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Farmworker children's residential non-dietary exposure estimates from micro-level activity time series

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ABSTRACT

Farmworkers' children may have increased pesticide exposure through dermal absorption and non-dietary ingestion, routes that are difficult to measure and model. The Cumulative Aggregate Simulation of Exposure (CASE) model, integrates the complexity of human behavior and variability of exposure processes by combining micro-level activity time series (MLATS) and mechanistic exposure equations. CASE was used to estimate residential non-dietary organophosphate pesticide exposure (i.e., inhalation, dermal, and non-dietary ingestion) to California farmworker children and evaluate the micro-activity approach. MLATS collected from children and distributions developed from pesticide measurements in farmworkers' residences served as inputs. While estimated diazinon exposure was greater for inhalation, chlorpyrifos exposure was greater for the other routes. Greater variability existed between children ($\sigma^2_B = 0.22–0.39$) than within each child's simulations ($\sigma^2_W = 0.01–0.02$) for dermal and non-dietary ingestion. Dermal exposure simulations were not significantly different than measured values from dosimeters worn by the children. Non-dietary ingestion exposure estimates were comparable to duplicate diet measurements, indicating this route may contribute substantially to aggregate exposure. The results suggest the importance of the micro-activity approach for estimating non-dietary exposure. Other methods may underestimate exposure via these routes. Model simulations can be used to identify at-risk children and target intervention strategies.

1. Introduction

The Food Quality Protection Act (FQPA) of 1996 requires the United States Environmental Protection Agency (US EPA) set pesticide food tolerances accounting for aggregate (multiple route) and cumulative (multiple chemicals exhibiting a common mechanism of toxicity) exposures through drinking water, dietary and non-dietary pathways with an emphasis on children. Compared to adults, young children are more susceptible to pesticide exposure due to their unique activities and physiological characteristics. They more frequently mouth their hands and objects and spend more time playing and crawling on the floor, which may lead to increased non-dietary exposure to contaminants (Goldman, 1998; Lewis et al., 1994; Tulve et al., 2002; Zartarian et al., 1998). Physiologically, young children are more susceptible to adverse health effects due to their developing organs, nervous and immune systems, low body weights and high exertion levels (Crom, 1994; Milsap and Jusko, 1994). Farmworkers' children may have higher levels of pesticides in their residential environments compared to children from non-agricultural families, which may be due to aerosol drift or occupational take-home contamination on clothing, shoes or skin (Arcury et al., 2006; Bradman et al., 1997, 2007; Curl et al., 2002; Eskenazi et al., 1999; Fenske et al., 2000b, 2002, 2005; Fenske, 1997; Lambert et al., 2005; McCauley et al., 2001; Petchuay et al., 2006; Simcox et al., 1995).

In response to the FQPA, US EPA identified dermal and non-dietary ingestion exposure assessments as high priorities (Cohen Hubal et al., 2000). These exposure routes are difficult to measure due to complex human behavior and exposure mechanisms (Fenske, 1993; Van Hemmen and Brouwer, 1995; Zartarian and Leckie, 1998) and modeling requires detailed mouthing and dermal contact activity data. Videotaping methods to obtain micro-activity data (Ferguson et al., 2006; Zartarian et al., 1997) and the Cumulative Aggregate Simulation of Exposure (CASE) model that utilizes this data to estimate non-dietary exposure have been previously developed (Canales and Leckie, 2007). Specifically, micro-level activity time series (MLATS) preserve the sequence of contact events and locations visited by a child, providing the basis for CASE calculations (Fig. 1).

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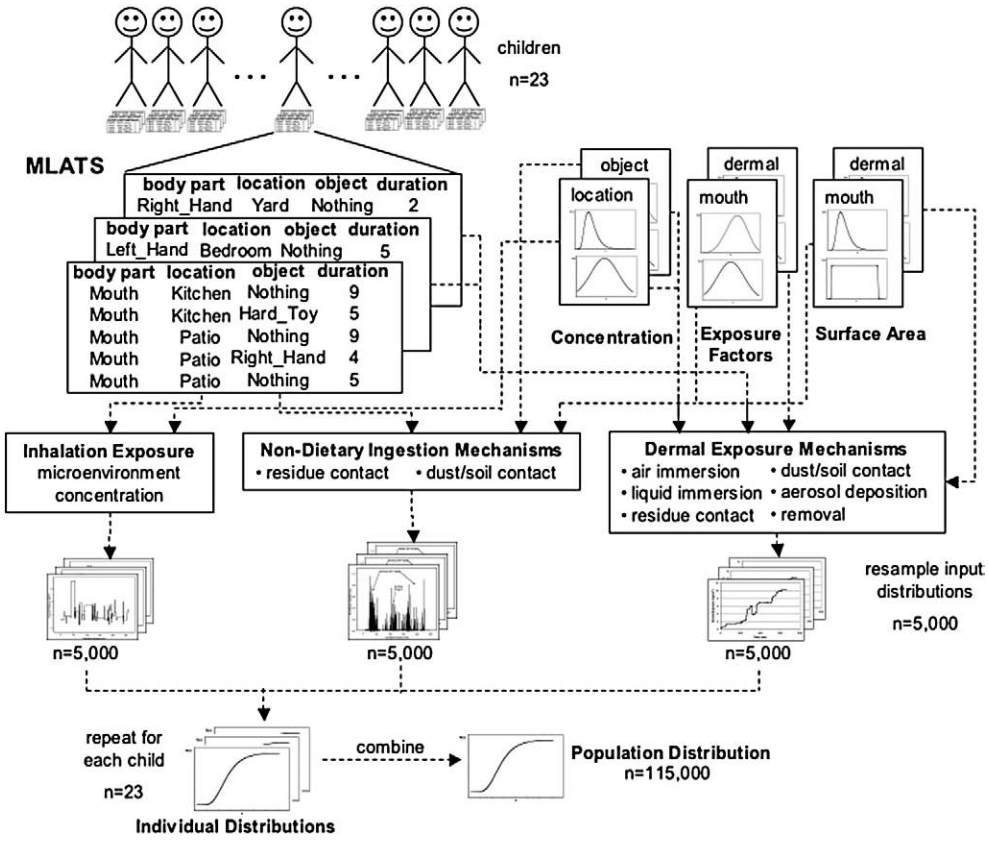

Fig. 1. CASE Framework. Each contact represented by a line in the MLATS is assigned an exposure mechanism corresponding to a unique equation. Concentration and exposure factor input distributions are sampled to generate exposure profiles for each MLATS. To propagate uncertainty and variability, 5000 simulations were conducted for each MLATS to generate 23 individual exposure distributions that were combined to generate a population distribution with 115,000 exposure scenarios.

Each line of a MLATS file represents a new mouth or hand contact with an object and is assigned an exposure mechanism corresponding to a specific equation in CASE (i.e., air immersion, liquid immersion, residue contact, soil/dust adherence, aerosol deposition, and removal) (Canales and Leckie, 2007). Incorporation of micro-activity data and multiple exposure mechanisms into CASE allows for a more detailed representation of dermal and non-dietary ingestion exposure not possible from other forms of activity data (Cohen Hubal et al., 2000; Tulve et al., 2002). Stochastic inputs and Monte Carlo simulations can yield estimates of individual and population exposure distributions. By preserving the sequence of loading and removal actions in MLATS, resulting exposure profiles from model simulations can highlight which micro-activities lead to significant exposures and aid development of intervention strategies.

The goal of this paper is a methodological evaluation of the micro-activity approach by using CASE to estimate residential exposure to the organophosphate pesticides chlorpyrifos and diazinon for a population of farmworkers' children in the Salinas Valley of California. These pesticides were chosen because of their historical residential and continuing agricultural use, common mechanism of toxicity (inhibition of acetylcholinesterase and developmental neurotoxicity), prevalence in residential environments and density of available literature data necessary to provide model input parameters (Bradman et al., 2007; Morgan et al., 2005; Pang et al., 2002; Rudel et al., 2003; Slotkin and Seidler, 2007). MLATS collected from the children ($n=23$) in conjunction with residential pesticide concentrations measured in farmworker residences ($n=20$) served as inputs (Beamer et al., 2008; Bradman et al., 2007). This work provides an evaluation of the micro-activity approach and is the first published example in the peer-reviewed literature that micro-activity data and environmental measurements collected simultaneously have been combined in a modeling framework to estimate non-dietary exposures with results compared to concurrent exposure measurements from the population.

2. Methods

CASE, a physical-stochastic model, combines equations describing physical exposure processes with parametric distributions of environmental concentrations (e.g., contaminants in indoor air, dust, and on surfaces) and exposure factors (e.g., transfer efficiency, soil-skin adherence, and contact area) for each contact in an MLATS file to yield exposure profiles (Fig. 1). Model construct, equations and output options, developed in accordance with exposure and contact boundary definitions presented in Zartarian et al. (Zartarian et al., 1997), have been discussed elsewhere (Canales and Leckie, 2007). MLATS are imported directly into the CASE modeling environment. The user assigns exposure mechanisms and input parameters for each location and object in the MLATS file. Input parameters can be point-estimates, empirical or parametric distributions allowing us to propagate model input variability through Monte Carlo simulations and generate individual and population exposure distributions.

2.1. Activity pattern collection

MLATS for these simulations were collected, according to previously developed and standardized methods, from farmworkers' children in the Salinas Valley of California during summer 2001 (July–October) and 2002 (June–August) (Beamer et al., 2008). All 23 participating children (8 female and 5 male infants (6–13 months of age), 5 female and 5 male toddlers (20–26 months of age) were videotaped at home for approximately 4 h ($\mu=4$; $\sigma=0.6$). Video footage was translated into MLATS for both hands and the mouth using Virtual Timing Device™ software (Beamer et al., 2008; Ferguson et al., 2006).

MLATS were edited for computational efficiency. Repetitive contacts were assumed to alternate between contacts with the surface/object and air ("Nothing") at the rate of two contacts per second (Beamer et al., 2008; Ferguson et al., 2006). All occurrences of "Not_In_View" were also changed to nothing for both non-dietary ingestion and dermal exposure simulations.

2.2. Environmental concentration distributions

Only during the second summer (June–August 2002), were pesticides measured in indoor and outdoor air, surface and toy wipes, house dust, duplicate diets, and union suit and sock dosimeters for 20 children residing in the Salinas Valley, including 11 who were videotaped for MLATS. However, the children did not wear the dosimeters while being videotaped. One sample of each media type was taken in each home. Chlorpyrifos and diazinon were detected in all media. Details on sampling procedures and analyses are presented elsewhere (Bradman et al., 2007). Agricultural use of chlorpyrifos and diazinon is widespread throughout the Salinas Valley (McKone et al., 2007), yet there is likely high variability of contamination within each home (Egeghy et al., 2004). The objective was to estimate and characterize the variability of non-dietary pesticide exposure of farmworkers' children as a population, and not of each child individually from their own home measurements as has been done previously (Bradman et al., 2007). Since families reported no residential applications of these pesticides (Bradman et al., 2007), measurements of chlorpyrifos and diazinon from the homes were assumed to represent variability that children in this unique population might encounter within their homes and throughout the Salinas Valley. Pesticide concentration probability distributions were developed from house dust, toy wipes, and air measurements (Table 1). Kolmogorov–Smirnov goodness-of-fit tests confirmed that all pesticide measurements were log-normally distributed.

While the MLATS provide detailed data on microenvironments visited and objects contacted, environmental concentrations collected from the farmworker homes were not obtained for each of the unique microenvironments or objects. Therefore, several assumptions were made in selecting the distributions for location and object concentrations. The 9 unique location categories visited by the children were grouped into indoor (bathroom, bedroom, kitchen, and living room/den) and outdoor (garage, patio, street/sidewalk, vehicle, and yard) locations. Distributions for object/surface concentrations were assigned according to the exposure mechanism and are described in the next section.

2.3. Assignment of exposure mechanisms

Because none of the families reported directly applying pesticides in their homes, it was assumed that the predominant pathways of residential contamination would be aerosol drift from agriculture and occupational take-home contamination on the parents' clothing, shoes or skin (Bradman et al., 1997; Eskenazi et al., 1999; Fenske et al., 2000a, 2002). Most likely, pesticides in homes would be adhered to soil or dust rather than as direct residues. Therefore, the majority of objects were assigned to the soil/dust adherence mechanism and house dust concentration distributions (Table 1) were used for contaminant loading. These objects are: animal, floors, dirt, toys, footwear, paper, vegetation, fabric, metal, rock/brick and plastic surfaces.

Wipes were taken from toys given to the children by researchers that had been in the houses for only a few days (Bradman et al., 2007). Wipes were assumed to represent contaminant loading for surfaces that are cleaned more frequently (i.e., food containers, body, head, clothes, and towel/washcloth). These objects, along with hands when assessing non-dietary ingestion exposure, were assigned to the residue transfer mechanism. Hand concentration values for hand-to-mouth contacts were sampled from each child's unique empirical dermal loading distribution from left and right hand simulations.

Concentration distributions were developed by excluding samples below the limit of detection (LOD). However, the CASE framework samples from the lower tail of the distribution extending below the LOD according to the proportion of the original non-detectable values. Chlorpyrifos was only detected in 35% of the toy wipes. To avoid bias in distribution development, non-detectable observations were replaced with random numbers between 0 and the limit of detection prior to distribution development.

Hand or mouth contacts with food were assumed to result in no non-dietary residential exposure. Hand contacts with "Nothing" were assigned to the air immersion mechanism for dermal exposure simulations with air concentration corresponding to the current microenvironment. Hand contacts with the mouth and water were assumed to result in a reduction in dermal exposure through the removal mechanism.

2.4. Exposure factor distributions

Exposure factor values (Table 2) were obtained from relevant experimental data in the literature, assumed, or derived from related experimental data (Beamer et al., 2009; Yamamoto et al., 2006; Zartarian et al., 2005; Zartarian, 1996). Exposure factors were assumed to be pesticide-independent. Lognormal probability distributions for

Table 1
Environmental concentration distributions developed from pesticide measurements taken in the farmworker homes (GM = geometric mean, GSD = geometric standard deviation, df = detection frequency).[a]

	Chlorpyrifos			Diazinon		
	df	GM	GSD	df	GM	GSD
Indoor air concentration [ng/m^3][a]	100	1.8	1.6	100	2.5	2.7
Outdoor air concentration [ng/m^3][a]	85	1.1	1.9	100	3.3	2.6
House dust [ng/g][b]	95	61.8	3.3	100	21.6	3.3
Toy wipe [ng/cm^2][c]	30	185.4	4.6	60	153.5	3.1

[a] Limit of detection (LOD) was 1 ng total for both pesticides for indoor and outdoor air.
[b] LOD was 2 ng/g for both pesticides in house dust.
[c] LOD was 5 and 2 ng total for chlorpyrifos and diazinon in wipe samples.

Table 2
Distributions representing exposure factors for CASE simulations (see supporting information).

Exposure factor	Distribution[a]	Parameter 1	Parameter 2	Source
Soil/dust-to-skin adherence [g/m^2]	Weibull	0.79	0.15	Yamamoto et al. (2006)[b]
Residue transfer [−]				
Rough objects	Lognormal	−4.26	0.54	Beamer et al. (2009)
Smooth objects	Lognormal	−3.30	0.85	Beamer et al. (2009)
Air zone height [m]	Uniform	0.001	0.003	Zartarian (1996)
Hand-washing removal [−]	Beta	32	22	Zartarian et al. (2005)
Residue-to-mouth removal [−]	Beta	14.5	4.1	Zartarian et al. (2005)
Soil/dust-to-mouth removal [g/m^2]	Weibull	0.79	0.15	Current study[c]
Hand contact surface area [m^2]	Uniform	0.1	0.5	Current study
Mouthing surface area [m^2]	Uniform	0.00078	0.0022	Current study

[a] Distribution (parameter 1, parameter 2) = [beta (shape 1, shape 2), lognormal, (lognormal mean, SD), normal (mean, SD), uniform (min, max), Weibull (shape, scale)].
[b] Yamamoto et al. (2006) divided by 7.
[c] Derived by multiplying dust–skin adherence distribution with mouthing residue removal efficiency distribution.

dermal residue transfer efficiency were developed for chlorpyrifos from carpet, vinyl and foil surfaces previously (Beamer et al., 2009). Dermal residue transfer efficiency from carpets was assumed to represent textured surfaces (i.e., head, hands, and body), while the distribution for vinyl could be used to represent smooth surfaces (food container).

Studies have demonstrated that particles adhered to hands are generally < 63 μm in size (Choate et al., 2006; Yamamoto et al., 2006), thus the same distribution was used for soil and dust adherence. Yamamoto et al. (2006) present a distribution for soil/dust adhered to children's hands following playing. Cohen Hubal et al. (2005) report that there is negligible transfer after 7 hand contacts. Therefore, the values presented by Yamamoto et al. (2006) were divided by 7 to develop the soil/dust adherence distribution for individual contacts.

The air contact zone height is a necessary parameter for estimation of dermal exposure from air immersion. It is defined as the height in which any molecule has a 100% probability of intersecting the skin contact boundary in the specified time interval (Zartarian, 1996; Zartarian et al., 1997). Based on dermal contact times of 5–50 s with "Nothing" from an earlier videotape translation study of farmworker children (Zartarian et al., 1997) and a diffusivity of 0.01 cm^2/s for gases in air (Cussler, 1984; Schwarzenbach et al., 1993), Zartarian (1996) estimated a range of 1–3 cm for the air contact zone height using film theory, penetration theory and surface renewal theory. As not much information is known on this parameter, a uniform distribution was assumed for this parameter, bound by the range calculated above.

Distributions of mouthing removal of residues and removal by washing hands were obtained from Zartarian et al. (2005). Data for mouthing removal of dust/soil from hands and/or objects are scarce (Canales, 2004). These values are different from the unitless mouthing removal of residues, because they have units of mass per area, similar to dust-to-skin adherence. The dust adherence distribution (Yamamoto et al., 2006) was multiplied by the mouthing removal distribution (Zartarian et al., 2005) using a Monte Carlo simulation to construct a distribution for mouthing removal of dust/soil.

Data is scarce for the contact-specific surface area for each mechanism. A uniform distribution of 0.1 to 0.5 was assumed for fractional surface area for hand contacts with all objects including the mouth, based on experience with translating MLATS from a study of suburban children for surface area (Ferguson et al., 2006). This represents that either the front or back of the hand is in contact with an object, and this contact can range from a full hand press to just contact with the finger tips. Mouthing contact-specific surface area data for adults were obtained (Leckie et al., 2000) that were adjusted for children using allometric methods (O'Flaherty, 1994).

2.5. Aggregate cumulative exposure simulations and data analysis

CASE was used to estimate farmworkers' children residential exposure to chlorpyrifos and diazinon simultaneously. Monte Carlo simulations were conducted, using input distributions representing exposure factors and environmental concentrations for chlorpyrifos and diazinon, for each MLATS file to obtain individual exposure distributions for each route. To achieve stability in results, 5000 simulations were completed for each child, resulting in 115,000 unique exposure scenarios that were combined to obtain population exposure distributions (Fig. 1). MLATS files for mouthing behavior were utilized to estimate hourly non-dietary ingestion and temporally-averaged inhalation exposure, while hand-specific temporally-averaged dermal exposure was estimated from left and right hand MLATS individually. Although person-oriented simulations were not completed where each child's exposures were only calculated based on the environmental measurements from their own homes, the variability within and between the simulations for each child was examined to understand the role of environmental concentrations and MLATS in the overall variability observed in the population. Within-individual variance and between-individual variance were calculated using log transformed values according to Rappaport (Rappaport, 2000). The exposure simulations were tested for differences between age groups (i.e., infants and toddlers) and gender using the Wilcoxon rank sum test.

3. Results

3.1. Inhalation exposure

Temporally-averaged inhalation exposure estimates for the farmworkers' children population are depicted in Fig. 2. Median estimated inhalation exposure for the population was 1.8 and 4.0 ng/m^3 for chlorpyrifos and diazinon, respectively. Within-child variability ($\sigma_W^2 = 0.04–0.18$) was higher than between-child variability ($\sigma_B^2 = 0.003–0.02$). See supplementary material for complete results.

3.2. Dermal exposure

Temporally-averaged right hand dermal exposure estimates are presented in Fig. 3. The median estimated chlorpyrifos dermal exposure for the population was 0.094 and 0.075 ng/cm^2 for the left and right hands, respectively. Estimated dermal exposure from diazinon was lower, with the median for the population equal to 0.041 and 0.032 ng/cm^2 for the left and right hands, respectively. For dermal exposure, there was a much greater variability between children ($\sigma_B^2 = 0.22–0.39$) and much smaller variability within each child's distribution ($\sigma_W^2 = 0.01–0.02$) compared to inhalation exposure. Given that the same pesticide concentration and exposure factor distributions were used for each child, and the variability in simulations within each child due to resampling was small, the differences between the children are most likely attributed to their individual activity patterns. The chlorpyrifos dermal loading profile of a right hand of a twelve-month-old crawling boy is shown in Fig. 4. Dermal loading on his hand arises from spending time crawling outdoors. He also had removal from mouthing his hands, resulting in non-dietary exposure.

3.3. Non-dietary ingestion exposure

Hourly non-dietary ingestion exposure estimates are depicted in Fig. 5. Median estimated non-dietary ingestion exposure for the population was 27.9 and 15.5 ng/h for chlorpyrifos and diazinon, respectively. Fig. 6 illustrates the non-dietary ingestion exposure profile for a 20-month old child, highlighting that many events resulting in non-dietary ingestion exposure occurred within a short period of time. The activities with the largest contribution to his non-dietary ingestion exposure were eating with hands, and sucking fingers while watching television. As with dermal exposure, there was much greater between-child variability ($\sigma_B^2 = 0.36–0.37$) compared to smaller within-child variability ($\sigma_W^2 = 0.01–0.02$). This again illustrates that differences between children's exposure estimates are most likely attributed to their unique activity patterns preserved in the MLATS file.

3.3. Population sub-group differences

Infants had significantly higher estimated left hand dermal exposure for chlorpyrifos (p-value = 0.01) and diazinon (p-value = 0.01) than toddlers. No other

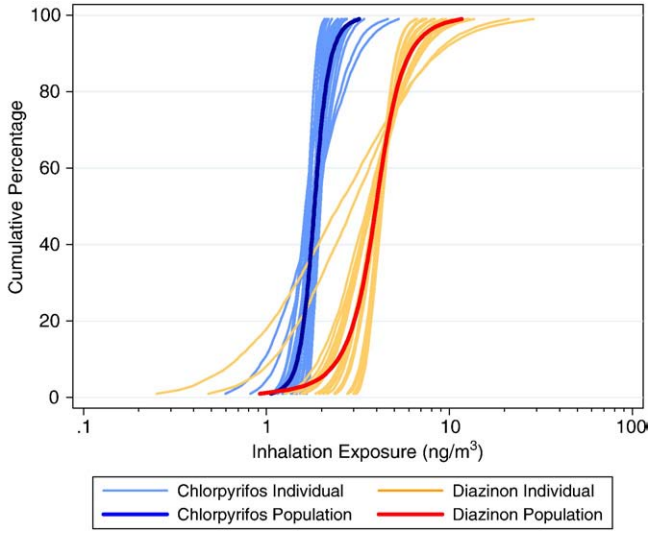

Fig. 2. Cumulative diazinon and chlorpyrifos inhalation exposure distributions for each of the 23 farmworker children ($n = 5000$) and population simulations ($n = 115,000$).

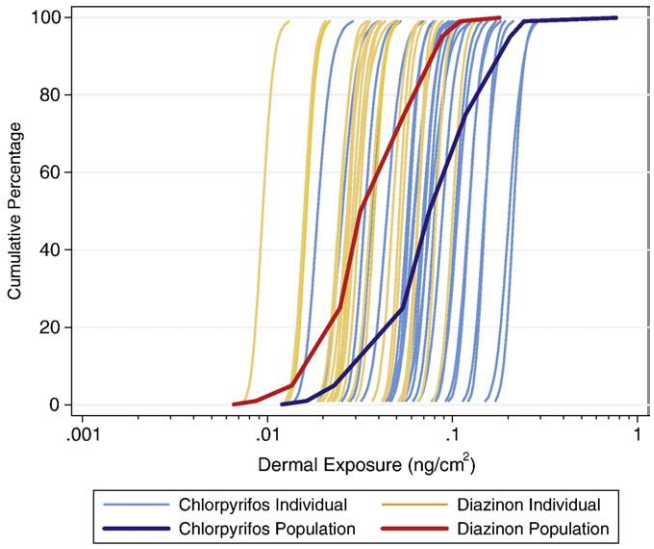

Fig. 3. Cumulative diazinon and chlorpyrifos right hand dermal exposure distributions for each of the 23 farmworker children ($n=5000$) and population simulations ($n=115{,}000$).

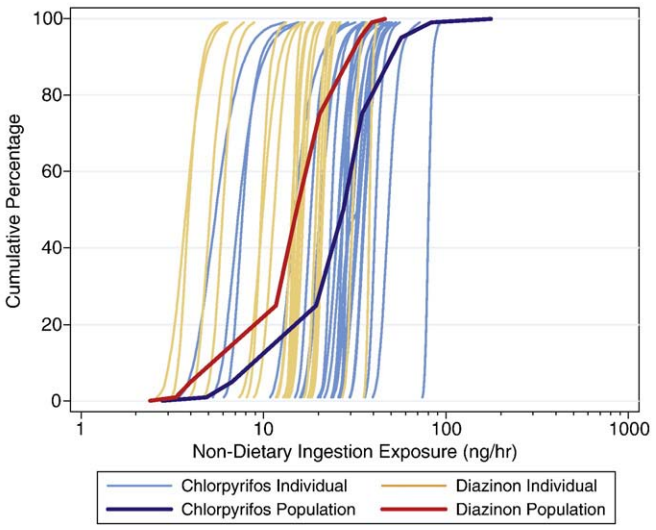

Fig. 5. Cumulative diazinon and chlorpyrifos non-dietary ingestion exposure distributions for each of the 23 farmworker children ($n=5000$) and population simulations ($n=115{,}000$).

significant differences were found for any exposure routes as a function of age or gender.

4. Discussion

CASE was used to estimate residential exposures to pesticides in a population of farmworkers' children. While diazinon exposure was higher for the inhalation route, chlorpyrifos exposure was higher for other routes (dermal and non-dietary ingestion). Diazinon had a higher concentration in both indoor and outdoor air compared to chlorpyrifos. During the sampling year 24,104 kg of chlorpyrifos compared to 65,032 kg of diazinon were applied in Monterey County for agricultural use (DPR, Cal EPA, 2002). In addition, diazinon has a higher vapor pressure than chlorpyrifos (0.012 vs. 0.0027 Pa). The outdoor concentration of diazinon was higher than the indoor concentration of diazinon, indicating that there was a significant outdoor source such as use in nearby agricultural fields. Chlorpyrifos has lower vapor pressure and is likely adhered to aerosols, dust and soil in the fields and contributing more to take-home contamination on the clothes and shoes of farmworkers. This may lead to higher concentrations of chlorpyrifos in house dust and on surfaces and increased dermal and non-dietary ingestion exposure compared to diazinon.

Because the same input distributions were used for simulating exposure for each child, variation in children's individual exposure distributions is mostly a result of differences in the children's unique MLATS. Due to the large between-child variability for both non-dietary ingestion and dermal exposure routes, multimodal distributions were obtained for population estimates (Figs. 3 and 5). For example, one child (Fig. 4) had high dermal exposures from crawling outdoors, resulting in abrupt slope changes at very high dermal exposure estimates (Fig. 3). Similarly, the children with the higher non-dietary ingestion exposure estimates contributed to the slope change observed at the higher non-dietary ingestion values (Fig. 6). All of the population distributions for each route are skewed, with low median values relative to long upper tails of the distributions. Thus the most at-risk children may have much higher exposures than the majority of the children. MLATS were only recorded for 4 h. Longer durations or multiple video collection of the same child at different times of day may reduce inter-individual variability as a result of capturing more activities. Observation of multimodal distributions likely indicates that additional MLATS recorded for longer durations may aid in fully characterizing the range of children's behaviors for this population.

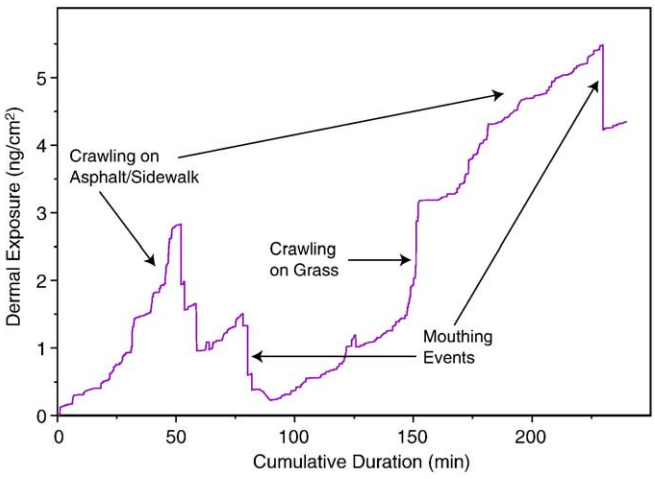

Fig. 4. Chlorpyrifos dermal right hand exposure profile for a 12 month old male child.

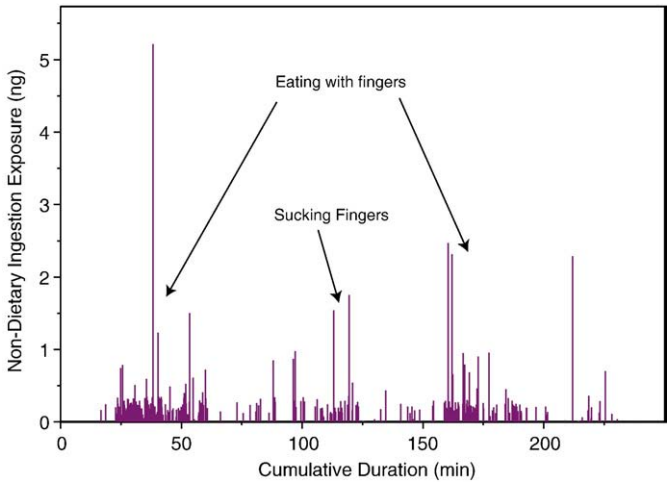

Fig. 6. Diazinon non-dietary ingestion exposure profile for a 20 month old male child.

While MLATS provide detailed data on microenvironments visited and objects contacted, the environmental concentration data were not measured with the same level of detail. In the future, if environmental concentrations are sampled from a wider variety of microenvironments and objects, more comprehensive exposure estimates could be obtained and used to assess the importance of children's activities on their exposure. Another limitation of this study is that environmental concentration distributions were developed from measured values taken in several homes. As a result, variability in these distributions is a representation of variability in environmental concentrations between homes and not of variability that might be observed within each home. Additionally, better experimental measures of exposure factors may reduce uncertainty in these exposure estimates.

Uncertainty was propagated for each of the exposure equations used in the CASE simulations based on uncertainty associated with concentration and exposure factor measurements according to error analysis theory (Bevington, 1969; Meyer, 1975). The relative uncertainty was 7% for inhalation, 10–13% for non-dietary ingestion, and 11–16% for dermal exposure calculations. These values are small compared to the range of values observed individually (see supporting information) and for the population. An uncertainty analysis could also be completed to assess treatment of values < LOD. Although the theoretical distribution was extended below the LOD, and sampled in proportion to the number of non-detected values other treatments could include assuming that values < LOD are equal to zero, half the LOD or the LOD. Future work will entail completing 2-dimensional Monte Carlo simulations to assess uncertainty associated with exposure factor estimates (i.e., air contact zone height, transfer efficiency, soil/dust adherence, and mouthing removal), assignment of objects to exposure mechanisms, duration of MLATS, and sampling techniques to identify which variables would benefit most from uncertainty reduction to ultimately reduce uncertainty in the exposure estimates.

Concurrent pesticide exposure and environmental measurements with videotaping, provide a unique opportunity to evaluate the estimates from CASE. Unfortunately, hand wipe samples were not taken of these children. However, the dermal exposure estimates from CASE were not statistically significant (Wilcoxon rank sum test) from measured loadings of chlorpyrifos and diazinon on sock dosimeters worn by the same children (Fig. 7). The similarity between modeled and measured values in the same children indicates success of CASE and the micro-activity approach in estimating dermal exposure at the population level.

Each exposure route is measured and quantified in different units due to differences in the contact boundary, making it difficult to compare relative contribution of each exposure route (Zartarian et al., 1997). Child respiratory rates were used from the US EPA Child-Specific Exposure Factor Handbook (CS-EFH) to estimate inhalation intake for each child (US EPA, 2008). Estimated median inhalation intake for the farmworker children population was 0.6 and 1.0 ng/h for chlorpyrifos and diazinon, respectively. This is low relative to the estimated median non-dietary ingestion intake of 27.9 and 15.5 ng/h for chlorpyrifos and diazinon. Twenty-four hour duplicate diets were collected from the children at the time of pesticide sampling in the home. However, only 4 and 2% of the duplicate diet samples had detectable values for chlorpyrifos and diazinon, due to dilution from aggregated samples. Substituting the detection limit divided by the square root of 2 for samples below the detection limit (Bradman et al., 2007), a potential median dietary intake of 24 (range = 4–118) and 15 (range = 4–80) ng/h was calculated for chlorpyrifos and diazinon respectively. Considering that these are relatively conservative estimates of dietary exposure, it is likely that non-dietary ingestion exposure may contribute substantially more than other routes to aggregate exposure in this population of farmworker children. Future work entails development of a pharmacokinetic model to assess route contribution to uptake of pesticides including dermal exposure.

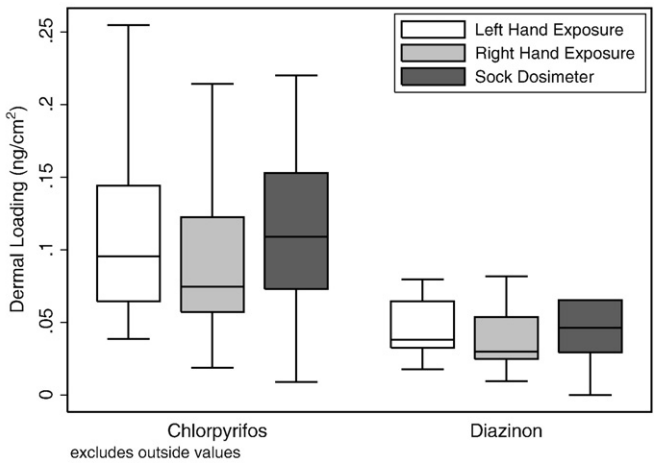

Fig. 7. Comparison of dermal exposure estimates from CASE with measured dermal loading measurements from QEA via a sock dosimeter.

The findings were consistent with other studies of residential inhalation pesticide exposure. Clayton et al. (2003) measured pesticide concentrations in personal air for 102 children in Minnesota. The median personal air concentration was 1.58 and 0.28 ng/m^3 for chlorpyrifos and diazinon, respectively. While the personal air concentration for chlorpyrifos is quite close to the median estimated value from the present study, the personal air concentration for diazinon is much lower than the estimated median value from the present study. This discrepancy may be due to heavy agricultural diazinon use in Monterey County (65,032 kg for the year 2002) where the Salinas Valley is located (DPR, Cal EPA, 2002). No agricultural use of diazinon in Minnesota has been reported for the years 1990–2006 (NASS, USDA, 2008). Morgan et al. (2005) estimated inhalation intake of chlorpyrifos based on measured indoor and outdoor concentrations, the amount of time children spent in those locations, a ventilation rate of 6.8 m^3/day and 50% absorption across the lungs. The median inhalation intake for these children in North Carolina was 0.8 ng/kg-day. Using the same ventilation and absorption rates with CASE estimates, the median chlorpyrifos inhalation intake for the population of farmworkers' children is 0.6 ng/kg-day.

Because the micro-activity data necessary (Cohen Hubal et al., 2000) for estimating non-dietary ingestion and dermal exposure are scarce, estimates are usually based on many assumptions regarding frequency of soil and dust ingestion and dermal contact. To provide comparison for the CASE simulations, dermal exposure was estimated according to current methods and exposure factors recommended by CS-EFH using the pesticide measurements from the farmworker homes (US EPA, 2008). See supplementary material for calculations. Based on one contact a day with soil, as specified (US EPA, 2008), a median dermal exposure of 0.005 and 0.002 ng/cm^2 was estimated for chlorpyrifos and diazinon respectively — one order of magnitude lower than the estimates from CASE. Currently, CS-EFH and supporting documents do not provide guidance on estimating dermal exposure from air immersion and residue contacts, and they do not account for dermal loading removal mechanisms (US EPA, 2008). The farmworker children that participated in videotaping had a median hand contact frequency of 0.5 events/h (mean = 3.8) with soil and a median hand contact frequency of 689.4 events/h (mean = 686.3) with all objects combined (Beamer et al., 2008). The assumption of dermal exposure arising from one contact with soil per day, underestimates dermal exposure for this population from soil adherence and other exposure mechanisms. However, the CASE model with appropriate distributions provides reasonable approximations of dermal exposure as demonstrated by comparison with the sock dosimeters.

Similarly, recommendations from the CS-EFH (US EPA, 2008) were explored to estimate non-dietary ingestion. Although mouthing frequency values are provided, the CS-EFH does not provide recommendations for saliva removal efficiency and other parameters. Therefore, based on the CS-EFH, non-dietary ingestion was estimated from only soil/dust to be 0.4 and 0.1 ng/h for chlorpyrifos and diazinon, respectively (see supporting information for calculations). These CS-EFH based estimates are much lower than the estimates from CASE simulations. There is no current method to directly measure non-dietary ingestion exposure, and as a result there are not suitable data sets to evaluate modeled non-dietary ingestion exposure estimates from either the CS-EFH or CASE (Shalat et al., 2003). However others (Morgan et al., 2005) using methods based on CS-EFH failed to account for over 60% of the chlorpyrifos metabolites measured in urine, indicating that exposure from this route may have been significantly underestimated (see supplementary material). While there are not any non-dietary ingestion exposure values measured directly to assess the ability of CASE to estimate this route, CASE does utilize a more detailed micro-activity approach accounting for additional exposure mechanisms to estimate non-dietary ingestion exposure. It is possible daily dust and soil ingestion rates utilized by others (Morgan et al., 2005; Pang et al., 2002) significantly underestimate this route.

MLATS are very expensive and time-consuming to collect. Not only is time spent videotaping children in the field, but substantial time is also needed for video preparation, translation and appropriate quality control measures. Several protocols have been developed that can help improve quality control and improve efficiency of the process (Ferguson et al., 2006; Beamer et al., 2008). Future work entails using the CASE model in conjunction with MLATS to develop dust/soil ingestion rates to be used in lower tier modeling frameworks. Eventually if enough MLATS are collected from individuals of different ages, engaged in various activities age-specific and activity-specific dust/soil ingestion rates could be developed to provide more complexity to modeling estimates. Hopefully, validated methods can be developed for simulating MLATS from existing MLATS to develop additional exposure scenarios for CASE simulations.

The only significant difference in exposure estimates as a function of age or gender was that infants had higher left hand dermal exposure estimates than toddlers. Left hand dermal exposure was significantly correlated with hand contact duration with toys ($\rho = 0.44$ for chlorpyrifos and diazinon) and negatively correlated with hand mouthing duration ($\rho = -0.81$ for chlorpyrifos; $\rho = -0.71$ for diazinon). Although not significantly different, toddlers have greater hand mouthing duration and less hand contact duration with toys (Beamer et al., 2008). This relationship was less pronounced for right hands. Left hand contact duration with toys was also significantly negatively correlated with hand mouthing duration ($\rho = -0.44$). When a child is busy playing with toys they are probably less likely to place their hands in their mouths, however additional MLATS recorded for longer durations should be collected to examine this issue.

In conclusion, if appropriate MLATS and stochastic inputs are used, CASE can provide realistic simulations of residential exposure. These simulations highlight object types, activities, microenvironments and additional conditions that contribute to residential exposure. Comparison of CASE estimates with measured values and estimates of non-dietary exposure from other methods provided a successful evaluation of the micro-activity approach. For this population of farmworkers' children, non-dietary residential exposure estimates were higher for chlorpyrifos than for diazinon, except for the inhalation route. The high variability observed between the individual non-dietary ingestion and dermal exposure distributions indicates the importance of a child's unique activity patterns and highlights potentially at-risk children. The potential substantial contribution of non-dietary ingestion exposure underscores the importance of characterizing aggregate exposure and cumulative risk when setting pesticide food tolerances as required by the FQPA.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envint.2009.08.003.

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