Journal of Exposure Science and Environmental Epidemiology (2009) 19, 613–623

1559−0631/09/$32.00

www.nature.com/jes

Children's inhalation exposure to methamidophos from sprayed potato ...elds in Washington State: Exploring the use of probabilistic modeling of meteorological data in exposure assessment

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We examined the signi...cance of meteorology and postspray volatilization of methamidophos (an organophosphorus insecticide) in assessing potential inhalation risk to children in an agricultural community. We combined ...uxes from sources and dispersion modeling with a range of possible local meteorology to create output to study the variability in potential community exposure as a result of changing temperature, wind speeds and wind directions. This work is based on an aerial spray drift study where air sampling measurements of methamidophos were made before, during and after a spray event were used to examine acute inhalation risk for children living in an Eastern Washington State community in close proximity (between 15 and 200 m) to sprayed potato ...elds. We compared the measured average air concentrations of methamidophos in the community to a ''no observed adverse effect level'' for subchronic inhalation to characterize acute and subchronic inhalation risks. The baseline estimates of inhalation exposure were below Environment Protection Agency's (EPA) level of concern based on a target margin of exposure of 300. As meteorological conditions during and after spraying in...uence the amount of material moving into areas where children reside we used historical meteorological data to drive model simulations that predicted likely air residue concentrations under different wind and temperature conditions. We also added variability to the decay constant and initial emission ...uxes to create a 2−D simulation of estimated air concentrations in the community near the ...elds. This work provides a methodological framework for the assessment of air concentrations of pesticides from agricultural sprays in the absence of extended measurements, although including variability from meteorological conditions. The deterministic as well as the probabilistic risk analyses in this study indicated that postspray volatilization in the speci...c spray situation analyzed (methamidophos applied on potato ...elds in Eastern Washington) did not pose acute or subchronic risks as de...ned by the EPA. However, this study did not consider any pathway of exposure other than inhalation (e.g. diet, dermal, etc.) and the risk assessment should be evaluated in that context.
Journal of Exposure Science and Environmental Epidemiology (2009) 19, 613–623; doi:10.1038/jes.2008.66; published online 29 October 2008

Keywords: inhalation risk, methamidophos, volatilization, meteorology, probabilistic modeling, pesticides.

Introduction

We have examined the potential inhalation risk to children in an agricultural community from exposure to air residues of the organophosphorus (OP) pesticide methamidophos (O,S−dimethyl phosphoramidothioate) generated from postspray volatilization. In Washington State during 2003, methami−dophos was used on 57% of the planted potato acres (a total use of 65,500 kg), thus creating a high potential for exposure in nearby residential communities (USDA NASS, 2004). Methamidophos poses a signi...cant hazard because it is a category I OP (Environment Protection Agency's; EPA's category for most acutely toxic) insecticide. Postapplication volatilization represents a secondary but signi...cant source of tropospheric pesticide concentrations (Taylor and Spencer, 1990) and may be a signi...cant pathway of exposure to humans in nearby residential communities. Harnly et al. (2005) noted that agricultural applications of OPs may have substantial volatilization and off−...eld movements and are a probable source of exposures of public health concern. The amount volatilized from agricultural ...elds can be consider−able F for some pesticides, up to 90% of the application

1. Abbreviations: AI, active ingredient; EPA, Environment Protection Agency; FDM, fugitive dust model; FQPA, Food Quality Protection Act; HQ, hazard quotient; LOC, level of concern; MOE, margin of exposure; NOAEL, no observed adverse effect level; OP, organopho−sphorus; RED, registration eligibility decision; RfD, reference dose; VP, vapor pressure

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Received 5 November 2007; accepted 11 September 2008; published online 29 October 2008.

amount may volatilize (Umsworth et al., 1999; Van den Berg et al., 1999; Bedos et al., 2002). In a study by Hatzilazarou et al. (2004), air concentrations of methamidophos and chlorothalonil were measured in a greenhouse, after application of the pesticides. The concentrations of methamidophos were highest 2 h after application because of its higher volatility. Residential proximity to agricultural ...elds has been associated with elevated exposures to OP insecticides. Lowenherz et al. (1997) compared urinary concentrations of pesticide metabolites in children of agricultural applicators in an intensive fruit production region of Washington State. Children living less than 200 ft from an orchard had higher frequencies and higher levels of detectable urinary dimethyl thiophosphate levels than children living farther away, indicating that proximity to spraying was an important factor contributing to magnitude of exposure. Lee et al. (2002) assessed inhalation risks to California communities from airborne pesticides and found that exposure estimates greater than or equal to non-cancer reference values occurred for 50% of the exposed populations for chronic and subchronic exposures to several pesticides. They concluded that pesticide vapor pressure (VP) was a better predictor of inhalation exposure and risk than rankings by chronic reference dose (RfD) or cancer potency factors. Lee's conclusion is consistent with observations that gas phase concentrations of pesticides in and around agricultural areas originate mostly from volatilizing active ingredients (AIs). If the conditions are right, material volatilizes off plant and soil surfaces for several days after the spray. High temperatures increase the rate of volatilization signi...cantly (Ramaprasad et al., 2004), thus increasing the potential for exposure.

The high volatility and high toxicity of methamidophos combine to make its postspray volatilization a potential hazard for inhalation exposure. In the spring of 2006 farmworker community members tested the air at two different locations in the Yakima Valley with the assistance of the Farm Worker Pesticide Project and Pesticide Action Network (Dansereau and Perez, 2006). Results showed that during the chlorpyrifos spray season measurable values were found in the air over a 28-day period. Also, Lee et al. (2002) found that the short-term chlorpyrifos exposure estimates exceeded the acute reference value for 50% of the children in the exposed population. Methamidophos is of higher volatility than chlorpyrifos and of comparable toxicity to chlorpyrifos. Temperatures in Eastern Washington, where this study is based, can get very high in the summers around the time when potato ...elds are sprayed with methamidophos. As a matter of fact, the day of our aerial spray drift ...eld study was the hottest day locally in 10 years! All this combined with the close proximity of the sprayed ...elds to the community (Weppner et al., 2006) makes the case for studying the impacts of volatilization and inhalation risks.

We evaluated the potential inhalation risk to children contributed by surface volatilization of methamidophos residues following an aerial application. Potential atmospheric dispersal and residence times of organophosphates after agricultural applications are not well understood and are driven by many interwoven factors including application methods, temperature, rainfall and wind (Whang et al., 1993; Bedos et al., 2002). We also examined how exposure might be affected by meteorological variability during and immediately after spraying. This was accomplished by combining ...uxes from sources and dispersion modeling with a range of possible local meteorology derived from historical records of temperature, wind speeds and wind directions.

Our goals in this paper were twofold: ...rst we used a set of limited measurements made before, during and immediately after a spray conducted in potato ...elds in Eastern Washington, to develop a case study-based deterministic risk assessment of inhalation riskFboth acute and subchronic for children. Acute inhalation risk (up to 24 h after spraying) is of interest because of the volatility (especially under the high temperature conditions during the spraying) and toxicity of methamidophos. The subchronic inhalation risk (exposure of about 30 days in this case) is of greater interest than the chronic inhalation risk (430 days of exposure) because the compound has been found to remain in the environment for approximately 30 days after its release. Secondly, because there is no mandatory reporting of pesticide spraying in the state of Washington, nor do we have routine air sampling of pesticides, we extended the deterministic assessment to a probabilistic one that would model the impact of meteorological variability in air concentrations of the pesticide. We used historical meteorological data with dispersion modeling to estimate air concentrations in the community under different weather conditions. The ...eld data (air concentration measurements) were used to validate the model dispersion results.

Methods

Deterministic Risk Assessment: Case Study

The current analysis is an extension of previous work that combined spray drift characterization with environmental and biological sampling as well as child activity data to study exposure pathways (Elgethun, 2004; Ramaprasad et al., 2004; Tsai et al., 2005; Weppner et al., 2006). Data related to the surface deposition and exposure by other pathways has been examined in one or more of these studies. The study was conducted in a small farm community that consisted of residences surrounded by potato, corn and wheat ...elds. The community had a centrally located playground and soccer ...eld. The households that participated in the study were within 15–200 m of the nearest treated ...eld. Eight children participated in the studyFfour boys and four girls (see Elgethun, 2004; Weppner et al., 2006) for details on this). The children participating in the study were between the ages of 2 and 11 years. The data sources were ...eld measurements of air residues collected before, during and after an aerial methamidophos application to a potato ...eld. The details of the air sampling protocol, outdoor sampler locations and residue data used to conduct the inhalational risk assessment were reported in Elgethun (2004), Ramaprasad et al. (2004), and Weppner et al. (2006). Figure 1 shows a map of the study site where ...ve crop circles surround the residential community. The order in which the ...elds were sprayed are indicated by the A–Q letters. The ...elds located in the North, Southwest, West and East of the community were sprayed from 0500 to 0930 hours. The ...eld located to the South was sprayed from 1400 to 1500 hours. The ...elds were sprayed only after making sure (using a smoke trail) that the wind directions would not lead to a direct drift into the community. Table 1 shows the mean mass air concentrations of AI measured before, during and after the spray. The averaging time periods were based on how long the samplers measured the ...ow of air.

Model Inputs for Risk Characterization Because the scope of the modeling is primarily to evaluate the transport of volatilized material from the ...eld toward the community the model does not deal with transport of aerosolized material to the community during the spray event. This has been discussed in detail in Ramaprasad et al. (2004) and does not appear to contribute to the inhalation risk. Postspray volatilization of drifted material that has settled in the community is not included in the modeling either. This is based on ...ndings by Tsai et al. (2005) showing that the surface loading on the applied ...elds was several orders of magnitude higher than the deposition in the community.

The following parameters were used in evaluation of acute and subchronic inhalational risks for the deterministic modeling: (1) exposure time outside vs inside, (2) inhalation rate (IR), (3) toxicological data and (4) measured air concentrations of methamidophos. A discussion of the effects of meteorological variability and the probabilistic analysis to

Table 1. Average mass concentrations of methamidophos (of all samplers, n ¼ 10) measured before, through and after the day of the spray.

Time period	Mean mass concentration measured (mg/m^3)	SE of measured concentration
Before	0.0475	0.03
0530–1030 hours	0.174	0.13
1130–0430 hours	0.479	0.26
0530 hours of spray day F 0930 hours of following day	0.121	0.06

Figure 1. Application map showing order of spray and wind direction for community and surrounding ...elds. The community area is indicated by the rectangle within the grid area. There are ...ve potato crop circles labeled as SW, W, N, E and S. The arrows indicate the initial 15−min wind direction when spraying began on that particular ...eld. The letters A–Q represent the ordered sequence of 15−min swathes that were sprayed by the plane (adapted from Tsai et al., 2005). The location of outdoor air samplers is shown.

investigate the impact of meteorological variability also is included in this section.

1. Exposure Time Outside vs Inside: In the absence of indoor monitoring data the daily exposure can be assumed as the 24−h exposure at the ambient outdoor concentrations as carried out by Lee et al. (2002), who have cited other studies to justify this approach (e.g. Camann et al., 1993). In this case study, we had a partitioning of time spent indoors vs outdoors (Elgethun, 2004; Weppner et al., 2006) and we used this information to calculate exposure. The indoor–outdoor fraction (IOF) represented the portion of time spent outdoors in a 24 h time period. This IOF is speci...c to the spray event being reported and discussed in this study. To address a conservative exposure scenario, we set the IOF to one if even one child was outside during any portion of the period that the exposure was being evaluated, and we set it to 0 if not even one child was outside.

2. Inhalation Rate: According to the Child Specific Exposure Factors Handbook (USEPA, 2002a,b: Tables 7–11) the IR for 3 to 10−year−old boy children is 2.40 m^3/h and for 3 to 10−year−old girl children is 2.28 m^3/h for high activity levels. We used an average of these two values, normalized by the body weight of 23 kg (average body weight for 3 to 10−year olds) to get a conservative IR value for the children sampled in the study during outdoor activities, of 2.44 m^3/kg/day.

3. Toxicological Data: The revised toxicology paper of the Methamidophos Registration Eligibility Decision (RED), (USEPA, 2000) reviewed all the required regulatory toxicol−ogy studies of the acute, subchronic and chronic effects of methamidophos. A subchronic 90−day inhalation toxicity study was classi...ed as acceptable by the EPA. This study was the only available toxicological study of exposure by inhalation, so we used it as the basis for characterizing inhalation risks.

The no observed adverse effect level (NOAEL) identi...ed by the EPA in the inhalational study was 0.001 mg/l based on plasma, erythrocyte and brain cholinesterase inhibition at 0.005 mg/l (the lowest observed adverse effect level). EPA stated ''the NOAEL of 1.1 mg/m^3 is selected for all exposure periods because this value is derived from the only study available for inhalation risk assessment.''

EPA set the margin of exposure (MOE) for acute, subchronic and chronic toxicity from non−occupational exposures at 300 (10 for intraspecies variation, 10 for interspecies extrapolation and 3 from the Food Quality Protection Act or FQPA (USEPA, 2000). The FQPA factor lowers acceptable exposures downward by incorporating an uncertainty factor when the toxicology database is incom−plete, and/or there are concerns about the enhanced susceptibility of children, neurotoxicity, or endocrine system toxicity.

Inhalation exposure was also compared to the acute population adjusted dose (aPAD), which is typically used by EPA for the characterization of acute dietary risk. The aPAD of 0.001 mg/kg/day is derived from the MOE adjusted (factor of 300) NOAEL (0.3 mg/kg/day) from an acute neurotoxicity study with rodents (USEPA, 2002a,b). Esti−mated exposures would not exceed EPA's level of concern (LOC) if the ratio of the PAD to the estimated exposure expressed as a percentage does not exceed 100%. EPA's expression of risk is equivalent to the hazard quotient (HQ) concept, where a toxicologically relevant level is ratioed to an exposure and expressed as a simple ratio (Eq. (8)). EPA considers an exposure to be above the LOC when the HQ41.

4. Measured Air Concentrations of Methamidophos (mg/m^3): Methamidophos applications to the potato ...elds occurred in two time periods lasting 4 h in the morning and 1 h in the afternoon. Air samplers operated in the morning between 0530 and 1030 hours and in the afternoon between 1130 and 1630 hours. Air samplers also were operated the day before spraying and overnight after spraying ended until the next morning (1730–0930 h). Table 1 shows the residue data averaged over each of four time periods F the day before application, the morning spray, the afternoon spray and the overnight postspray period. Postapplication mea−sured air concentrations were signi...cantly higher than those on the day before the spray (Ramaprasad et al., 2004; Weppner et al., 2006) suggesting volatilization of previously deposited residues.

Peak gas phase residues were observed during the after−noon period in association with the highest temperatures of the day. Air residues during this time period, as well as those collected after spraying ended, were likely to have resulted from volatilization rather than generated as aerosols during spraying (Ramaprasad et al., 2004).

Measured Air Concentrations: Acute Exposure As part of the Washington Aerial Spray Drift Study (Weppner et al., 2006), air sampling was also conducted within residential homes. Because indoor air samples were near or below detection limits (Elgethun, 2004) it was determined that children playing outdoors were more likely to have been exposed to volatilized methamidophos residues than children playing indoors. Children's activity preapplication, during and postapplication were recorded using GPS tracking (Elgethun, 2004). For a point estimate of the acute inhalation risk during and immediately following spraying, we used a residue air concentration of 0.48 mg/m^3 (Table 1). This concentration is used in the MOE calculations for the time immediately after the spray. (The MOE is de...ned by the EPA as the ratio of the NOAEL to the estimated exposure dose.)

We also estimated the acute risk for the period of 26 h following the spray (we had available measurements over a 26 h period). This risk is estimated numerically using the HQ approach. The HQ is expressed as the ratio of the estimated intake to the RfD. To estimate the HQ, we calculated an average daily intake (ADI). Most of the air residues within residence homes were not detected. The highest indoor air concentration of methamidophos was 0.03 pg/m^3, seven orders of magnitude lower than the outdoor air samples (Elgethun, 2004; Weppner et al., 2006). We assumed that children could be outside anytime following the end of the spray period, that is after 1730 h. Inhalation exposure was calculated as a time-weighted average of the measured concentrations (C_{twa}) over the time periods during and after the pesticide application (Eqs. (1) and (2)).

$$C_{twa} = \sum C(t)\, t \quad (h) \qquad (1)$$

where C(t) represents the concentration at any time interval and t represents the number of hours in that interval (based on sampling intervals shown in Table 1).

$$C_{twa} = ((0.174\ (mg/m^3) \times 5\ (h)) + (0.479\ (mg/m^3) \times 5\ (h)) + 0.121\ (mg/m^3) \times 16\ (h)))/26\ (h) = 0.20\ ug/m^3 \qquad (2)$$

ADI (ADI_A for acute exposure and ADI_{SC} for subchronic exposure) was calculated using the formula below:

$$ADI_{AI}(mg/kg/day) = \frac{C_{twa}(mg/m^3)\ IOF(t)}{IR\ (m^3/kg/day)} \qquad (3)$$

(IR = inhalation rate (m^3/kg/day); IOF(t) = Indoor–outdoor factor = 1 if any child in the dataset was outside, IOF(t) = 0 if no child is outside).

From the observations (data on the children's locations and activities collected as part of the study and documented in Elgethun (2004)) we see that at least one child was outside during all or part of the time periods considered. We calculate an ADI as

$$ADI_{A2} = 0.20 \times 10^{-3} \times 2.44\ mg/kg/day = 4.88 \times 10^{-4}\ mg/kg/day$$

This amounts to the very conservative assessment of inhalation dose as the IOF = 1, and IRs were always assumed for high activity levels. However, this approach sets an upper bound to the risk as far as time spent outdoors by any of the children.

Measured Air Concentrations: Subchronic Exposure Subchronic risk is calculated from exposures occurring during one spray season. According to methamidophos usage statistics in Washington State (USDA NASS, 2004), potatoes receive an average of 1.6 applications per season. These applications are used to control aphids and thus are likely to occur within a single month during the summer when plants are most susceptible to rapidly developing populations. Because methamidophos residues in the houses were near or below detection limits (Elgethun, 2004; Weppner et al., 2006), we modified the approach taken by Lee et al. (2002) to estimate subchronic inhalation risk by applying an IOF to account for actual time only spent outdoors. We calculated the ADI (ADI_{SC}) from inhalation using the following formula (Eq. (3)):

$$ADI_{SC}(mg/kg/day) = C_{air}\ IR\ IOF$$

C_{air} = air concentrations of methamidophos (mg/m^3) time weighted over a 30-day period.

According to the EPA perspective of pesticide residue dissipation on surfaces following spraying, the concentration decreases exponentially to 0 over a period of 30 days (USEPA, 1994). This 30-day period is the time estimated for 99% of the material to have left the surface through runoff, surface volatilization, etc. The half-life values chosen were selected after an analysis that looked into which range of values would best validate the measurements we had. For the purpose of validation with air concentration measurements made on the spray day, the half-life of methamidophos was set at 36 h to include losses from plant and soil uptake as well as volatilization. This is consistent with decay constants calculated from half-life values for methamidophos loss from soil (1.9–12 days – U.S. EPA, 1989) and vegetative surfaces (4.8–5.9 days – Antonious and Snyder, 1994).

Applying the exponential decay constant to the highest mean air concentration (C_0), we calculated the time-weighted average methamidophos air concentrations for a 30-day postapplication period (Eq. (4)). We then substituted this average concentration for the air concentration in the calculation of the ADI and then the MOE.

$$C_{avg} = \frac{1}{t}\int_0^t C(t)\,dt = \frac{1}{t}\int_0^t C_0 \exp(-\lambda t)\,dt \qquad (4)$$

where C_{avg} = time-weighted average concentration of pesticide in community air ($\approx 0.03 \times 10^{-3}$ mg/m^3); C_0 = 0.48 mg/m^3 and C(t) = concentration at any time interval.

Probabilistic Risk Assessment

Effects of Meteorological Variability: Analysis of Historical Data The distribution of sprayed and volatilized material moving from the targeted application areas into the community was influenced by the meteorological conditions on and immediately after the day of the spray. Characterization of acute inhalation risk based on study specific conditions would only be descriptive of exposures occurring at the time of the application. To extrapolate risk to other meteorological scenarios we extracted historical meteorological data (specifically temperature, wind speed and wind direction) over an 11-year period for the local area. The data were collected and archived by the Washington Agricultural Weather Network (AgWeatherNet; http://weather.wsu.edu/awn.php), formerly knows as the Washington State University Public Agricultural Weather System. We simulated the transport of volatilized material from the ...ve sprayed ...elds using the EPA fugitive dust model (FDM−modeling details discussed in Ramaprasad et al., 2004; Tsai et al., 2005) for varying wind directions, using a reference wind speed (3 m/s) and temperature (300 K or 26.81C). These data were used to estimate the transport of volatilized material into the community under different meteorological conditions than those that occurred on the spray day studied.

The meteorological data (temperatures, wind speeds and wind directions) over an 11−year period (1994–2004) were analyzed for the local area of the pesticide application. The hourly temperatures on the day of spraying during 2002 and the long−term (11 years) statistical average distribution are shown in Figures 2 and 3, respectively. The maximum temperature on the day of the spray observed in the case study was the highest recorded temperature in July for the period from 1994 to 2004, which meant that the volatilization estimates on that day were higher than average. Figure 4

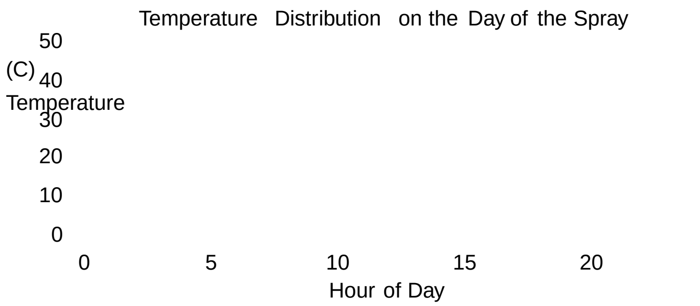

Figure 2. Temperature distribution in spray area on the day of the spray. Zero on the x−axis is 1200 hours on the day of the spray.

is a wind rose of wind speeds measured every 15 min on the day of spraying in July 2002. The maximum frequency of winds arose along the 292–3151 vector with a lesser frequency occurring between 3151 and 3301. In contrast, to the July 2002 meteorological conditions, 11−year historical winds occurred more frequently along the 225–2471 vector (Figure 5). The second most frequent wind directions occurred along the 270–292.51. The difference between the frequency of winds on the day of application and the historical records suggest exposures during July could be quite different depending on the emissions from speci...c ...elds relative to the location of the community.

Probabilistic Analysis to Investigate the Impact from Meteorological Variability For a better understanding of the impact of variable wind speeds and wind directions on air concentrations in the community, we conducted a probabilistic analysis, which included bootstrap sampling of temperature and wind conditions from the historic data to generate a distribution of possible air concentrations in the community.

1. We combined historical meteorological data with a dispersion model to simulate effects of meteorological variability. The dispersion model predicts concentrations at different receptor locations corresponding to the homes in the community for different initial meteorological conditions.

We created a database of various possible meteorological events using the 11−year meteorological database, that included 15−min temperature, wind speed and wind directions for each July of the 11 years. The look−up table of wind directions vs concentrations was developed from the FDM

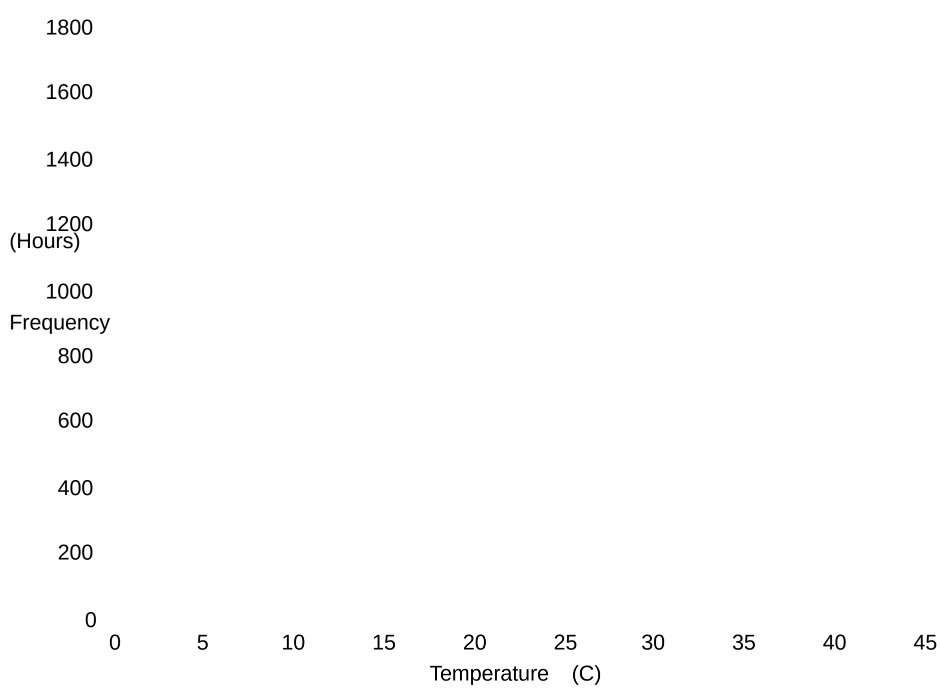

Figure 3. July temperature distribution in spray area analyzed over a 11−year period (total number of measurements ¼8183).

N

20%

NW

15%

NE

10%

W

E

N = 95

Calm winds 0%

Bars indicate the frequency of winds of a given speed from the plotted direction.

SW

SE

S

Wind Speed (m/s)

0−1.5 1.5−2.5 2.5−3.5 3.5+

Figure 4. Fifteen minutes wind direction distribution on the day of the spray.

simulations for a temperature of 300 K (26.8°C) and a wind speed of 3 m/s as mentioned in ''Probabilistic risk assessment under effects of meteorological variability: analysis of historical data'' section. The air concentrations of the AI averaged over all receptor locations in the community was calculated based on the wind direction value in the historical database for each 15-min interval, that is the air concentration in the community was accessed from the database for each 15-min time interval using the wind direction at that time period. Because this concentration was simulated for a reference temperature of 300 K (26.8°C) and wind speed of 3 m/s, it was adjusted for the wind speed and temperature at the relevant time interval in the archival database. The wind speed adjustment is a linear scaling relative to the reference wind-speed of 3 m/s (Eq. (6.2) Pasquill and Smith, 1983). The temperature is used to adjust the methamidophos flux emitted from the fields (Woodrow and Seiber, 1997) because the volatilization emission flux, Q, is a function of temperature according to:

$$Q_1 = e^{(11.79+(0.85543\log(P)))} \quad (5)$$

$$P = P_{300}e^{(-A((1/T)-(1/300)))} \quad (6)$$

where P_{300} is the VP corresponding to 26.8°C (a reference temperature and pressure), P is the VP corresponding to the temperature, T, in the 15 min interval and A is a constant in Eq. (6) (Clausiu–Clapeyron equation).

2. This approach to modeling community air concentrations was validated using meteorological data for July 12th, 2002 — the day of the case study spray event — from the database. The measured methamidophos air concentrations were used to validate the simulations. The model slightly underpredicted the measured concentrations during two of the time periods, and slightly overpredicted them during one time period. The predicted value was 0.07 mg/m^3 vs the 0.17 mg/m^3 measured in the morning, 0.59 mg/m^3 predicted vs 0.48 mg/m^3 measured in the afternoon of the spray day, and 0.07 mg/m^3 predicted vs 0.12 mg/m^3 measured for the day after the spray.

3. A Monte Carlo simulation was developed to investigate the impacts of meteorology and uncertainty in the decay rate and initial amount of the AI, that is superficially available for volatilization on the concentrations in the community. This was implemented by using a bootstrap of observations of meteorological conditions from the historical dataset along with a modeled uncertainty in the volatilization decay rate. The amount of material available to be volatilized from the applied surface is a function of many different losses — soil absorption, runoff, volatilization and plant uptake, etc. We have combined all the losses into two parameters — an initial

N
20%
NW
15%
NE
10%
W
E
N = 26301
Calm winds 0.11%
SW
SE
Bars indicate the frequency of winds
of a given speed from the plotted direction.
S
Wind Speed (m/s)
0−2.5 2.5+

Figure 5. Distribution of hourly wind directions in the spray area in July analyzed over a 11−year period from 1994 to 2004.

adjustment for the emission factor and the half−life. We used a triangular distribution (a continuous distribution de...ned by a lower limit, a mode and an upper limit) to sample for the half−life and the emission factor. The parameters of the distribution for the half−life were (min ¼ 24 h, mode ¼ 36 h and max ¼ 96 h, based on the half−life variability from 1 to 4 days, a subset of the values in U.S. EPA (1989). As mentioned in ''Deterministic risk assessment: case study'' under Methods section, a half−life value of 36 h was used as the mode because it best validated our measurements. The initial emission rate varies from 0.1 to 0.75 of the applied amount, in our distribution. This range is estimated based on the partitioning of the AI into other compartments where it would not be available for immediate volatilization. These are bounding estimates that are uncertain because of lack of speci...c data on this in the current literature. The mode of 0.25 for emission rate was used in the distribution because it best validated the measurements.

Given that the initial emission rate distribution was uncertain we explored the impact of choosing a uniform distribution, which has more frequent extreme values. The use of a uniform distribution instead of a triangular distribution for the emission rates resulted in mean concentrations proportional to mean emission rates as expected from the triangle distribution case. The variability also scaled proportionately with emission rates and amounted to a 10% increase in the variability in concentrations in the community compared to the triangle distribution case. This additional variability is small as compared to the overall variability in concentrations from meteorological inputs (see Figure 6) and so the choice of the distribution function does not appear to have a major in...uence on the simulation results.

The Monte Carlo simulation was carried out to calculate the range in community concentrations of AI because of variability in the meteorological conditions, emission rate and decay rate. Instead of the conventional approach of constructing a frequency distribution of wind speeds, wind directions and temperatures, we sampled from the historical data directly. The advantage of this is that the inherent covariances in the data are preserved. A 15−min interval was randomly picked from the database as a starting point for the analysis. Only start times that were between 0600 and 1800 hours were selected as suitable for continuing this analysis because, that is the most representative of the possible postspray acute (24 h) risk that we were attempting to characterize. At each successive 15−min interval for the next 24 h following the initial start time, a community concentration is calculated using the FDM output and the look−up table of meteorological variables.

The distribution of 24 h average air concentrations in the community was estimated from a dataset of 400 realizations of dispersion simulations. A total of 59 such datasets each

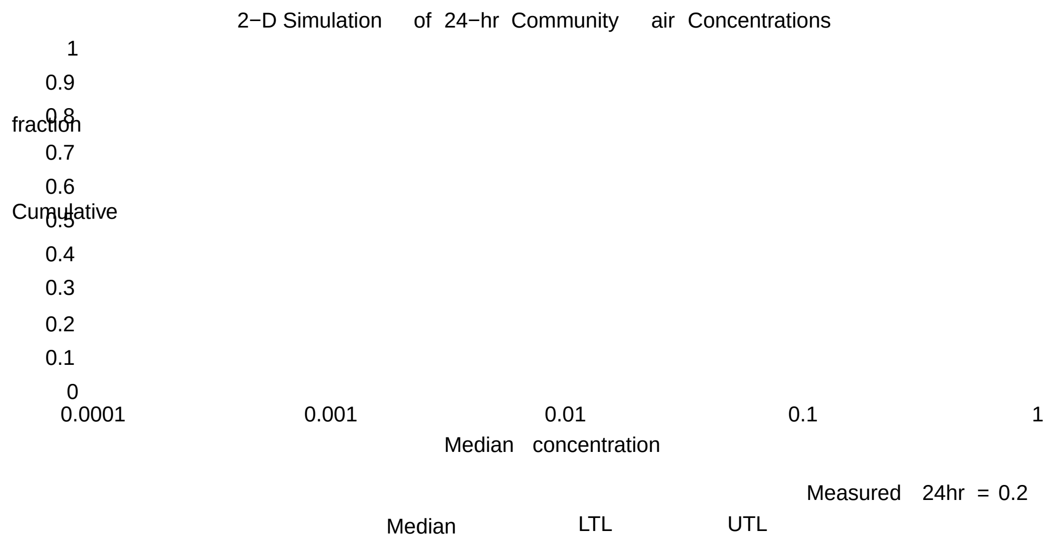

Figure 6. Simulation of variability of concentrations in the community with variability in meteorological conditions and decay rate.

with 400 realizations was performed (23,600 realizations). Each of the 59 datasets was ranked to obtain estimates of the percentiles of the 24−h concentration distribution, and the median value within each percentile was calculated along with the maximum and minimum in each percentile from the 59 datasets. The matrix size of 400 59 realizations was chosen based on sample size calculations for the tolerance limits on the percentiles of the distribution. According to Conover (1980), the median value estimated from a set of 400 realizations has a 95% chance of containing the true population median, and other percentiles will be estimated with at least 95% con...dence. Also, the maximum or minimum percentile values selected from a set of 59 values constitute upper and lower 95% tolerance limit on the population percentile value with 95% con...dence.

Results

Deterministic Analysis

Acute Inhalation Risk Immediately Following the Spray We evaluated the risk of acute inhalation toxicity from volatilization of methamidophos in a scenario where children come out to play immediately after cessation of spraying. Results from the ...eld study (Elgethun, 2004; Weppner et al., 2006) demonstrated that children were indoors during spraying but played outside for a short time after spraying. Elgethun (2004) measured and analyzed the location of the children in relationship to the location where surface pesticide residues were present near and within the community. It was found that children, on average, spent the majority of their outdoor time on the spray day between 30 and 150 m of the edge of the nearest upwind treated ...eld.

The calculated MOE (Eq. (7)) was approximately eight−fold greater than EPA's LOC (equivalent to MOE 300).

$$MOE_{calc} = \frac{NOAEL}{\text{Air concentration}} = \frac{1100\ \mathrm{ug/m^3}}{0.48\ \mathrm{ug/m^3}} = 2292 \qquad (7)$$

$$HQ = \frac{\text{Average daily intake (mg/kg/day)}}{\text{Population adjusted dose (mg/kg/day)}} \qquad (8)$$

$$HQ = \frac{0.00049\ \mathrm{mg/kg/day}}{0.001\ \mathrm{mg/kg/day}} = 0.49$$

As EPA's LOC occurs when $HQ > 1$ we see that we are well below this value in this example. It is important to note that this is an upper bound for the HQ because we used conservative estimates for the IRs (high activity levels) and an IOF = 1 if even one child was outside for any part of the period. We also note that the ADI value here does not include non−inhalation sources of exposure like the dermal or oral routes.

SubChronic Risk for a Spray Season Using C_{avg} as calculated in Methods section, we calculated a MOE of 11,000 (based on the inhalation toxicity NOAEL). The subchronic HQ was based on the 30−day ADI adjusted by the IOF. The ADI was calculated as 7.32 10^{5} mg/kg/day (0.03 10^{3} 2.44 1). The HQ was conservatively determined using the chronic oral RfD (1 10^{4} mg/kg/day, USEPA, 2002a,b) as the toxicological comparison level, similar to the approach of Lee et al. (2002). The HQ was under EPA's LOC of 1 even when considering the upper bound conservative scenario of IOF = 1, and an IR for high

Table 2A. Acute and subchronic risk for spray event F margin of exposure calculation

Risk	Estimated exposure (mg/m^3)	ReferenceF [a]NOAEL	Margin of exposure
AcuteFimmediately after the spray	0.48 (concentrations in the evening of spray when children came outside)	1100	2292
Subchronic	0.03	1100	36,666

[a]NOAEL F no observed adverse effect level.

Table 2B. Acute subchronic risk for spray event F hazard quotient calculation

Risk	Average estimated exposure (mg/m^3)	Duration of exposure	Average daily intake (ADI; mg/kg/day)	Reference	Hazard quotient
Acute− for the period of 26 h following the spray	0.2	26 h	0.0194 10^{3}	[a]aPAD ¼ 0.001	0.194
Subchronic	0.03	30 days	7.32 10^{5}	Chronic oral RfD ¼ 1 10^{4}	0.732

[a]aPAD F acute population adjusted dose.

levels of activity. The acute and subchronic risk estimates are laid out in Tables 2A and 2B.

The average daily exposure and subchronic risk character− izations relied upon an assumed rate of residue decay from surfaces postapplication. Although this rate was validated by previously reported foliar half−lives (e.g. Antonious and Snyder, 1994), continuous monitoring of the concentrations for several days after a spray would have given a more accurate estimate of the subchronic risks associated with inhalational exposures.

Probabilistic Analysis

The air concentration distribution that was created with the Monte Carlo simulation was lognormal with a geometric mean of 0.05 mg/m^3 and geometric standard deviation of 3.4. The interquartile range of the simulated values of concentra− tions was 0.02–0.11 mg/m^3. The observed value of 0.2 mg/m^3 (based on measurements on the spray day) fell in the 90th percentile of the distribution.

The median value of the 95th percentile of air concentra− tions was 0.28 mg/m^3, the upper tolerance level was 0.35 and the lower tolerance level was 0.22 (see Figure 6). These simulated concentrations corresponded to a HQ of 0.68 with upper threshold level HQ of 0.85 and lower threshold level HQ of 0.54, all of which were below the LOC corresponding to a HQ of 1.

Discussion and conclusions

We used measurements of methamidophos in air made during and after an aerial pesticide spraying to examine potential acute and subchronic risk for children who live in communities very close to agricultural ...elds sprayed with pesticides. From this set of observations, we calculated average concentrations in the community and compared them against the available RfD information for acute and subchronic inhalation risks.

The baseline estimates of the acute and subchronic risk for children were well within acceptable margins of exposure when the risk was characterized using measured air concentrations and a mean IR for active children of 2.44 m^3/kg/day. However, the 99.9th percentile IR (USEPA, 2002a,b), would have raise inhalation exposure estimates by about threefold. Nevertheless, even a fourfold change in IR would still result in an MOE at least twofold greater than EPA's LOC of 300.

The meteorological conditions during and after spraying can be highly variable, resulting in large ...uctuations in the amount of material translocating into areas where children may live and play. Modeling showed that changing wind directions during the spray period can contribute to increased surface deposition of insecticide residues within the commu− nity (Tsai et al., 2005).

A probabilistic analysis of variability in community air concentrations based on historical meteorological conditions in the sprayed area indicated that the inhalation risk to children from postspray volatilization of methamidophos applied to potato ...elds surrounding a residential community was below EPA's LOC. We emphasize here that the exposures and risks estimated here are only for the inhalation pathway.

The various deterministic risk estimates based on measured air concentrations also showed that the postspray volatiliza− tion in this case did not pose acute or subchronic risks as de...ned by the EPA. In contrast, Lee et al. (2002) did ...nd risks in compounds that were similar to methamidophos in toxicity and VP. For example, they found that ''short−term chlorpyrifos exposure estimates exceeded the acute reference value for 50% of children in exposed populations.'' One difference in the two studies was that they had more extensive air measurements from which they built lognormal distribu−

tions of air concentrations to use in the risk analysis. The Lee et al. (2002) analysis was applicable to an agricultural region of California wherein the air concentrations represented multiple emission sources, not just one source as in our study. Also, the intensity and extent of pesticide use, as well as the layout of the ...elds are different in Eastern Washington State than in California. Other important differences were that we did not assume that the indoor air concentrations were the same as the outdoor concentrations (based on results reported by Elgethun, 2004; Weppner et al., 2006), and we did not include variability in IRs for exposure assessment, but instead used a value for ''active'' children to get a conservative estimate of the risk.

An important aspect of this study was to estimate a distribution of possible air concentrations using available data along with meteorological measurements and dispersion modeling. As is often the case, the ...eld data gives a limited set of air concentration measurements as compared to the entire universe of possibilities concerning variability in different parameters. Although the measured data does not account for the full range of concentration values that would occur over many spray seasons it is essential in benchmarking and validating the model results. We have set up a methodology to use historical meteorological data and dispersion modeling, and used it along with measurements from the spray, to estimate the distribution air concentration near sprayed ...elds. In situations where modest air concen−tration data are available this approach provides a metho−dology to incorporate variability in the different emission and dispersion parameters to assess exposure and risk, as opposed to relying on isolated data points.

Acknowledgements

This study was supported by the US EPA (RD−83170901−0), the National Institute of Environmental Health Sciences (2P01ES09601) Child Health Centers Program and the Agricultural Centers Program of the National Institute for Occupational Safety and Health (5450OH07544). We thank Vince Hebert (Washington State University) for invaluable help with data collection.

References

Antonious G.F., and Snyder J.C. Residues and half−lives of acephate, methamidophos,and pirimiphos F methyl in leaves and fruit of green−house−grown tomatoes.Bull Environ Contam Toxicol 1994:52: 141–148.

Bedos C., Cellier P., Calvert R., Barruso E., and Gabrielle B. Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: overview. Agronomie 2002:22: 21–33.

Camann D.E., Geno P.W., Harding H.J., Giardio N.J., Bond A.E., Lewis R.G., and Akland G.G. A pilot study of pesticides in indoor air in relation to agricultural applications. In: Seppanen O. (Ed.). Indoor Air 1993: Proceedings of the Sixth International Conference on Indoor Air Quality and Climate, Helsinki, Finland, 4–8 July, Vol. 2, Helsinki 1993.

Conover W.J. Practical Nonparametric Statistics. John Wiley, New York, 1980, 493p.

Dansereau C., and Perez M. Poisons on the wind−Community Air Monitoring for Chlorpyrifos in Yakima Valley. A Report by Farmworker Pesticide Project & Pesticide Action Network North Americ; Dec 2006, http://www.panna.org/docsdrift/POWExSumEng.pdf.

Elgethun K. Global positioning system (GPS) tracking to characterize children's exposure to pesticides, PhD dissertation University of Washington, 2004.

Harnly M., McLaughlin R., Bradman A., Anderson M., and Guneir R. Correlating the use of OPs with outdoor air concentrations: a particular concern for children. Environ Health Perspect 2005:113(9): 1184–1189.

Hatzilazarou S., Charizopoulos M., Papadopoulo−Mourkidou E., and Economou A.S. Pesticide dissipation in the greenhouse environment during hydroponic cultivation of Gerbera. Proceedings of XXVI IHC F Horticulture, Human Well−Being and Life Quality 2004.

Lee S., McLaughlin R., Harnley M., Gunier R., and Kreutzer R. Community exposures to airborne agricultural pesticides in California F ranking of inhalation risks. Environ Health Perspect 2002:110: 1175–1184.

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

Pasquill F., and Smith F.B. Atmospheric Diffusion F Study of the Dispersion of Windborne Material from Industrial and Other Sources, 3rd edn. Ellis Horwood Series in Environmental Science 1983.

Ramaprasad J., Tsai M.Y., Elgethun K., Hebert V.R., Felsot A., Yost M.G., and Fenske R.A. The Washington Aerial Spray Drift Study: assessment of off−target organophosphorus insecticide atmospheric movement by plant surface volatilization. Atmos Environ 2004:38: 5703–5713.

Taylor A.W., and Spencer W.F. Volatilization and Vapor Transport Processes Pesticides in the Soil Environment: Processes, Impacts and Modeling, SSSA Book Series, Vol. 2 Soil Science Society of America, Madison, WI, 1990, pp. 213–269.

Tsai M.Y., Elgethun K., Ramaprasad J., Yost M.G., Felsot A.S., Hebert V.R., and Fenske R.A. The Washington Aerial Spray Drift Study: modeling pesticide spray drift from an aerial application. Atmos Environ 2005:39: 6194–6203.

Umsworth J.B., Wauchope R.D., Klein A.W., Dorn E., Zech B., Yeh S.M., et al. International Union of Pure and Applied Chemistry (IUPAC) pesticide report 41. Signi...cance of the long range transport of pesticides in the atmosphere. Pure Appl Chem 1999:71: 1359–1383.

U.S. EPA. Pesticide Environmental Fate One Line Summary: methamidophos. U.S. EPA Environmental Fate and Effects Division, Washington, DC, 1989.

U.S. EPA. 1994. Emission Factor Documentation for AP−42, Section 922 Pesticide Applications. EPA Contract No. 68−D2−0159 Midwest Research Institute, Kansas City, MO, September. URL: http://www.epa.gov/ttn/chief/ap42/ch09/bgdocs/b9s02−2.pdf.

U.S. EPA. 2000. Methamidophos Revised Toxicology Chapter for RED, URL: http://www.epa.gov/oppsrrd1/op/methamidophos.htm.

USEPA. Child Specific Exposure Factors Handbook. National Center for Environmental Assessment, Washington, DC, 2002a. EPA/600/P−00/002B. Available from National Information Service, Spring...eld, VA; PB2003−101678 http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid¼55145.

USEPA. Interim Reregistration Eligibility Decision for Methamidophos, Case No 0043 2002b: http://www.epa.gov/oppsrrd1/op/methamidophos.htm.

USDA NASS (U. S. Department of Agriculture National Agricultural Statistics Service). 2004. Agricultural Chemical Usage 2003 Field Crops Summary p. 71 http://usda.mannlib.cornell.edu/MannUsda/viewDocumentInfo.do?documentID¼1001.

Van den Berg F., Kubiek R., Benjey W., Majewski M., Yates S., Reeves G., et al. Emission of pesticides in the air. Water Air Soil Pollut 1999: 115: 195–218.

Weppner S., Elgethun K., Lu C., Hebert V., Yost M.G., and Fenske R.A. The Washington Aerial Spray Drift Study: children's exposure to methamidophos in an agricultural community following ...xed−wing aircraft applications. J Expo Anal Environ Epidemiol 2006:16: 387–396.

Whang J.M., Schomburg C.J., Glotfelty D.E., and Taylor A.W. Volatilization of tomofos, chlorpyrifos and atrazine from conventional and no−till surface soils in the ...eld. J Environ Qual 1993:22: 173–180.

Woodrow J.E., and Seiber J.N. Correlation techniques for estimating pesticide volatilization ...ux and downwind concentrations. Environ Sci Technol 1997:31: 523–529.