May to November) to the inland agricultural area (November to May). The elevated ΣENDO observed is likely due to the local agricultural usage. HCHs, chlordanes, *trans*-nonachlors, and dieldrin were more evenly distributed across the country likely due to them being aged residues and more diffuse in the environment. In contrast, hotspots of endosulfans, DDTs, and toxaphenes were observed as they were heavily used in localized agricultural or malarious regions of Mexico.

Introduction

Mexico is known for its long history of organochlorine pesticides (OCs) usage in malaria control and agriculture. According to Li and MacDonald (*1*), Mexico ranked sixth in the world for the overall use of dichlorodiphenyltrichloroethane (DDT). Approximately 250 kt of DDT was used between 1947 and 2000. Under North American Regional Action Plans (NARAPs) initiated by the North American Commission for Environmental Cooperation, Mexico is phasing out usage of DDT, chlordane and lindane (γ-

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[*] Corresponding author e-mail: terry.bidleman@ec.gc.ca; phone: 1-705-458-3322; fax: 1-705-458-3301.

[†] Centre for Atmospheric Research Experiments, Science and Technology Branch, Environment Canada.

[‡] Instituto de Investigaciones Oceanológicas, Universidad Autónoma de Baja California.

[§] Facultad de Ciencias Biológicas y Agropecuarias, Región Orizaba-Córdoba, Universidad Veracruzana.

[||] Centro de Investigación en Materiales Avanzados, Chihuahua.

[⊥] Department of Chemistry, University of Toronto.

[#] Department of Environmental Science, Policy and Geography, University of South Florida.

[▽] Sustancias Tóxicas En Suelos y Residuos, Centro Nacional de Investigación y Capacitación Ambiental.

[○] Facultadde Ingeniería, Universidad Autónoma de San Luis Potosí.

[◆] Departamento de Ingeniería Civil y Ambiental, Universidad de Las Americas-Puebla.

[¶] Jefa del Sistema Integral de Monitoreo Ambiental Agencia de Protección al Medio Ambiente y Recursos Naturales.

[$] Centro Universitario de Investigaciones en Ciencias del Ambiente, Universidad de Colima.

[%] Laboratorio de Toxicología, Facultad de Ciencias del Mar, Univeridad Autónoma de Sinaloa.

[&] Cinvestav del IPN, Unidad Merida.

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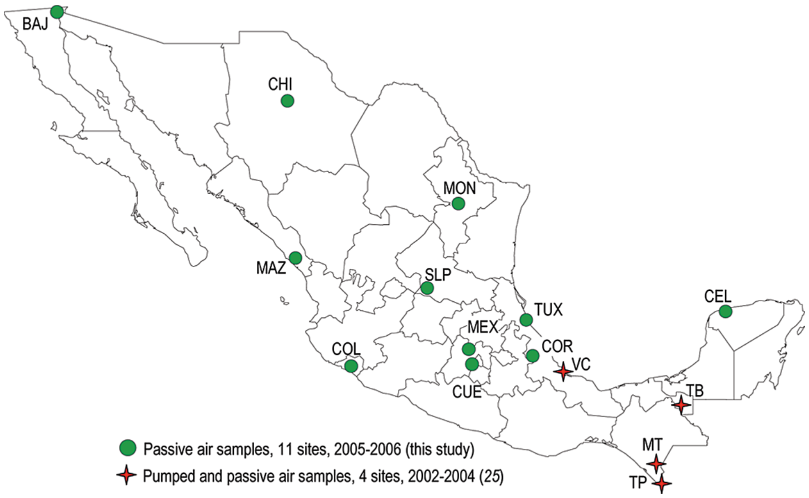

FIGURE 1. Map of air sampling sites in Mexico during 2005−2006 (this study) and 2002−2004 (*25*). BAJ = Baja California, CHI = Chihuahua, CEL = Celestun, COL = Colima, COR = Cordoba, CUE = Cuernavaca, MAZ = Mazatlan, MEX = Mexico City, MON = Monterrey, SLP = San Luis Potosi, TUX = Tuxpan, TB =Tabasco, MT = Chiapas mountain, TP = Tapachula, VC = Veracruz.

hexachlorocyclohexane) (*2*−*4*). Mexico exceeded this target and was successful in halting DDT use by 2000 (*5*). Elimination of chlordane use was achieved in 2003 (*6*) and Mexico has agreed to phase out lindane in the coming years (*4*).

Most of the studies on OCs in Mexico have been focused on human blood or tissues (*7*−*11*), sediment (*12*−*16*), coastal waters (*16*−*18*), marine biota (*19*−*21*), and food products (*22, 23*). Information on the atmospheric levels of OCs in Mexico is scarce. Previous studies in southern Mexico found that DDT and toxaphene concentrations in air were 1−2 orders of magnitude above levels in the Laurentian Great Lakes and arctic regions (*24*−*26*). Atmospheric levels in southern Mexico were generally higher than those in central Mexico (*27*), Costa Rica (*28, 29*) and Cuba (*30*), and comparable to those in Belize (*31*). Until now, no atmospheric data for OCs have been available for the larger area of Mexico, and establishing baseline data across the country would be useful for developing a long-term air monitoring program. The current study is an extension to an earlier effort by Alegria et al. (*25*) and Wong et al. (*32*) who investigated airborne OCs at four sampling sites located in southern Mexico during 2002−2004. Here we report results of a passive air sampling campaign from the south to north of Mexico during 2005−2006.

Materials and Methods

Air Sampling. Passive air samplers (PAS) were deployed at eleven sampling sites across Mexico during 2005−2006. Locations of the sampling sites and four stations in southern Mexico where pumped and passive samples were collected in 2002−2004 (*25*) are illustrated in Figure 1. Samples were collected every three to four months during which about 350 m^3 air was sampled. Duplicate PAS were deployed at each site within 3 m. Details about each site and sampling schedule are given in Supporting Information, SI-1.

PAS consisted of polyurethane foam (PUF) disks enclosed in a stainless steel housing. Design and theory behind PAS are described in Shoeib and Harner (*33*). Similar PAS have been used in air sampling campaigns worldwide (*34*−*39*). The PUF disks (PacWill Environmental, Stony Creek, ON, Canada) were rinsed with tap water, Soxhlet extracted once with acetone for 22 h and two times with petroleum ether for 22 h, and dried in a vacuum desiccator.

To determine the sampling rate ($m^3\ d^{-1}$), 30 mL of a petroleum ether solution containing a suite of depuration compounds (DCs) was spiked onto the PUF disks prior to field deployment. DCs included 262 ng of $[^2H_6]$-γ-hexachlorocyclohexane (HCH), 120 ng of $[^{13}C_{12}]$-polychlorinated biphenyl (PCB) 52, 8 ng of PCB107, and 8 ng of PCB198. Period 3 and Period 4 samples were also spiked with 100 ng of $[^{13}C_{12}]$-PCB9 and 100 ng of $[^{13}C_{12}]$-PCB32. The procedure for deriving the sampling rate using DCs can be found in Gouin et al. (*37*) and SI-2. Annual mean sampling rates for all sites ranged from 3.0 to 7.7 $m^3\ d^{-1}$ and they are consistent with those previously measured elsewhere (*26, 30, 37*).

Extraction and Analysis. Extraction was achieved by Soxhlet apparatus using 400 mL of petroleum ether for 18 h. Prior to extraction, samples were fortified with surrogate recovery compounds: 20 ng of $[^2H_6]$-α-HCH, 20 ng of $[^{13}C_{10}]$-heptachlor *exo*-epoxide (HEPX), 20 ng of $[^{13}C_{10}]$-*trans*-nonachlor (TN), 20 ng of $[^{13}C_{12}]$-dieldrin (DIEL), and 100 ng of $[^2H_8]$-*p,p*′-DDT. Cleanup procedures followed those in Alegria et al. (*25*). The final extract was concentrated to 500 μL in isooctane. The duplicate samples were analyzed individually for most compounds. To improve detectability, extracts of duplicate samples were combined, given an additional cleanup by shaking with 15% fuming sulfuric acid, blown down to 150 μL, and quantitatively analyzed for toxaphenes. These combined extracts were also used for chiral analysis.

OCs were determined using capillary gas chromatography−electron capture negative ion mass spectrometry (GC-ECNI-MS), on an Agilent 6890 GC−5973 MSD with a 60-m DB-5 column (0.25 mm i.d., 0.25 μm film, J&W Scientific, U.S.A.). Toxaphene was determined using GC-ECNI-MS on a Hewlett-Packard 5890 GC−5989B MS-Engine with a 60-m DB-5 column (0.25 mm i.d., 0.25 μm film, J&W Scientific, U.S.A.). The ΣTOX residues were quantified versus technical toxaphene as the sum of 7-Cl, 8-Cl, and 9-Cl homologues (*40, 41*). Eight individual peaks were also quantified versus Parlar congeners 26, 39, 40, 41, 42, 44, 50, and 63. Details of the operating condition, ions monitored, and sources of chemical standards are found in Alegria et al. (*25*).

Enantiomer separations of *trans*-chlordane (TC), *cis*-chlordane (CC) and *o,p*′-DDT were performed as described by Kurt-Karakaus et al. (*42*). Chiral results were expressed as the enantiomer fraction, EF = peak areas of the $(+)/[(+)+(-)]$ enantiomers and also as deviation from racemic, DEVrac = the absolute value of $(0.500 - \mathrm{EF})$ (*42*). A racemic EF = 0.500 (DEVrac = 0) whereas preferential degradation of the (+) or (−) enantiomer yields EFs <0.500 and >0.500, respectively (DEVrac >0 in both cases).

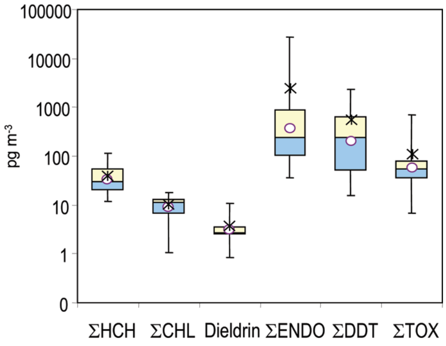

FIGURE 2. Box–whisker plot of organochlorine pesticides (pg m^{-3}) in this study and the 2002-2004 sampling campaign (*25*). The top end of the box represents the 75th percentile of the data, and the bottom of the box represents the 25th percentile. The horizontal line between the boxes is the median, the circle is the geometric mean, and the asterisk is the arithmetic mean. The whiskers on the top and bottom of the boxes indicate the maximum and minimum ($^1/_2$ LOD in some cases) values of the data set. ΣHCH = α-HCH + γ-HCH. ΣCHL = TC + CC + TN. ΣENDO = ENDO I + ENDO II + ESUL. ΣDDT = p,p′-DDT + o,p′-DDT + p,p′-DDE + o,p′-DDE + p,p′- DDD + o,p′-DDD. ΣTOX = quantified as technical toxaphene.

Quality Control. Limit of detection (LOD) was defined as mean blank + 3 times the standard deviation. If a chemical was not found in the blanks, LOD was defined as instrumental detection limit (IDL), which was estimated by injecting low concentrations of target analytes until a small peak at ~3:1 signal/noise ratio was obtained. LODs are expressed in pg m^{-3} considering ~170 m^3 of air volume (350 m^3 for ΣTOX) and a final sample volume of 500 μL (150 μL for ΣTOX). IDLs ranged from 0.08 to 22 pg m^{-3} for individual OCs and 5.1 pg m^{-3} for ΣTOX. Values are listed in SI-3. Recovery percentages for the spiked surrogates were (n = 112): [$^2H_6$]-α-HCH: 78 ± 7%; [$^{13}C_{10}$]-HEPX: 101 ± 14%; [$^{13}C_{10}$]-TN: 80 ± 6%; [$^{13}C_{12}$]-DIEL: 95 ± 11%; [$^2H_8$]-*p,p′*-DDT: 86 ± 9%.

Duplicate samples agreed within 20% for three-quarters of the measurements and within 35% for 90% of the measurements. Decisions as to whether a particular sample contained racemic or nonracemic residues were made by determining whether the EF for the compound in question fell within or outside of the ± 95% confidence interval of the standards EFs. Air concentrations were calculated from the mean of the duplicate sampler results, with the exception of ΣTOX, in which case the combined extract from duplicates was used.

Results and Discussion

Air Concentrations of OCs. Discussions in this paper include pumped air data collected in a 2002–2004 study where sampling was conducted at four sites in southern Mexico: suburban Tapachula (TP) and a mountain site (MT) in Chiapas, Veracruz City (VC), and rural Tabasco (TB) (*25, 32*).These sites are also shown in Figure 1. In that study, results from colocated passive and pumped samplers were compared for γ-HCH, chlordanes, endosulfans, *p,p′*-DDT, *p,p′*-DDE, and *o,p′*-DDT. Mean values of passive/pumped ratios ranged from 0.76 for *p,p′*-DDT to 1.5 for endosulfans, with an overall average of 1.0 for all compounds (*25*). Figure 2 shows a box–whisker plot summarizing the OCs concentrations in air at all sites as the sums within each compound class. The most abundant OCs were the ΣDDT = *p,p′*-DDT + *o,p′*-DDT + *p,p′*-DDE + *o,p′*-DDE + *p,p′*-DDD + *o,p′*-DDD, ΣENDO = endosulfan I (ENDO I) + endosulfan II (ENDO II) + endosulfan sulfate (ESUL), and ΣTOX. Considering all sites and deployment periods, detection frequencies of the OC classes were: DDTs, chlordanes, HCHs, endosulfans, toxaphenes 100%, heptachlor 18%; heptachlor *exo*-epoxide 8%, aldrin 0%, and dieldrin 88%. Annual mean concentrations of the OC species at individual sites are presented in SI-3.

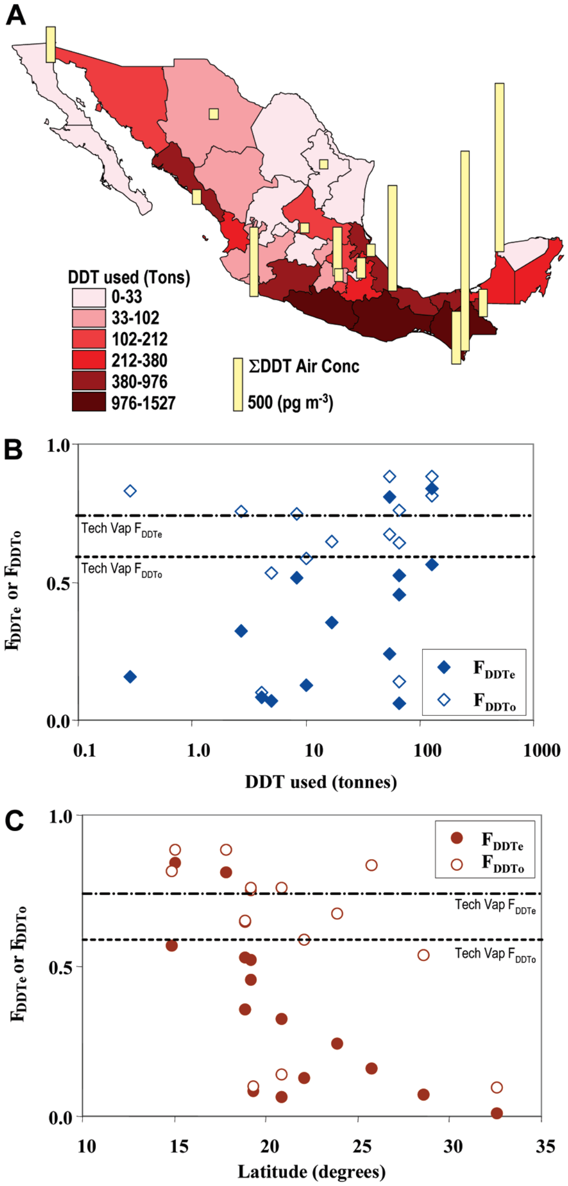

FIGURE 3. (A) Spatial distribution of ΣDDT in air (pg m^{-3}) and DDT used for public health purposes between 1989 and 1999 (*44*). (B) F_{DDTe} and F_{DDTo} vs DDT used. (C) F_{DDTe} and F_{DDTo} vs latitude. F_{DDTe} is significantly positively correlated with DDT used for malaria control (r^2 = 0.45, p = 0.01) and negatively with latitude (r^2 = 0.57, p = 0.001). F_{DDTo} is not significantly correlated with either usage or latitude. Tech Vap = technical vapor. These figures included data from Alegria et al. (*25*).

DDT. The ΣDDT ranged from 15 to 1975 pg m^{-3} in this study, and 239–2360 pg m^{-3} at the southern Mexico sites in 2002–2004 (*25*). The arithmetic and geometric mean (AM and GM) concentrations for both studies were 558 and 200 pg m^{-3}. The highest concentration was found at MT and the lowest was at MON. Figure 3A shows the spatial distribution of ΣDDT tended to be higher in the south (MT 2360 pg m^{-3}, CEL 1975 pg m^{-3}, VC 1200 pg m^{-3}, TP 547 pg m^{-3}, TB 239 pg m^{-3}) and some central sites (COL 750 pg m^{-3}, CUE 500 pg m^{-3}, COR 129 pg m^{-3}). Most sampling sites located in central (SLP 21 pg m^{-3}, MON 15 pg m^{-3}, MEX 55 pg m^{-3}, TUX 50 pg m^{-3}, MAZ 76 pg m^{-3}) and northern (CHI 34 pg m^{-3}) Mexico had lower ΣDDT concentrations. An exception was 338 pg m^{-3} at the most northern station, BAJ, which is located in an agricultural region of the Mexicali valley where DDT may have been used in the past. BAJ is also close to southern California, where ΣDDT in the hundreds to thousands of ng g^{-1} have been reported in agricultural soils (*43*). DDT levels observed at MEX were consistent with those previously reported with mean of 110 pg m^{-3} at an urban site in Mexico city (*27*). Air concentrations of ΣDDT at most Mexico sites were 1−2 orders of magnitude greater than in Costa Rica, where ΣDDT ranged from 10 to 16 pg m^{-3} in samples collected between 2001 and 2004 (*26, 28*).

The endemic malarious areas in Mexico extended from the south (comprising the states of Chiapas, Yucatan, Campeche, Veracruz, and Tabasco) to the north along the Pacific coast (Oaxaca, Guerrero, Jalisco, and Sinaloa). These areas were heavily sprayed with DDT in past sanitary campaigns (*44*). The total amount of DDT applied by the government from 1989 to1999 was the greatest in the south and decreased to the north (Figure 3A). This is consistent with results showing that the sites in southern Chiapas (TP, MT), Yucatan (CEL), and Colima (COL) had relatively high ΣDDT in air. It should be noted that Chiapas consumed 16% (i.e., 1527 tons) of the total DDT used in Mexico during 1989−1999, more than any other state (*44*). However, the correlation between DDT used in malaria campaigns and atmospheric concentration of ΣDDT is not significant ($r^2 = 0.13$, $p = 0.19$) and there is also no significant relationship with latitude ($r^2 = 0.17$, $p = 0.13$). Since these samples were collected in urban, rural, and agricultural sites, sources of DDT at each site would be different. Urban sites would likely be a reflection of DDT used in sanitary campaigns, whereas the agricultural sites would be more related to soil emissions from the former use of DDT in agriculture. DDT use in agriculture began to decline in the 1970s, and by 1997 DDT was registered only in government-sponsored public health campaigns (*2*). However the spatial distribution of DDT consumption in agriculture is not available and thus cannot be accounted for in Figure 3A. Another possibility is atmospheric transport from southern neighboring countries. As shown in the air trajectory analysis by Alegria et al. (*25*), southern Mexico is often impacted by air parcels that passed over Guatemala, Honduras, and Belize. ΣDDT levels in Belize air are similar to those that have been reported in southern Mexico (*26, 31*).

To gain further insight to sources and age of DDT residues, the relative amounts of *p,p′*-DDT, *p,p′*-DDE, and *o,p′*-DDT were expressed as fractional values, $F_{DDTe} = p,p'$-DDT/(p,p'-DDT + p,p'-DDE) and $F_{DDTo} = p,p'$-DDT/(p,p'-DDT + o,p'-DDT) (*45*). F_{DDTe} and F_{DDTo} of technical DDT are 0.95 and 0.84, respectively, assuming the World Health Organization (*46*) reported composition for technical DDT: 77%, *p,p′*-DDT, 15% *o,p′*-DDT, 4% *p,p′*-DDE. Fractionation of these compounds during evaporation of technical DDT was estimated using liquid-phase vapor pressures at 25 °C, resulting in $F_{DDTe} = 0.75$ and $F_{DDTo} = 0.59$ for technical DDT vapor. Field experiments conducted by sampling air close to an agricultural soil indicate that F_{DDTe} and F_{DDTo} in the overlying air can be predicted from those in the soil using relative vapor pressures (*45*). F_{DDTe} close to the vapor-phase technical DDT value suggests emissions from recent use while a lower F_{DDTe} suggests a greater proportion of the metabolite *p,p′*-DDE and an older residue.

F_{DDTe} in the current study ranged from 0.01 to 0.56, indicating the presence of residual *p,p′*-DDE at all sites. F_{DDTe} reported for the 2002−2004 campaign in southern Mexico ranged from 0.45 to 0.83. Highest F_{DDTe} in both sampling campaign were found at MT (0.83) and TB (0.74), suggestive of "fresh" DDT. F_{DDTe} in VC and TP were 0.45 and 0.55, respectively, and indicated more aged residues (*25, 32*). When combined with the larger passive sampling data set from this study, F_{DDTe} shows a significant positive correlation with DDT used ($r^2 = 0.45$ and $p = 0.01$) and negative correlation with latitude ($r^2 = 0.57$ and $p = 0.001$) (Figure 3B and C). This implies fresher DDT residues in air are associated with a higher (and probably more recent) DDT application in southern Mexico. Thus, it is suggested that southern Mexico is subjected to recent DDT input either locally or from atmospheric transport from neighboring countries.

F_{DDTo} was not significantly related to DDT used with $r^2 = 0.08$ and $p = 0.30$ nor with latitude with $r^2 = 0.20$, and $p = 0.09$ (Figure 3B and C). Including the four sites from the 2002−2004 sampling campaign (*25*), 12 out of 15 sites exceeded the F_{DDTo} of the WHO DDT technical vapor of 0.59 and these sites were often associated with higher ΣDDT. However, the relationship between F_{DDTo} and the "freshness" of the DDT residue is not clear. Similar degradation rates for *p,p′*-DDT and *o,p′*-DDT in soil would lead to residues with F_{DDTo} unchanged from the technical product. For example, F_{DDTo} in an Ontario farm soil where the last DDT application was 3 decades ago was 0.77, similar to $F_{DDTo} = 0.84$ in technical DDT (*45*). The variability of F_{DDTo} can also be due to the origin of the technical DDT, as it has been reported that the proportion of *o,p′*-DDT in technical DDT can be quite different depending on the manufacturer (*47*). Mexico manufactured DDT, but the composition of its technical product is not known.

The EFs of *o,p′*-DDT ranged from 0.480 to 0.510, showing a mix of racemic and nonracemic signatures. Since degradation of *o,p′*-DDT in soils is ambivalent, with approximately equal proportions of residues with EFs <0.5, = 0.5, and >0.5 (*42*), deviation from racemic (DEVrac) is reported to indicate degradation regardless of which enantiomer is depleted (*42*). Figure SI-4 showed significant relationships of DEVrac versus DDT used ($r^2 = 0.33$, $p = 0.03$) and latitude ($r^2 = 0.57$, $p = 0.001$). More nearly racemic *o,p′*-DDT at southern Mexico sites agrees with the relative "freshness" indicated by the higher F_{DDTe} in that region, as mentioned earlier. This may also suggest the lack of enantioselective degradation of *o,p′*-DDT in sites with higher DDT applications.

Endosulfan. An extremely high annual mean concentration (26,800 pg m^{-3}) of ΣENDO was measured at Mazatlan (MAZ), which is located in the agricultural area of western Sinaloa. Endosulfan is the only currently used pesticide that is reported here and it is commonly used worldwide. It is one of the most frequently detected pesticides in the estuarine sediments and waters of Ensenada del Pabellion and Bahia et Santa Maria which are located in Sinaloa, Mexico (*16*). High levels of ENDO had also been reported in the sediments of San Blas, Nayarit which located ~300 km south of MAZ (*15*).

Excluding MAZ, ΣENDO ranged from 36 to 3730 pg m^{-3} in this study and 92 to 341 pg m^{-3} in the 2002−2004 sampling campaign (*25*). The AM and GM measured at all sites from both sampling campaigns are 2400 and 368 pg m^{-3}, respectively. High ΣENDO was not always associated with agricultural sites. For example, a suburban site COL had the second highest ΣENDO (3730 pg m^{-3}) and moderate level was observed at another suburban site CUE (1280 pg m^{-3}). ΣENDO at 23 sites in Costa Rica ranged from 5 to 17,300 pg m^{-3} with AM and GM of 342 and 109 pg m^{-3} (*29*). Isomers of parent endosulfan are expressed as F_{ENDO}, which defined as F_{ENDO} = ENDO I/(ENDO I + ENDO II). ENDO II is often found to be more vulnerable to degradation (*48*), hence a higher F_{ENDO} indicates an aged compound. Technical endosulfan has ENDO I/II of 2.3 (*49*) and the ratio of liquid-phase vapor pressures is 1.39 (*50*), leading to a vapor ratio of 3.2 for the technical product and gives a F_{ENDO} of 0.76.

The range of F_{ENDO} from both sampling campaigns is 0.66−0.88 with a mean of 0.82. This is close to the F_{ENDO} of technical endosulfan which suggests recent application in the region.

Toxaphene. Toxaphene is a complex pesticide containing hundreds of chlorobornane congeners. The ΣTOX reported here is the sum of hepta-, octa-, and nonachlorobornanes (SI-3). The ΣTOX in this study ranged from 27 to 689 pg m^{-3}, and 6.2 to 229 in the 2002−2004 sampling campaign. The AM and GM for both studies were 108 and 58 pg m^{-3}. Highest ΣTOX was found at BAJ (689 pg m^{-3}), TP (229 pg m^{-3}), and MAZ (150 pg m^{-3}), all in or near cotton-growing regions in northwest Mexico and Chiapas. SI-5 summarizes the proportion of toxaphene congeners in air collected in this study and the 2002−2004 sampling campaign (*32*). This includes octachlorobornanes (Parlar numbers P26, P39, P42, and P44+) and nonachlorobornanes (P50 and P63). The symbol 44+ is used to indicate that the chromatographic peak at this retention time consists of P44 and other unidentified octachlorobornane (*51, 52*). These proportions are normalized to coeluting P40 + 41. The samples showed depletion in P39 amd P42 and enrichment of P26 and P44+. Since vapor pressures of P39 and P42 are similar (*53*), fractionation due to volatility difference is unlikely. Hence, the depletions of P39 and P42 are likely reflecting the toxaphene congener pattern in soils (*32*). Enrichment of P26 is due to its higher liquid-phase vapor pressure (*51*) and hence it is preferentially volatilized into the air. P50 showed a similar proportion as the technical TOX (0.91) at most sites except that depletion was observed at BAJ (0.55), CHI (0.73), MAZ (0.54), and MON (0.72). Depletion of P63 was observed in all the air samples. The congener pattern observed here is a typical soil emission signature which has been reported in the southern U.S. (*54*).

Chlordane and Related Compounds. Chlordane (CHL) was used in Mexico for agriculture and as a termiticide until 1992, when it was restricted to termiticide use only. Between 1992 and 1996, 212 tons of chlordane was imported from the U.S. (*3*). The ΣCHL (TC + CC + TN) concentrations in this campaign was low, ranging from 1.0 to 18 pg m^{-3}. These levels were consistent with those reported for southern Mexico in 2002−2004 (*25*), and the AM and GM for both sampling campaign were 10 and 8.8 pg m^{-3} respectively. The ΣCHL concentrations were significantly higher in urban−suburban areas (CHI, MEX, SLP, COL, COR, CUE, TP, VC; AM = 12 ± 3.4 pg m^{-3}) than at rural and agricultural sites (BAJ, CEL, MAZ, MON, TUX, MT, TB; AM = 7.3 ± 4.1 pg m^{-3}) at $p = 0.006$. Higher chlordanes in the urban area of Mexico City (11 pg m^{-3}) than its rural area (2.1 pg m^{-3}) were similarly reported by Bohlin et al. (*27*). Chlordanes in air of Mexico are far lower than those in U.S. and Canadian cities where ΣCHL levels from ~70−600 pg m^{-3} are reported (*26, 35, 40, 55−58*). The chlordane-related compounds heptachlor (HEPT) and heptachlor *exo*-epoxide (HEPX) were low; only 3 out of 15 sites had detectable levels in both sampling campaigns. The range of positive values over both sampling campaigns was <1.0−5.0 pg m^{-3} for HEPT and <1.3−5.9 pg m^{-3} for HEPX.

Isomers of chlordanes are expressed as fraction of TC (F_{TC}), which defined as TC/(TC + CC). Technical TC vapor has F_{TC} of 0.62 (*40*). F_{TC} averaged 0.52 ± 0.19 at agricultural−rural sites and 0.62 ± 0.13 at urban−suburban sites but not statistically different with $p = 0.11$. Lower F_{TC} at nonurban sites was observed in the Great Lakes region (*55*). The average F_{TC} in Costa Rican air was 0.58 (*28*), which is similar to that of Mexico.

Enantiomeric fractions of *trans*-chlordane (TC) and *cis*-chlordane (CC) are presented in SI-6. EFs of TC and CC averaged 0.499 ± 0.009 and 0.507 ± 0.003 at agricultural−rural sites, and 0.492 ± 0.006 and 0.509 ± 0.003 at urban−suburban sites. The urban and nonurban means are not significantly different ($p > 0.05$) in each case. The average EFs for all sites, TC = 0.495 ± 0.008 and CC = 0.508 ± 0.004, were closer to racemic than for chlordanes in the Great Lakes region (means: TC = 0.473, CC = 0.513), where emission of aged residues in soils is thought to be a contributor to atmospheric levels (*26, 55*). EFs in Costa Rican air averaged 0.488 for TC and 0.518 for CC (*28*).

Lindane and HCH isomers. There is no production of lindane (γ-HCH) in Mexico and about 20 tons per year is imported. Lindane is mainly used for seed treatment for oats, barley, and beans. Currently, it is listed as a restricted pesticide that is authorized for parasite control on livestock and for pharmaceutical use (*4*). Lindane measured ranged from 8.2 to 104 pg m^{-3} in this study and 12 to 52 pg m^{-3} in the 2002−2004 sampling campaign (*25*). Combining data from both studies results in AM and GM of 30 pg m^{-3} and 23 pg m^{-3}, respectively. Highest concentration was observed at the most northern site: BAJ (104 pg m^{-3}). Other isomers in formerly used technical HCH were sought. α-HCH was measured in both studies ranged from 1.9 to 20 pg m^{-3} with AM 10 pg m^{-3} and GM 8.8 pg m^{-3}) but β-HCH and δ-HCH were not found.

Dieldrin. Low levels of dieldrin were found, ranging from 1.6 to 7.8 pg m^{-3} in this study and 0.86 to 11 pg m^{-3} in the 2002−2004 sampling campaign (*25*). Concentrations were distributed fairly evenly across the country, with slightly higher levels at MT (11 pg m^{-3}). The AM and GM for both sampling campaign were 3.8 and 3.2 pg m^{-3}, respectively. Much higher levels of dieldrin, averaging 1200 pg m^{-3} and accompanied by similarly high levels of aldrin, were found in Belmopan, Belize during 1995−1996 (*31*), and 260 pg $m^{-3}$of dieldrin was reported in 2000−2001 (*26*). Levels of dieldrin in Costa Rica in 2004 ranged from 0.4 to 27 pg m^{-3} (*28*), which is consistent with this study.

Seasonal Variation of OCs. Seasonal trends for selected OCs in relation to 3-day back trajectory airshed maps are shown for each site in SI-7. In general, there were not large differences in airshed maps among the four sampling periods at a particular site. The strongest seasonality observed was at Mazatlan, Sinaloa (MAZ). ENDO I showed a sharp increase at MAZ during Periods 3 (November to February) and 4 (February to May) and this may be explained by examining the back trajectory airshed map shown in SI-7.7. Methods of generating the airshed maps are described in Gouin et al. (*37*). The airshed maps show where the air most frequently passed within three days before arriving at the sampling site. At MAZ, the air mostly originated from the Pacific Ocean during Periods 1 (May to August) and 2 (August to November), but flowed from inland during Periods 3 and 4. It is suggested that endosulfans measured during the Periods 3 and 4 were due to local agricultural usage, while during Periods 1 and 2 the site was mainly impacted by the cleaner air mass that came from the ocean which led to lower concentrations. Colima also showed strong seasonality for ENDO I with peak level observed in Period 3 (November to February). SI-7.4 shows that the air during this period mainly comes from inland which could account for the source of ENDO I.

Robledo-Marenco et al. (*15*) indicated that highest concentration of pesticides in the San Blas, Nayarit estuaries appeared during October to February, where it coincided with the time during which pesticides are applied in the agricultural areas in the region. Presumably the pesticide application time is the same in Mazatlan and Colima; this would explain our results, as our sampling time during Periods 3 and 4 (November to May) corresponded to the pesticide application period. In other cases, air pathways do not explain the concentrations observed. Examples are BAJ (SI-7.1) and Cuernavaca (SI-7.5), which show similar airshed maps for the sampling periods, yet large differences in seasonal concentrations for some pesticides. It is cautioned that the back trajectory airshed analysis does not consider the "quality" of the region through which the air has traveled. Even if the probability of air passing through a particular region is low its impact may still be high if the emission source is strong. Furthermore, back trajectory alone may not be sufficient to explain the seasonal difference in air concentration. Seasonal variation is likely due to a combination of factors, such as current and historical regional usage pattern, wind speed, precipitation, temperature, and other meteorological factors.

This study has provided some baseline data on the organochlorine pesticide levels in the atmosphere of Mexico which could be useful for establishing long-term atmospheric monitoring program in the country. This study has also demonstrated the cost-effectiveness of using passive air sampling technique for mapping regional differences in air concentrations as has been demonstrated in other studies worldwide (*26−28, 30, 35−37, 39, 59*). Although this study has identified some hotspots, other areas of potentially high emissions have not been covered. These include Oaxaca, the state with the highest DDT consumption in the country during 1989−1999 (*16*), inland agricultural areas of Sinaloa, and cotton-growing regions in Sonora.

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Supporting Information Available

Information about the sampling sites and schedule, sampling rates, annual mean OCs concentration, chiral signatures of *o,p′*-DDT, TC and CC, toxaphene congener profiles, three-day back trajectory airshed maps and seasonality of OC concentrations at each site. This information is available free of charge via the Internet at http://pubs.acs.org.

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