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The Washington aerial spray drift study: Children's exposure to methamidophos in an agricultural community following fixed-wing aircraft applications

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This study characterized exposures of eight children living in an agricultural community near potato fields that were treated by aerial application with the organophosphorus (OP) insecticide, methamidophos (*O*,*S*-dimethyl phosphoramidothioate). Exposure monitoring included air and deposition samples in the outdoor community environment, outdoor and indoor air samples at each residence, wipe samples of playground equipment, toys, indoor surfaces, and children's hands, and periodic urine samples. Monitoring occurred prior to, the day of, and 1 day following applications. Methamidophos deposition in the community was very low compared to deposition inside the boundaries of the treated fields. Community air concentrations increased from 0.05 $\mu g/m^3$ (prespray) to 0.11 and 0.48 $\mu g/m^3$ (spray day morning and afternoon, respectively), decreasing to 0.10 $\mu g/m^3$ on the postspray day. Air concentrations outside residences followed a similar pattern; indoor levels did not exceed 0.03 pg/m^3. Methamidophos residues were found on playground equipment following applications, but not on indoor residential surfaces. The median hand wipe levels increased from <0.02 (prespray) to 0.08 μg/sample (spray day), decreasing to 0.05 μg/sample (postspray day). Median concentrations of the primary methamidophos urinary metabolite were 61 μg/l before 1100 hours on the spray day, 170 μg/l after 1100 hours on the spray day, and 114 μg/l on the postspray day. Spray day metabolite levels were correlated with time outside on the spray day ($r_s = 0.68$), with spray day hand wipe levels ($r_s = 0.67$), and with postspray day metabolite levels ($r_s = 0.64$). Postspray day metabolites levels were also positively associated with postspray day hand wipe levels ($r_s = 0.66$). The documentation of children's exposure in this study does not necessarily mean that risks for these children were significantly altered, since nearly all children in the United States are exposed to some level of OP pesticides through dietary intake and other pathways. The association of metabolite levels with time spent outside, and the absence of methamidophos in homes indicates that children's exposures occurred primarily outdoors.
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Introduction

Pesticides become airborne during and after aerial and ground applications, sometimes resulting in significant off-target pesticide movement and potential exposure to workers and individuals near sprayed fields (Richter et al., 1986, 1992). Distance from source, wind direction, and wind speed have been identified as primary determinants of off-target movement (Barnes et al., 1987; Richards et al., 2001). Several studies in agricultural communities have found organophosphorus (OP) pesticide residues in house dust and yard soil, as well as OP pesticide metabolites, inversely associated with distance from treated fields (Simcox et al., 1995; Loewenherz et al., 1997; Lu et al., 2000). However, a recent study did not confirm this relationship (Royster et al., 2002).

Past studies of off-target pesticide drift have characterized the movement of the pesticide spray using tracer dyes, deposition and air sampling, foliar residues, and modeling techniques (Draper et al., 1981; Barnes et al., 1987; Gilbert and Bell, 1988; Riley et al., 1989; Clark et al., 1991; Salyani and Cromwell, 1992; Woodrow et al., 1997; Garcia et al., 2000; Richards et al., 2001; Woods et al., 2001). No studies to date have incorporated environmental sampling and biomarkers of exposures before, during, and following applications when assessing children's potential for exposure to pesticide drift. In most human exposure studies, symptoms and health effects attributable to pesticide drift most often have been gathered through questionnaires

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after an exposure event (Goldman et al., 1987; Ames et al., 1993).

The current study was initiated to investigate the role of off-target drift as a pathway for human exposure in nearby communities. This paper focuses on off-site deposition patterns, community and residential air concentrations, residue levels on community and residential surfaces, and residue levels on children's hands of methamidophos (*O*,*S*-dimethyl phosphoramidothioate). Urinary excretion of *O*,*S*-methyl hydrogen phosphorothioate (*O*,*S*-DMPT), a specific biomarker of methamidophos, was additionally monitored preapplication, during, and postapplication in children. Children's activities were monitored during this study with a new portable global positioning system (GPS) instrument (Elgethun et al., 2003). Data from this study have been used to develop models for the volatilization of residues (Ramaprasad et al., 2004), and the movement of particles into community and residential environments (Tsai et al., 2005). These models will be used in conjunction with the GPS-based children's activity data to develop refined estimates of children's exposure pathways in a subsequent paper.

Methods

Study Population

Study participants lived in a farm housing community surrounded by potato, corn, and wheat fields in central Washington State. The community had a centrally located park with a playground and soccer field. Participating households were within 800 m of each other and were within 15–200 m of the nearest treated field.

Families were invited to an informational meeting, and bilingual research staff explained the study purpose and answered questions. Families were eligible if they resided in the study community, and had at least one toilet-trained child between 2 and 12 years old living at home. Six families with eight children (four female, four male) aged 2–12 years were enrolled. Parents were interviewed (in Spanish or English as appropriate) regarding home and occupational pesticide use, and their child's hand-to-mouth behavior. Participants provided informed consent or informed assent, and all study procedures were approved by the University of Washington Human Subjects Division.

Application Procedures

Cultivated potato fields were treated by aerial application with Monitor 4® in late July to control green peach aphids. The farm operator reported that this insecticide had not been applied to neighboring potato crops earlier in the growing season.

A single 1340S2R Thrush aircraft with a 400-gallon tank flying at approximately 180 km/h (110 mph) and a maximum 3 m (10 ft) above the crop canopy sprayed five fields for a total of 283 ha (700 acres). The aircraft was equipped with 60 ASAE medium-sized whirl jet nozzles (1.4–1.5 kg/cm^2 (20–22 psi) oriented 180° from the direction of flight and 2–3 ft (< 1 m) below the wing. The spray boom was located forward of the wing and was 75% of the aircraft's wingspan. Swath width was approximately 14 m (45 ft). Methamidophos in liquid formulation (40% *O*,*S*-dimethyl phosphoramidothioate, 60% inert ingredients), known as Monitor 4®, was applied at a rate of 1.12 kg/ha (1 lb/acre) active ingredient beginning at 0500 hours on the day of application. Four fields located to the north, southwest, west, and east of the community were sprayed from 0500 to 0930 hours. Spray was suspended due to wind speeds greater than 8 km/h (5 mph) at 0930 hours. Spraying of the South field took place in the afternoon, between 1400 and 1500 hours.

Meteorological Conditions

Wind speed and direction data were collected from the Washington State University Public Agricultural Weather System. This system has a measurement station ~3 km (2 miles) south of the study site, and provides data as 15-min averages. The terrain in this part of the state is flat, and the station's reports were considered a good representation of wind conditions at the study site.

Sampling Design

Sampling was designed to capture potential exposures from a series of aerial applications. The types and numbers of samples collected at specific times are presented in Table 1. Baseline samples were collected in May, approximately 2 months prior to the spray event. Additional samples were collected 1 day prior to the spray event, the day of the event, and the day following the spraying. Children's time–location information was collected with a small GPS unit (Elgethun et al., 2003), and will be reported in a subsequent paper.

Deposition Sampling

Silica gel chromatography plates (20 × 20 cm) were placed throughout the community to measure methamidophos deposition. Deposition plates were mounted on stands 25 cm above the ground, and spaced approximately 15 m (50 ft) apart along a transect starting just inside the perimeters of two potato fields. A second transect was placed along the length of the community park, and in participants' yards nearest to one of the sprayed fields. Methamidophos was not detected on the five deposition plates collected prior to application. Deposition plates from both transects were collected after the morning spray; a second set was collected following the afternoon spray. Deposition plates were wrapped in tin foil at the time of collection, placed in plastic bags, and put on ice until transport to the analytical laboratory.

Table 1. Sample collection schedule for the Washington aerial spray drift study.

Sample type	Baseline	Study period		
		Preapplication day	Application day	Postapplication day
Deposition in community	—[a]	5/day	22/morning; 22/afternoon	—
Community outdoor air (four sites)	—	1/site	1/site, morning; 1/site, afternoon	1/site
Off-site outdoor air (one site)	—	1/site	1/site	1/site
Residential outdoor air (four homes)	—	1/home	1/home	1/home
Indoor air (four homes)	—	1/home	1/home	1/home
Playground wipes	—	5/day	5/morning; 5/afternoon	—
Surface, toy, apple wipes (five homes)	2/home	4/home	4/home	4/home
Hand wipes (seven children)	1/child	1/child	3/child	4/child
Urine (seven children)	1/child	1/child	1–2/child before 1100 hours 4–8/child after 1100 hours	3–4/child

[a]No samples collected during this time period.

Air Sampling

All samplers were equipped with polyurethane foam (PUF) cartridges for collection of methamidophos residues in air. Two medium flow Staplex® air samplers that sampled air at ca. 3 m^3/h and two high flow Thermo Anderson® samplers (model PS-1) that sampled air at ca. 12 m^3/h were placed in the community's public space. The Stablex samplers extracted ambient air through two colocated PUF cartridges. Residues from the tandem cartridges were averaged to represent a single sample for the purposes of this paper. An additional high volume sampler was positioned upwind approximately 1.5 km from the community to serve as a reference. Each sampler collected a preapplication day sample, morning and afternoon application day samples, and a postapplication day sample. Flow rates (l/min) for the Stablex air samplers were calibrated at the beginning and end of each sampling period. Mean flow rates for the Thermo Anderson samplers were calibrated at the beginning of the study following calibration methods provided by the manufacturer.

For outdoor residential air sampling, a medium flow SKC Hi-Lite® sampler (flow rate ca. 1.8 m^3/h) was placed in the yard of each participating family. The PUF cartridges were positioned 1 m from ground level to approximate a child's breathing space. SKC samplers were also placed inside each participating family residence. The physical pump assembly was situated outside the kitchen window to minimize indoor noise. Plastic tubing was run through the window, with the PUF cartridge supported on the windowsill. Windows were sealed with duct tape around the tubing to prevent outdoor air from entering the houses. Samples were collected prior to the application, on the day of application, and on the day after application.

All PUF cartridges were handled with new latex gloves, sealed in glass jars, and kept in the refrigerator of a mobile laboratory at approximately 1°C until transport on ice to the analytical laboratory. Samples were not kept at 1°C longer than 4 h.

Playground Equipment Wipe Sampling

Wipe samples were collected from playground equipment for the following surfaces: monkey bar crossbars and sidebars, a tire swing, a baby swing, and swing chains. Two gauze wipes wetted to near saturation with 10% isopropanol (i.e., misting gauze pad with 2–3 ml from a spray bottle) were used to wipe each surface. In order to standardize the sampling method, the entire surface area of the equipment (e.g., entire surface area of two crossbars on the north side of monkey bar set) was sampled. Playground equipment wipes were collected from the same surface once prior to, and twice following the start of the spray event (approximately 6 and 11 h after aerial application began).

Residential Wipe Sampling

Two nights before the spray event, a precleaned plastic ball (855 cm^2) was placed in each participant's yard. An additional ball was placed on the soccer field near the community playground. Wipe samples were collected prior to and 6 h after the beginning of spraying. Surface wipe samples were collected from kitchen tables and counters using a plastic template (10 × 10 cm), and from precleaned apples (195 cm^2). Sampling occurred during baseline sampling and approximately 15 and 36 h after the beginning of spraying. Two gauze wipes wetted to near saturation with 10% isopropanol (i.e., misting gauze pad with 2–3 ml with a spray bottle) were used to wipe each surface. Wipes were placed into plastic bags and stored in a cooler with ice until they reached the analytical laboratory.

Child Hand Wipe Sampling

Hand wipe samples were collected from each child by research staff the day before methamidophos applications, on

the spray day before the application began, twice after spraying began, and three or four times on the postspray day. Hands were wiped with precleaned gauze pads wetted to near saturation with 10% isopropanol (i.e., misting gauze pad with 2–3 ml from a spray bottle). One gauze pad was used to thoroughly wipe the palm of each hand and a second pad was used to wipe the palm side of the fingers, so that the entire palm side of the hand was wiped. Both hands were wiped and a total of four gauze pads were used and placed in a prelabeled jar and treated as one sample. If the child was unreceptive when approached, hand wipe samples were postponed until a later time. In one case, parents collected two of the eight hand wipe samples at the request of the child. The removal efficiency of methamidophos from skin is not known, so the values reported are the amounts of residue removed by this procedure.

Urine Samples

Spot urine samples were collected during the baseline sampling period, and the evening immediately preceding the spray. To the extent possible, a complete 24-h urine void was then collected from each child starting the morning of the spray, and three spot urine samples were collected the day following the spray. Parents were provided with urine collection jars and specimen pans for the toilet. Contents of the specimen pan were emptied into the appropriate urine collection jar, and the jars were refrigerated until pickup by the field staff.

Sample Handling

All samples were transported on the day of sampling and immediately placed in cold storage at the Washington State University Food and Environmental Quality Laboratory (FEQL) in Richland, WA, USA. Wipe, deposition plate, and PUF air samples were stored at -20°C and spot urine samples at -80°C until residue determination. To evaluate the stability during storage, replicate wipe, deposition plate, and PUF blank samples were fortified with a known amount of methamidophos and then stored at -20°C. The storage stability of each fortified matrix was determined after their respective longest storage interval.

Sample Analysis

Gauze pads (Johnson & Johnson, 3×3 inch 100% cotton) were precleaned by Soxhlet extraction with acetyl acetate before field use. Each wipe sample (consisting of two to four gauze pads), deposition plate, or PUF sampler was submerged in ethyl acetate and sonicated. Two sequential ethyl acetate extractions were performed followed by suction filtration. The two suction-filtered solvent extracts were combined. The total solvent extract volume was reduced to just dryness by rotary-evaporation under reduced pressure at 40°C. The sample extract was redissolved in ethyl acetate and quantitatively transferred to a preconditioned 500-mg carbograph SPE column. The sample extract was eluted using ethyl acetate under slight negative pressure. The sample eluent volume was reduced under nitrogen at 35°C to a desired final volume for residue determination.

Air, wipe, and deposition samples were analyzed by gas chromatography employing a Varian Star 3400CX with 8200CX Auto Liquid Sampler using pulsed flame photometric detection (PFPD) in phosphorus mode. A fused silica megabore EC-1 (100% methyl silicone phase), $15\,\text{m} \times 0.53\,\text{mm}$ i.d. $\times\, 1.20\,\mu\text{m}$ film thickness column was used with a flow rate of 10–13.5 ml/min. The PFPD temperature was set at 310°C. Injector port temperature was programmed from 200°C to 250°C at 250°C/min. Oven temperature was programmed to increase from 80°C to 270°C at 20°C/min and hold at a final temperature for 5 min. Injection volume was $2\,\mu$l.

Data were considered to be acceptable if variation between bracketed single point calibration standards was $<15\%$ (averaged during run) and linearity as measured by the regression r^2 was >0.995. A limit of quantitation (LOQ) for air, wipe, and deposition samples was established based on the lowest reproducible level of quantification to be $0.1\,\mu$g/sample with an estimated limit of detection (LOD) of $0.02\,\mu$g/sample ($\sim 4\times$ of the background chromatographic signal).

Recoveries of methamidophos from PUF, wipe, and deposition samplers were determined by fortifying the sample media with a known amount of methamidophos. Analytical sets consisted of four to eight samples followed by two quality control (QC) samples. Blank media were also extracted and analyzed in each analytical set to serve as controls. Gauze wipes were routinely fortified with 0.1–20 μg of methamidophos during residue analyses; average fortified percent recovery was $101 \pm 13\%$. Average fortified percent recovery for silica gel deposition plates was $81 \pm 8\%$. No detectable residues were recovered from blank samples. Data were considered acceptable if variation between bracketed single point calibration standards was $<15\%$ (averaged during run) and linearity as measured by the regression r^2 was >0.995.

Urine samples were analyzed at the University of Washington's Environmental Health Laboratory for the metabolite of methamidophos, *O*,*S*-DMPT, under procedures based on the method of Tomaszewska and Hebert (2003). Urine aliquots (2.5 ml) were freeze-dried at -6°C for about 15 h, and then derivatized with *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide and 1% *tert*-butyldimethylchlorosilane (MTBSTFA + 1% TBDMCS) for analysis by gas chromatography (PFPD). In all, 15 urine samples, fortified with known concentrations of *O*,*S*-DMPT at the time of sample collection, were analyzed with the field samples; no degradation of the metabolite was observed. Laboratory and field blank samples did not contain measurable *O*,*S*-DMPT. The average recovery for

O,*S*-DMPT from 12 laboratory spiked samples (spiking levels of 43 and 430 μg/l) was 92 $\pm$ 42%. The LOD was 9 μg/l, and the LOQ was 18 μg/l.

Results

Deposition Samples

The locations of deposition plates are plotted on an aerial photo (Figure 1), and methamidophos residues found on deposition plates are summarized in Table 2. Plates 1–10 were placed along the edge of the community's park, 68–75 m from the North field, and 217–325 m from the South field. Plate 11 was placed 1 m inside the North field. Plates 12–22 were placed in a line extending from several of the homes to the edge of the East field, with plate 22 placed 1 m inside the East field. Morning deposition plates were set up at 0530 hours and were in the field for approximately 6 h. Afternoon plates were set up between 1200 and 1300 hours and remained in the field approximately 5 h.

Figure 2 illustrates wind direction, magnitude, and frequency with a wind stick graph during and after application. During the morning spray period, winds were generally from the south-southwest. Wind direction shifted between 0900 and 1000 hours, and winds were from the north-northwest for the rest of the day. Fields located to the north, west, and east of the community were sprayed while the prevailing wind blew from the south-southwest, and fields to the south were sprayed while winds blew from the north-northwest, effectively carrying the primary drift away from the community in each case.

Median surface loadings following morning application of methamidophos on fields north, west, and east of the community were 13.8 ng/cm^2 for plates 1–10 and 13.3 ng/cm^2 for plates 12–21. In contrast, the plates located just within the boundaries of the fields (plates 11 and 22) had substantially higher deposition levels (7990 and 20,400 ng/cm^2, respectively). The median surface loadings following the afternoon application on the field south of the community were 9.8 ng/cm^2 for plates 1–10 and 1.3 ng/cm^2 for plates 12–21. Again, residue levels on plates within the boundaries of the fields (plates 11 and 22) were higher than those in the community. The median values for the four deposition plate sets were inversely associated with median distances of the plate sets from the nearest sprayed field ($R^2 = 0.94$; $P = 0.03$).

Air Samples

The off-site (upwind) sampler recorded methamidophos concentrations at or below the LOD throughout the 3-day sampling period (Table 3). The median outdoor air concentration in the community increased from a preapplication day level of 0.05 to 0.11 μg/m^3 for the application day morning,

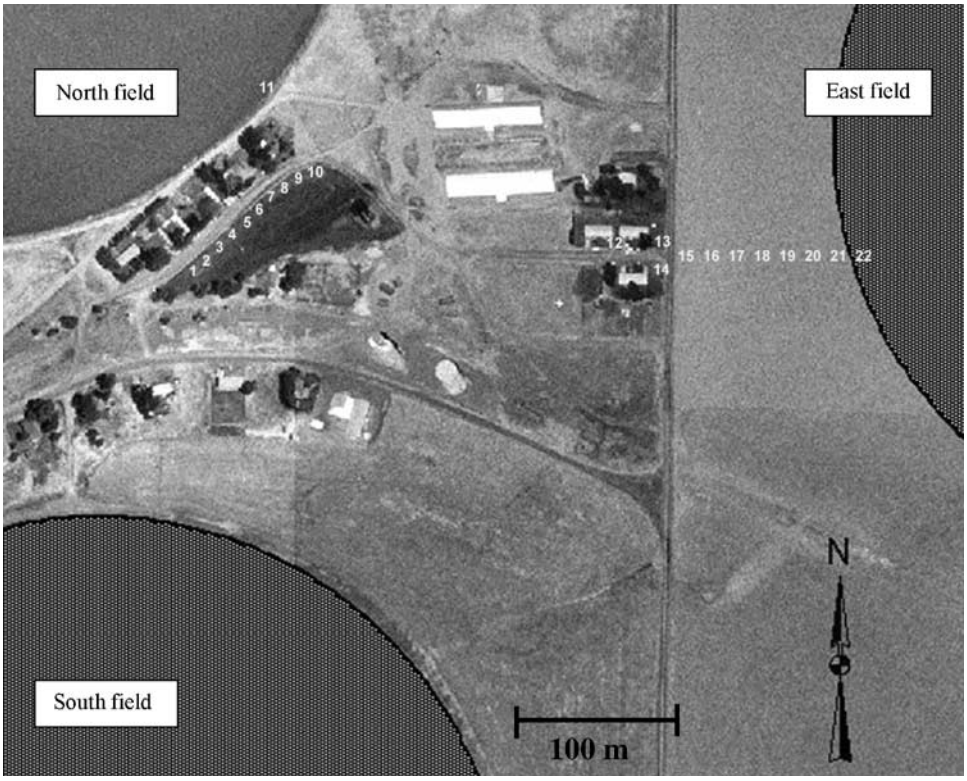

Figure 1. Deposition plate locations are numbered from 1 to 22: plates 1–10 were placed on the edge of the community park; plates 12–14 were placed near residences; and plates 11 and 22 were located just inside the boundaries of the sprayed fields.

Table 2. Methamidophos deposition in the community on the spray day (ng/cm^2), and distance of deposition plates from nearest sprayed field (m)[a].

Location	Morning[b]		Afternoon[b]	
	Distance to the nearest sprayed field (m)[c]	Loading (ng/cm^2)[d]	Distance to the nearest sprayed field (m)[c]	Loading (ng/cm^2)[d]
1	77	12.6	217	6.8
2	76	8.5	229	16.0
3	74	12.5	241	8.3
4	72	13.4	253	8.6
5	70	3.4	265	11.3
6	68	15.4	276	10.1
7	68	15.6	288	12.2
8	70	16.8	300	12.1
9	70	14.1	312	9.5
10	73	15.4	325	7.6
Median	71	13.8	270	9.8
Range	68–77	3.4–16.8	217–325	6.8–16
11	0[e]	7990	372	77.9
12	179	25.5	374	2.5
13	134	10.7	381	1.5
14	131	8.1	401	1.6
15	107	9.9	412	1.3
16	91	14	429	1.3
17	76	115	445	1.3
18	61	11.3	462	1.1
19	46	12.5	479	1.9
20	30	16.7	495	1.1
21	15	20.3	512	1.1
Median	84	13.3[f]	437	1.3[f]
Range	15–179	8.1–115	374–512	1.1–2.5
22	0[e]	20,400	529	5.3

[a]Median distance and median loading were inversely associated; $R^2 = 0.94$; $P = 0.03$.
[b]Morning samples were in the field for 6.75 h; afternoon samples were in the field for 5 h.
[c]Distances were measured using global positioning system (GPS) coordinates: distances for locations 1–11 were measured from the North field in the morning, and from the South field in the afternoon; distances for locations 12–22 were measured from the East field in the morning, and from the South field in the afternoon.
[d]The limit of detection was 0.05 ng/cm^2; the limit of quantitation was 0.25 ng/cm^2.
[e]Deposition plates 11 and 22 were placed 1 m inside the sprayed field.
[f]Median morning loading for deposition plates 12–21 was greater than median afternoon loading (Wilcoxon's signed-rank test, $P = 0.005$).

and to 0.48 μg/m^3 for the application day afternoon (Table 3). The median concentration for the day postapplication (0.10 μg/m^3) was about twice that of the preapplication day, and was comparable to the application day morning value. Application day and postapplication values were significantly higher than preapplication day values (Wilcoxon's signed-rank test, $P < 0.05$). The community air sampler closest to the nearest upwind treated field recorded the highest concentrations.

Median outdoor air concentrations for samplers at residences increased from a preapplication day level of 0.03 to 0.15 μg/m^3 for the application day morning, and to 0.36 μg/m^3 for the application day afternoon (Table 3). The median concentration for the day postapplication (0.13 μg/m^3) was about four times higher than that of the preapplication day, and comparable to the application morning value.

The range of application day concentrations was notably higher for the outdoor residential samplers, presumably because several of the residence yards were very close to the nearest upwind treated field (within 10–20 m). The highest outdoor residential air sample was 0.98 μg/m^3 during the application day afternoon, whereas the highest community air sample was 0.68 μg/m^3 for the same time period.

The highest indoor air concentration recorded indoors during the study was 0.03 pg/m^3, approximately seven orders of magnitude lower than the outdoor samples. Most indoor air samples were near or below the LOD. It was noted during the study that the doors and windows of the residences were closed during the applications, and that air conditioning was used during these periods.

Surface Wipe Samples

All preapplication playground equipment wipe samples had low but measurable methamidophos residues (Table 4). Median playground equipment loadings at preapplication, and 6 and 11 h following the start of application were 0.04, 0.57, and 1.04 ng/cm^2, respectively. Methamidophos residues on playground equipment at both 6 and 11 h after aerial applications began were significantly higher than preapplication levels ($P = 0.04$ in each case, Wilcoxon's signed-rank test). No significant difference was found between playground equipment samples at 6 and 11 h.

No detectable methamidophos residues were found on the six outdoor toys prior to application, whereas four of the toys had measurable methamidophos residues after the applications (0.11–0.37 ng/cm^2). There were no detectable residues for any of the apples placed inside the residences, or for any of the indoor residential surfaces.

Child Hand Wipe Samples

None of the baseline and only a few of the prespray day hand wipe samples contained detectable methamidophos (Table 5 and Figure 3). The median hand loading on the spray day (0.08 μg/sample) was significantly higher than the baseline or prespray loadings ($P = 0.03$, Wilcoxon's signed-rank test), and was also higher than the median postspray hand loading ($P = 0.05$). The median postspray day hand loading was also higher than baseline or prespray loadings ($P = 0.02$). Spray day and postspray day hand loadings were correlated (Spearman's rank-correlation test, $r_s = 0.84$; $P = 0.02$).

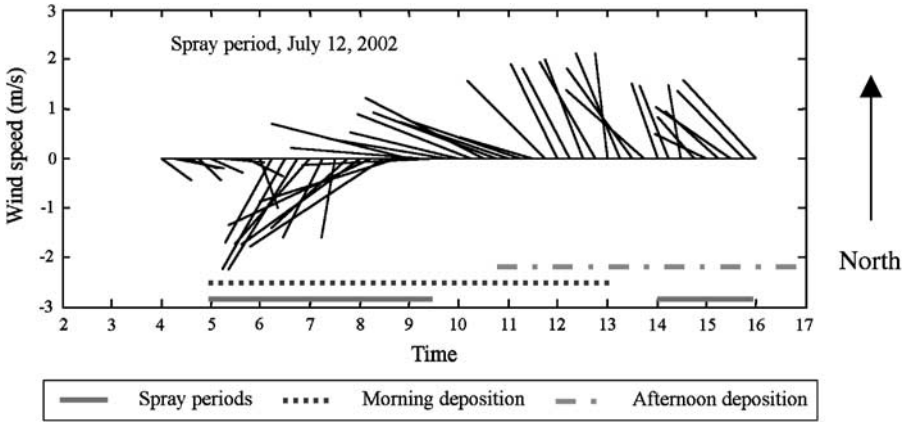

Figure 2. The 15-min average wind direction and magnitude during study period. Wind data were obtained from Washington State University Public Agricultural Weather System. Wind sticks represent direction and magnitude along a 24-h scale timeline. Wind direction follows the stick toward the *x*-axis. Magnitude is represented by stick length. All sticks are scaled equally regardless of direction to the *y*-axis.

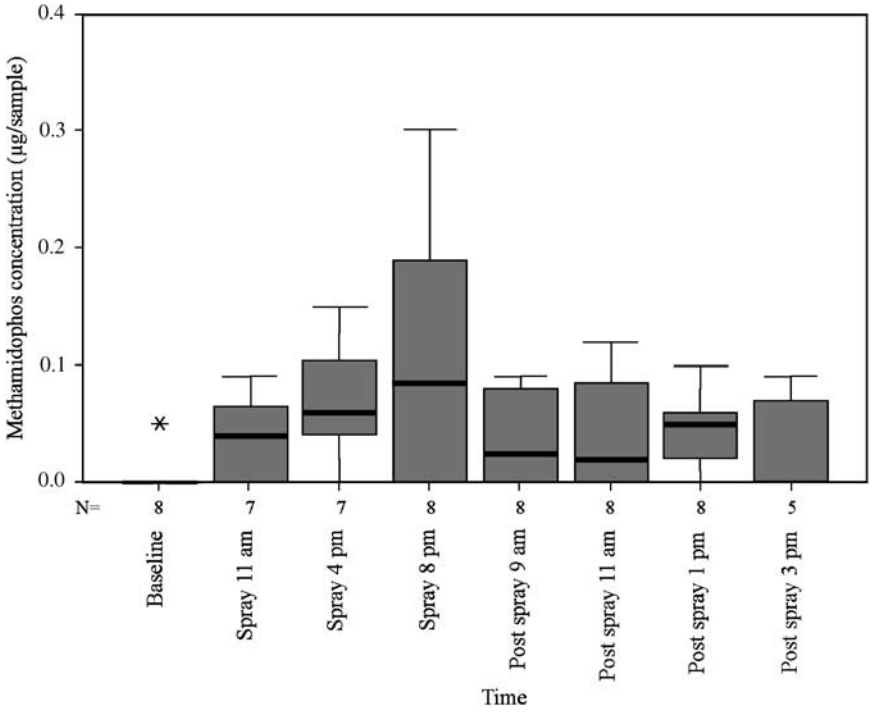

Figure 3. Hand wipe residues (μg/sample) by day and time of sample collection: boxplot bars represent the 25th and 75th percentiles; and dark lines within bars represent median values for seven children. All baseline samples were less than the LOD.

Urine Samples

Eight children provided a total of 100 urine samples for analysis. Eight samples were collected during baseline sampling, eight the day before spraying, 59 on the day of spraying, and 25 on the day after spraying. Of the 100 samples, 15 were not analyzed successfully: three did not have sufficient urine volume for analysis, and 12 did not derivatize successfully. Of the remaining 85 samples, 18 were below the LOD ($<9\ \mu$g/l), and seven were between the LOD and the LOQ (9–18 μg/l). The remaining 60 samples ranged in concentrations from 23 to 927 μg/l.

The *O*,*S*-DMPT concentrations in urine are presented in Table 6. Child 1 was omitted from the analysis, since only one sample was provided on the day of spraying, and this sample did not derivatize successfully. Baseline and prespray values are each based on a single sample from each child. The other values in Table 6 are volume-weighted averages of multiple samples. Relatively high values were recorded during the baseline and prespray day sampling for three of the children; the source of methadmidophos exposure for these children prior to the aerial applications is not known.

Table 3. Methamidophos air concentrations in community and residential samples ($\mu g/m^3$)[a].

Sampling period[b]	Outdoor off-site[c]	Outdoor community[d]		Outdoor residential[e,f]	
		Median[g]	Mean	Median[g]	Mean
Prespray day	0.006	0.05	0.05	0.03	0.50
Spray day: a.m.	0.02	0.11	0.14	0.15	0.20
Spray day: p.m.	<0.02	0.48	0.49	0.36	0.46
Postspray	<0.02	0.10	0.10	0.13	0.13

[a]The limit of detection (LOD) was 0.02 μg/sample; the limit of quantitation was 0.10 μg/sample.
[b]Samples were collected in the afternoon on the prespray day; from approximately 0500 to 1000 hours on the spray day morning; from approximately noon to 2000 hours on the spray day afternoon; and from approximately 2100 hours on the spray day to 0900 hours the following day (postspray).
[c]One high-volume sampler was located 1.5 km upwind from the community.
[d]Four high-volume samplers were located within the community.
[e]High-volume samplers were placed in the yards of the four study homes in the community.
[f]High-volume samplers were also placed inside the four study homes; concentrations did not exceed 0.03 pg/m^3, and these data are not included in this table.
[g]Spray day and postspray concentrations were higher than prespray day concentrations for the outdoor community samples and the outdoor residential samples (Wilcoxon's signed-rank test, $P<0.05$).

Table 4. Playground equipment samples: surface areas and methamidophos loadings.

Playground equipment sampled	Equipment material	Surface area (cm^2)	Concentration[a] (ng/cm^2)		
			Prespray	Morning (1100 hours)	Afternoon (1600 hours)
Monkey bars: two crossbars	Painted metal	1122	0.24	2.09	2.00
Monkey bars: three crossbars; two side bars	Painted metal	3395	0.04	0.57	1.04
Monkey bars: entire East-facing side bar	Painted metal	5069	0.04	0.38	0.32
Tire swing: entire top surface	Rubber	3098	0.03	0.36	0.98
Baby swing: handles (20 chain lengths) and seat	Unpainted metal and rubber	724	0.10	2.96	5.10
Median			0.04[b]	0.57[b]	1.04[b]

[a]Limits of detection (LODs) and limits of quantitation (LOQs) varied for each playground equipment sample due to differing surface areas. LODs ranged from 0.006 to 0.03 ng/cm^2; LOQs ranged from 0.02 to 0.15 ng/cm^2.
[b]Median morning and afternoon spray day concentrations were significantly different from prespray day concentrations (Wilcoxon's signed-rank test, $P=0.04$ in each case).

Median concentrations from spray day samples collected after 1100 hours were higher than spray day levels before 1100 hours (Wilcoxon's signed-rank test, $P=0.06$), as were the postspray day concentrations ($P=0.06$). Spray day (after 1100 hours) metabolite levels were correlated with time outside (see Table 5) on the spray day (Spearman's rank-correlation test, $P=0.09$, $r_s=0.68$), with spray day hand wipe levels ($P=0.10$, $r_s=0.67$), and with postspray day metabolite levels ($P=0.12$, $r_s=0.64$). Postspray day metabolites levels were correlated with postspray day hand wipe levels (Spearman's rank-correlation test, $P=0.11$, $r_s=0.66$).

Discussion

Methamidophos residues found on deposition plates, playground equipment, toys, and childrens' hands confirmed that drift occurred in this community following aerial application. The presence of the primary methamidophos metabolite, *O*,*S*-DMPT, at elevated levels in urine following spray indicates exposure among the children in the study. One striking finding from the deposition plates was the disparity between residues within the boundaries of the treated fields compared to those on adjacent samples outside the treated areas: these residue levels differed by approximately three orders of magnitude (8–20 $\mu g/cm^2$ vs. 13–14 ng/cm^2). These data indicate that the aerial application was very well controlled, and that nearly all of the material applied reached the targeted fields, at least along those boundaries where measurements were taken. It seems likely that the presence of our field investigation team had an influence on the application procedures. According to the farm operator, the pilot scheduled for the aerial application observed our field sampling apparatus from the air and chose to return to base prior to spraying. The application that was the focus of this study occurred the next day with a different pilot.

We did not find methamidophos residues inside homes, but one recent study of propanil drift from rice fields to nearby

Table 5. Methamidophos residue levels on children's hands (μg/sample), and time spent outdoors in the residential community.

Child[a]	Baseline[b]	Methamidophos residues on hands[c] (μg/hand wipe)			Time outside[d] (min)	
		Prespray[e]	Spray day[f]	Postspray day[g]	Spray day[h]	Postspray day[i]
2	<0.02[j]	0.04	0.12	0.05	251	76
3	<0.02	0.04	0.08	0.06	148	223
4	<0.02	<0.02	0.28	0.06	84	45
5	<0.02	0.03	0.22	0.1	169	224
6	<0.02	<0.02	0.08	0.03	207	181
7	<0.02	<0.02	0.02	0.02	19	179
8	<0.02	<0.02	<0.02	0.02	28	179
Mean	<0.02	0.022	0.12	0.049	129	158
Median	<0.02	<0.02	0.08[k,l]	0.05[m,l]	148	179

[a]Child 1 did not provide an adequate number of samples, and was omitted from analysis.
[b]Baseline hand wipes were collected approximately 2 months before the spray day.
[c]Hand wipe values represent wipes from both hands as described in the Methods section.
[d]Time outside is based on global positioning system (GPS) measurements on children.
[e]Prespray hand wipes are the average of samples collected the day before the spray and those collected before 1100 hours on the morning of the spray (two samples per child).
[f]Spray day levels are the average of samples collected at 1600 and 2000 hours on the spray day (two samples per child).
[g]Postspray day levels are the average of samples collected on the day following the spray (four samples per child).
[h]Time outside on the spray day began after 1000 hours for all children; all children were indoors during the afternoon spray (1400–1500 hours).
[i]Time outside on the postspray day began after 1100 hours for all children.
[j]Residue levels less than the limit of detection (0.02 μg/sample) were assigned one-half the limit of detection for calculating averages.
[k]Spray day residues were greater than baseline or prespray levels ($P = 0.028$); and were greater than postspray day residues ($P = 0.046$); Wilcoxon's signed-rank tests.
[l]Spray day residues and postspray day residues were correlated ($P = 0.019$); Spearman's rank-correlation test, $r_s = 0.84$.
[m]Postspray day residues were greater than baseline and prespray residues ($P = 0.017$); Wilcoxon's signed-rank tests.

Table 6. Methamidophos metabolite (*O*,*S*-DMPT) concentrations in child urine samples (μg/l)[a].

Child[b]	Baseline[c]	Prespray day[d]	Spray day before 1100 hours[e]		Spray day 1100–2400 hours		Postspray day	
2	<9[f]	514	25	(1)	535	(6)	191	(3)
3	71	41	61	(2)	188	(8)	356	(2)
4	450	658	162	(1)	270	(4)	264	(3)
5	<9	317	174	(2)	109	(7)	114	(3)
6	NS[g]	<9	109	(1)	170	(7)	64	(1)
7	27	14	<9	(1)	10	(7)	73	(3)
8	<9	75	<9	(1)	80	(5)	76	(2)
Mean	94	232	77		195		163	
Median	16	75	61		170[h,i]		114[j,k]	

[a]Concentrations for spray day and postspray day are volume-weighted averages (VWA); number within parentheses is number of samples. VWA (μg/l) = $\sum[C_i\ (\mu g/l) \times V_i\ (l)]/\sum[V_t\ (l)]$ where C_i = urinary concentration; V_i = volume of the corresponding urine sample; and V_t = total urine volume.
[b]Child 1 did not provide an adequate number of samples, and was omitted from analysis.
[c]Baseline samples were collected approximately 2 months before the spray day.
[d]Prespray samples were collected the day before the spray.
[e]Children first went outside between 1000 and 1100 hours on the spray day.
[f]Limit of detection = 9 μg/l; one-half the LOD (4.5 μg/l) is used in calculations.
[g]NS = no sample available or sample did not derivatize successfully.
[h]Spray day (after 1100 hours) metabolite levels were higher than spray day levels before 1100 hours ($P = 0.063$; Wilcoxon's signed-rank test).
[i]Spray day (after 1100 hours) metabolite levels were correlated with time outside on spray day (Spearman's rank-correlation test, $P = 0.094$, $r_s = 0.68$), with spray day hand wipe levels ($P = 0.10$, $r_s = 0.67$), and with postspray day metabolite levels ($P = 0.12$, $r_s = 0.64$).
[j]Postspray day metabolite levels were higher than spray day levels before 1100 hours ($P = 0.063$; Wilcoxon's signed-rank test).
[k]Postspray day metabolites levels were correlated with postspray day hand wipe levels (Spearman's rank-correlation test, $P = 0.11$, $r_s = 0.66$).

homes (<150 m) found detectable levels of propanil on sampling surfaces within three of four houses where the prevailing wind direction was toward the home (Richards et al., 2001). The investigators noted differences in home integrity (i.e., open windows, drafts through the walls) and travel in and out of the houses that may have allowed

residues to enter the home. In our study, participants in all six homes kept their doors and windows closed and had air conditioners operating throughout the spray and postspray day due to extreme temperatures (average afternoon temperatures during the spray day and postspray day were 39.2°C and 38.3°C (102.5°F and 101°F), respectively. We also observed that the children were inside while spraying occurred, and that they spent the majority their time indoors on the study days.

The source of methamidophos found on participants' hands is not known, but the absence of methamidophos on indoor surfaces suggests that exposure occurred outdoors. The increase in methamidophos residues on playground equipment following the spray, and the presence of residues on toys placed outside during the spray suggest an opportunity for children to contact pesticides when playing outdoors after the applications. The presence of measurable methamidophos levels on children's hands and the corresponding methamidophos metabolites in their urine confirm that these children were exposed as a result of their normal activities, both on the spray day and on the postspray day. The positive association between spray day metabolite levels and time spent outside further supports the conclusion that exposures occurred outside the home. GPS data from the children indicate that none entered the treated fields on either study day.

The documentation of children's exposure in this study does not necessarily mean that risks for these children were significantly altered. Nearly all children in the United States are exposed to some level of OP pesticides through dietary intake and other pathways. A subsequent paper will incorporate source–receptor models (Ramaprasad et al., 2004; Tsai et al., 2005), children's activities, and urinary metabolite data to produce refined exposure estimates, as well as dose estimates for this study population.

In conclusion, this study demonstrates that pesticide drift into a residential community occurred during and following application. It was apparent that the application was well executed as demonstrated by the large difference between in-field deposition and community deposition. Children's exposure to methamidophos was most likely the result of outdoor activities in their community.

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