Pesticide Measurements from the First National Environmental Health Survey of Child Care Centers Using a Multi-Residue GC/MS Analysis Method

NICOLLE S. TULVE,*,† PAUL A. JONES,† MARCIA G. NISHIOKA,‡ ROY C. FORTMANN,† CARRY W. CROGHAN,† JOEY Y. ZHOU,§ ALEXA FRASER,|| CAROL CAVE,⊥ AND WARREN FRIEDMAN#

National Exposure Research Laboratory, U.S. Environmental Protection Agency, MD-E20504, Research Triangle Park, North Carolina 27709, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201, U.S. Army Center for Health Promotion and Preventive Medicine, Environmental Medicine Program, Attn: MCHB-TS-EMP, Bldg E-1570 Stark Road, Aberdeen Proving Grounds, Maryland 20101-5403, Westat, Inc., 1650 Research Boulevard, Rockville, Maryland 20850, U.S. Consumer Product Safety Commission, 4330 East West Highway, Bethesda, Maryland 20814, Office of Healthy Homes and Lead Hazard Control, U.S. Department of Housing and Urban Development, 451 7th Street, SW, Washington, DC 20410

The U.S. Department of Housing and Urban Development, in collaboration with the U.S. Consumer Product Safety Commission and the U.S. Environmental Protection Agency, characterized the environments of young children (<6 years) by measuring lead, allergens, and pesticides in a randomly selected nationally representative sample of licensed institutional child care centers. Multi-stage sampling with clustering was used to select 168 child care centers in 30 primary sampling units in the United States. Centers were recruited into the study by telephone interviewers. Samples for pesticides, lead, and allergens were collected at multiple locations in each center by field technicians. Field sampling was conducted from July through October 2001. Wipe samples from indoor surfaces (floors, tabletops, desks) and soil samples were collected at the centers and analyzed using a multi-residue GC/MS analysis method. Based on the questionnaire responses, pyrethroids were the most commonly used pesticides among centers applying pesticides. Among the 63% of centers reporting pesticide applications, the number of pesticides used in each center ranged from 1 to 10 and the frequency of use ranged from 1 to 107 times annually. Numerous organophosphate and pyrethroid pesticides were detected in the indoor floor wipe samples. Chlorpyrifos (0.004−28 ng/cm^2), diazinon (0.002−18 ng/cm^2), *cis*-permethrin (0.004−3 ng/cm^2), and *trans*-permethrin (0.004−7 ng/cm^2) were detected in >67% of the centers. Associations exist between residues measured on the floor and other surfaces for several pesticides (p-values range from <0.0001 to 0.002), but to a lesser degree between floor and soil and other surfaces and soil. Regional analyses indicate no differences in mean level of pesticide loading between the four Census regions ($0.08 < p < 0.88$). Results show that there is the potential for exposure to pesticides in child care centers.

* Corresponding author phone: (919) 541-1077; fax: (919) 541-0905; e-mail: tulve.nicolle@epa.gov.
† U.S. Environmental Protection Agency.
‡ Battelle Memorial Institute.
§ U.S. Army Center for Health Promotion and Preventive Medicine.
|| Westat, Inc.
⊥ U.S. Consumer Product Safety Commission.
U.S. Department of Housing and Urban Development.

Introduction

Approximately 13 million children in the United States (U.S.) are placed in non-parental child care during some portion of the work day. Children can spend as many as 10 hours per day in a child care center (*1*). However, children's exposures to chemicals in child care centers have not been well characterized. The Food Quality Protection Act of 1996 (FQPA) requires the U.S. Environmental Protection Agency (EPA) to upgrade the risk assessment process for setting pesticide residue tolerances in food by considering the potential susceptibility of infants and children to both aggregate and cumulative exposures to pesticides. Exposure assessments must include data from all sources, routes, and pathways of potential exposure. Most importantly, FQPA requires risk assessments to use high quality and high quantity exposure data. Current reports of environmental health issues (e.g., asthma, lead, injuries, pesticides) assessed in child care centers have been limited by geographic area, locations sampled within centers, diversity of analytes, and/or accompanying survey and questionnaire data (*2*−*7*). To understand children's aggregate exposures to pesticides, data are needed for environmental concentrations and exposure factors in all locations where they spend time, including child care centers.

The First National Environmental Health Survey of Child Care Centers was a collaborative project of the U.S. Department of Housing and Urban Development (HUD), the U.S. Consumer Product Safety Commission (CPSC), and EPA. The study was designed and implemented by HUD and CPSC with EPA providing expertise on pesticides. The data presented here are the pesticide results from this first probability-based national study of child care centers.

The objectives of the pesticide portion of the study were to (*1*) evaluate pesticide use patterns in child care centers including both the type and frequency of pesticide use, and (*2*) measure pesticide residue concentrations in and around child care centers. Questionnaires and environmental analyses were used to evaluate pesticide use patterns in the centers. Due to financial constraints and field logistics, only surface wipes and soil samples were collected. Air samples were not logistically feasible since no return visits were scheduled and a sample collection visit needed to be completed in under 4 h. However, the collection of surface wipes and soil samples would allow us to demonstrate the presence of pesticides inside and outside the building. Knowledge of the presence of pesticides inside and outside the building is an important first step in estimating the potential for dermal and indirect ingestion exposures, the likelihood for track-in, and the likelihood that inhalation exposure may occur due to resuspension of the pesticides.

Experimental Section

A detailed description of the methods is provided in the study report (*8*). A brief description of the center and room selection criteria and pesticide methods is provided below.

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Center and Room Selection. Licensed, institutional child care centers serving children <6 years of age within the 48 contiguous United States were randomly selected for participation. Multi-stage sampling with clustering resulted in the selection of 334 child care centers with 168 eligible centers completing the survey (*8*). Details on the selection of the child care centers are presented in the Supporting Information.

Up to two classrooms and one multipurpose room where children <6 years of age regularly spent time were randomly selected for sample collection. If a center contained more than six classrooms or multipurpose rooms, then an additional room of that type was sampled. A total of 336 rooms were sampled (*8*). The study was staged such that field sampling was occurring in all Census regions simultaneously.

Pesticide Data Collection. A survey questionnaire was administered by telephone to each center director prior to field sample collection. This questionnaire collected information on the center including building age and characteristics, play equipment and playground maintenance, number and type of rooms, funding source, pesticide use practices, recorded bug problems, and child demographics. In cases where the center director was unable to provide the requested information, the director provided permission for a telephone surveyor to contact the professional applicator.

After obtaining permission, the technician collected the environmental samples. Where applicable, the technician also collected soil samples from designated play areas located on center property. Details concerning the lead and allergen data can be obtained in their respective final reports (*9*, *10*). The focus of this manuscript is on the pesticide data.

Sample Collection Methods. One floor wipe and one surface wipe sample were collected in each sampled room. The floor wipe sample was collected from a location in the room where the children spent a significant amount of time. The surface wipe sample was collected from a desk or tabletop that the children used while in the room. Floor and surface wipe samples (area sampled = 929 cm^2) were collected from hard surfaces and in the same room. To collect a wipe sample, the technician poured a 10-mL aliquot of isopropanol (high purity, Fisher Scientific) onto a sterile non-woven gauze dressing sponge (100% rayon, 4 in. × 4 in., 6-ply, Johnson & Johnson SOF-WICK). Using an S-shaped wiping motion, the technician wiped from left to right in the marked sampling area; then, turning the same dressing sponge inside out, wiped from right to left. This used dressing sponge was then placed in a certified pre-cleaned glass container (57-mL straight-sided amber glass jar cleaned via Procedure A and Level 1, Scientific Specialties Services, Inc.). The same area was then wiped with a second wetted dressing sponge from top to bottom and then bottom to top with one final wipe around the perimeter. This used dressing sponge was added to the jar containing the first dressing sponge.

Soil samples were collected using a scraping technique in which the top 0.5 centimeter of bare soil was removed with a clean stainless steel spatula and placed in a clean glass jar. Soil was collected from multiple play locations until a 57-mL glass sampling jar was full.

Field and quality control samples were collected between July and October 2001 by trained field technicians using the described methods and sent to EPA's contract laboratory for sample extraction, analysis, and reporting. Established laboratory quality control procedures were implemented during sample extraction and analysis. EPA compiled the database for statistical analysis and reporting. Sampling weights were developed to adjust for possible bias due to non-response and to provide national estimates and appropriate confidence intervals (*11*).

Multi-Residue Analysis Method. A multi-residue analysis method was developed and validated for this study. The method included 22 organophosphate (OP) pesticides, 13 synthetic pyrethroid pesticides, pyrethrins I and II, one synergist (piperonyl butoxide), and one phenyl pyrazole (fipronil) (Supporting Information, Table S1). Surrogate recovery standards (SRSs) representative of the major compound classes included fenchlorphos for the nonpolar OPs, diethylacetamidomalonate (DEAA) for the polar OPs, and $^{13}C_6$-*trans*-permethrin for the pyrethroids. The internal standard method of quantification was used and analyte concentrations were corrected by the appropriate SRS recovery.

Room-temperature equilibrated wipe samples (one sample = two wipes collected from a given location) were packed into a 22-mL accelerated solvent extraction (ASE) cell, fortified with 100 ng of each SRS, extracted at 2000 psi and 100 °C with dichloromethane (DCM) for two extraction cycles (Dionex 200), concentrated to 1 mL in a Kuderna−Danish apparatus, and solvent exchanged to hexane. The extract was then eluted through a conditioned silica solid-phase extraction cartridge (1 g BakerBond, JT Baker) in sequence with hexane (3 mL), 15% diethyl ether in hexane (two aliquots of 6 mL each), DCM (6 mL), and 20% acetone in ethyl acetate (three aliquots of 6 mL each). The hexane fraction was discarded; the remaining three eluents were collected as one fraction, concentrated to 1 mL using a nitrogen evaporator, fortified with 100 ng of the internal standard (IS) 4,4′-dibromobiphenyl, and stored at −20 °C until analysis. Laboratory blank and spike samples consisted of two dressing sponges moistened with isopropanol (5 mL), fortified with SRSs (blanks and spikes) and analytes (spikes), and analyzed. Field blank and spike samples consisted of two dressing sponges moistened with isopropanol (20 mL) and fortified with analytes (spikes), but these samples were taken to the field, stored, handled, and processed the same as the field samples.

Soil samples were prepared as follows. A 1-g aliquot free of debris (e.g., pebbles, twigs, grass blades) was weighed, fortified with 100 ng of each SRS, mixed with 6 g of muffled sodium sulfate, and loaded into an 11-mL ASE cell. Prior to extraction, the remaining cell volume was filled with muffled sand. After preparation, soil samples were extracted using the same procedure as the wipes. Laboratory blank and spike samples used 1-g aliquots of a high humic acid garden soil that contained a low level of chlorpyrifos (~10 ng/g). Fortified samples were corrected by this blank level prior to recovery calculations.

A 7-point calibration curve was prepared that spanned the concentration range of 2.5−50× the instrument detection limit for each analyte. Samples and standards were analyzed using an Agilent/HP 6890 gas chromatograph/5973 mass selective detector in the multiple ion detection mode using an embedded standard approach in which the standards were interspersed with the field samples within the run sequence. Details on the chromatographic conditions are presented in the Supporting Information. For samples where an analyte(s) exceeded the maximum calibration concentration by >15%, the solution was diluted, re-spiked with IS, and re-analyzed.

In developing the database for analysis, wipe samples were blank- and surrogate-recovery corrected, while soil samples were surrogate-recovery corrected. For those centers where multiple samples were collected, results for samples of the same type were averaged so that only a single value was reported for each sample type.

Results and Discussion

1. Multi-Residue Method Performance. The goal of any multi-residue method is for the analysis of as many high-priority analytes as possible with the greatest degree of precision and accuracy. Since analytes included in the method encompass a wide range of physicochemical characteristics, the resulting method will not be optimal for all

analytes, either due to low recovery, high variability, or interferences. Therefore, it is very important to include class-specific SRSs in the method. The performance of the multi-residue method is described in detail in the Supporting Information and summarized below.

1.a. Method Quantitation and Detection Limits. The method quantitation limit (MQL) and the method detection limit (MDL) were based on instrumental performance only. The MQL was determined as the analyte level giving 10:1 S/N in a wipe extract fortified with a known amount of analyte just prior to GC/MS analysis. The MDL was determined as the analyte level giving 3:1 S/N in a wipe extract fortified with a known amount of analyte just prior to GC/MS analysis. The method detection limits (MDLs) ranged from 0.002 to 0.016 ng/cm^2 for the pyrethroids and from 0.002 to 0.027 ng/cm^2 for the OPs (Supporting Information, Table S1). An alternate approach for calculating the MDL for chlorpyrifos is presented in the Supporting Information.

1.b. Field and Laboratory Blank Samples. Forty-two field and 51 laboratory blanks were analyzed with the 248 field wipe samples. Field blanks were blind to the laboratory carrying out the analyses. One laboratory blank was analyzed with each analysis set.

Most analytes (>80%) were not detected in the laboratory and field blanks above a frequency rate of 2% (Supporting Information, Table S2). For those analytes with detectable blank levels, all values were averaged, and nondetects were assigned a zero value for calculation. Although the pesticide levels in the blanks were extremely low, they were measurable and significantly different from zero. Therefore, all wipe samples were corrected for field blank levels.

Nine field and 14 laboratory blanks were analyzed with the 117 field soil samples. The garden soil used for laboratory QC purposes had trace levels of several pesticides. The field blanks had trace detectable levels of azinphos methyl (7.7 ± 23.2 ng/g), while the laboratory blanks had trace detectable levels of bifenthrin (0.5 ± 1.9 ng/g), esfenvalerate (2.0 ± 7.4 ng/g), chlorpyrifos (7.2 ± 7.7 ng/g), diazinon (0.5 ± 1.9 ng/g), and phosmet (0.3 ± 1.0 ng/g). For each spike and blank pair, the blank level was subtracted before calculation of the spike recovery. The nine field QC soil samples were prepared at the EPA laboratories, shipped to the field, taken to the sampling locations, and then shipped with the field samples to the analysis laboratory. The fact that these soil samples showed essentially no detectable residue levels indicated very good control of shipping and storage conditions.

1.c. Recovery Data for Laboratory Spike Samples. For the wipe samples, recovery averaged 96 ± 28% for all analytes. For the soil samples, recovery averaged 74 ± 38% for all analytes (Supporting Information, Table S1).

1.d. Wipe Field Controls. Forty wipe samples were spiked with 11 target pesticides at the EPA laboratory, shipped to the field, taken to sampling locations, and then shipped with field samples to the analysis laboratory. The pyrethroids were chosen to cover a range of physicochemical properties and the OPs were chosen as the OPs most likely to be encountered in a child care center. These samples were blind to the analytical laboratory. With the exception of diazinon, average recoveries were >80% (81−137%). Average recovery for diazinon was 65%. We typically observe a lower recovery for diazinon as compared to other pesticides possibly due to hydrolysis. The pesticides, spiking levels, and percent recoveries are listed in Table S3 (Supporting Information).

2. Pesticide Distributions. Weighted summary statistics for the first nationally representative data reporting pesticide concentrations in child care centers are reported in Table 1. All summary statistics are reported as weighted national estimates as described by Rogers (*11*).

All 13 synthetic pyrethroids and the two pyrethrins targeted for quantitation were detected in the floor wipe samples, with seven detected at ≥5% of the centers. Fifteen OPs were detected, with five detected at ≥5% of the centers. Both piperonyl butoxide and fipronil were detected in the floor wipe samples. At the time of this study (2001), chlorpyrifos and diazinon were still registered for indoor use. However, the data in Table 1 suggest that *cis*- and *trans*-permethrin were detected almost as frequently. Eight of the 13 synthetic pyrethroids and pyrethrin II were detected on other surfaces in the centers, but only *cis*- and *trans*-permethrin, cypermethrin, resmethrin, and *lambda*-cyhalothrin were detected in ≥5% of the centers. Eight synthetic pyrethroids and seven OPs were also detected in the soil samples, but at a much lower frequency of detection as compared to the wipe samples. The results show that a large variety of pesticide active ingredients are being used in and around child care centers.

The pesticides measured in the highest weighted mean concentrations in the floor wipe samples include chlorpyrifos, diazinon, *cis*- and *trans*-permethrin, piperonyl butoxide, and cypermethrin; whereas the pesticides measured in the highest weighted mean concentrations on other surfaces in each sampled room were *cis*- and *trans*-permethrin. The mean concentration of *cis*- and *trans*-permethrin residues measured on the other surfaces (e.g., desktops, tables) are more than an order of magnitude greater than what was measured on the floor. The summary data suggest that the pesticides for which there is the highest potential for exposure are chlorpyrifos, diazinon, and *cis*- and *trans*-permethrin because these pesticides were measured in numerous locations in and around the centers. In addition, Table 1 also reports the summary data for the soil samples collected from each center that had an outdoor location where the children were allowed to play. Mean soil pesticide residue concentrations were greater than 5 ng/g for those pesticides detected at >5% of the centers, and higher than other mean soil pesticide residue concentrations reported for child care centers (*12*, *16*, *17*). For example, in a Pilot Study of Children's Total Exposure to Pesticides and Other Persistent Organic Pollutants (CTEPP) study, the mean diazinon concentration was less than the detection limit (0.5 ng/g) as compared to a weighted mean of 910 ng/g for this study (*12*). Furthermore, the data suggest that diazinon was heavily used in the outdoor environment at the time of this study.

Spearman rank correlation coefficients were calculated to evaluate the relationship of the pesticide residue concentrations between the floor wipes, other surface wipes, and soil samples (Table 2). A positive and statistically significant correlation existed between residues measured on the floor wipes and other surface wipes for bifenthrin, chlorpyrifos, cyfluthrin, cypermethrin, diazinon, diazinon oxon, and piperonyl butoxide. This suggests that as the pesticide residue concentration on the floor increases, the likelihood that the pesticide residue concentration on other surfaces in the sampled rooms also increases. However, it should be noted that if the field blank calculated-MDL data are used for chlorpyrifos, the correlation measured on the floor wipes and other surface wipes is not significant. There was a statistically significant association between residues measured on the floor wipes and soil samples for bifenthrin and cyfluthrin. The only significant relationship between the other surface wipes and soil samples was for malathion. The relationship between the floor wipe residue concentrations and the soil sample concentrations may be related to track-in.

It is rather challenging to compare the pesticide concentrations in the CCC study with other studies because there are only a handful of studies that report pesticide loadings in child care centers, and none are nationally representative. In the CTEPP study, dust samples were collected using the HVS3 in day care centers located in NC and OH, but these data are not directly comparable to the surface wipe data

TABLE 1. Weighted Summary Statistics for Selected Pesticides Measured in Floor Wipe Samples (ng/cm^2), Other Surface Wipe Samples (ng/cm^2), and Soil Samples (ng/g) in the CCC Study (See Text for Weight Details)

compound	% detect	mean	SE	GM	50th P	75th P	90th P	95th P	max
Floor Wipes[a] (*N* = 168; *cis/trans*-permethrin: *N* = 167)									
chlorpyrifos	89 (34)[b]	0.42 (0.45)[b]	0.21 (0.21)[b]	0.03 (0.11)[b]	0.02 ( )[b,c]	0.13 (0.13)[b]	0.51 (0.51)[b]	0.88 (0.88)[b]	28 (28)[b]
trans-permethrin	72	0.30	0.09	0.03	0.03	0.17	0.79	1.5	7
cis-permethrin	72	0.16	0.04	0.03	0.03	0.09	0.42	1.02	2.8
diazinon	67	0.33	0.24	0.01	*c*	0.06	0.26	0.53	18
cypermethrin	23	0.26	0.09	0.01	*c*	*c*	0.4	2.02	22
piperonyl butoxide	23	0.30	0.16	0.01	*c*	*c*	0.09	0.81	11
malathion	18	0.02	0.003	0.01	*c*	*c*	0.04	0.08	0.21
diazinon oxon	17	0.01	0.01	0.002	*c*	*c*	0.01	0.03	0.55
fipronil	8	0.01	0.01	0.005	*c*	*c*	*c*	0.03	0.42
lambda-cyhalothrin	7	0.02	0.004	0.005	*c*	*c*	*c*	0.03	0.44
cyfluthrin	7	0.13	0.07	0.01	*c*	*c*	*c*	0.73	6.9
esfenvalerate	6	0.02	0.01	0.01	*c*	*c*	*c*	0.05	1.9
bifenthrin	5	0.01	0.002	0.004	*c*	*c*	*c*	0.01	0.27
trans-mevinphos	5	0.004	<0.001	0.004	*c*	*c*	*c*	0.004	0.04
Other Surface Wipes[d] (*N* = 80)									
chlorpyrifos	93 (51)[b]	0.19 (0.21)[b]	0.07 (0.07)[b]	0.04 (0.1)[b]	0.05 ( )[b,c]	0.14 (0.14)[b]	0.28 (0.28)[b]	0.64 (0.64)[b]	4.3 (4.3)[b]
trans-permethrin	65	4	3.5	0.03	0.03	0.13	0.27	0.78	220
diazinon	60	0.11	0.07	0.01	*c*	0.02	0.09	0.36	2.4
cis-permethrin	48	1.9	1.5	0.02	*c*	0.07	0.25	0.43	90
piperonyl butoxide	11	0.13	0.09	0.01	*c*	*c*	0.01	1.3	3.7
fipronil	10	0.02	0.01	0.01	*c*	*c*	0.02	0.03	0.52
cypermethrin	9	0.19	0.12	0.01	*c*	*c*	*c*	0.65	23
diazinon oxon	9	0.01	0.01	0.002	*c*	*c*	*c*	0.03	0.18
resmethrin	6	0.01	0.002	0.01	*c*	*c*	*c*	0.06	0.1
lambda-cyhalothrin	5	0.01	0.004	0.005	*c*	*c*	*c*	0.06	0.18
malathion	5	0.01	0.003	0.01	*c*	*c*	*c*	0.05	0.2
Soil[e] (*n* = 117)									
trans-permethrin	11	6	1	4	*c*	*c*	9	12	140
chlorpyrifos	11	24	14	5	*c*	*c*	13	21	1200
bifenthrin	10	7	1.7	4	*c*	*c*	7	13	310
diazinon	8	910	855	2.1	*c*	*c*	*c*	18	110000
cis-permethrin	7	5	1	4	*c*	*c*	*c*	8	130

[a] Pesticides with % detect <5% in floor wipes: pyrethrin II = 4; resmethrin = 3; acephate = 3; sumithrin = 2; delta/tralomethrin = 2; tetramethrin = 2; *cis*- and *trans*-allethrin = 2; methamidophos = 2; phosmet = 2; pyrethrin I = 1; chlorpyrifos oxon = 1; methidathion = 1; azinphos methyl = 1; ethion = 1; ethyl parathion = 1; dimethoate = 0; fonofos = 0; demeton-S = 0; disulfoton = 0; malathion oxon = 0; methyl parathion = 0; naled = 0; dichlorvos = 0. [b] Results using the field matrix blank calculated − MDL. See Supporting Information for details. [c] At this percentile, all values were below the detection limit. [d] Pesticides with % detect <5% in other surface wipes: bifenthrin = 4; cyfluthrin = 1; pyrethrin II = 1; sumithrin = 1; methamidophos = 1; chlorpyrifos oxon = 1; methidathion = 1; esfenvalerate = 0; delta/tralomethrin = 0; tetramethrin = 0; *cis*- and *trans*-allethrin = 0; pyrethrin I = 0; *trans*-mevinphos = 0; acephate = 0; phosmet = 0; azinphos methyl = 0; ethion = 0; ethyl parathion = 0; dimethoate = 0; fonofos = 0; demeton-S = 0; disulfoton = 0; malathion oxon = 0; methyl parathion = 0; naled = 0; dichlorvos = 0. [e] Pesticides with % detect <5% in soil: esfenvalerate = 4; azinphos methyl = 4; cyfluthrin = 3; cypermethrin = 3; *trans*-mevinphos = 3; *lambda*-cyhalothrin = 2; pyrethrin II = 2; diazinon oxon = 2; delta/tralomethrin = 1; malathion = 1; acephate = 1; fonofos = 1; piperonyl butoxide = 1; resmethrin = 0; sumithrin = 0; tetramethrin = 0; *cis*- and *trans*-allethrin = 0; pyrethrin I = 0; *cis*-mevinphos = 0; methamidophos = 0; phosmet = 0; chlorpyrifos oxon = 0; methidation = 0; ethion = 0; ethyl parathion = 0; dimethoate = 0; demeton-S = 0; disulfoton = 0; malathion oxon = 0; methyl parathion = 0; naled = 0; dichlorvos = 0; fipronil = 0.

reported here. Detectable levels of chlorpyrifos (NC: $N = 19$, mean = 0.21 ng/cm^2; OH: $N = 23$, mean = 0.19 ng/cm^2), diazinon (NC: $N = 19$, mean = 0.57 ng/cm^2; OH: $N = 23$, mean = 0.1 ng/cm^2), *cis*-permethrin (NC: $N = 20$, mean = 5.4 ng/cm^2; OH: $N = 23$, mean = 0.78 ng/cm^2), and *trans*-permethrin (NC: $N = 20$, mean = 5.6 ng/cm^2; OH: $N = 22$, mean = 0.73 ng/cm^2) were measured at all centers in both states (*12*).

The only probability-based study found in the literature was the California Portable Classrooms (CPC) study. This study was conducted to assess the environmental conditions in California's portable classrooms (*13*). Using the Data Vac 2 vacuum cleaner, floor dust samples were collected from each classroom and analyzed for 20 different pesticides, including chlorpyrifos, diazinon, and *cis*- and *trans*-permethrin. Chlorpyrifos (mean = 0.09 ng/cm^2), *cis*-permethrin (mean = 0.07 ng/cm^2), and *trans*-permethrin (mean = 0.12 ng/cm^2) were detected in over 80% of the classrooms (*13*). Diazinon was measured in 48% of the portable classrooms and had a mean loading of 0.02 ng/cm^2 (*13*). Even though the sample collection methods were different for the studies, all three studies reported that chlorpyrifos and *cis*-and *trans*-permethrin were detected in the greatest frequencies.

In the CCC study, the number of pesticides in each media type ranged from 0 to 13. Thirty-one percent of the centers had 3−4 pesticide residues detected in the floor wipe samples. Fifty percent of the centers had 3−4 pesticide residues detected in the other surface wipe samples. Sixty-two percent of the centers had zero pesticide residues detected in the soil samples (Figure 1).

Three of the four centers with the highest number of pesticides detected in the floor wipe samples were located in the Southern U.S. region. Therefore, a regional analysis was conducted in order to identify any regional differences. The regional analysis was conducted for the following pesticides: bifenthrin, chlorpyrifos, diazinon, esfenvalerate, fipronil, malathion, piperonyl butoxide, cyfluthrin, cypermethrin, *cis*- and *trans*-permethrin, and *lambda*-cyhalothrin. The four Census regions included the Northeast, Midwest, South, and West. To evaluate the association between regional differences with respect to the number of detected pesticides, we used the Chi-Square test. The Chi-Square test was not valid for bifenthrin and fipronil because they were not detected in the West. However, for all other pesticides, the Chi-Square test suggested that statistically significant associations existed between the number of detects for the

TABLE 2. Correlations Between the Floor Wipes, Other Surface Wipes, and Soil Samples Using the Spearman Rank Correlation Coefficient Evaluation

compound	floor wipe vs other surface wipe ($N = 80$) *r* value, *p* value	floor wipe vs soil ($N = 117$) *r* value, *p* value	other surface wipe vs soil ($N = 59$) *r* value, *p* value
bifenthrin	0.57, <0.0001	0.24, 0.008	0.14, 0.3
chlorpyrifos	0.45, <0.0001	0.19, 0.04	0.09, 0.51
	(0.26, 0.02)[a]	(0.21, 0.025)[a]	(0.23, 0.09)[a]
cis-permethrin	0.23, 0.04 ($N = 79$)	0.04, 0.67 ($N = 111$)	−0.05, 0.72
cyfluthrin	0.38, <0.0005	0.25, 0.007	*b*
cypermethrin	0.44, <0.0001	−0.09, 0.36	−0.11, 0.4
diazinon	0.42, <0.0001	0.1, 0.29	0.19, 0.16
diazinon oxon	0.37, 0.0008	0.04, 0.69	−0.06, 0.64
esfenvalerate	*b*	0.04, 0.67	*b*
fipronil	0.13, 0.26	−0.10, 0.28	−0.07, 0.61
lambda-cyhalothrin	−0.07, 0.57	0.05, 0.57	0.16, 0.22
malathion	0.16, 0.15	0.11, 0.23	0.39, 0.002
piperonyl butoxide	0.35, 0.002	−0.01, 0.92	−0.1, 0.46
resmethrin	−0.03, 0.82	−0.04, 0.64	−0.05, 0.69
trans-permethrin	0.17, 0.13 ($N = 79$)	0.04, 0.68 ($N = 116$)	0.09, 0.49
trans-mevinphos	*b*	−0.07, 0.48	*b*

[a] Results using the field matrix blank calculated − MDL. [b] Not enough data to evaluate relationship.

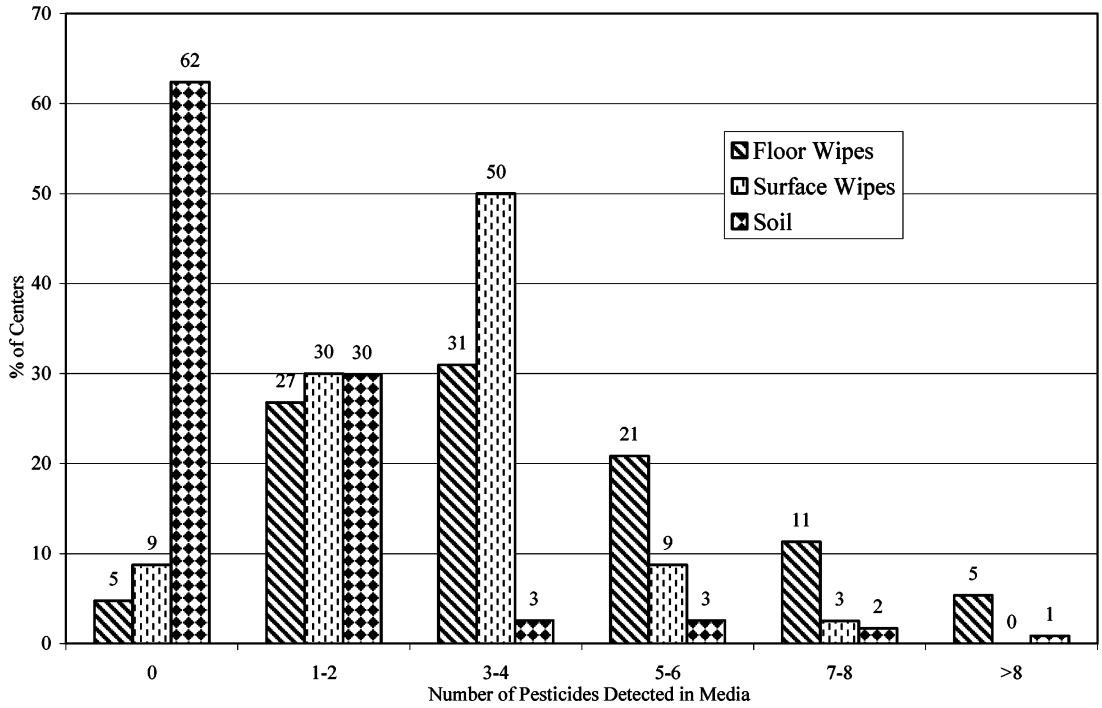

FIGURE 1. Number of pesticides detected in each media type.

various pesticides in the Census regions ($p < 0.0001$). Chlorpyrifos, diazinon, malathion, piperonyl butoxide, cypermethrin, *cis*- and *trans*-permethrin, and *lambda*-cyhalothrin had the greatest number of detects in the South and the least number in the West.

A second regional analysis was conducted to evaluate whether pesticide concentrations were statistically significantly different in the four Census regions, but the differences were not significant ($0.08 < p < 0.88$). Contrary to our study finding, Colt and colleagues (*14*) reported that pesticide levels were consistent with geographic variations due to geographic differences in pesticide use practices. To arrive at this conclusion, these researchers collected used vacuum cleaner bags between February 1999 and May 2001 and analyzed the contents for 30 pesticides, including chlorpyrifos, diazinon, and *cis*- and *trans*-permethrin. However, the Colt et al. (*14*) data are based on four locales (the Detroit, MI metropolitan area; the state of Iowa; Los Angeles County, CA; and the Seattle, WA metropolitan area), while the data presented in this paper are nationally representative.

Questionnaires were used to collect information about specific usage in the indoor and outdoor environments of the child care centers. An estimated 75% (weighted) of the centers reported at least one pesticide application, 18% (weighted) reported no pesticide applications, and 7% (weighted) were unsure of a pesticide application in the last year. Thirty-one percent of the centers applied pesticides in both inside and outside locations. A total of 375 different pesticide products were reported used by the centers. Among centers applying pesticides, pyrethroids were the most commonly used pesticides in indoor and outdoor locations. Individual centers reported using anywhere from 1 to 10 pesticide products (mean = 3, SD = 1.9). In addition, the frequency of pesticide applications ranged from 1 to 107

times annually ($N = 123$ centers reporting), with most centers in the range from 5 to 39 annual pesticide applications (10th to 95th percentiles). Of the 375 different pesticide products reported as used, 107 pesticide products contained one or more of the 39 active ingredients measured in this study. Of these 107 pesticide products, 57% were found in buildings that were greater than 30 years old. Center directors were asked about cleaning frequency and 87% reported daily cleaning in the center.

We conducted a comparison of the pesticide questionnaire responses and what was measured in the floor wipe samples. We limited the comparison to two specific pesticides (chlorpyrifos and permethrin) and three pesticide classes (OPs, pyrethroids, phenyl pyrazoles) that we had targeted for quantitation. A positive match is defined as finding the pesticide in the floor wipe sample and the response in the questionnaire stated that it was used, or not finding the pesticide in the floor wipe sample and the response in the questionnaire stated that it was not used. The comparison of the questionnaire responses to the environmental measurements showed that for all 115 pesticides that were detected in the floor wipe samples there was a positive match 48% of the time. There were positive matches 35% of the time for the OPs and 43% of the time for the pyrethroids. These results strongly suggest that questionnaire responses are not adequate in predicting pesticide residue occurrence on surfaces or predicting potential exposure in the child care center.

Results of this first nationally representative sample of surface and soil pesticide concentration data for child care centers show that there is the potential for exposure to pesticides in child care centers because 63% of the centers reported using pesticides and at least one pesticide (chlorpyrifos) was detected in over 89% of the centers. Up to 13 different pesticide residues were measured in the floor wipe samples, with chlorpyrifos, diazinon, and *cis*- and *trans*-permethrin most often detected. Although these data demonstrate the potential for exposure, they cannot be used to quantitatively estimate exposures due to the lack of ancillary data needed for the exposure algorithms (*15*). Because these field samples were collected in 2001 it is also important to recognize that, at this time or in the future, different pesticides or building treatment practices may be in use (e.g., integrated pest management), and chlorpyrifos and diazinon are no longer registered for indoor use. Routine measurements in buildings such as child care centers are important to document changes in pesticides that may be found in young children's environments. In order to accurately estimate young children's aggregate exposures, it is essential to characterize all of the environments where they may spend time.

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Supporting Information Available

Details on the child care center selection, chromatographic conditions, and quality assurance data. This material is available free of charge via the Internet at http://pubs.acs.org.

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