EXPLORATION OF CUSHION FOAM CORE SAMPLES TO ASSESS HISTORICAL RESIDENTIAL EXPOSURE TO PESTICIDES

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Introduction

Semivolatile organic chemicals (SVOCs) redistribute among the gas phase, airborne particles, settled dust, and other surfaces in indoor environments as a function of vapor pressure.[1] Pulling air through polyurethane foam (PUF) is a widely used method to collect pesticides and other SVOCs for measurement of their concentrations in air.[2] Mattresses, pillows, sofa cushions and toys with PUF foam interiors will also collect the pesticide and other SVOC residues from the air during decompression after being compressed when used, and may thus serve as passive samplers of past residential SVOC exposure. Foam core samples from furnishings with a known period of use in a residence or in a series of the family's residences since purchased new may indicate the cumulative exposure of the residents to the measured SVOCs. Foam samples from a chair, house dust, and wipe and air samples were collected from two homes, along with wipe samples from a third home, to investigate SVOC migration within the residence and to explore if past residential exposure could be inferred from pesticides measured in the chair foam.

Materials and Methods

Paired foam core samples (0.4 – 1.7 g) were collected with a knife, scissors, and tweezers from the outer edge and from the interior (~ 4 cm deep) of the cushion of a chair, as shown in Figure 1, from two homes in San Antonio in July 2006: from a condominium built in 1987 (Condo:1987) and from a single-family house built in 1989 (House:1989). Vacuum cleaner bag dust was also collected from both homes. Condo:1987 had been treated repeatedly with pesticides by a prior owner before June 2004, when the new owner removed the carpet, all fleecy surfaces, and nearly all furnishings, cleaned aggressively, introduced whole-house HEPA and activated charcoal/potassium permanganate air-filtration, took indoor air samples, and ceased pesticide treatments except for a bait with sulfluramid. The only furnishing retained in Condo:1987 in June 2004 by the new owner was the chair whose cushion foam was later sampled. The chair sampled in House:1989 was purchased new in 1998 when the new owner moved in, and remained in the house thereafter; indoor pesticide use was discontinued in September 2000. Wipe samples were also collected with isopropanol-wetted gauze in two single-family homes: from the wood flooring beneath the refrigerator and from above the sill of the door-frame (~ 8-foot separation) in House:1989, and from sheet vinyl flooring under the stove and from above the sill of the door-frame in another room (~ 30-foot separation) in House:1940. Indoor air samples from Condo:1987 and House:1989 had previously been collected onto a quartz fiber filter and PUF between June 2004 and May 2005. The foam core and wipe samples and 1 g of fine (< 150 um) dust were each soxhlet-extracted with 6% diethyl ether/hexanes and analyzed by GC/MS selected ion monitoring for 45 pesticides, 4 phthalates, and 4 BDE and 5 PCB congeners. The filter and PUF of each air sample were extracted together in a soxhlet with 6% diethyl ether/hexanes and analyzed by GC/MS selected ion monitoring for a subset of these pesticides.

Results and Discussion

The concentrations of detected pesticides, phthalates and BDE congeners in the paired cushion foam and dust samples from Condo:1987 and House:1989 in July 2006, and of these pesticides in earlier indoor air samples from these homes and in three blank PUF matrices, are presented in Table 1. Detected pesticide concentrations in the cushion foam were consistently higher than in three blank PUF matrices (untreated high- and low-density PUF and new polyfoam), except for the disinfectant ortho-phenylphenol. A concentration gradient, with a higher concentration present in the outer surface foam than in the interior foam, is evident for seven of the pesticides (bifenthrin, chlorpyrifos, α-chlordane, γ-chlordane, 4,4'-DDE, propetamphos, and propoxur) in the Condo:1987 chair cushion, and for six of the pesticides (chlorpyrifos, α-chlordane, γ-chlordane, diazinon, fipronil, and ortho-phenylphenol) in the House:1989 chair cushion. These pesticides have partially migrated from the indoor air into the cushion foam, with repeated decompressions after sitting in the chair, but have not completely penetrated to establish equilibrium throughout the foam. Some of these pesticides were still present in the house dust in July 2006

and in prior indoor air (bifenthrin, chlorpyrifos, 4,4'-DDE, and propoxur in Condo:1987 and chlorpyrifos, diazinon, and ortho-phenylphenol in House:1989), but others were no longer detected indoors. The non-volatile pyrethroids (cyfluthrin, cypermethrin, cis-permethrin, trans-permethrin) were detected only in the vacuum bag dust, but the more volatile pyrethroid bifenthrin was detected in the chair foam and house dust. High concentrations of diazinon (> 4 μg/g), ortho-phenylphenol (> 2 μg/g), and propetamphos (0.9 - 2 μg/g) were present in the foam of the chair cushion in Condo:1987. The more volatile chemicals (diazinon and ortho-phenylphenol) had equilibrated within this foam cushion. The recent indoor air and dust levels are too low to account for the measured concentrations of diazinon, propetamphos, α-chlordane, γ-chlordane, and propoxur in the Condo:1987 chair foam. Thus we infer that the former residents of Condo:1987 were likely exposed to substantial levels of diazinon and propetamphos and to indeterminate levels of α-chlordane, γ-chlordane, and propoxur during those years between 1987 and 2004 when the chair was in that condominium. Similarly, the current residents of House:1989 were likely exposed to indeterminate levels of α-chlordane, γ-chlordane, fipronil, and chlorpyrifos between 1998 and 2000.

The extraordinarily high levels (0.8 – 5.7 mg/g) of BDE flame retardants detected in the House:1989 chair foam demonstrate pretreatment of the foam, and illustrate the inability to assess historical BDE exposure using foam samples. However, the paired foam cores show a concentration gradient of some diester phthalates which is suggestive of past exposure; a higher concentration is present in the outer surface foam than in the interior foam of di-n-butyl phthalate in the Condo:1987 chair cushion, and of di-n-butyl phthalate, benzylbutyl phthalate and diethylhexyl phthalate in the House:1989 chair cushion. Nevertheless, foam core samples are less suitable to assess historical phthalate exposure, due to variable levels of foam pretreatment with phthalates.

The removed loadings of detected pesticides, phthalates and BDE congeners in the paired wipes of the kitchen floor and doorframe sill in House:1940 and House:1989 are shown in Table 2. The same pesticides found in kitchen floor wipe samples were usually detected in the doorframe sill wipe from the same house, with twelve at similar or higher sill loadings, and thirteen at higher floor loadings. Loadings of phthalates and BDEs were usually similar in these kitchen floor and doorframe sill wipes, although the high DEHP content of the vinyl flooring of House:1940 resulted in a huge removed DEHP wipe loading (223 mg/m^2). The similarity of the loadings removed by paired sill and floor wipes illustrates the relatively uniform redistribution of more volatile (diazinon, chlorpyrifos, fipronil, diethyl phthalate) and less volatile (cis-permethrin, trans-permethrin, cypermethrin) SVOCs within the residence, as previously documented after application of diazinon and chlorpyrifos.[3]

Based on pesticide concentrations measured in paired interior and outer foam samples from a chair cushion, supplemented by the chair history, recent avoidance of indoor pesticide use, and pesticides measured in other indoor samples, we were able to infer the pesticide exposure of the residents of two homes during specific earlier time periods when that chair was in use in the home. Pesticide concentrations measured in foam core samples from a resident's mattress, pillow, or toys with a documented usage history may provide a good indication of historical pesticide exposure. Suitable blank foam samples are necessary to rule out migration of pesticides into the foam prior to use in the residence. Foam cores with a documented history may be useful as an inexpensive available sample to assess past exposure.

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References:

1. Weschler CJ, Nazaroff WW (2008); *Atmos Environ.* 42(40): 9018-40
2. Lewis RG, Gordon SM (1996) 401-470, in Keith LH (ed.) Principles of Environmental Sampling American Chemical Society, Washington, DC
3. Lewis RG, Fortune CR, Blanchard FT, Camann DE (2001); *J Air & Waste Manage Assoc.* 51: 339-51.

Table 1. Detected Concentrations (µg/g) of Pesticides, Phthalates and BDE Congeners in Inner and Outer Foam of a Chair Cushion and in House Dust in Two Homes in 2006 and Earlier in Indoor Air (ng/m^3), San Antonio, TX

Structure: Year Built	Condo: 1987					House: 1989				Foam QC, µg/g	
Month Collected:	July 2006			May 2005	Jun 2004	July 2006			Aug 2004		
Detected SVOC Chemicals	Cushion Foam Inner	Cushion Foam Outer	House Dust	Indoor Air	Indoor Air	Cushion Foam Inner	Cushion Foam Outer	House Dust	Indoor Air	Usual DL	Range in 3 PUF Blanks
Pyrethroid Pesticides and Synergist											
Bifenthrin	0.07	0.12	0.07						NM[a]	0.01	
Cyfluthrin								1.78	NM	0.06	
Cypermethrin			1.25					5.66	NM	0.04	
cis-Permethrin			0.48					0.59		0.01	
trans-Permethrin			0.88					1.14		0.02	
Piperonyl butoxide			0.23					0.20		0.005	
Other Pesticides											
Chlorpyrifos	0.10	0.29	0.37	0.4	2.1, 2.2	< 0.002	0.20	0.14	6.8	0.002	
α-Chlordane	0.09	0.22		NM[a]	NM	< 0.007	0.04		NM	0.01	ND – 0.01
γ-Chlordane	0.13	0.34		NM	NM	< 0.007	0.08		NM	0.01	ND – 0.01
4,4'-DDT			1.15	NM	NM				NM	0.01	
4,4'-DDE	0.04	0.16	0.28	NM	NM				NM	0.01	
Diazinon	4.48	4.07		0.3		0.02	0.05	0.06	1.8	0.003	ND – 0.04
Fipronil					NM	< 0.007	0.12		NM	0.01	
ortho-Phenylphenol	2.50	2.34	0.14	6.1	7.3, 7.9	0.19	0.63	0.12	26	0.05	ND – 0.67
Propetamphos	0.93	2.03			NM			0.26	NM	0.02	
Propoxur	0.12	0.26	0.02					0.04	5.2	0.006	
Sulfluramid	NM	NM	NM	10.1	< 2.1	NM	NM	NM	NM		NM
Diester Phthalates											
Diethyl	23.5	19.0	760	NM	260, 360	4.9	5.9	1320	NM		2.0 - 15.3
Di-n-butyl	40.4	122	3.3	NM	210, 240	2.5	17.1	4.0	NM		3.0 - 10.6
Benzyl butyl	< 5.7[b]	1.1	72.2	NM	NM	0.4	2.5	22.1	NM		0.4 – 4.1
Diethyl hexyl (DEHP)	29.6	34.1	23.9	NM	NM	1.5	8.6	21.0	NM		0.6 – 132
Brominated Diphenyl Ether Congeners											
BDE 47	0.15	0.13	0.92	NM	NM	2060	2980	0.62	NM		0.15 – 0.59
BDE 99	0.24	0.14	1.29	NM	NM	4170	5650	1.09	NM	0.02	ND – 0.25
BDE 100		0.02	0.14	NM	NM	826	990		NM	0.02	ND – 0.03
BDE 153			0.23	NM	NM	1360	1450	0.10	NM	0.02	

Entry is left blank when chemical was measured but not detected (ND).

[a] NM = not measured. [b] Interference elevated detection limit.

Yellow-highlighted = > 2-fold concentration gradient from outer to inner cushion foam.

Table 2. Detected Removed Loadings (µg/m^2) of Pesticides, Phthalates and BDE Congeners in Wipes of Kitchen Floor and Sill above Door Frame in Two Homes and Concentrations (µg/g) in House Dust, San Antonio, TX, 2006

Structure: Year Built	House: 1940		House: 1989		
Detected SVOC Chemicals	Vinyl Kitchen Floor	Sill above Door	Wood Kitchen Floor	Sill above Door	Dust Conc, µg/g
Pyrethroid Pesticides and Synergist					
Bifenthrin		4.1	3.7	5.8	
Cyfluthrin		9	91		1.78
λ-Cyhalothrin	41	10	10		
Cypermethrin			18	26	5.66
cis-Permethrin			5.9	6.8	0.59
trans-Permethrin			9.1	8.2	1.14
Piperonyl butoxide	222	33	42	3.4	0.20
Other Pesticides					
Chlorpyrifos	2	2	6	6	0.14
α-Chlordane	77	37			
γ-Chlordane	104	47			
4,4'-DDT	261	58			
4,4'-DDE	44	18			
4,4'-DDD	73				
Diazinon			1	3	0.06
Fipronil	10		4	17	
ortho-Phenylphenol	17	7	5	5	0.12
Propetamphos			4	6	0.26
Propoxur	63	10			0.04
Diester Phthalates					
Diethyl	198	223	93	101	1320
Di-n-butyl	649	801	285	752	4.0
Benzyl butyl	27300	4550	829	729	22.1
Diethyl hexyl (DEHP)	223000	767	744	729	21.0
Brominated Diphenyl Ether Congeners					
BDE 47	23	6	19	18	0.62
BDE 99	65	64	35	19	1.09
BDE 100	6	4	3	2	
BDE 153	75	18			0.10

Entry is left blank when chemical was measured but not detected (ND).

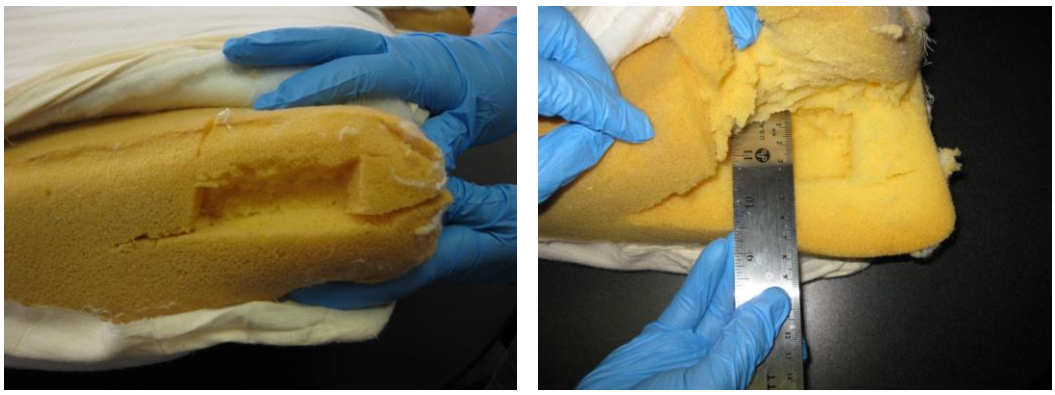

Figure 1. Collection of foam core samples from an outer edge and the interior of a chair cushion