Journal of Exposure Science and Environmental Epidemiology (2007) 17, 331–349

www.nature.com/jes

Pesticides and their Metabolites in the Homes and Urine of Farmworker Children Living in the Salinas Valley, CA

ASA BRADMAN[a], DONALD WHITAKER[b], LESLIAM QUIRÓS[a], ROSEMARY CASTORINA[a], BIRGIT CLAUS HENN[c], MARCIA NISHIOKA[d], JEFFREY MORGAN[e], DANA B. BARR[f], MARTHA HARNLY[g], JUDITH A. BRISBIN[h], LINDA S. SHELDON[b], THOMAS E. MCKONE[a,i] AND BRENDA ESKENAZI[a]

[a]*Center for Children's Environmental Health Research, School of Public Health, University of California, Berkeley, CA, USA*
[b]*US Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development, Research Triangle Park, NC, USA*
[c]*ASPH Environmental Health Fellow, US Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Office of Research and Development, Research Triangle Park, NC, USA*
[d]*Battelle Memorial Institute, Columbus, OH, USA*
[e]*US Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development, Cincinnati, OH, USA*
[f]*National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, Georgia, USA*
[g]*Environmental Health Investigations Branch, California Department of Health Services, Richmond, CA, USA*
[h]*Oak Ridge Institute for Science and Technology, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Cincinnati, OH, USA*
[i]*Lawrence Berkeley National Laboratory and University of California, Berkeley, CA, USA*

In support of planning efforts for the National Children's Study, we conducted a study to test field methods for characterizing pesticide exposures to 20 farmworker children aged 5–27 months old living in the Salinas Valley of Monterey County, California. We tested methods for collecting house dust, indoor and outdoor air, dislodgeable residues from surfaces and toys, residues on clothing (sock and union suits), food, as well as spot and overnight diaper urine samples. We measured 29 common agricultural and home use pesticides in multiple exposure media samples. A subset of organophosphorus (OP), organochlorine (OC) and pyrethroid pesticides were measured in food. We also analyzed urine samples for OP pesticide metabolites. Finally, we administered four field-based exposure assessment instruments: a questionnaire; food diary; home inspection; and a self-administered child activity timeline. Pesticides were detected more frequently in house dust, surface wipes, and clothing than other media, with chlorpyrifos, diazinon, chlorthal-dimethyl, and *cis*- and *trans*-permethrin detected in 90% to 100% of samples. Levels of four of these five pesticides were positively correlated among the house dust, sock, and union suit samples (Spearman's $\rho = 0.18$–0.76). Pesticide loading on socks and union suits was higher for the group of 10 toddlers compared to the 10 younger crawling children. Several OP pesticides, as well as 4,4′-DDE, atrazine, and dieldrin were detected in the food samples. The child activity timeline, a novel, low-literacy instrument based on pictures, was successfully used by our participants. Future uses of these data include the development of pesticide exposure models and risk assessment.
Journal of Exposure Science and Environmental Epidemiology (2007) **17,** 331–349; doi:10.1038/sj.jes.7500507; published online 31 May 2006

Keywords: *pesticides, children, exposure, agriculture, union suits.*

Introduction

Since the publication of 'Pesticides in the diets of infants and children' in 1993 (NRC, 1993) and the passage of the Food Quality Protection Act (FQPA) in 1996, public health concerns about pesticide exposures to young children have received increased attention. Recent studies have confirmed pesticide contamination in home and day care environments where children spend most of their time (Adgate et al., 2001; Karmaus et al., 2001; Fenske et al., 2002a; Curl et al., 2003; Wilson et al., 2004). Biomonitoring studies have demonstrated that children are widely exposed to a number of pesticides, including organophosphorus (OPs), pyrethroid, fungicide, and organochlorine (OC) pesticides (Bradman et al., 1997, 2003; Aprea et al., 2000; Fenske et al., 2000a; Adgate et al., 2001; Lu et al., 2001; Wilson et al., 2003; Barr et al., 2005). The effects of these exposures on children's health are largely unknown. However, epidemiologic studies are currently investigating whether pre- and/or postnatal exposure to pesticides is associated with adverse health outcomes such as poorer growth and neurodevelopment in children (Berkowitz et al., 2004; Eskenazi et al., 2004, Whyatt et al., 2004; Young et al., 2005). Additionally, key

1. Address all correspondence to: Dr. Asa Bradman, Center for Children's Environmental Health Research, School of Public Health, University of California, Berkeley, 2150 Shattuck Avenue, Suite 600, Berkeley, CA 94720-7380, USA.
Tel.: +1 510 643 3023. Fax: +1 510 642 9083.
E-mail: abradman@socrates.berkeley.edu
Received 19 October 2005; accepted 4 May 2006; published online 31 May 2006

hypotheses of the National Children's Study, a multiagency longitudinal cohort study of 100,000 children to be followed from conception until young adulthood, focus on the association of pesticide exposure with adverse health effects in children (Branum et al., 2003).

In contrast to risk assessment studies that attempt to classify the range of exposures in a population, epidemiological studies require accurate classification of individual-level exposures. However, accurately characterizing children's exposures to current-use pesticides is challenging because of the nonpersistent nature of these chemicals and the variability in how they are metabolized (Cohen Hubal et al., 2000a, b; Fenske et al., 2002a, b; Branum et al., 2003; Clayton et al., 2003; Bradman and Whyatt, 2005).

Several studies suggest that children living in agricultural areas or with farmworker families are exposed to OP pesticides (Simcox et al., 1995; Loewenherz et al., 1997; Lu et al., 2000; O'Rourke et al., 2000; McCauley et al., 2001; Koch et al., 2002; Quandt et al., 2004). Farmworker children may be particularly vulnerable to pesticide exposure because they can experience exposures via multiple pathways such as pesticide drift from nearby fields, parental take-home exposure, and breast milk from the farmworker mother (Camann et al., 1995; Simcox et al., 1995; Fenske, 1997; Eskenazi et al., 1999; Fenske et al., 2000b, 2002b; Lu et al., 2000; McCauley et al., 2001; Curl et al., 2002; Thompson et al., 2003; Quandt et al., 2004; Lambert et al., 2005). In support of the National Children's Study and our own exposure modeling efforts, we conducted a study to test multimedia sampling methods to assess pesticide exposure to farmworker children living in the agricultural area of the Salinas Valley, CA.

Methods

Study Population

We enrolled a convenience sample of 20 children residing in the Salinas Valley, Monterey County, California. Families were recruited through local community clinics, social service organizations, and word-of-mouth. Eligible participants were either 6–12 months old and not able to walk (crawling) or approximately 24 months old and able to walk (toddler), and had at least one farmworker parent 18 years or older living in the same household. A total of 10 boys and 10 girls were recruited, with equal gender distribution in each age group. All sampling occurred between June and September, 2002. All procedures were reviewed and approved by the University of California, Berkeley Institutional Review Board (IRB).

Data Collection/Field Instruments

For each family participating in the study, we performed a total of three visits over 3 days. During the first study visit, we obtained signed informed written consents from participants. In addition, we provided an overview of the urine and environmental sampling procedures, provided supplies for overnight urine sample collection, and distributed the toys and teething rings. During the second study visit, we administered questionnaires, collected spot urine samples, retrieved overnight urine samples, provided an overview and demonstration of the CAT and recall log, distributed union suits and socks, performed home inspections, collected surface wipe and press samples, set up indoor and outdoor air samplers, and collected house dust and food samples. During the third study visit, we retrieved indoor and outdoor air samplers, food 2005, union suit, and sock samples. In addition, we collected toy and teething ring wipe samples, and administered the child activity recall logs and 24-h food diaries. The field instruments and sample collection methods are summarized in Table 1 and described below.

Questionnaire Bilingual/bicultural study staff administered questionnaires in either English or Spanish to the child's parents. Information obtained included a household enumeration, the parents' and other household members' occupations, behaviors potentially related to take-home exposures, home pesticide use, pets in the home, the child's activities, and exposure-related behaviors.

Home Inspection At the home inspection, staff recorded the types of floor surfaces (wood, linoleum, carpet, etc.) in each room, distance of the home to the closest agricultural field or orchard, overall quality of the housekeeping, and an inventory of all home pesticides and active ingredients.

Child Activity Timeline and Recall Log A time-activity diary was created for the mother or adult relative to record the child's location and activity during the 24-h period coincident with collection of the personal and air samples (see below). Each page of the form covered a 12 h period. Parents were asked to record the dominant activity and room the child was in for 30 min increments. Six activity levels were defined: sleeping, eating, quiet play (e.g., drawing), active play (running or jumping), watching television, and sitting in a stroller, carriage or car seat. Macro-location (i.e., inside or outside home) and microlocation (i.e., room in the house) categories were specifically defined and made visually distinct. Pictures were used to represent locations and activities to facilitate use by low-literacy respondents. Extensive training on how to complete the CAT was provided by study staff to ensure accurate completion. At the end of the 24-h sampling period, study staff verified responses with participants while transferring information from the child activity timeline (CAT) into a computer-codeable form for data entry (Recall Log). While completing the Recall Log, additional information was also obtained on the amount of time children spent on specific surfaces (e.g., wood floor, carpet, grass) and garments worn by the children during the

Table 1. Collection methods and field instruments for pesticide samples.

Matrix	Collection method/exposure information attained
House dust	HVS3 vacuum cleaner and HVS3 attachment
Air (indoor, outdoor)	24-h integrated sample (target flow rate 2.5 l/min)
Surface press (floor)	5-min sample (total contact area of 114 cm^2 and a contact pressure of 11.8 g/cm^2)/Two C_{18} 90 mm extraction disks (3M EmporeTM)
Surface and toy wipe	Soft-wick sponges (2 $4'' \times 4''$ 6-ply sponges with 10 ml isopropanol)
Duplicate food (solid)	Plastic zip closure bags in two sizes (quart and gallon size)
Duplicate food (liquid)	Nalgene bottle (quart size)
Leftover handled food (solid, liquid)	Plastic zip closure bags in two sizes (quart and gallon size) and Nalgene bottle (quart size)
Clothing	Cotton union suits and cotton socks (sampling time: 3–4 h)
Urine	Sterile U-bag/Specipan or urine collection cup 10–25 ml aliquots and diaper. One spot sample and one overnight diaper sample were collected
Study instruments	
Questionnaires	Occupational pesticide contact, proximity to fields, use and storage of home pesticides, and child's activities and diet
Home inspections	Home inspection to record details of home and surroundings (i.e., proximity to agricultural fields), room-by-room assessment, overall conditions of the home, and home pesticide use and active ingredient(s)
Child activity timelines (CAT)	Self-administered visual diary for participant's parents to record child's activities and location during the 24-h monitoring period
Recall log	Numerically coded log to improve reliability and accuracy of child activity timeline (CAT)
Food diaries	Self-administered diary for participants' parent(s) to record child's daily food intake.

sampling period (long *versus* short pants, long *versus* short sleeve shirts, etc).

Food Diary Parents were asked to record all food items consumed by the child during the 24-h period after consent was obtained. Information recorded included type of food, portion size, and time of consumption. Study staff reviewed the food diary with the parent(s) to determine how representative this sample was of the child's typical diet.

Environmental, Personal, and Biological Sample Collection Over 3 days of sampling, we collected house dust, surface press, surface and toy wipe and 24-h indoor and outdoor air samples from 20 farmworker homes. We also collected children's clothing samples, 24-h duplicate diet and leftover handled food samples, as well as one spot urine and one overnight diaper urine sample (Table 1).

House Dust We used the High Volume Surface Sampler (HVS3) (Roberts et al., 1991) to collect carpet dust samples from mostly carpeted living area floors and, in one case, a carpeted dining room, where children spent time playing. One sample was collected from a bare wood floor. Samples were collected from one square meter areas according to procedures defined in the American Society for Testing Materials (ASTM) Standard Practice D 5483–94 (ASTM, 1997).

Surface Wipes (Floors and Toys/Pacifiers) Approximately 1.5 days (range: 1–6 days) before sampling, study staff provided a teething ring (area = 99.2 cm^2) and a small ball (area = 283.5 cm^2) to the crawling children and toddlers, respectively. We collected surface wipes from the floors and age-appropriate toys. Floor wipes were obtained from a central location, usually the kitchen or dining area, near the boundary with carpeted floors. A defined surface area on the floor or indoor play area of 30×30 cm and the entire surface of the toys were thoroughly wiped using 10×10 cm Johnson and Johnson SOF-WICK rayon dressing sponges dampened with reagent-grade isopropanol alcohol (Geno et al., 1996).

Surface Presses We used a surface press to estimate transferable residues from floors to skin. The press consisted of a custom built sampling device based on the EL press sampler (Edwards and Lioy, 1999). C_{18} impregnated Teflon extraction disks (3M Empore disks) were mounted on the press, which was then placed on hard floor surfaces (linoleum or wood), with the exception of one sample that was collected from a carpeted surface.

Indoor/Outdoor Air Indoor monitors were placed in the main living area approximately 0.5–1.5 m above the floor. Outdoor monitors were placed in a central area in the yard and, when possible, at least 6 m away from driveways and roadways. Indoor and outdoor air samples were collected over a 24-h period using polyurethane foam (PUF) cartridges, resulting in a nominal sampled air volume of 3,600 l. The target flow rate for the cartridges was 2.5 l/min. Pumps were secured in a tamper resistant box for indoor monitoring and a tamper- and weather-resistant box for outdoor monitoring. At the end of the monitoring period, the PUF cartridge was placed in a glass jar, capped, and stored until shipped for laboratory extraction and analysis.

Duplicate Diet and Leftover Handled Food To estimate pesticide levels in ingested food, 24-h duplicate diet samples were collected from each child's family. Parents were asked to prepare twice the amount of food normally prepared for the child and to collect the same amount of food the child ingested throughout the day. Liquid diet (including formula) or duplicate beverage samples and solid foods were collected for the crawling children and placed in a container provided by the study staff. For the toddlers, liquid and solid foods were collected in separate containers that were provided to participants. To estimate residues transferred to foods from the children's hands or from contaminated dusts in the home, leftover handled solid foods, when available, were also collected for this age group.

Union Suits and Socks In order to assess potential dermal loading, participants were provided cotton one-piece playsuits (union suits) and socks. Participants wore the garments while at home for an average duration of 4.0 h. (SD = 2.3). At the end of the activity period, garments were removed, cut into segments, and stored in plastic zip closure bags prior to shipping to the laboratory for pesticide analysis.

Child Urine Two urine samples were collected from each child during the 24-h sampling period: one spot sample and one overnight diaper sample. Procedures used were those outlined by the Centers for Disease Control and Prevention (CDC) for use in the National Health and Nutrition Examination Survey 1999–2000 (NHANES) (CDC, 2003). For the spot urine samples, toilet-trained children were asked to void in a cleaned specimen container (Specipan; Baxter Scientific, McGaw Park, IL). For children who were not toilet-trained, a standard infant urine collection bag (Hollister) was affixed by its adhesive surface to the pubic area and held in place with the diaper. The bag was removed at the end of the visit. If, for any reason, the child could not provide any of the samples during the visit, a spot sample was collected on the day after the overnight diaper was collected (see below). For the overnight diaper sample, we provided the adult respondent with a disposable diaper containing a sewn-in Johnson and Johnson SURGIPAD combine dressing (Hu et al., 2000). The next morning, study staff collected this diaper when the air and food samples were collected. The total weight of the diaper was recorded, and then the insert was expressed and the volume recorded. For quality control purposes, frozen field blanks and spikes, prepared earlier by CDC, were defrosted, re-packaged in the field according to collection procedures for actual samples, and then shipped blind with the unknown samples to CDC.

Laboratory Analysis

Environmental and Clothing Samples All environmental and clothing samples were stored on ice packs in the field and during transport to the field laboratory, where they were stored at $-80^{\circ}C$ until shipment to the analytical laboratory (Battelle Memorial Institute, Columbus, Ohio). Samples were stored at the laboratory at $-20^{\circ}C$ until extraction and analysis.

Environmental (house dust, indoor/outdoor air, surface wipes, and C_{18} surface press disks) and clothing samples (union suits and socks) were analyzed for 12 OP pesticides, 13 pyrethroids, two fungicides, two OCs, and one herbicide (Tables 2 and 3). Target analytes were chosen based on the amount of local agricultural use, the likelihood of home pesticide use, and laboratory feasibility. All sample types were spiked with a mixture of surrogate recovery standards (SRSs), cleaned with a solid phase extraction (SPE) method (except for C_{18} press disk samples), and analyzed using gas chromatography/mass spectrometry (GC/MS) in selected ion monitoring (SIM) mode. Extract concentrations were quantified based on a 7-point linear calibration curve. The SRSs were chosen to reflect general compound classes and/or polarity ranges of the analytes; they were spiked at 100 ng for air and C_{18} press disks and 250 ng for other matrices. The SRSs included $^{13}C_{12}$-p, p′-DDE, $^{13}C_{12}$- p,p′-DDT, 1:1 mix of $^{13}C_6$-*cis*-permethrin and $^{13}C_6$-*trans*-permethrin, fenchlorphos, d_{10}–diazionon, and $^{13}C_1$-diethyl acetamidomalonate ($^{13}C_1$-DEAA).

Dust samples were sieved to obtain the dust fraction $<150\,\mu$m for analysis. A 0.5 g aliquot was spiked with the SRSs, and extracted by sonication with 12 ml of 1:1 hexane:acetone. The SPE cleanup step on silica (1 g, BakerBond) included sequential elution with hexane, 15% diethyl ether in hexane, dichloromethane (DCM) and 20%

Table 2. Limits of detection and detection frequencies for the target analytes in multimedia samples.

Analyte	House dust (ng/g)		Indoor air (ng total)		Outdoor air (ng total)		Surface wipe (ng total)		Toy wipe (ng total)		Cotton socks (ng total)		Union suits (ng total)[a]	
	LOD	DF (%)	LOD	DF (%)	LOD	DF (%)	LOD	DF (%)	LOD	DF (%)	LOD	DF (%)	LOD	DF (%)
Organophosphorous pesticides														
Acephate	10	0	10	0	10	0	50	0	50	5	50	0	100	0
Chlorpyrifos	2	95	1	100	1	85	5	95	5	30	5	89	4	100
Diazinon	2	100	1	100	1	100	2	95	2	60	2	95	2	100
Dichlorvos	10	0	2	5	2	10	10	5	10	0	2	0	4	0
Dimethoate	10	0	10	0	10	0	25	0	25	0	50	5	200	0
Fonofos	2	0	1	0	1	0	2	0	2	5	2	0	4	0
Malathion	2	20	2	15	2	40	10	20	10	5	25	16	20	25
Phosmet	2	0	2	0	2	0	2	0	2	0	25	0	25	5
Azinphos-Methyl[b]	25	0	50	0	50	0	25	0	25	0	25	0	—[c]	—[c]
Chlorpyrifos Oxon[b]	10	0	2	0	2	0	10	0	10	0	50	0	50	0
Methidathion[b]	10	0	2	0	2	0	5	0	5	0	25	0	4	0
Pyrethroids														
cis-Allethrin	5	25	2	15	2	0	5	20	5	0	5	10	10	20
trans-Allethrin	5	25	2	15	2	0	5	20	5	0	5	10	10	20
Bifenthrin	1	5	1	5	1	5	1	5	1	5	2	32	4	30
Cyfluthrin[d]	200	10	100	0	100	0	200	5	200	0	1000	5	800	5
λ-Cyhalothrin	10	20	10	0	10	0	10	5	10	0	25	0	100	5
Cypermethrin[d]	200	40	100	5	100	0	200	40	200	0	1000	5	800	0
Deltamethrin	200	5	50	0	50	0	250	0	250	0	500	0	200	0
Esfenvalerate	10	5	25	0	25	0	10	0	10	0	25	10	50	0
cis-Permethrin	2	100	2	40	2	30	2	85	2	15	2	100	4	100
trans-Permethrin	2	100	2	16[e]	2	0[e]	2	95	2	15	2	100	4	100
Resmethrin	5	0	2	0	2	0	10	0	10	0	10	10	100	0
Sumithrin	2	20	2	10	2	0	2	15	2	0	10	10	50	5
Tetramethrin	4	0	4	0	4	0	4	0	4	0	20	0	8	10
Other														
Chlorthal-dimethyl (herbicide)	2	100	0.5	100	0.5	100	1	100	1	55	2	95	2	100
p,p′-DDE (OC)	2	60	1	30	1	40	1	15	1	0	2	74	4	55
p,p′-DDT (OC)	10	10	5	5	5	0	10	0	10	0	10	5	50	10
Iprodione (fungicide)	10	35	25	0	25	0	10	20	10	0	250	10	200	10
Vinclozolin (fungicide)	10	0	2	0	2	0	10	0	10	0	10	0	20	0

[a]Union suit sample is a composite of four sections: leg, arm, upper and lower torso.
[b]Analytes not detected in any of these seven matrices.
[c]No calibration curve obtained, due to injector fouling.
[d]Detection limit when all four chromatographically resolved isomers are detected.
[e]One sample missing.
Abbreviations: DF = Detection frequency; LOD = Limit of detection; OC = Organochlorine.

acetone in ethyl acetate. The hexane fraction was discarded. Since p,p′-DDE eluted partially in the discarded hexane fraction, the recovery of SRS $^{13}C_{12}$-p,p′-DDE was used to correct for this planned loss of p,p′-DDE. The internal standard (IS) dibromobiphenyl (100 ng) was added to the final 1 ml extract.

Air (indoor and outdoor) and surface wipe samples were extracted using accelerated solvent extraction (ASE) at 2000 psi and 100°C. Samples were extracted in sequence with 9:1 and 1:1 hexane:acetone. Extracts were combined, cleaned up as described above, and analyzed using GC/MS/SIM.

The C_{18} surface press disks were extracted on a shaker table for 30 min in 1:1 DCM:ethyl acetate, and concentrated to 1 ml for analysis.

Before sampling, union suits were washed multiple times in hot water and mild detergent. After sampling, they were cut into four segments (upper torso, arms, bottom torso, and legs), and each segment was extracted separately in a Soxhlet extractor with 250 ml of DCM for 14–16 h. Similar extraction methods were used for socks. A gelatinous flocculate formed during the concentration step and became more pronounced with the solvent exchange of the extracts

Table 3. Pesticide concentrations in multimedia samples ($n = 20$ children)[a].

	House dust[b] (ng/g)				Indoor air (ng/m^3)				Outdoor air (ng/m^3)			
Analyte	p25	p50	p75	Range	p25	p50	p75	Range	p25	p50	p75	Range
Organophosphorous pesticides												
Acephate	—	—	—	—	—	—	—	—	—	—	—	—
Chlorpyrifos	40	49	76	ND-1,200	9.4	11	15	4.0–36	4.0	6.0	9.0	ND-36
Diazinon	10	21	32	4.0–810	9.4	12	21	5.9–260	11	17	35	6.2–140
Dichlorvos	—	—	—	—	—	—	—	ND-150	—	—	—	ND-200
Dimethoate	—	—	—	—	—	—	—	—	—	—	—	—
Fonofos	—	—	—	—	—	—	—	—	—	—	—	—
Malathion	—	—	—	ND-480	—	—	—	ND-50	—	—	18	ND-90
Pyrethroids												
cis-Allethrin	—	—	70	ND-2,500	—	—	—	ND-63	—	—	—	—
trans-Allethrin	—	—	60	ND-2,800	—	—	—	ND-61	—	—	—	—
Bifenthrin	—	—	—	ND-30	—	—	—	ND-3.1	—	—	—	ND-2.8
λ-Cyhalothrin	—	—	—	ND-140	—	—	—	—	—	—	—	—
Cyfluthrin	—	—	—	ND-300	—	—	—	—	—	—	—	—
Cypermethrin	—	100	420	ND-1,500	—	—	—	ND-380	—	—	—	—
Deltamethrin	—	—	—	ND-560	—	—	—	—	—	—	—	—
Esfenvalerate	—	—	—	ND-50	—	—	—	—	—	—	—	—
cis-Permethrin	57	150	210	13–2,900	—	—	5.4	ND-8.2	—	—	7.1	ND-8.0
trans-Permethrin[c]	140	230	570	22–5,800	—	—	—	ND-11	—	—	—	—
Resmethrin	—	—	—	—	—	—	—	—	—	—	—	—
Sumithrin	—	—	—	ND-5,500	—	—	—	ND-96	—	—	—	—
Other												
Chlorthal-dimethyl (herbicide)	19	31	61	6.5–110	7.5	12	19	1.8–43	11	25	46	5.0.-83
p,p′-DDE (OC)	—	17	20	ND-860	—	—	2.0	ND-28	—	—	4.6	ND-10
p,p′-DDT (OC)	——	—	—	ND-140	—	—	—	ND-31	—	—	—	—
Iprodione (fungicide)	—	—	20	ND-1,400	—	—	—	—	—	—	—	—

	Surface(floor) wipe(ng/cm^2)				Toy wipe (ng/cm^2)				Cotton socks[d] (ng/sample)			
Analyte	p25	p50	p75	Range	p25	p50	p75	Range	p25	p50	p75	Range
Organophosphorous pesticides												
Acephate	—	—	—	—	—	—	—	ND-0.20	—	—	—	—
Chlorpyrifos	0.017	0.046	0.079	ND-0.20	—	—	0.052	ND-0.15	14	24	37	ND-66
Diazinon	0.011	0.038	0.066	ND-0.096	—	0.014	0.034	ND-0.27	5.7	11	20	ND-590
Dichlorvos	—	—	—	ND-0.083	—	—	—	—	—	—	—	—
Dimethoate	—	—	—	—	—	—	—	—	—	—	—	ND-54
Fonofos	—	—	—	—	—	—	—	ND-0.084	—	—	—	—
Malathion	—	—	—	ND-0.69	—	—	—	ND-0.21	—	—	—	ND-300
Pyrethroids												
cis-Allethrin	—	—	—	ND-2.0	—	—	—	—	—	—	—	ND-1,600
trans-Allethrin	—	—	—	ND-2.2	—	—	—	—	—	—	—	ND-1,500
Bifenthrin	—	—	—	ND-0.035	—	—	—	ND-0.14	—	—	19	ND-92
λ-Cyhalothrin	—	—	—	ND-0.026	—	—	—	—	—	—	—	—
Cyfluthrin	—	—	—	ND-0.40	—	—	—	—	—	—	—	ND-1,400
Cypermethrin	—	—	0.34	ND-2.8	—	—	—	—	—	—	—	ND-2,400
Deltamethrin	—	—	—	—	—	—	—	—	—	—	—	—
Esfenvalerate	—	—	—	—	—	—	—	—	—	—	—	ND-230
cis-Permethrin	0.053	0.10	0.21	ND-1.7	—	—	—	ND-0.053	50	120	380	17–5,600
trans-Permethrin	0.14	0.23	0.39	ND-3.6	—	—	—	ND-0.072	140	220	490	10–9,200
Resmethrin	—	—	—	—	—	—	—	—	—	—	—	ND-130
Sumithrin	—	—	—	ND-3.5	—	—	—	—	—	—	—	ND-2,100

Table 3. *Continued.*

Analyte	Surface(floor) wipe(ng/cm^2)				Toy wipe (ng/cm^2)				Cotton socks[d] (ng/sample)			
	p25	p50	p75	Range	p25	p50	p75	Range	p25	p50	p75	Range
Other												
Chlorthal-dimethyl (herbicide)	0.022	0.044	0.079	0.0018–0.28	—	0.0059	0.012	ND-0.035	9.8	16	31	ND-200
p, p′-DDE (OC)	—	—	—	ND-0.15	—	—	—	—	—	28	52	ND-86
p, p′-DDT (OC)	—	—	—	—	—	—	—	—	—	—	—	ND-13,000
Iprodione (fungicide)	—	—	—	ND-0.53	—	—	—	—	—	—	—	ND-11,000

[a]Analyte concentrations presented only when detectable levels were measured in 1 or more matrices.
[b]House dust samples are collected from 1 square meter surface.
[c]One missing *trans*-permethrin house dust sample measurement.
[d]One participant's sock sample was missing.
Abbreviations: '—' and ND = Nondetectable; OC = Organochlorine.

into hexane prior to SPE cleanup. The extract was centrifuged at 3000 r.p.m., and the supernatant was removed for SPE cleanup. When flocculate again formed after SPE cleanup, ethyl acetate was added and a small portion of this extract was then filtered into the GC vial. Although analytical recoveries were acceptable (see below), performance of the GC/MS injection liner, column, and ion source was compromised by the flocculate, and these parts had to be cleaned or replaced frequently.

The extracts were analyzed using a Hewlett Packard (HP) 6890 GC interfaced to an HP 5973 MS. The gas chromatography conditions included: a DB-1701 column (30 m × 0.25 mm id × 0.15 μm film thickness); temperature program of 70°C for 2 min, then 70–130°C at 25 C/min, 130–220°C at 2 C/min, and 220–280°C at 10 C/min.

For each sample type, the analyses included multiple (2–5) field matrix blanks and spikes, laboratory matrix blanks and spikes, and duplicate analyses of house dust. Field matrix spiked samples were fortified with all analytes, then handled, transported, stored and analyzed as field samples. Laboratory matrix spiked samples were fortified just before extraction with all analytes. Analyte spike levels were 250 ng of each analyte, with the exception of acephate, naled, and the pyrethroids, which were spiked at 1000 ng. Naled was detected as its degradation product dichlorvos. There were no field matrix spikes for the dust or the union suit matrices (although there were multiple laboratory spiked samples of these matrices); the field spiked sock matrix was used to represent the union suit matrix.

With the exception of *cis*- and *trans*-permethrin in the sock and union suit matrices (215 ± 62 ng/sample and 52 ± 3 ng/sample for *cis*- and *trans*-permethrin in socks; 31 ± 10 ng/sample and 54 ± 55 ng/sample for *cis*- and *trans*-permethrin in union suits), there were only rare instances when any analyte was detected in a field or laboratory matrix blank. Recoveries of the pyrethroids in all field spiked matrices averaged 87% (90% for related SRSs); recoveries of the OPs and other compounds (chlorthal-dimethyl, iprodione, vinclozoline) in all field spiked matrices averaged 76% (99% for related SRSs). Recoveries of the pyrethroids in all laboratory spiked matrices averaged 87% (87% for related SRSs); recoveries of the OPs and other compounds in all laboratory spiked matrices averaged 78% (89% for related SRSs). Duplicate analysis of one dust sample showed very good agreement for the three analytes detected: 3.5 ± 0.5 ng/g for diazinon, 9.5 ± 0.5 ng/g for chlorthal-dimethyl, and 14 ± 1 ng/g for *cis*-permethrin.

Food Samples Target analytes for the food analyses included a range of OP, OC, and pyrethroid pesticides and fungicides. Food samples were stored on ice packs in the field and during transport to the field laboratory, where they were stored at −80°C, until shipment on dry ice to the analytical laboratory (US EPA, National Exposure Research Laboratory, Office of Research and Development, Cincinnati, Ohio). Food samples were defrosted and homogenized. For analysis of OP pesticides, solid food and beverage samples were extracted using pressurized fluid extraction with methylene chloride:acetone (1:1 v:v). Extracts were cleaned up using a diatomaceous earth chromatography column attached to the top of a C_{18} column. Organo-phosphorus pesticides were eluted with acetonitrile saturated with hexane. Analysis was performed using gas chromatography with pulsed flame photometric detection (GC/PFPD). The initial analysis was performed on an OP Pesticide column, 30 m × 0.32 mm ID (Restek, Bellefonte, PA, USA). Confirmation analysis was performed on an OPPesticide2 column (Restek, Bellefonte, PA, USA).

For non-OP pesticides, homogenized solid food and beverage samples were extracted using pressurized fluid extraction with hexane:acetone (1:1, v:v). Extracts were cleaned up using a diatomaceous earth chromatography column eluted with acetonitrile saturated with hexane followed by an alumina column eluted with methylene chloride:hexane (70:30, v:v). Analysis was performed using GC/MS in the SIM mode (Rosenblum et al., 2001). The

average recovery of non-OPs from composite solid foods was 79% and ranged from 60% to 108% for 22 of 23 analytes tested. Recovery of one analyte, chlorothalonil, was below 60%. The average recovery of non-OPs from composite beverages was 72% and ranged from 61% to 79% for 17 of 23 analytes tested. Recovery of aldrin, chlorthalonil, heptachlor, hexachloro-benzene, simazine and trifluralin was below 60%. The average recovery of OPs from composite solid foods was 84% and ranged from 65% to 106%. The average recovery of OPs from composite beverages was 76% and ranged from 60% to 94%. Detection limits for all target analytes ranged from 0.5 to 6 ng/g (Table 7).

Urine Samples The urine samples were stored on ice packs in the field and during transport to the field laboratory, where they were stored at -80°C until shipment to the laboratory for analysis (CDC, National Center for Environmental Health, Atlanta, Georgia). Six non-specific dialkyl phosphate (DAP) OP metabolites were measured — three dimethyl phosphates: dimethylphosphate (DMP), dimethylthiophosphate (DMTP), and dimethyl-dithiophosphate (DMDTP); and three diethyl phosphates: diethylphosphate (DEP), diethylthiophosphate (DETP), and diethyldithiophosphate (DEDTP). These metabolites derive from approximately 28 OP compounds registered in the US, representing approximately 81% of OP pesticide use in the Salinas Valley. Urine specimens were lyophilized to remove water then the residue was redissolved in acetonitrile:diethyl ether (1:1). The DAPs were derivatized to their chloropropyl phosphate esters. The concentrated extracts were then analyzed by isotope dilution gas chromatography-tandem mass spectrometry (GC-MS/MS) (Bravo et al., 2004), which is widely regarded as the definitive technique for trace analysis for DAP metabolites with detection limits of 1 ppb or less (Shealy et al., 1996; Barr et al., 1999). Creatinine concentrations in urine were determined using a commercially available diagnostic enzyme method (Vitros CREA slides, Ortho Clinical Diagnostics, Raritan, NJ, USA).

Laboratory quality control included repeat analysis of three in-house urine pools enriched with known amounts of pesticide residues whose target values and confidence limits were previously determined. The validity of each analytical run was determined using the Westgard rules for quality control (Westgard, 2003). Limits of detection (LODs) ranged from 0.08 μg/l for DMDTP to 0.4 μg/l for DMP. We assigned an imputed value of the LOD/$\sqrt{2}$ to levels below the detection limit (Hornung and Reed, 1990; Barr et al., 2004). For one toddler, the level for one of the six metabolites (DMTP) from the overnight diaper sample was not readable due to analytic interference. As metabolites within the dimethyl phosphate group were highly correlated, the missing value was imputed using regression analysis to predict the missing metabolite level based on the other metabolite levels for that child and that sample type.

Field quality control samples included blank, spike, and duplicate urine samples. No metababolites were measured in blank samples indicating that no contamination occurred in the field during processing or shipment to the laboratory. For field spiked samples, laboratory methods yielded an average percent recovery of 96% for total DAPs.

As many OP pesticides devolve to more than one metabolite in their class (diethyl or dimethyl phosphates), quantities were converted to molar concentrations (nmol/l) and summed to obtain the total concentrations of the diethyl and dimethyl phosphates (Barr et al., 2004). We performed all statistical analyses using both the creatinine-adjusted and non-adjusted urine data and there were no significant differences in our results. We chose not to adjust the metabolite levels for creatinine due to concerns regarding the validity of such adjustments for children (Barr et al., 2005).

Data Analysis
Summary statistics were computed for all media. Spearman correlation coefficients were calculated for overnight and spot urine samples as well as for environmental and clothing samples. All data analysis was performed with Stata Version 8 (StataCorp LP, College Station, TX, USA).

Results

Population Characteristics
The mean age of the crawling children ($n = 10$) was 8.3 months (range = 5–11) and of the toddlers ($n = 10$) was 23.5 months (range = 21–27). Gender was evenly distributed in both age groups. Study participants generally represent the farmworker population in the Salinas Valley agricultural area, which is primarily low income, Spanish-speaking, from Mexico or of Mexican descent, and low-literacy. In all, 40% of participants had household members besides the parent(s) working in agriculture, 50% of participants used some type of pesticide in or around their homes in the three months prior to the study visit, and 35% of participants lived within 400 m of the nearest agricultural field or orchard. In all, 40% of participants stored some type of pesticide in or around their homes; active ingredients included piperonyl butoxide and pyrethrin and pyrethroid compounds. Pesticides were used to kill fleas, flies and fungus.

Environmental and Clothing Samples
Analytical LODs and detection frequencies for the seven sampled exposure media are presented in Table 2. Three of the eleven OP pesticides measured (azinphos-methyl, chlorpyrifos oxon and methidathion), plus the fungicide vinclozolin were not detected in any of these media (Table 2).

Table 3 presents results for the pesticides detected in house dust, indoor and outdoor air, surface (floor) wipes, toy wipes, and socks. A higher number of pyrethroids was detected (11 analytes) when compared to the number of OP pesticides detected (eight analytes). Pyrethroids were the class of pesticides detected at the highest concentrations in house dust, indoor air, and surface wipes. Only two pyrethroids were detected in outdoor air, whereas indoor air samples contained seven pyrethroids. No analytes were detected in surface press samples (data not shown), and fewer analytes were detected in toy wipes than in floor wipes (Table 2). The highest detection frequencies were found in house dust samples, where concentrations ranged from <2.0 to 5,800 ng/g. Chlorpyrifos, diazinon, malathion, bifenthrin, *cis*-permethrin, and chlorthal-dimethyl were found in all the environmental media listed above (Table 3).

Data from sock samples are presented in Table 3. The most frequently detected analytes ($>70\%$) in the cotton socks were chlorpyrifos, diazinon, *cis*-permethrin, *trans*-permethrin, chlorthal-dimethyl, and p,p′-DDE (Table 2). The highest concentration detected was 13,000 ng/sample for p,p′-DDT. Similar to union suit samples, more pyrethroids were detected than OP pesticides (11/13 *versus* 4/11 analytes, respectively), and concentrations of pyrethroids were generally higher than OP pesticides (ranges of <2.0–9,200 ng/sample *versus* <2.0–590 ng/sample, respectively). Also, among the most frequently detected analytes ($\geqslant 90\%$ detection frequency), higher concentrations were detected for the older toddler children (Table 5). Other analytes detected in socks include malathion, bifenthrin, *cis*-allethrin, *trans*-allethrin, cyfluthrin, cypermethrin, esfenvalerate, resmethrin, sumithrin, and iprodione.

In the cotton union suit samples, the most frequently detected ($\geqslant 90\%$) analytes were chlorpyrifos, diazinon, *cis*-permethrin, *trans*-permethrin, and chlorthal-dimethyl (Tables 2 and 4). For most analytes, higher concentrations were present in composite lower torso and leg sections than on top torso and arm sections. More pyrethroids than OP pesticides were detected (9 *versus* 3 analytes in composite union suits), and pyrethroids were detected at higher concentrations than OP pesticides (6.4–42,000 ng/sample for pyrethroids *versus* 2.0–2,100 ng/sample for OP pesticides). Ranges of total detected union suit analyte concentrations for fungicides were <200–19,000 ng/sample, <4.0–560 ng/sample for the OCs and <2.0–350 ng/sample for the herbicide chlorthal-dimethyl (Table 4). Table 5 presents results for the composite union suit and sock samples for the five most frequently detected analytes. For four of the five analytes, median and geometric mean levels were consistently higher for the older children (toddlers) compared to the younger crawling children. The ratio of geometric mean pesticide levels in the toddler *versus* crawling children ranged from 1.1 to 2.6 ng/sample in the union suits and from 1.5 to 3.0 ng/sample in the socks. Table 6 presents the Spearman rank sum correlation matrix for the five most frequently detected analytes across the environmental and clothing sampling media.

Food

Data from duplicate diet samples are presented in Table 7. In all, 10 combined (liquid and solid) food samples from the crawling children were analyzed, and 10 solid and 9 (one missing) liquid food samples were analyzed from the toddlers. In all, 15 leftover handled food samples (i.e., leftover liquid and/or solid food samples) were also collected from the children and the majority of these samples were from the toddlers (10/15). Out of 46 analytes, 13 were detected in food samples. Detection frequencies were $\leqslant 30\%$ for these compounds. Solid and leftover handled food samples had the highest number of detected analytes (6/46), followed by combined food samples (5/46), and liquid food samples (3/46). The highest analyte concentration detected was in a solid food sample for a 22-month-old child (7.8 ng/g of malathion). Analytes detected in the duplicate diet and leftover handled food samples include: chlorpyrifos, diazinon, dieldrin, malathion, methamidophos, 4,4′-DDE, and endosulfan. The dieldrin concentration in the leftover handled food sample was slightly greater than that found in the duplicate solid food sample (6.1 *versus* 4.8 ng/g) and the malathion concentration in the leftover handled food sample was lower than that in the duplicate solid food sample (1.8 *versus* 7.8 ng/g). Diazinon was only detected in the leftover handled food. The only analyte detected in all food sample types was methamidophos.

Urine

Results for spot and overnight diaper sample urinary metabolite levels, unadjusted for creatinine, are presented in Table 8. Median spot and overnight urine dimethyl phosphate levels were higher than diethyl levels for both age groups (Table 8). In all cases, diethyl phosphates were lower in overnight diaper samples than in spot samples, while for toddlers dimethyl phosphates were higher in overnight diaper samples. Median overnight total DAP metabolite concentrations were higher for the older *versus* the younger children (180 *versus* 84 nmol/l, respectively), whereas the spot total DAP levels were more similar (100 and 130 nmol/l). Median total DAP concentrations for all children were higher in the overnight samples compared to the spot samples (140 *versus* 100 nmol/l), however, these differences were not statistically significant (Wilcoxon signed-rank test).

Table 9 presents Spearman correlations calculated for spot and overnight urine samples by age. The dimethyl phosphate concentrations for the spot and overnight samples for all children were significantly correlated ($\rho = 0.53$; $p = 0.02$). The diethyl phosphate concentrations for the spot and overnight diaper samples were also correlated ($\rho = 0.48$; $p = 0.03$). Total DAP metabolites in spot and overnight

Table 4. Pesticide concentrations in cotton union suits ($n = 20$ children).

	Lower torso (ng/sample)				Upper torso (ng/sample)				Arms (ng/sample)				Legs[a] (ng/sample)				Total burden (composite of all 4 sections) (ng/sample)[b]			
Analyte	p25	p50	p75	Range	p25	p50	p75	Range	p25	p50	p75	Range	p25	p50	p75	Range	p25	p50	p75	Range
Organophosphorus pesticides																				
Chlorpyrifos	11	19	28	6.7–93	12	15	22	ND-53	6.9	11	20	ND-44	9.9	16	30	4.5–94	45	59	100	15–290
Diazinon	6.4	10	22	3.4–490	6.6	12	19	2.4–1803	4.6	6.9	12	ND-210	5.3	10	20	2.2–1,200	26	43	72	14–2,100
Malathion	—	—	35	ND-230	—	—	—	ND-410	—	—	—	ND-470	—	—	45	ND-190	—	—	80	ND-1,300
Phosmet	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	ND-66	—	—	—	ND-66
Pyrethroids																				
cis-Allethrin	—	—	—	ND-1,400	—	—	—	ND-1,700	—	—	—	ND-670	—	—	—	ND-1,900	—	—	—	ND-5,700
trans-Allethrin	—	—	—	ND-1,600	—	—	—	ND-1,600	—	—	—	ND-1,100	—	—	—	ND-2,600	—	—	—	ND-6,800
Bifenthrin	—	—	12	ND-30	—	—	4.1	ND-32	—	—	7.1	ND-33	—	—	9.1	ND-23	—	—	29	ND-120
Cyfluthrin	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	ND-3,400	—	—	—	ND-3,400
λ-Cyhalothrin	—	—	—	—	—	—	—	ND-330	—	—	—	—	—	—	—	ND-130	—	—	—	ND-460
Cypermethrin	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	ND-1,700
Esfenvalerate	—	—	—	—	—	—	—	ND-230	—	—	—	—	—	—	—	—	—	—	—	ND-230
cis-Permethrin	98	190	330	6.4–17,000	110	150	260	30–6,000	81	120	260	25–5,100	99	150	300	31–11,000	470	597	1,100	200–39,000
trans-Permethrin	42	59	100	ND-11,000	40	64	200	8.3–8,400	20	43	103	13–7,500	30	58	170	10–15,000	160	280	390	39–42,000
Resmethrin	—	—	—	—	—	—	—	ND-150	—	—	—	—	—	—	—	—	—	—	—	ND-150
Sumithrin	—	—	—	ND-91	—	—	—	ND-96	—	—	—	—	—	—	—	ND-700	—	—	—	ND-940
Tetramethrin	—	—	—	ND-290	—	—	—	ND-250	—	—	—	ND-240	—	—	—	ND-350	—	—	—	ND-1,100
Other																				
Chlorthal-dimethyl	12	24	35	2.3–120	9.5	21	30	2.3–100	6.5	14	22	ND-100	11	22	34	2.6–78	48	80	120	8.8–350
p, p'-DDE	—	—	20	ND-130	—	—	40	ND-280	—	—	6.7	ND-56	—	—	28	ND-150	—	34	180	ND-500
p, p'-DDT	—	—	—	ND-56	—	—	—	ND-96	—	—	—	ND-560	—	—	—	ND-69	—	—	—	ND-560
Iprodione	—	—	—	ND-4,500	—	—	—	ND-5,400	—	—	—	ND-4,500	—	—	—	ND-4,200	—	—	—	ND-19,000

[a]One section is missing for one subject for all analytes; *trans*-permethrin missing from one section of an additional subject's section due to chromatographic interferences.
[b]Range values reported consist of the composite data: bottom, top, arm and leg sections.
'—' and ND = Nondetectable.

Table 5. Comparison of most frequently detected analytes (⩾90%) in union suits and socks by children's age ($n = 20$)[a].

	Union suits — composite (ng/sample)[b,c]					Socks (ng/sample)[d]				
Analyte	*n*	Range	GM	Median	Ratio[e]	*n*	Range	GM	Median	Ratio[e]
Chlorpyrifos										
Crawling children	10	28–280	60	56		9	4.5–37	17	22	
Toddlers	10	15–130	66	73	1.1	10	2.9–66	27	32	1.5
Chlorthal-dimethyl										
Crawling children	10	8.8–300	53	68		9	1.8–26.0	9.5	16	
Toddlers	10	16–350	84	91	1.6	10	6.8–200	29	28	3.0
Diazinon										
Crawling children	10	14–130	39	41		9	3.6–29	8.1	7.0	
Toddlers	10	20–2,100	66	43	1.7	10	0.0–590	24	15	2.9
cis-Permethrin										
Crawling children	10	38–1,200	440	550		9	17–870	100	110	
Toddlers	10	140–39,000	960	820	2.2	10	28–5,600	190	180	1.8
trans-Permethrin[f]										
Crawling children	10	40–3,500	220	260		9	10–770	160	260	
Toddlers	10	120–42,000	580	300	2.6	10	110–9,200	360	200	2.3

[a]Values below detection limit = DL/$\sqrt{2}$.
[b]Composite of all four union suit sections.
[c]Data for one section of one toddler's union suit is missing.
[d]One crawling child's sock sample is missing ($n = 9$).
[e]Ratio of geometric mean pesticide levels: Toddlers *versus* crawling children.
[f]*trans*-Permethrin data for one section is missing for three toddlers.
Abbreviations: GM = geometric mean.

samples were positively correlated for all children ($\rho = 0.57$; $p = 0.009$).

Correlations Between Sampled Media

Table 6 presents Spearman correlations for the five most frequently detected analytes across all the sampling media. With the exception of chlorpyrifos, pesticides in house dust, sock, and union suit samples were positively correlated and had Spearman correlation coefficients ranging from 0.18 to 0.76 for the most frequently detected analytes (Table 6). Indoor and outdoor air were moderately to strongly correlated for diazinon, chlorpyrifos, and chlorthal-dimethyl. Except for diazinon, levels on toys were not consistently correlated with other media.

Correlations between diazinon and chlorpyrifos levels in environmental media and overnight and spot urine diethyl phosphate metabolite levels are also presented (see urine methods, above). Except for toys ($\rho = 0.50$; $P < 0.05$), total diethyl phosphate metabolites were weakly or negatively correlated with levels of chlorpyrifos in other media (Table 6). Total diethyl metabolites were positively correlated with diazinon in house dust, socks, and union suits ($\rho = 0.069$–0.49; with overnight urine and dust significantly correlated, $P < 0.05$). Total diethyl phosphate metabolite levels were also nonsignificantly associated with diazinon levels on toys ($\rho = 0.20$–0.33) (Table 6). We also evaluated the association of total diethyl urinary metabolite levels with the molar sum of diazinon and chlorpyrifos in each medium. Correlations between these media and urine were generally weak ($\rho = -0.17$ to 0.24). Total diethyl metabolite levels in overnight urine were moderately correlated with the molar sum of diazinon and chlorpyrifos on toys ($\rho = 0.62$; $P < 0.05$).

Child Activity Timeline and Recall Log

The majority of participating parents (~80%) understood the Child Activity Timeline (CAT) and completed it properly. In most cases, it took approximately 15 min to explain the CAT to parents and to demonstrate filling it out, and about 10 min to review it with the parents on the final visit. Completing the Recall Log, however, appeared to be a burden both to staff and to participating parents. The most time-consuming components involved questions about the specific surfaces contacted by the children and clothing worn for each 30-min time interval. In most cases, parents were unable to recall the amount of time the participating child spent on each surface. This was particularly a problem for the older, more active children.

Table 10 presents 24-h time activity and recall log information for 10 crawling children and 10 toddlers. The

Table 6. Spearman rank sum correlation matrix for the five most frequently detected analytes across sampling media[a]

	Dust	Socks	Union suit	Surface wipe	Indoor air	Outdoor air	Toy	Overnight urine	Spot urine
Chlorpyrifos									
Dust	1								
Socks	−0.25	1							
Union suit	−0.24	0.54*	1						
Surface wipe	0.14	−0.056	0.16	1					
Indoor air	0.36	0.012	0.11	0.030	1				
Outdoor air	0.16	−0.037	−0.083	−0.24	0.46*	1			
Toy	−0.087	−0.19	−0.34	0.17	0.44	−0.11	1		
Overnight urine	−0.24	0.057	−0.17	0.021	0.14	0.17	0.50*	1	
Spot urine	−0.39	0.12	0.19	−0.091	−0.089	0.31	0.056	0.48*	1
Chlorthal-dimethyl									
Dust	1								
Socks	0.39	1							
Union suit	0.50*	0.76*	1						
Surface wipe	0.053	0.37	0.080	1					
Indoor air	0.63*	0.40	0.57*	0.048	1				
Outdoor air	0.58*	0.27	0.56*	0.19	0.92*	1			
Toy	0.075	−0.043	0.13	−0.22	0.23	0.12	1		
Diazinon									
Dust	1								
Socks	0.52*	1							
Union suit	0.47*	0.76*	1						
Surface wipe	0.29	0.25	0.16	1					
Indoor air	0.57*	0.52*	0.55*	0.36	1				
Outdoor air	0.24	0.24	0.48*	0.30	0.77*	1			
Toy	0.33	0.76*	0.52*	0.28	0.59*	0.33	1		
Overnight urine	0.49*	0.25	0.069	0.081	0.063	−0.20	0.33	1	
Spot urine	0.40	0.11	0.27	−0.14	0.076	−0.027	0.20	0.48*	1
cis-Permethrin									
Dust	1								
Socks	0.43	1							
Union suit	0.40	0.18	1						
Surface wipe	0.39	0.44	0.32	1					
Indoor air	0.072	0.078	0.21	0.18	1				
Outdoor air	−0.18	0.12	−0.39	−0.22	0.058	1			
Toy	0.22	0.30	0.036	0.061	0.057	−0.29	1		
trans-Permethrin									
Dust	1								
Socks	0.58*	1							
Union suit	0.52*	0.45	1						
Surface wipe	0.40	0.34	0.26	1					
Indoor air	0.39	0.30	0.13	0.20	1				
Outdoor air	−0.34	−0.42	−0.17	−0.19	−0.26	1			
Toy	0.33	0.44	0.13	−0.098	0.23	−0.16	1		

[a]Spot and overnight urine samples are total diethyl phosphate metabolite levels (nmol/l). *Statistically significant Spearman rho ($P<0.05$).

children spent a large amount of time sleeping, with the crawling children sleeping on average 12.6 h/day and the toddlers sleeping on average 13.2 h/day. The crawling children spent slightly more time eating than the toddlers (mean = 3.2 h/day *versus* 2.2 h/day, respectively). The younger crawling children spent significantly more time in quiet play compared to the toddlers (mean = 5.0 h/day *versus* 1.4 h/day, respectively; $t = 3.4$ $P < 0.05$), while the toddlers spent more time compared to the crawling children engaged in active play (mean = 4.4 h/day *versus* mean = 1.7 h/day, respectively; $t = 2.53$ $P < 0.01$). Further, the toddlers spent significantly more time watching television than the crawling children (mean = 1.8 h/day *versus* 0.4 h/day, respectively; $t = 3.3$ $P < 0.01$). All children spent most of their day inside

Table 7. Pesticide levels in children's liquid, solid and combined food samples ($n = 20$ children)[a].

Analyte		Combined food samples for crawling children (ng/g) $n = 10$		Liquid food samples for toddlers (ng/g) $n = 9$		Solid food samples for toddlers (ng/g) $n = 10$		Leftover handled food samples (ng/g)[b] $n = 15$	
	LOD (ng/g) (L, S)	Range	DF(%)	Range	DF(%)	Range	DF(%)	Range	DF(%)
Organophosphorous pesticides									
Acephate	0.50, 0.81	—	—	—	—	<0.81–1.0	10	—	—
Chlorpyrifos	0.98, 1.4	<0.98–1.4	10	—	—	—	—	<0.98–1.0	6.7
Diazinon	0.58, 1.2	—	—	—	—	—	—	<0.58–0.62	6.7
Dimethoate	0.50, 0.81	<0.50–0.88	20	—	—	<0.50–0.88	10	—	—
Isofenphos	1.0, 1.8	—	—	<0.50–1.4	20	—	—	—	—
Malathion	0.52, 1.6	<0.52–1.0	30	—	—	<1.6–7.8	10	<0.52–1.8	13
Methamidophos	0.61, 2.3	<0.61–0.80	20	<0.61–0.85	30	<0.61–2.2	10	<0.61–0.66	6.7
Phosmet	2.0, 1.9	<1.9–4.1	10	—	—	—	—	—	—
Other									
4,4′-DDD	2.0, 4.6	—	—	<2.0–5.3	10	—	—	—	—
4,4′-DDE	3.5,1.8	—	—	—	—	—	—	<1.8–3.5	6.7
Atrazine	3.9, 1.9	—	—	—	—	<1.9–2.0	10	—	—
Dieldrin	2.0, 1.5	—	—	—	—	<1.5–4.8	10	<1.5–6.1	6.7
Endosulfan	6.1, 4.5	—	—	—	—	—	—	<4.5, 5.1	6.7

Nondetected analytes in food samples[c]

Acetochlor (L = 1.7/S = 1.7)	Demeton O&S (L = 1.0/S = 2.1)	Hexachlorobenzene (L = 2.3/S = 2.9)	*cis*-Permethrin (L = 6.5/S = 4.5)
a-Chlordane (L = 1.8/S = 1.8)	Dichlorvos (L = 1.0/S = 4.1)	Lindane (L = 2.7/S = 3.5)	*trans*-Permethrin (L = 3.0/S = 2.9)
Alachlor (L = 1.1/S = 2.7)	Disulfoton (L = 0.6/S = 2.3)	Malathion Oxon 2 (L = 0.8/S = 2.2)	Parathion (L = 0.6/S = 1.2)
Aldrin (L = 5.5/S = 2.0)	Endrin (L = 1.3/S = 3.1)	Methidathion (L = 0.5/S = 1.2	Phorate (L = 1.3/S = 2.1)
g-Chlordane (L = 2.1/S = 1.7)	Ethion (L = 0.7/S = 1.2)	Methyl Parathion (L = 0.6/S = 2.0)	Simazine (L = 6.4/S = 3.5)
Chlorothalonil (L = 1.2/S = 2.1)	Fenamiphos (L = 0.7/S = 1.2)	Metolachlor (L = 1.1/S = 1.7)	Trifluralin (L = 1.1/S = 4.2)
Chlorpyrifos Oxon (L = 1.6/S = 2.0)	Fonofos (L = 0.6/S = 1.9)	Mevinphos (L = 0.7/S = 2.0)	Vinclozolin (L = 2.7/S = 2.4)

[a]One participant had two liquid and two solid food samples and another participant had two liquid food samples: the second aliquot from each was not analyzed.

[b]10 24-month olds and five 6-month olds had leftover handled food samples. Leftover handled foods are those that were liquid and/or solid leftover samples.

[c]Numbers in parentheses represent the LOD of the liquid (L) and solid food (S) samples, respectively.

'—' = Non detected.

Table 8. Dialkyl phosphate metabolite levels in children's spot and overnight urine samples[a].

	Spot Samples (nmol/l)						Overnight Samples (nmol/l)[b]					
Crawling children	n	GM	p25	p50	p75	Range	n	GM	p25	p50	p75	Range
Total diethyls	10	16	1.3	24	41	1.3–240	10	4.6	1.3	2.7	13	1.3–65
Total dimethyls	10	71	8.9	110	250	4.1–1,100	10	52	5.9	81	230	4.1–4,400
Total DAPs	10	117	37	130	450	5.4–1,300	10	71	15	84	230	5.4–4,400
Toddlers												
Total diethyls	10	8.0	1.3	4.5	46	1.3–310	10	4.3	1.3	1.3	11	1.3–210
Total dimethyls	10	62	12	81	220	7.0–1,100	10	102	89	130	250	4.1–400
Total DAPs	10	83	14	100	330	8.3–1,100	10	120	91	180	350	5.4–440
All children												
Total diethyls	20	11	1.3	13	44	1.3–310	20	4.4	1.3	1.3	12	1.3–210
Total dimethyls	20	66	11	85	240	4.1–1,100	20	73	11	130	240	4.1–4,400
Total DAPs	20	99	32	100	390	5.4–1,300	20	92	18	140	310	5.4–4,400
Creatinine (mg/dL)	20	31	16	28	60	7.6–150	20	37	22	40	57	13–120

[a]Values below detection limit = DL/$\sqrt{2}$, consistent with NHANES data published by CDC (CDC, 2003).
[b]One toddler is missing an overnight sample DMTP measurement; thus, total dimethyl and DAP metabolite concentrations were imputed for that child (see Methods).
Notes: Detection limits and detection frequencies (%) for urinary metabolite data: DMP = 0.4 μg/l (46.2); DMTP = 0.3 μg/l (82.1); DMDTP = 0.08 μg/l (33.3); DEP = 0.1 μg/l (38.5); DETP = 0.1 μg/l (43.6); DEDTP = 0.1 μg/l (2.6).

Table 9. Spearman "ρ" correlation between spot and overnight urine samples[a].

	Diethyl phosphate			Dimethyl phosphate			Total DAP		
Age group	n	ρ	*P*-value	n	ρ	*P*-value	n	ρ	*P*-value
Crawling children	10	0.43	0.22	10	0.60	0.07	10	0.66	0.04
Toddlers	10	0.48	0.16	10	0.53	0.12	10	0.65	0.04
All children	20	0.48	0.03	20	0.53	0.02	20	0.57	0.009

[a]One toddler is missing an overnight sample DMTP measurement; thus total dimethyl and DAP metabolite concentrations were imputed for that child (see Methods).

the home (mean = 21.3 h/day) compared to outside in the yard (mean = 0.9 h/day) or away from home (1.8 h/day).

Discussion

We collected multimedia exposure samples from the homes of 20 farmworker children living in the Salinas Valley, CA, an agricultural region. Measurable levels of OP, OC, and pyrethroid pesticides were detected in house dust, indoor and outdoor air, surface wipes, clothing, and food. The pesticides chlorpyrifos, diazinon, *cis*- and *trans*-permethrin, and chlorthal-dimethyl were commonly detected in most media. Pesticide residues on clothing (union suits and socks) were consistently higher in the older group of children (21–27 months) compared to the younger children (5–11 months). In addition, spot and overnight diaper urine samples were collected successfully and analyzed for DAP metabolites. We found measurable levels of DAP metabolites in all the children's urine. DAP metabolites in spot and overnight diaper samples were correlated ($\rho \sim 0.6$), suggesting that spot urine samples may be valid indicators of total daily metabolite excretion.

The greatest number and type of pesticides were detected in house dust, surface wipes, and clothing compared to other environmental media. Thus, these media may be the best indicators of which pesticides are present in a given home. Detectable levels of pesticides were measured on age-appropriate toys distributed just a few days before the home sampling visit, demonstrating that pesticides can quickly transfer to toys that are handled and explored orally by children. While the levels of pesticides in dust and clothing were only moderately correlated (Table 6), the presence or absence of a pesticide in one medium generally indicated the presence or absence in the other medium.

Higher concentrations of the most frequently detected analytes on the clothing of the older age group may be attributed to the fact that toddlers are more actively walking, running, crawling, and playing than younger children, and are thus potentially more exposed to pesticide residues from residential surfaces. This hypothesis is supported by the higher DAP metabolite levels in older children (Table 8); however, the older children's exposures may be due, in part, to differences in diet.

This study is the first to report data on a broad range of pyrethroid pesticides in the home environments of children.

Table 10. 24 h time activity information for crawling children and toddlers ($n = 20$).

		Hours spent per activity	
Activity	*N*	Range	Mean (SD)
Sleeping			
Crawling children	10	10.5–15	12.6 (1.5)
Toddlers	10	10–19	13.2 (2.3)
Eating			
Crawling children	10	0–5	3.2 (1.4)
Toddlers	10	1–5	2.2 (1.2)
Quiet play			
Crawling children	10	1–10	5.0 (2.9)
Toddlers	10	0–4	1.4 (1.6)
Active play			
Crawling children	10	0–6.5	1.7 (2.4)
Toddlers	10	0–8.5	4.4 (2.3)
Watching TV			
Crawling children	10	0–1.5	0.4 (0.6)
Toddlers	10	0–4.5	1.8 (1.2)
Sitting in a stroller or car seat			
Crawling children	10	0–3.5	1.2 (1.2)
Toddlers	10	0–4.5	1.1 (1.4)
Inside home			
Crawling children	10	14.5–24	21.6 (3.1)
Toddlers	10	16.5–23.5	21.1 (2.2)
Outside home			
Crawling children	10	0–2	0.6 (0.8)
Toddlers	10	0–2.5	1.2 (0.9)
Away from home			
Crawling children	10	0–9.5	1.9 (3.2)
Toddlers	10	0–7.5	1.7 (2.2)

Table 11. Usage in the Salinas Valley (2002)[a] of pesticides frequently detected in multimedia samples.

Pesticide	Kilograms applied in 2002
Chlorpyrifos[b]	23,576
Diazinon[b]	65,127
Permethrin[c,d]	11,365
Chlorthal-dimethyl[e]	32,865
Total	132,933
Other:	
Acephate[f]	31,471
Dimethoate[g]	15,905
Dieldrin	0
Iprodione	23,349
Malathion[g]	39,713
Phosmet[g]	1,463

[a]Includes agricultural, landscape maintenance, structural pest control and roadside pesticide usage; agriculture represents 99% of total use (DPR 2001).
[b]Diethyl OP pesticide.
[c]Quantities of *cis*- and *trans*-permethrins are combined.
[d]Pyrethroid pesticide.
[e]Herbicide.
[f]OP pesticide that does not devolve to DAP urinary metabolites.
[g]Dimethyl OP pesticide.

Consistent with the low vapor pressure of pyrethroids, relatively low levels of these compounds were detected in air. The pyrethroids *cis*- and *trans*-permethrin were, however, the most frequently detected pesticides in dust and clothing and were also present at the highest levels. Our findings reflect the increasing use of pyrethroid pesticides in home environments as manufacturers substitute these materials for restricted-use OP pesticides (DPR, 2004). Other studies in the US (Colt et al., 2004) and other countries have found permethrins to be the most abundant pesticides routinely detected in dust (Butte and Heinzow, 2002).

Chlorpyrifos and diazinon were detected in all of the sampling media. These compounds may persist longer in indoor environments compared to outdoor environments due to the lack of sunlight, moisture, and soil microorganisms (Lewis et al., 1994) and have been detected in many studies of home environments (Butte and Heinzow, 2002; Colt et al., 2004; Egeghy et al. 2005). Chlorpyrifos and diazinon are no longer licensed for home pesticide use (U.S. EPA, 2000, 2001) and no participants reported using these pesticides. The residues we found may be due to previous home use or local agricultural pesticide use.

We detected chlorthal-dimethyl in all house dust, indoor air, outdoor air, surface wipe, union suit, and some toy samples. Chlorthal-dimethyl is a semi-volatile chlorinated phthalate herbicide used primarily in agriculture (the parent product is known as Dacthal). Chlorthal-dimethyl has an estimated half-life of 36 days in air (HSDB, 2005) and is commonly present in the air of agricultural valleys in California (Ross et al. 1990; USGS, 2002) and elsewhere (Rawn and Muir, 1999), and in the soil and sediment in Monterey County (DPR, 1988). Chlorthal-dimethyl has also been detected in air samples taken from a region with low agricultural and home pesticide use (Whitmore et al., 1994), suggesting the potential for long-range transport (Rawn and Muir, 1999). It has also been detected in the dust of farmers' homes and, at lower levels, in control homes (Starr et al., 1974).

Of the five commonly detected analytes, only *cis*- and *trans*-permethrin and chlorthal-dimethyl are licensed for use in and around the home. In this population, however, home use of these pesticides was rarely or never reported. Table 11 summarizes possible sources of these contaminants, including agricultural, landscape maintenance, structural pest control, and roadside pesticide use in the Salinas Valley (DPR, 2002).

Duplicate diet and surface press samples were less promising methods of assessing pesticide exposure in this study. Pesticides were not detected in any of the surface press samples. As shown recently (Cohen Hubal et al., 2005), transfer efficiencies of chlorpyrifos and allethrin from carpeted and laminate surfaces to the C_{18} Press Sampler are quite low, on the order of 0.01–0.55%. While other studies have suggested that food ingestion may be one of the major routes of children's exposure to pesticides (Clayton et al., 2003; Wilson et al., 2003), we were not able to adequately assess the relative importance of diet as a route of exposure. Owing to the small volume sampled and relatively high limits of detection, analyte detection frequencies in food samples were low compared to those found in the environmental and clothing samples. The limits of detection for chlorpyrifos and dieldrin reported by Wilson et al. (2003) were almost two orders of magnitude lower than those in this study (0.04 *versus* 1 and 2 ng/g, respectively). These detection limits, however, may not be directly comparable because they were not calculated in the same manner (i.e., detection limits based on signal to noise ratios *versus* detection limits based on spiked matrix replicates).

We developed four field survey instruments (questionnaire, home inspection, food diary, and CAT/recall log) to help characterize children's pesticide exposure pathways. These instruments were well received by the participating families as well as by study staff. In general, the CAT was easy to use and consumed little time. Providing extensive instruction and training to parents gave them confidence in completing the form and improved the quality and reliability of the information attained. A surprising finding based on the CAT data was that all the children in the study spent most of their day inside the home (mean = 21.3 h/day) compared to outside in the yard (mean = 0.9 h/day) or away from home (1.8 h/day). However, this is consistent with the quality of participants' housing, which was generally small and crowded with little or no yard space.

For future studies, we recommend that the CAT be divided to cover shorter time periods (i.e., six instead of 12 h), presented on several sheets to make it less visually crowded, and modified to provide a more complete list of age-specific activities and common locations (e.g., time in daycare, time at school for older children, etc.). In contrast to the CAT, the Recall Log was difficult and time-consuming to complete. Specifically, use of the Recall Log to collect additional information not recorded on the CAT, such as spent on different surface types and clothing worn, was tedious and may have contributed to errors by study staff when coding responses. The Recall Log should be simplified to directly mirror the CAT for all data collected. Finally, it is unlikely that resolution of data about which room the child was in and clothing worn is feasible for time increments less than 30 or 60 min, especially for older children.

Urinary DAP metabolite concentrations reported in this study were similar to levels found in other children. For example, children ages 2–5 living in an agricultural community of Washington State had geometric mean urinary metabolite levels for diethyl and dimethyl phosphates of 36 and 80 nmol/l, respectively (Koch et al., 2002). In another study of Washington children living in an agricultural area, spot urine samples collected from farmworker children ages 2–6 years had median levels of diethyl and dimethyl phosphate metabolites of 60 and 80 nmol/l, respectively (Curl et al., 2002). Finally, median total DAP levels in spot urine samples for our population of 5–27 month old children were similar to NHANES levels for children 6–11 years old (median = 113 nmol/l)(Barr et al. 2004). These populations are not directly comparable, however, due to the differences in their ages.

Dimethyl phosphate metabolite levels were higher than diethyl phosphate metabolites, a finding consistent with previous studies in other populations (Koch et al., 2002; Barr et al., 2004). The molar ratio of dimethyl to diethyl metabolites in the participants' urine was 8:1, which is higher than would be expected given the 3:2 ratio of dimethyl (e.g., malathion) to diethyl (e.g., chlorpyrifos) OP pesticides that is typically used in the Salinas Valley (DPR, 2001, 2002). The discrepancy may be explained by alternate exposure pathways, such as diet and home pesticide use. It is also possible that diethyl pesticides and metabolites degrade more rapidly than dimethyl OP pesticides. This hypothesis is supported by our finding that diethyl phosphates were lower in overnight diaper samples than in spot samples.

We did not observe strong correlations between diethyl phosphate urinary metabolites and levels of diazinon and chlorpyrifos, which devolve to these metabolites, in environmental and personal media. The correlations we do report, although weak to moderate, tended to be more consistent for diazinon compared to chlorpyrifos or the molar sum of diazinon and chlorpyrifos. We have no ready explanation for this finding. It is possible that diazinon in the home environment is more likely to be absorbed, inhaled, or ingested by a child. The overall lack of strong correlations may be due to high variability in the environmental or urinary measurements that would obscure meaningful associations, especially given the small sample size. It is also possible that the diethyl metabolites in the children were due to exposures to other diethyl phosphate metabolites in the environment or diethyl OP pesticides, which are used locally in agriculture. In the future, we intend to measure pesticide-specific metabolites to, at least partially, address this possibility. Finally, one recent study found that diet is the primary source of children's OP pesticide exposure (Lu et al., 2005), suggesting that environmental concentrations may not be associated with exposure biomarkers.

This study has several limitations. First, the study had a small sample size and took place in an agricultural region;

thus observed pesticide exposures cannot be generalized to a larger agricultural or general population. Additionally, the relatively low sensitivity of our analytical methods for food may have reduced the detection frequencies of some pesticides. Future studies using clothing samples should use 100% polyester union suits to avoid the formation of gelatinous flocculates. The flocculate appears to be organic material extracted from the cotton fibers, and thus washing and/or pre-extraction will not reduce this material to an acceptable level. In subsequent work, we have found that extraction of 100% polyester union suits does not yield this flocculate.

We provide unique data on the likely range of pesticide exposures to young children living in an agricultural community and how exposures may differ due to age. The presence of permethrins, chlorpyrifos, diazinon, and chlorthal-dimethyl in most environmental samples suggests that these compounds were ubiquitous in the homes and further research is needed on the environmental fate of these compounds.

In future analyses, we will explore potential relationships between pesticide exposure factors, based on questionnaire, child activity, and home inspection data, and specific and nonspecific urinary OP metabolites. We will also focus on apportioning routes of exposure and estimating relative contributions of exposure media. Additionally, a pesticide exposure model is currently being developed to determine the behavior and activity patterns of children resulting in dermal and nondietary exposure from pesticide residues on surfaces in and around the home environment. These data and models will be used to characterize and assess aggregate exposure in children and to develop exposure and risk assessment models.

Acknowledgements

The United States Environmental Protection Agency through its Office of Research and Development partially funded and collaborated in the research described here under RD 83171001 to the U.C. Berkeley Center for Children's Environmental Health Research. It has been subjected to Agency review and approved for publication. This research was also funded by NIEHS grant PO1 ES009605. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the funding agencies. T. McKone was supported in part by the U.S. EPA National Exposure Research Laboratory through Interagency Agreement DW-988-38190-01-0 with Lawrence Berkeley National Laboratory through the US Department of Energy under Contract Grant No. DE-AC02-05CH11231. The authors declare they have no competing financial interests. We gratefully acknowledge Katherine Kogut for her technical assistance, the field staff, and, especially, the families that participated in this study for their valuable time and commitment.

References

Adgate J.L., Barr D.B., Clayton C.A., Eberly L.E., Freeman N.C., and Lioy P.J., *et al.* Measurement of children's exposure to pesticides: analysis of urinary metabolite levels in a probability-based sample. *Environ Health Perspect* 2001: 109: 583–590.

Aprea C., Strambi M., Novelli M.T., Lunghini L., and Bozzi N. Biologic monitoring of exposure to organophosphorus pesticides in 195 Italian children. *Environ Health Perspect* 2000: 108: 521–525.

ASTM. Standard Practice for Collection of Dust from Carpeted Floors for Chemical Analysis. Standard Practice D 5438–94. *Annual Book of ASTM Standards*, Vol. 11.03. American Society of Testing and Materials, West Conshohoken, PA, 1997, pp. 517–523.

Barr D.B., Barr J.R., Driskell W.J., Hill R.H., Ashley D.L., and Needham L.L., *et al.* Strategies for biological monitoring of exposure for contemporary-use pesticides. *Toxicol Ind Health* 1999: 15(1–2): 168–179.

Barr D.B., Bravo R., Weerasekera G., Caltabiano L.M., Whitehead Jr R.D., Olsson A.O., Caudill S.P., Schober S.E., Pirkle J.L., Sampson E.J., Jackson R.J., and Needham L.L. Concentrations of dialkyl phosphate metabolites of organophosphorus pesticides in the U.S. population. *Environ Health Perspect* 2004: 112(2): 186–200.

Barr D.B., Wilder L.C., Caudill S.P., Gonzalez A.J., Needham L.L., and Pirkle J.L. Urinary creatinine concentrations in the U.S. population: implications for urinary biologic monitoring measurements. *Environ Health Perspect* 2005: 113(2): 192–200.

Berkowitz G.S., Wetmur J.G., Birman-Deych E., Obel J., Lapinski R.H., Godbold J.H., Holzman I.R., and Wolff M.S. In utero pesticide exposure, maternal paraoxonase activity, and head circumference. *Environ Health Perspect* 2004: 112(3): 388–391.

Bradman A., and Whyatt R.M. Characterizing exposures to nonpersistent pesticides during pregnancy and early childhood in the National Children's Study: a review of monitoring and measurement methodologies. *Environ Health Perspect* 2005: 113(8): 1092–1099.

Bradman A., Barr D.B., Claus Henn B.G., Drumheller T., Curry C., and Eskenazi B. Measurement of pesticides and other toxicants in amniotic fluid as a potential biomarker of prenatal exposure: a validation study. *Environ Health Perspect* 2003: 111(14): 1779–1782.

Bradman M.A., Harnly M.E., Draper W., Seidel S., Teran S., and Wakeman D., *et al.* Pesticide exposures to children from California's Central Valley: results of a pilot study. *J Expo Anal Environ Epidemiol* 1997: 7(2): 217–234.

Branum A.M., Collman G.W., Correa A., Keim S.A., Kessel W., Kimmel C.A., Klebanoff M.A., Longnecker M.P., and Mendola P., *et al.* The National Children's Study of environmental effects on child health and development. *Environ Health Perspect* 2003: 111(4): 642–646.

Bravo R., Caltabiano L.M., Weerasekera G., Whitehead R.D., Fernandez C., Needham L.L., Bradman A., and Barr D.B. Measurement of dialkyl phosphate metabolites of organophosphorus pesticides in human urine using lyophilization with gas chromatography-tandem mass spectrometry and isotope dilution quantification. *J Expo Anal Environ Epidemiol* 2004: 14(3): 249–259.

Butte W., and Heinzow B. Pollutants in house dust as indicators of indoor contamination. *Rev Environ Contam Toxico* 2002: 175: 1–46.

Camann D.E., Harding H.J., Clothier J.M., Kuchibhatla R.V., and Bond A.E. Dermal and in-home exposure of the farm family to agricultural pesticides. In: *Proceedings of Measurement of Toxic and Related Air Pollutants Symposium*, 16–18 May 1995, Research Triangle Park, NC. A&WMA Publication VIP-50 Pittsburg, PA: Air and Waste Management Association, 1995 pp. 548–554.

CDC. Second national report on human exposure to environmental chemicals. NCEH Pub. No. 02–0716. Atlanta: Centers for Disease Control and Prevention: National Center Environmental Health, 2003.

Clayton C.A., Pellizari E.D., Whitmore R.W., Quackenboss J.J., Adgate J., and Sefton K. Distributions, associations, and partial aggregate exposure of pesticides and polynuclear aromatic hydrocarbons in the Minnesota Children's Pesticide Exposure Study (MNCPES). *J Expo Anal Environ Epidemiol* 2003: 13: 106–111.

Cohen Hubal E.A., Sheldon L.S., Burke J.M., McCurdy T.R., Berry M.R., Rigas M.L., Zartarain V.G., and Freeman N.C. Children's exposure assessment: a review of factors influencing children's exposure, and the data available to characterize and assess that exposure. *J Expo Anal Environ Epidemiol* 2000a: 10: 638–649.

Cohen Hubal E.A., Sheldon L.S., Zufall M.J., Burke J.M., and Thomas K.W. The challenge of assessing children's residential exposure to pesticides. *Environ Health Perspect* 2000b: 108(6): 475–486.

Cohen Hubal E.A., Suggs J.C., Nishioka M.G., and Ivancic W.A. Characterizing residue transfer efficiencies using a fluorescent imaging technique. *J Expo Anal Environ Epidemiol* 2005: 15: 261–270.

Colt O.S., Lubin J., Camann D., Davis S., Cerhan J., Severson R.K., Cozen W., and Hartge P. Comparison of pesticide levels in carpet dust and self-reported pest treatment practices in four US cities. *J Expo Anal Environ Epidemiol* 2004: 14: 74–83.

Curl C.L., Fenske R., and Elgethun K. Organophosphorus pesticide exposure of urban and suburban preschool children with organic and conventional diets. *Environ Health Perspect* 2003: 111(3): 377–382.

Curl C.L., Fenske R.A., Kissel J.C., Shirai J.H., Moate T.F., Griffith W., Coronado G., and Thompson B. Evaluation of take-home organophosphorus pesticide exposure among agricultural workers and their children. *Environ Health Perspect* 2002: 110(12): A787–A792.

DPR. Endosulfan and chlorthal-dimethyl residues in soil and sediment of Monterey County. Sacramento, CA: Department of Pesticide Regulation, California Environmental Protection Agency, 1988: http://www.cdpr.ca.gov/docs/empm/pubs/ehapreps/eh8806.pdf.

DPR. Pesticide use report, annual 2001, indexed by chemical and by crop. Sacramento, CA: Department of Pesticide Regulation, California Environmental Protection Agency, 2001.

DPR. Pesticide use report, annual 2002, indexed by chemical and by crop. Sacramento, CA: Department of Pesticide Regulation, California Environmental Protection Agency, 2002.

DPR. Study 224: A preliminary assessment of pyrethroid contamination of surface waters and bed sediments in high pyrethroid-use regions of California. Sacramento, CA: Department of Pesticide Regulation, California Environmental Protection Agency. 2004, July 6, 2004. Available: http://www.cdpr.ca.gov/docs/empm/pubs/protocol/prot224.pdf.

Edwards R.D., and Lioy P.J. The EL Sampler: a press sampler for the quantitative estimation of dermal exposure to pesticides in house dust. *J Expo Anal Environ Epidemiol* 1999: 9: 521–529.

Egeghy P.P., Quackenboss J.J., Catlin S., and Ryan P.B. Determinatnts of temporal variability in NHEXAS-Maryland environmental concentrations, exposures, and biomarkers. *J Expo Anal Environ Epidemiol* 2005: 15: 388–397.

Eskenazi B., Bradman A., and Castorina R. Exposures of children to organophosphate pesticides and their potential adverse health effects. *Environ Health Perspect* 1999: 107(3): 409–419.

Eskenazi B., Harley K., Bradman A., Weltzien E., Jewell N.P., Barr D.B., Furlong C.E., and Holland N.T. Association of in utero organophosphate pesticide exposure and fetal growth and length of gestation in an agricultural population. *Environ Health Perspect* 2004: 112(10): 409–419.

Fenske R. Pesticide exposure assessment of workers and their families. *Occup Med* 1997: 12(2): 221–237.

Fenske R., Kedan G., Lu C., Fisker-Andersen J.A., and Curl C.L. Assessment of organophosphorus pesticide exposures in the diets of preschool children in Washington State. *J Expo Anal Environ Epidemiol* 2002a: 12: 21–28.

Fenske R., Lu C., Barr D., and Needham L. Children's exposure to chlorpyrifos and parathion in an agricultural community in Central Washington State. *Environ Health Perspect* 2002b: 5: 549–553.

Fenske R.A., Kissel J.C., Lu C., Kalman D.A., Simcox N.J., Allen E.H., and Keifer M.C. Biologically based pesticide dose estimates for children in an agricultural community. *Environ Health Perspect* 2000a: 108: 515–520.

Fenske R., Lu C., Simcox N.J., Loewenherz C., Touchstone J., Moate T., Allen E.H., and Kissel J.C. Strategies for assessing children's organophosphorus pesticide exposures in agricultural communities. *J Expo Anal Environ Epidemiol* 2000b: 10: 662–671.

FQPA. *Food Quality Protection Act of 1996*, http://www.epa.gov/opppsps1/fqpa/fqpa-iss.htm.

Geno P.W., Camann D.E., Harding H.J., Villalobos K., and Lewis R.G. Handwipe sampling and analysis procedure for the measurement of dermal contact with pesticides. *Arch Environ Contam Toxicol* 1996: 30: 132–138.

Hazardous Substances Data Bank [Internet], Bethesda (MD): National Library of Medicine (US); [Last Revision Date 2002 Nov 8; cited 2005 Sept 27]. Chlorthal-dimethyl; Hazardous Substances Databank Number: 358. 2005, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

Hornung R.W., and Reed L.D. Estimation of average concentration in the presence of nondetectable values. *Appl Occup Env Hyg* 1990: 5(1): 46–51.

Hu Y.A., Barr D.B., Akland G., Melnyk L., Needham L., Pellizzari E.D., Raymer J.H., and Roberds J.M. Collecting urine samples from young children using cotton gauze for pesticide studies. *J Expo Anal Environ Epidemiol* 2000: 10(6 Pt 2): 703–709.

Karmaus W., DeKoning E.P., Kruse H., Witten J., and Osius N. Early childhood determinants of organochlorine concentrations in school aged children. *Pediatr Res* 2001: 50: 322–323.

Koch D., Lu C., Fisker-Andersen J., Jolley L., and Fenske R.A. Temporal association of children's pesticide exposure and agricultural spraying: Report of a longitudinal biological monitoring study. *Environ Health Perspect* 2002: 110: 829–833.

Lambert W.E., Lasarev M., Muniz J., Scherer J., Rothlein J., Santana J., and McCauley L. Variation in organophosphate pesticide metabolites in urine of children living in agricultural communities. *Environ Health Perspect* 2005: 113(4): 504–508.

Lewis R.G., Fortmann R.C., and Camann D.E. Evaluation of methods for monitoring the potential exposure of small children to pesticides in the residential environment. *Arch Environ Contam Toxicol* 1994: 26(1): 37–46.

Loewenherz C., Fenske R.A., Simcox N.J., Bellamy G., and Kalman D. Biological monitoring of organophosphorus pesticide exposure among children of agricultural workers in central Washington State. *Environ Health Perspect* 1997: 105(12): 1344–1353.

Lu C., Fenske R.A., Simcox N., and Kalman D. Pesticide exposure of children in an agricultural community: evidence of household proximity to farmland and take home exposure pathways. *Environ Res* 2000: 84(3): 290–302.

Lu C., Knutson D.E., Fisker-Andersen J., and Fenske R.A. Biological monitoring survey of organophosphorus pesticide exposures among pre-school children in the Seattle metropolitan area. *Environ Health Perspect* 2001: 109: 299–303.

Lu C., Toepel K., Irish R., Fenske R.A., Barr D.B., and Bravo R. Organic diets significantly lower children's dietary exposure to organophosphorus pesticides. *Environ Health Perspect* 2005; doi:10.1289/ehp.8418. [Online 1 September 2005] http://ehp.niehs.nih.gov/docs/2005/8418/abstract.html.

McCauley L.A., Lasarev M.R., Higgins G.R., Muniz J., Ebbert C., and Phillips J. Work characteristics and pesticide exposure among migrant agricultural families: a community-based research approach. *Environ Health Perspect* 2001: 109(5): 533–538.

National Research Council (NRC). *Pesticides in the Diets of Infants and Children*. Washington: National Academy Press, 1993.

O'Rourke M.K., Lizardi P.S., Rogan S.P., Freeman N.C., Aguirre A., and Saint C.G. Pesticide exposure and creatinine variation among young children. *J Expo Anal Environ Epidemiol* 2000: 10: 672–681.

Quandt S.A., Arcury T.A., Rao P., Snively B.M., Camann D.E., Doran A.M., Yau A.Y., Hoppin J.A., and Jackson D.S. Agricultural and residential pesticides in wipe samples from farmworker family residences in North Carolina and Virginia. *Environ Health Perspect* 2004: 112(3): 382–387.

Rawn D.K., and Muir D.C.G. Sources of chlorpyrifos and dacthal to a small Canadian priarie watershed. *Environ Sci Technol* 1999: 33: 3317–3323.

Roberts J.W., Budd W.T., and Ruby G. A small high volume surface sampler (HVS3) for pesticides, lead and other toxic substances in house dust. In: *Proceedings of the Annual Meeting of the Air and Waste Management Association*. Pittsburg, PA, 1991.

Rosenblum L., Hieber T., and Morgan J. Determination of pesticides in composite dietary samples by gas chromatography/mass spectrometry in the selected ion monitoring mode by using a temperature-programmable large volume injector with preseparation column. *J AOAC Int'l* 2001: 84(3): 891–900.

Ross L.J., Nicosia S., McChesney M.M., Hefner K.L., Gonzalez D.A., and Seiber J.N. Volatilization, off-site deposition, and dissipation of DCPA in the field. *J Environ Qual* 1990: 19: 715–722.

Shealy D.B., Bonin M.A., Wooten J.V., Ashley D.L., Needham L.L., and Bond A.E. Application of an improved method for the analysis of pesticides and their metabolites in the urine of farmer applicators and their families. *Environ Int* 1996: 22(6): 661–675.

Simcox N.J., Fenske R.A., Wolz S.A., Lee I.C., and Kalman D.A. Pesticides in household dust and soil-exposure pathways for children of agricultural families. *Environ Health Perspect* 1995: 103(12): 1126–1134.

Starr H.G., Aldrich F.D., McDougall W.D., and Mounce L.M. Contribution of household dust to the human exposure to pesticides. *Pesticides Monitoring J* 1974: 8(3): 209–212.

Thompson B., Coronado G.D., Grossman J.E., Puschel K., Solomon C.C., and Islas I., *et al.* Pesticide take-home pathway among children of agricultural

workers: study design, methods, and baseline findings. *J Occup Environ Med* 2003: 45: 42–53.

U.S. EPA. *Chlorpyrfos revised Risk Assessment and Agreement with Registrants. Office of Prevention, Pesticides, and Toxic Substances (7506C)*. U.S. Environmental Protection Agency. Washington, DC, 2000: http://www.epa.gov/pesticides/op/chlorpyrifos/agreement.pdf.

U.S. EPA. *Diazinon revised Risk Assessment and Agreement with Registrants. Office of Prevention, Pesticides, and Toxic Substances (7506C)*. U.S. Environmental Protection Agency. Washington, DC, 2001: http://www.epa.gov/pesticides/op/diazinon/agreement.pdf.

USGS. *Atmospheric Transport of Pesticides in the Sacramento, California, Metropolitan Area, 1996–1997*. U.S. Geological Survey Water Resources Investigations Report 02–4100 USGS. Sacramento, CA, 2002.

Westgard J.O. Westgard qc: Tools, technology, and training for healthcare laboratories, 2003: http://www.westgard.com[accessed January 10 2003].

Whitmore R.W., Immerman F.W., Camann D.E., Bond A.E., Lewis R.G., and Schaum J.L. Non-occupational exposures to pesticides for residents of two U.S. cities. *Arch Environ Contamin Toxicol* 1994: 26: 47–59.

Whyatt R.M., Rauh V., Barr D.B., Camann D.E., Andrews H.F., Garfinkel R., Hoepner L.A., Diaz D., Dietrich J., Reyes A., Tang D., Kinney P.L., and Perera F.P. Prenatal insecticide exposures and birth weight and length among an urban minority cohort. *Environ Health Perspect* 2004: 112(10): 1125–1132.

Wilson N.K., Chuang J.C., Iachan R., Lyu C., Gordon S.M., Morgan M.K., Ozkaynak H., and Sheldon L. Design and sampling methodology for a large study of preschool children's aggregate exposures to persistent organic pollutants in their everyday environments. *J Expo Anal Environ Epidemiol* 2004: 14: 260–274.

Wilson N.K., Chuang J.C., Lyu C., Menton R., and Morgan M.K. Aggregate exposures of nine preschool children to persistent organic pollutants at day care and at home. *J Expo Anal Environ Epidemiol* 2003: 13(3): 187–202.

Young J.G., Eskenazi B., Gladstone E.A., Bradman A., Pedersen L., Johnson C., Barr D.B., Furlong C.E., and Holland N.T. Association between in utero organophosphate pesticide exposure and abnormal reflexes in neonates. *Neurotoxicology* 2005: 26(2): 199–209.