Ambient Air Concentrations of Organochlorine Pesticides in Southern Mexico

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Introduction

The Mexico-Central America region has been historically characterized for its extensive use of organochlorine pesticides (OCPs) in agriculture and for vector disease control[1-3]. DDTs and chlordane have been banned in Mexico under North American Regional Action Plans (NARAPs), and others are expected to be prohibited under the UNEP Protocol. However, preliminary studies we carried out in Belize (Central America) and Chiapas (Mexico) suggest the continued use of some banned OCPs, perhaps from existing stockpiles[4,5]. As part of efforts aimed at determining if the Mexico – Central America region is a source region for North America, we have carried out further studies to determine ambient air concentrations of OCPs in the southern Mexican states of Chiapas, Tabasco and Veracruz.

Materials and Method

Air samples were collected bi-weekly at (i) an organic coffee plantation in Chiapas located at an elevation of ~1300 m (MT, n=19, 2002-03), (ii) a suburban site located ~5 km from the city centre of Tapachula, Chiapas (TP, n=14, 2002-03), (iii) a rural site in Tabasco (TAB, n=14, 2003-04), and (iv) an urban site in Veracruz City (VER, n=20, 2003-04). Figure 1 shows sampling locations. Samples were collected with the use of a high volume air sampler employing a glass fibre filter and one or two polyurethane foam (PUF) plugs to trap pesticides.

Filters and PUF plugs were soxhlet-extracted together overnight (16 h) with petroleum ether. Prior to extraction, PUF plugs were fortified with a mixture containing 20 ng each of a-HCH-d_6, $^{13}C_{10}$-heptachlor *exo*-epoxide (HEPX), $^{13}C_{10}$-*trans*-nonachlor (TN) and $^{13}C_{12}$-dieldrin, and 100 ng of p,p'-DDT-d_8 which served as surrogates for assessing method recoveries for each sample. Extracts were concentrated by rotary evaporation, blown down with a gentle stream of nitrogen and exchanged into isooctane. Extracts were cleaned up and fractionated on a column of neutral Al_2O_3 (1 g, 6% deactivation with H_2O) overlain with 1 cm anhydrous Na_2SO_4. The column was pre-eluted with 10 mL dichloromethane followed by 10 mL petroleum ether. Extracts were applied in ~ 1mL isooctane and the column was eluted with 15 mL 5% dichloromethane/petroleum ether. The eluate was concentrated by nitrogen blow down and solvent-exchanged into isooctane. Volumes were adjusted to ~ 1mL and $^{13}C_{10}$-PCB105 was added as an internal standard just prior to analysis.

Analysis

OC pesticides (except toxaphene) were quantified by gas chromatography – electron capture negative ion mass spectrometry (GC-ECNI-MS) on an Agilent 6890GC-5973 MS detector with a DB-5 capillary column (J&W, 60m x 0.25 mm i.d., 0.25 mm film thickness). Total toxaphene was quantified on a Hewlett – Packard 5890 GC – 5989B MS Engine, using the same type of column, as the sum of the 7-Cl, 8-Cl, and 9-Cl homologues. The detectors in both instruments were operated in the selective ion monitoring mode to enhance sensitivity. Specific details for the

monitored ions and operating conditions can be found elsewhere[1,6].

Results and Discussion

Table 1 summarizes the results from all four sites for selected OC pesticides. Levels of total DDTs (p,p'-DDT + o,p'-DDT + p,p'-DDE + o,p'-DDE + p,p'-DDD + o,p'-DDD) were in the order: Chiapas mountain site > Veracruz > Tapachula > Tabasco. DDT was used much more extensively in Chiapas and Veracruz for agriculture (in fact, Chiapas was the last state allowed to legally use DDT in agriculture) than in Tabasco, so it is tempting to attribute the concentrations seen air to simple recycling from soils[1,3,6]. However, an analysis of the proportions of total DDT components indicates that at least some of the DDTs measured in air are likely due to continued usage in the region. As shown in Figure 2, the percentages of "new" DDT (as indicated by p,p'-DDT concentrations compared to total DDTs) were in the order Chiapas mountain site ~ Tabasco > Tapachula > Veracruz. Thus, ambient air in the mountain site in Chiapas contained not only the highest concentrations of DDTs, but the "freshest, with p,p'-DDT accounting for >70% of total DDTs." On the other hand, levels of DDTs in Veracruz were second highest, but the relatively low proportion of p,p'-DDT (37%) suggests the most weathered source. While the levels of DDTs were lowest in Tabasco, the DDT profile resembles the Chiapas mountain site (63% p,p'-DDT) which suggests a fresh source.

In an effort to determine the potential sources of DDTs measured in air in the different sampling stations, air parcel back trajectories were calculated (at several altitudes) using the U.S. National Atmospheric and Oceanic Administration (NOAA) Hysplit4 model (available online at http://www.arl.noaa.gov/ready/open/hysplit4.html). There did not appear to be a clear difference in DDT levels or patterns depending on the air pathway. However, Tabasco was impacted more than Veracruz by air that had passed over Central America. The mountain site in Chiapas was also impacted significantly by air that had passed over Central America and, as in Tabasco, the DDT signature suggests a fresh source. It is possible that continued usage in neighbouring countries may explain the "fresher" signatures in Tabasco and the Chiapas mountain site. On the other hand, the high levels of total DDTs in Veracruz may be a result of recycling from local soils, especially considering the large quantities used in the state for agriculture and in the city for public health purposes. Waliszewski et al. (2001, 1998) have shown a decline in p,p'-DDT over time in human adipose tissue from samples taken in Veracruz, supporting the hypothesis of exposure to weathered sources over time[7,8]. The results of air parcel back trajectories cannot discard the possibility of continued local usage of DDTs in areas with a "fresher" DDT signature and high concentrations. During the sampling periods in Chiapas, for example, we obtained anecdotal evidence from local farmers of continued DDT uses in agriculture.

Concentrations of lindane (g-HCH) were uniformly higher than a-HCH, probably due to the more extensive and recent use of the former in the region. Levels of lindane were similar at all the sampling stations except the mountain site in Chiapas, which showed lower levels.

Total endosulfans (total ENDO = endosulfans I and II, and endosulfan sulfate) were higher in Chiapas (both sites) than in Tabasco and Veracruz. Endosulfan is still being used in agriculture, which probably explains the higher levels in Chiapas and even in rural Tabasco compared to the urban site in Veracruz.

Total chlordane compounds (total CHLOR =heptachlor + trans-chlordane + cis-chlordane + trans-nonachlor) were slightly higher at the urban sites (Tapachula and Veracruz) compared to the rural sites (Tabasco and mountain site in Chiapas). Interestingly, levels in the same site in Tapachula were much higher during 2000 – 2001 than in 2002 – 2003. Whether this reflects decreased usage in Mexico of chlordanes for termiticidal purposes is unclear.

Acknowledgement

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Fig. 1 Sampling locations

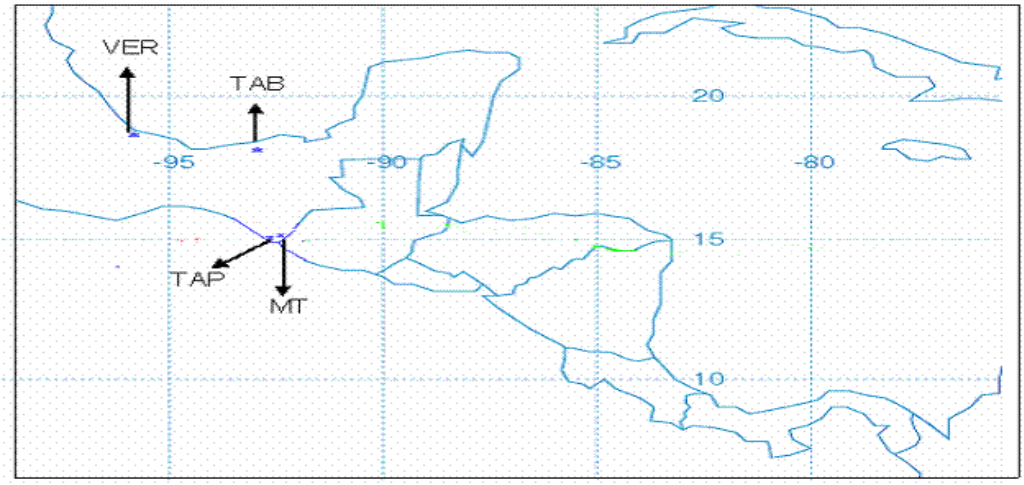

Table 1. Mean Concentrations of Selected OCPs in Southern Mexico

	TAP, 2002-03	MT, 2002-03	VER, 2003-04	TAB, 2003-04
t-DDTs	523±190	2310±785	1200±490	238±246
g-HCH	39±19	11±7	49±26	38±28
t-Chlordanes	14±7	7.9±6.5	12±4	7.3±1.9
Dieldrin	3±1.2	11±7	2.6±2.0	0.6±1.5
t-Endosulfans	309±326	225±125	98±71	93±59
Toxaphene	156±103	65±38	19±16	7±5

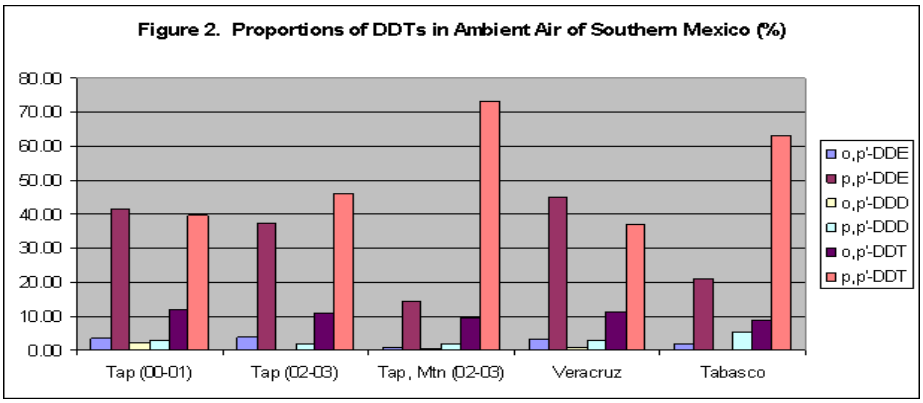
Figure 2. Proportions of DDTs in Ambient Air of Southern Mexico (%)
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Tap (00-01)
Tap (02-03)
Tap, Mtn (02-03)
Veracruz
Tabasco
o,p'-DDE
p,p'-DDE
o,p'-DDD
p,p'-DDD
o,p'-DDT
p,p'-DDT