DISTRIBUTIONS OF RESIDENTIAL ORGANOCHLORINE PESTICIDE RESIDUALS ALONG THE ARIZONA/MEXICO BORDER

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ABSTRACT
The use of DDT has been banned for many years in the United States. Mexico began a 10-year phase out of DDT in 1997. DDT was banned in the U.S. primarily because of its environmental persistence. Thus, DDT is still found in the outdoor and indoor environment. We report the results from samples collected in 83 homes in Arizona along the Arizona/Mexico border. The media sampled included indoor air, floor dust, dermal wipes, and blood serum. 4,4'-DDT was detected in 62% of the floor dust samples, 19% of the indoor air samples, and 31% of the dermal wipes. This may be from spray residuals in older housing stock, recent use of chemicals obtained in Mexico, track-in from outdoor usage, or other sources. We report on the concentrations found, examine the distributions of occurrence of DDT analogs in the various media and discuss possible sources of these occurrences.

INDEX TERMS
DDT, exposure, indoor air, house dust, dermal

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INTRODUCTION

Although the use of DDT, has largely been eliminated in the USA and many other countries, residues remain in the environment and are a subject of concern. For example, the Journal *Chemosphere* published 97 articles related to DDT from January, 1995 to January, 2002. The majority of the articles relate to the occurrence of DDT and other organochlorine pesticides in the outdoor environment (surface water, sediments, soil, fish, and other wildlife). The remaining articles mainly present results related to human exposure from studies of human biological specimens such as milk, blood and adipose tissue. One area that has received little attention is the persistence and levels of DDT and the degradation products DDE and DDD in the residential environment. (Note: all values reported here are for the 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD compounds.) In a 1968 study of 16 homes (182 samples) in Colorado the mean detected values for DDT, DDE, and DDD in urban house dust were respectively 6.90, 4.37, and 1.77 ug/g (Starr, Aldrich, McDougall, et al., 1974). In a 1970-1971 study in the Bahama Islands, mean house dust concentrations in 15 homes were DDT 122 ug/g, DDE, 3.7 ug/g, and DDD 2.2 ug/g (Davies, Edmundson, and Raffonelli, 1975). This study was prior to the ban on DDT usage and illustrates the high DDT/DDE ratios that indicate recent contamination. More recent work summarized the results of pesticide levels in house dust from seven different exposure studies conducted at various locations across the USA, for a total of 1040 samples (Camann, Colt, Teitelbaum, et al., 2000). Dust DDT concentration median values ranged from <0.02 to 0.3 ug/g with a 90th percentile range of 0.07 to 3.0 ug/g. DDE median values were <0.02 to 0.05 ug/g and the 90th percentile range was <0.09 to 0.25 ug/g.

The current work reports the DDT, DDE, and DDD levels found in house dust, indoor air, and dermal wipes for 83 homes in Arizona along the Arizona/Mexico border. The samples were collected as part of a larger study (Arizona Border Study) that compared exposures of the border residents to the exposures of the remainder of Arizona (National Human Exposure Assessment Survey-Arizona (NHEXAS-Arizona)) to a large number of environmental contaminants. The Arizona border is comprised of three, environmentally quite different population areas. The Douglas/Naco area is mountainous, with a history of mining and smelting. The Nogales area is primarily a border crossing, with a large amount of industry on the Mexican side of the border. The Yuma area is highly agricultural, with a long history of heavy pesticide use. DDT from Mexico might be used in the border area, since Mexico only recently started to phase out the use of DDT (Environmental Health Perspectives, 1997).

METHODS

All samples were collected and analyzed using the methods and quality control procedures specified in the Arizona Border Study Quality Systems Implementation Plan (QSIP) and Standard Operating Procedures (SOPs). These data will be available at http://www.epa.gov/heds/default.htm by October 2002. Prior to that time they are available from the authors. The methods are briefly summarized below.

Dermal wipes were collected by having the participant wipe their hands twice with isopropanol saturated gauze wipes (SOP UA-F-8.1). The wipes were processed by spiking with surrogate standards, Soxhlet extracted with 10% diethylether/hexane, and cleaned up using a Florisil solid phase extraction column (BCO-L-12.1). The analysis was performed using GC/MS in the selected ion monitoring mode with internal standard quantitation (SOP BCO-L-15.0).

Floor dust samples were collected by using a vacuum cleaner with a custom sampling head to vacuum a minimum of three-square meters in each of two rooms. If less than a total of two grams of fine dust appeared to have been collected, additional area was vacuumed (SOP UA-F-7.1). The dust was sieved through a 63 micrometer (no. 230) sieve and split into portions for pesticides and metals analysis (SOP UA-L-12.0). A one gram sample of dust was spiked with surrogate standard, sonicated with five mL of acetone, and cleaned up using a C-18 solid phase cartridge (SOP BCO-L-14.0). The extracts were analyzed using GC/MS in the selected ion monitoring mode with internal standard quantitation (SOP BCO-L-15.0).

Indoor air active samples were collected using a calibrated pump and a URG impactor with a PM_{10} cut point and a 25 mm Teflon coated fiberglass filter and a PUF cartridge. The flow rate was set at four liters per minute for three days (SOP UA-F-3.1). The samples were processed by spiking the PUF cartridge with a surrogate standard, Soxhlet extracting the filter and PUF with acetone, concentrating to one mL with Kuderna-Danish glassware and cleaned up using a C-18 solid phase extraction cartridge (SOP BCO-L-11). The analysis was performed using GC/MS in the selected ion monitoring mode with internal standard quantitation (SOP BCO-L-15.0).

Indoor air passive integrative samples were collected using Semipermeable Membrane Devices (SPMDs). SPMDs are constructed of low-density layflat polyethylene tubing (86.5 centimeters in length) containing one ml of triolein distributed as a thin film on the inside. The tubing is heat sealed at each end with a loop for hanging. The SPMDs are suspended from the ceiling with cotton cord and a pushpin. Four SPMDs were deployed in different locations in each residence for 30 days and composited for analysis. SPMDs were deployed in only 53 of the 83 homes (SOP UA-F-27.0). Samples were dialyzed into hexane, subjected to gel permeation chromatography and column cleanup, and analyzed by gas chromatography with an electron capture detector (Huckins, Manuweera, and Petty, et al., 1993), (Petty, Huckins, and Zajicek, 1993), (Petty, Huckins, and Orazio, et al., 1995).

The statistical analyses were performed using SPSS Version 9.0.1.

RESULTS

The dermal wipe, floor dust, and indoor active air samples were collected over a five day period. The indoor air sample was initiated the first day of the period. The dermal wipes and floor dust samples were collected at the end of the five days to reduce the potential for contaminating the air samples with particulates disturbed during floor dust collection. The frequency of detection of each compound in each media is given in Table 1. The most frequently detected compound was DDE. The difference in the percent detected between the active and passive air samplers may well be due to the difference in sampling time.

Table 1. Frequency of detection in environmental media

	Percent detected			Number of samples
	DDT	DDE	DDD	
Dermal Wipes	31	51	11	83
Floor Dust	62	77	18	83
Indoor Air Active sampler (Pump)	19	55	5	83
Indoor Air Passive sampler (SPMD)	39	94	30	53

The concentration distributions of DDT, DDE, and DDD in the various matrices are given in Table 2. The concentrations of DDT tend to be higher than those of DDE or DDD, even though DDE was detected in a larger number of samples.

Table 2. Concentration Distribution of samples with detected analytes

	DDT	DDE	DDD	Units
Dermal wipes	N=26	N=43	N=9	ug/sample
25th percentile	0.02	0.01	0.01	
50th percentile	0.045	0.02	0.03	
75th percentile	0.18	0.04	0.05	
90th percentile	0.28	0.046	0.21	
Mean	0.102	0.03	0.05	
	DDT	DDE	DDD	Units
Floor dust	N=52	N=64	N=15	ug/g
25th percentile	0.052	0.03	0.03	
50th percentile	0.13	0.05	0.09	
75th percentile	0.35	0.12	0.18	
90th percentile	1.29	0.21	0.65	
Mean	0.75	0.15	0.16	

	DDT	DDE	DDD	Units
Indoor air, active sampler	N=16	N=46	N=4	ng/m^3
25th percentile	1.12	0.4	0.6	
50th percentile	1.5	0.6	1.85	
75th percentile	3.05	0.8	7.67	
90th percentile	7.86	1.56	9.4	
Mean	2.75	0.88	3.37	
	DDT	DDE	DDD	Units
Indoor air, passive sampler	N=21	N=50	N=16	ng/sample
25th percentile	115	42	10	
50th percentile	249	110	15	
75th percentile	720	202	44	
90th percentile	5200	510	530	
Mean	1000	210	99	

The DDT/DDE ratios for the study samples are summarized in Table 3. The DDT/DDE ratio is often used as an indicator of the time since the application, with higher ratios indicating more recent applications.

Table 3. DDT/DDE ratios for study samples

Media	N	Minimum	Maximum	Mean
Dermal Wipes	19	0.2	8.3	2.5
Floor Dust	48*	0.3	11.6	3.2
Indoor Air (active sampler)	15	0.79	3.4	1.9
Indoor Air (passive sampler)	20	0.16	7	2.1

*One outlier value removed.

DISCUSSION

The ratio of DDT to DDE is used as an indicator of the time since the DDT was applied. Ratios in Alabama agricultural soil have been reported in the range of 0.5 to 1.35 (Harner, Wideman, Jantunten, et al., 1999). Assuming that DDT was heavily used in Alabama until it was banned, ratios of 0.5 to 1.35 are indicative of the type of ratio currently expected in agricultural soil after three decades. A long-term study of DDT in Maine forest soil, where the last application was in 1967, found ratios changing from approximately 13 in 1967 to 1.2 in 1993 (Dimond and Owen, 1996), which agrees with the Alabama data.

Overall, in the Arizona Border samples, we see a higher percentage of detects with DDE than DDT indicating normal degradation of DDT to DDE is occurring. However, examination of the concentration data reveals that the detected values of DDT are generally higher than the DDE detected concentrations. This may indicate that for some homes the DDT has degraded to below the limit of detection and thus only the DDE is detected.

The highest DDT concentrations were found in homes with the highest DDT/DDE ratios. Of the six floor dust samples with DDT concentrations of 1.0 ug/g and greater, four of these had DDT/DDE ratios greater than four. The highest floor dust sample concentration of 16.6 ug/g

had a ratio of 9.7 compared to the mean concentration of 0.75 ug/g DDT and a mean DDT/DDE ratio of 3.2. These values suggest DDT may have been used in the relatively recent past in some of the subject homes in the Arizona border area. These ratios must be interpreted with caution, since the reported environmental values show considerable variability and there is very little data available on the degradation rate of DDT in the indoor environment.

We also examined the relationship of the age of the home and the occurrence of DDT and DDE. No significant correlations were found at the 0.05 level using the Pearson correlation. This was somewhat surprising since one would expect DDT residues to be more prevalent in housing constructed before the use of DDT was banned. This lack of correlation could be due to the continued use of DDT or due to infiltration and track in of DDT and DDE residues in soil in homes built after 1970.

CONCLUSIONS

DDT was found in the floor dust of over 60 percent of 83 homes sampled in a population-based study along the Arizona/Mexico border. DDT and DDE residues were also found in air samples and in wipes of resident's hands. Sporadic use of DDT may still persist in the Arizona border region as seen in the few unusually high values of DDT in dermal wipes, floor dust, and indoor air samples. This concept is substantiated by the handful of high DDT/DDE ratios in these same samples.

The presence of DDT and DDE in the indoor air and the dermal wipe samples indicate that these compounds may be volatilizing and condensing on household surfaces. This is indicated by the dermal levels which are probably a result of surface contact and the continuing presence of DDT and DDE in the house dust, which would tend to be depleted through air exchange if recycling is not occurring. Volatilization rather than particle-bound distribution is suspected due to the uptake of DDT, DDE, and DDD by the passive air sampler, which uses vapor phase diffusion through a polyethylene membrane to retain the compounds of interest. Particle bound material should not pass through the membrane. This is an area of pesticide behavior in the residential environment that needs further investigation.

The levels of DDT, DDE, and DDD found in house dust in this study are similar those reported by Camann in seven recent residential studies.(Camann, Colt, Teitelbaum, et al., 2000). The levels are also similar to those reported in Maine forest soil (Dimond and Owen, 1996) and about an order of magnitude higher than those reported in Alabama agricultural soil (Harner, Wideman, Jantunten, et. al., 1999).

Potential sources of DDT, DDE, and DDD in the Arizona border region include: residential DDT usage prior to the 1977 ban, track-in or infiltration of dust from historical agricultural use, or from knowing or unknowing use of DDT in recent years. One potential source of DDT use is the illegal pesticide impregnated chalk products that are occasionally sold at flea markets and swap meets in Mexico and the U.S. These products lack proper labeling and may contain a variety of pesticides including DDT. Consumers are instructed to draw chalk lines on the floor to kill insects that crawl over the pesticide. This product is especially dangerous because children may mistake it for ordinary chalk and play with it (Federighi and Brank, 1998).

Future work will include estimating the contribution of the DDT from the residential environment to the total DDT intake for study participants. Blood serum samples from the

participants were also analyzed for DDT, DDE, and DDD. Preliminary results from these analyses have a range of 0.016 to 2.65 ng/mL serum for DDT and a range from nondetect to 93.3 ng/mL for DDE. When the results are finalized, we will determine if the serum levels are related to the residential levels found.

NOTICE

This work has been funded wholly or in part by the United States Environmental Protection Agency and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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16. ABSTRACT

THE USE OF DDT HAS BEEN BANNED FOR MANY YEARS IN THE UNITED STATES. MEXICO BEGAN A 10-YEAR PHASE OUT OF DDT IN 1997. DDT WAS BANNED IN THE U.S. PRIMARILY BECAUSE OF ITS ENVIRONMENTAL PERSISTENCE. THUS, DDT IS STILL FOUND IN THE OUTDOOR AND INDOOR ENVIRONMENT. WE REPORT THE RESULTS FROM SAMPLES COLLECTED IN 83 HOMES IN ARIZONA ALONG THE ARIZONA/MEXICO BORDER. THE MEDIA SAMPLED INCLUDED INDOOR AIR, FLOOR DUST, DERMAL WIPES, AND BLOOD SERUM. 4,4'-DDT WAS DETECTED IN 62% OF THE FLOOR DUST SAMPLES, 19% OF THE INDOOR AIR SAMPLES, AND 31% OF THE DERMAL WIPES. THIS MAY BE FROM SPRAY RESIDUALS IN OLDER HOUSING STOCK, RECENT USE OF CHEMICALS OBTAINED IN MEXICO, TRACK-IN FROM OUTDOOR USAGE, OR OTHER SOURCES. WE REPORT ON THE CONCENTRATIONS FOUND, EXAMINE THE DISTRIBUTIONS OF OCCURRENCE OF DDT ANALOGS IN THE VARIOUS MEDIA AND DISCUSS POSSIBLE SOURCES OF THESE OCCURRENCES.

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