The Washington aerial spray drift study: assessment of off-target organophosphorus insecticide atmospheric movement by plant surface volatilization

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Abstract

Post-application pesticide emissions from wetted leaf surfaces and soil may present a significant pathway of exposure to humans in nearby residential communities. In this study, high volume air sampling was performed to measure airborne concentrations of the pesticide methamidophos in a residential community in close proximity to aerial spraying. Sampling occurred before, during and 24 h post-application. To evaluate whether predictive models could reliably estimate residential exposure to methamidophos, an emission factor was used for estimating fluxes of volatilized material over the sprayed area for a 1-day post-application period. These flux estimates were then incorporated into a fugitive dust gaussian dispersion model (FDM) for assessing distribution of mass around the sprayed area. The predictive model output was compared with the field air sampler measurements. In our comparison, 1-day flux estimates from the model were found to be associated to observed field measurement data, with an $r^2 = 0.63$ the day of the spray and $r^2 = 0.67$ the day after the spray. The volatilization model however appears to underestimate surface emission flux immediately after the spray and overestimate the emission the next day.
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1. Introduction

The vast majority of pesticides that enter the lower atmosphere originate from agricultural use. Aspelin and Gruber (1999) reported that approximately 2 billion kilograms of pesticides are applied each year in the United States in agriculture. In high production agriculture in the Northwest, pesticides are formulated for application over wide acreages by aerial spray or using sprinkler and center pivot ground broadcast

sprayer application systems. To minimize the potential for pesticide drift from the application site, sprayer application systems are designed to dispense a coarse droplet spectrum (usually > 200 μm) that can gravitationally settle making rapid contact with the foliage/land surface (AgDrift 2.0, 2002). Even when sprayer equipment nozzles and line pressures are carefully selected and calibrated, a proportion of the pesticide spray will invariably exist as smaller spray droplets (i.e. < 100 μm) and stay suspended in the air mass. Under stable air application conditions, off-target drift may still have the potential to cause non-target crop damage

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with potential exposure risks to humans and sensitive ecosystems (Hebert, 2001; Pimentel and Levitan, 1986; Willis et al., 1983).

Besides physical drift, post-application volatilization from plant and soil surfaces represents a second and significant source of sustained tropospheric loading (Taylor and Spencer, 1990). Chemical evaporative flux from plant and soil surfaces can be appreciable for even moderate to low vapor pressure (VP) (10^{-1} to 10^{-5} Pa) pesticides. For example, cumulative volatilization losses were estimated to approach 25% after a wheat application of the semi-volatile isoctyl ester formulation of the chlorophenoxy herbicide 2,4-D (Grover, 1991). The organophosphorus (OP) insecticide diazinon when applied to soil has been observed to have a measured volatilization rate of about $0.27\,\mathrm{g\,ha^{-1}\,h^{-1}}$ ($\sim 10^{-2}$ Pa, summer) (Majewski et al., 1990), while residues of this insecticide showed a volatilization rate of about $9\,\mathrm{g\,ha^{-1}\,h^{-1}}$ ($\sim 10^{-3}$ Pa, winter) from an orchard canopy in California (Glotfelty et al., 1990).

Understanding pesticide volatilization is important for assessing the health impacts and risks to farm-workers, their families, and nearby residential communities. Especially for the more highly toxic OP insecticides, airborne residues represent a major inhalation and dermal contact health concern. Of immediate concern is acute dermal contact and inhalation exposure from OP insecticides to children living in close proximity to agricultural operations. Children have a higher inhalation rate to body weight ratio than adults and may have comparatively immature detoxification and clearance systems and therefore are at higher risk than adults to adverse effects from airborne toxicants. Lee et al. (2002) evaluated several predictors of chronic inhalation risks for pesticides using Spearman rank correlation coefficients. They found that the pesticide's VP was the best predictor of the child chronic risk ranking ($r = 0.70$, $p = 0.003$). They also found that VP was a better predictor of lifetime cancer risk ranking than the cancer potency factor. Among the 15 pesticides evaluated in their study, VP was highly correlated with geometric mean air concentrations in rural communities. Woodrow et al. (1997) also found high correlations between VP of a pesticide and its downwind concentration. The evaporation rate of the pesticide's active ingredient (AI) is determined in large part by its VP. Ignoring the effects of volatilization could significantly underestimate the ambient concentrations and hazards associated with inhalation exposure.

Although there has been considerable research effort to characterize volatile soil fumigant flux (Yates et al., 2003) relatively few field volatility experiments have been undertaken to reliably estimate human exposure for the majority of semi-volatile pesticides (Majewski and Capel, 1995). Studies on semi-volatiles have been problematic due to the wide range of pesticide physio-chemical properties and site-specific soil/climatic conditions that can greatly influence surface flux measurements (Haith et al., 2002; Yates et al., 2003). As a result, post-application predictive models that can reasonably estimate plant and soil surface pesticide volatilization with climatic condition inputs will be essential in human exposure assessments.

The objective of this paper is to compare actual pesticide residues in air samples on the day of a routine spray in a potato field in eastern Washington with concentrations predicted by the Environmental Protection Agency (EPA) Fugitive Dust Model (FDM). This gaussian dispersion model uses source emission terms for volatilization that are based on a simple representation of the mechanics of pesticide mobility through the environment and into the atmosphere. It has been previously shown to reliably estimate distribution of airborne mass from a source area (Kim and Larson, 2001). This readily available modeling approach was selected to evaluate its applicability and reliability for estimating plant surface volatilization shortly after a spray event.

2. Theoretical calculation of surface to atmosphere mass fluxes from volatilization

Several field and laboratory studies have been conducted to understand the processes that influence the emissions of pesticides from the surface to the atmosphere (Glotfelty et al., 1984; Taylor et al., 1976; Claith et al., 1980). Three factors found to have the greatest influence in the volatilization of pesticides are: (1) the physical properties and distribution characteristics of the AI (e.g. VP and Henry's Law constant), (2) meteorological conditions (e.g. surface emission rate is positively correlated with temperature, low relative humidity and wind speeds/turbulence) and (3) environmental factors that can influence movement from the land surface boundary conditions (Jury et al., 1983a, b). In the case of aerial spray, the physical properties of the active ingredient (VP) and the meteorological properties (temperature, wind speed) play a more important role than the soil adsorption coefficients which would be more significant in the case of pesticides mixed in with the soil.

2.1. Volatilization emission factor model (VEFM)

A predictive model was used to estimate the emission factor (EPA, 1994). This model was validated by the EPA from a limited database of field and laboratory studies and will be referred to hereafter as the VEFM. Emission estimates of the AI are based on the numerical averages of data for two ranges of AI VP. The model was developed for use with surface and soil applications

and does not account for evaporation from falling spray droplets during aerial application. The VEFM is used in this evaluation to calculate only volatilization from the wetted surfaces after the aerial application event. Volatilization is a dominant removal process for a period of time after field application. The VEFM estimates an emission factor over a 30-day period. After 30 days, however, other degradation processes such as surface run-off, plant uptake and soil adsorption can dominate (Jury et al., 1983a, b, 1984a, b). Furthermore, limited data are available in the published literature on pesticide volatilization in field application studies with sampling times greater than 30 days (EPA, 1994). The 30-day emission factor is used to calculate volatilization decay constant for a defined unit of time, such as 15 min or an hour. For AIs with VP > 0.013 Pa the data shows that on average the total loss of AI within 30 days after application was 58%. For AIs between 0.013 and 1.3×10^{-4} Pa, the data shows that on average the total loss over the 30 days was approximately 35%. The average percentage loss is subject to considerable uncertainty since within each of the VP groups there can be considerable variability of field conditions from one field test to the other. However, based on the constraints of the models and lack of field data for validation the use of the average percent values may well represent a best emission estimate. This model is a useful approximation for the volatilization source term of gas phase emissions. It provides a simple source term based on the applied mass and VP of a compound. The emission factor–VP relationship is represented as a discrete binary function. Although it accounts for some VP differences between compounds, it does not account very accurately for the temperature dependence of volatilization (i.e. higher volatilization at higher temperatures). The emission factor would ideally be more accurately represented as a continuous function of VP. Lastly, this algorithm accounts only for gas-phase emissions.

2.2. Methamidophos

Methamidophos in an emuslifiable liquid formulation (40% *O,S*-dimethyl phosphoramidothioate, 60% inert ingredients) was applied at a rate of 0.45 kg (1 lb) AI per acre. It is a semi-volatile OP insecticide with an estimated VP of 2.3×10^{-3} Pa at 20°C (Crop Protection Handbook, 2003). When applying the Clausius Clapeyron relationship (Perry and Green, 1997) the VP of methamidophos should increase to 4×10^{-2} Pa at 30°C. Methamidophos is also the breakdown product of acephate, which is a heavily used pesticide.

Applying the VEFM, the emission factor is estimated at 0.350 g/kg for AIs with 1.33×10^{-4} Pa < VP < 1.33×10^{-2} Pa and 580 g/kg for those with VP greater than 1.33×10^{-2} Pa. The half-life of methamidophos ranges

from several hours to several days depending on the soil type over which it is applied. The soil type in the area of the field site is silt loam (personal communication, Larry Hooker—USDA, WA). The half-life of methamidophos varies from 1.9 days for silt and 4 days for loam (US EPA 1989). This half-life is based on environmental losses through leaching (the most significant loss pathway for methamidophos based on its highly soluble nature), run off, soil adsorption, etc.

3. Spray event

A description of the spray event is provided in Weppner et al. (2004). The field site was a farm community of approximately 100 residents in east central Washington. The terrain is mostly flat surrounding the community for approximately 5 km in all directions. All participating families lived in farm housing surrounded by potato, corn and wheat fields (crops are rotated yearly). Participating households were within 800 m of each other and were within 15–200 m of the nearest treated field.

The locations of the houses, the coordinates of the edges of the sprayed fields, and the locations of deposition and air samplers were measured using a global positioning system (GPS-PAL, Enertech, Campbell, CA). These GPS coordinates were then mapped and used to inform drift modeling and exposure estimations.

Spray synopsis: Cultivated potato fields adjacent to the residences were scheduled for aerial application of methamidophos at an unspecified date in late July to control green peach aphids. A single 1340S2R Thrush aircraft with a 400-gallon tank flying at approximately 180 km h^{-1} (110 mph) and a maximum 3 m (10 ft) above the crop canopy sprayed 5 fields for a total of 700 ha. Methamidophos was applied at a rate of 0.45 kg (1 lb) AI per acre beginning at 5:00 a.m. on the day of application. Four fields located to the north, southwest, west and east of the community were sprayed from 5 a.m. to 9:30 a.m. A total of 700 ha of potatoes were aerially applied with the pesticide. Spray was suspended as wind speeds exceeded 8 km h^{-1} (5 mph) at 9:30 a.m. The winds abated and spraying recommenced in the afternoon at which time the south field was treated. The second spray began at 2:00 p.m. on the day of application and continued until 3:00 p.m.

Air sampling synopsis: Ambient air and deposition monitoring was initiated 12 h before, during and 24 h post-application in a community located nearby (within 50 m) of the applied fields (Fig. 1). Local meteorological data were obtained at 15 min intervals for the day of the spray from a Washington State University "PAWS network" weather station located 2 km south of the applied fields over flat terrain. On the day of the spray
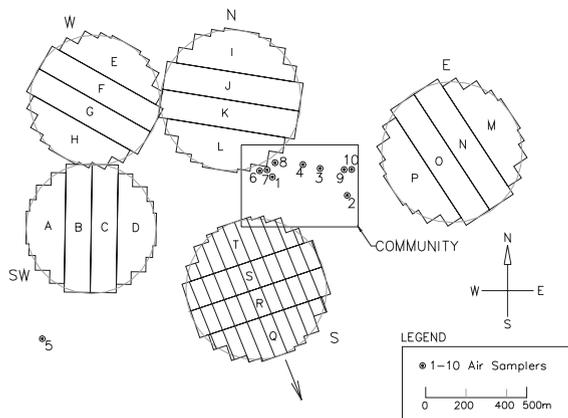
Fig. 1. Location of sprayed fields (circles) and samplers. Wind is blowing away from the community in the afternoon (as shown by the direction of the arrow). The south field labeled S is the field sprayed in the afternoon.
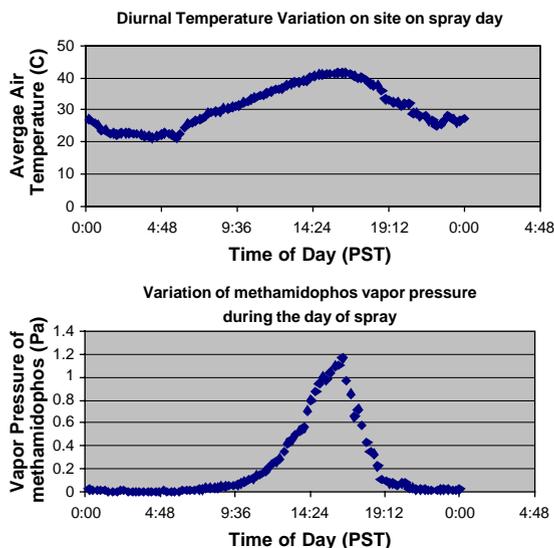

Fig. 2. Variation in temperature and VP on the day of the spray.

the temperatures rose to as high as 42°C (Fig. 2) and at this temperature the VP of methamidophos is significantly higher than at 25°C. The VP of methamidophos was calculated as it varied with temperature through the day, and this was used to calculate the emission factor as a function of temperature. When the temperature exceeded about 24°C the VP of methamidophos was over the threshold limit of 1.33×10^{-2} Pa, resulting in a step increase of the emission factor from 0.35 to 0.58 g kg^{-1}. Fig. 3 shows the estimated mass volatilizing through the day from a single sprayed patch.
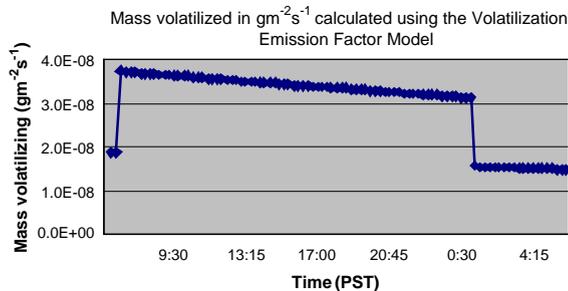

Fig. 3. Flux of mass volatilized from a sprayed patch through the day. This is derived from the Emission Factor in the VEFM. The patch was sprayed at 6:00 a.m. at a rate of 1 lb acre^{-1}.

3.1. Air sampler data collection and the fugitive dust model

Methamidophos was absorbed from outdoor air on polyurethane foam (PUF) with three different air samplers running at three different flow rates: in participants' yards at 20–28 lpm (SKC Hi Lite Pump); at either end of the community at 30–32 lpm (Staplex TFIA Pump, 2 PUFs per pump co-located); and at two locations in the center of the community at 180–200 lpm (Anderson High Volume Pump). Sampling began the night before the spray, and continued during and 12 h post-application. The PUFs were changed at least once every eight hours. PUF plugs were changed between the two spray periods on the spray day. The Food and Environmental Laboratory (FEQL) at Washington State University provided analytical support for quantifying methamidophos residues (AI in Monitor 4®) from air sampling adsorbents. PUF media used in trapping methamidophos from the ambient air were solvent extracted in ethyl acetate, and then ultrasonicated. The solvent volume was reduced by roto-evaporation before performing a carbograph solid phase cleanup. The solvent extracts were then analyzed to determine methamidophos residues by gas chromatography with pulsed-flame photometric detection.

Before performing actual residue analyses, a validation was performed. The validation was conducted by fortifying methamidophos at three concentration levels. Each concentration level was conducted in triplicate with the low-level spikes at the method's established limit of quantitation (LOQ) of 0.1 μg total methamidophos per PUF. The method was considered validated if recoveries fell within 70–120% for the analyte(s) with a combined coefficient of variation $<20\%$. For each set of prepared samples at least one recovery fortification sample was prepared by injecting a known volume of methamidophos solution (known concentration) into the PUF media. The recovery samples were extracted and analyzed in the same manner as the field ambient air

samples. For samples that could not be analyzed within 14 days from time of field sampling, separate storage stability studies for both small and large PUF were performed to demonstrate the analyte's integrity over the maximum frozen storage interval. Details on the quality assurance and quality control of the methods can be found in an analytical summary report by Tomasz-weska and Hebert (2003).

Fig. 1 shows a layout of the sprayed fields (circles) and the community location where the air samplers were placed. The patches represented in Fig. 1 were sprayed in sequence from A to T, with each patch corresponding to approximately a 15-min time interval. Patches A–P were sprayed in the morning and are part of the AM-spray event. Patches Q–T were sprayed in the afternoon and are part of the PM-spray event. Volatilization was assumed to start after the first patch was sprayed. It was anticipated that this and other patches would continue to volatilize through the day while emissions from other patches were added sequentially (from A to T) as spraying progressed through the day. Surface to air fluxes of methamidophos were calculated based on an initial spray amount of $1 \, lb \, acre^{-1}$, the temperature variation through the day and the relationship between VP and emission factor as defined by the VEFM. As each consecutive patch was sprayed, this new wetted area contributed to the source term for the volatilized component of the AI. Updated surface loadings for methamidophos were calculated every fifteen minutes based on an estimated conservative half-life of 3 days. These fluxes were used as source terms in the FDM (Tsai et al., 2004) for calculating downwind concentrations at distances equivalent to where the air sampler data were located.

The FDM is a robust gaussian dispersion model that computes transport of particles from fugitive dust sources (Users Guide for the FDM, 1993). It is used extensively for modeling dispersion of aerosols and has been used by Tsai et al. (2004) to predict the transport of aerially sprayed pesticide in the Washington Spray Drift Study (see Weppner et al. (2004) for study design description). Tsai et al. (2004) have validated the model output for the same spray event while examining transport and deposition of the sprayed particles. Although the FDM is applied for aerosol (dust) transport it is adapted here to model gas transport by

choosing a mono-dispersed particle size distribution that has a negligible gravitational settling rate. Since very small particles follow airflow like gases it is possible to simulate gas transport by choosing sufficiently small particle sizes (Hinds, 1982). Gravitational settling is increasingly important for sizes larger than $1 \, \mu m$ in diameter. Particles sized in the range from 0.1 to $1 \, \mu m$ show the minimum values of deposition velocity. A mean size of $0.3 \, \mu m$ is used here to represent gas transport in the model. The FDM uses meteorological data (temperature, wind speed, wind direction, stability), a particle size distribution and source emissions as input.

4. Results

Pre-application spray data were collected on the day before the application. The AM-spray data were collected between 5.30 a.m. and 10.30 a.m., while the PM-spray data were collected between 11 a.m. and 4.30 p.m. Post-spray measurements were made from the evening of the spray event through the next morning. Table 1 shows the mean and standard error for all samplers grouped by time.

A one-way analysis of variance of the air sampler measurements taken on the day of the spray found that air concentrations of AI during the afternoon spray event differed significantly from the mean values measured in the other two time periods. There were 4 h of spraying in the morning and only 1 h in the afternoon. However, temperatures were higher in the afternoon probably causing the sprayed AI on the wetted surfaces to volatilize more readily.

Figs. 4a and b show the FDM predicted results from model runs that describe volatilization. The 'during spray' (5:30 a.m. to 4:30 p.m. on the day of the spray) and 'post-spray' (5:30 p.m. to 9:30 a.m. of the following day) data were analyzed separately. There is good correlation between the modeled data and the measurements ($R^2 \sim 0.6$) both proximal to the spray application (i.e. within a few hours of it) and during the following day. However, the model underpredicts the mass concentrations immediately after the spray event, and overpredicts it later. The magnitude of this prediction error is indicated by the slope (b) of the correlation plots

Table 1
Average mass concentrations of AI (of all samplers) measured before, through and after the day of the spray

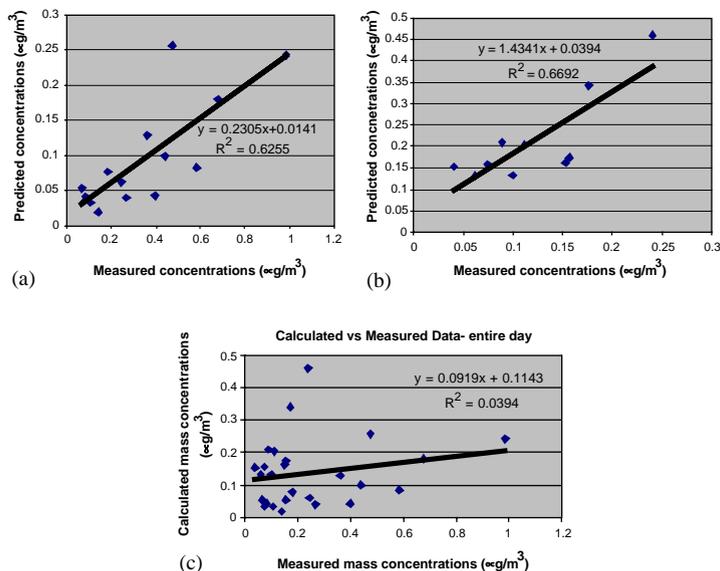| Time period	Mean mass conc. measured ($\mu g \, m^{-3}$)	SE of measured conc.	Sig. (p value of difference from mass in the 11:30 a.m.–4:30 p.m. period)
Before	0.0475	0.03	<0.00001
5:30 a.m.–10:30 a.m.	0.174	0.13	<0.01
11:30 a.m.–4:30 p.m.	0.479	0.26	
5:30 p.m. of spray day–9:30 a.m. of following day	0.121	0.06	<0.0001

Fig. 4. (a) Correlation between measured air sampler data and model predictions of distribution of the gases from volatilization of wetted fields—during the sprays. (b) Correlation between measured air sampler data and model predictions of distribution of the gases from volatilization of wetted fields—after the sprays. (c) Correlation between all measured and calculated data.

between the air samples and prediction results. In the period proximal to the spray event the model predicts levels that are only about 20% of the measured concentrations ($b = 0.23$), while on the following day the model predicts concentrations about 40% higher than the measurements ($b = 1.43$). When all the data from both spray periods is analyzed together there is poor correlation between the measured and calculated data sets (see Fig. 4c). The over-estimate in one period counters the under-estimate in the other period to bring down the overall correlation.

5. Discussion

The model calculations underpredict the air concentrations as compared to the measured values during the spray and overpredict in the hours after the spray. While there are strong correlations between measured and calculated values in the morning and afternoon individually, over-all there is poor correlation in the measured and calculated data. It is clear that volatilization from wetted fields is a process that changes significantly with time. It is likely to be most intense during the hours immediately following the spray and gradually decreases with time.

The measured air concentrations were significantly higher than the model calculated concentrations during the active spray period. The higher measured values may be due to any of the following reasons:

(a) Volatilization of the sprayed particles as they are released from the airplane contributes to the measured air concentrations.

To evaluate the potential contribution of evaporation from falling droplets a model run was conducted where it was assumed that all the sprayed material evaporated before reaching the fields. Air concentrations of volatilized AI were predicted from model runs using a size distribution with a mean of $0.3\,\mu m$ and geometric standard deviation (GSD) of 1 during the time of the sprays. This is an estimate of the gas phase transport of the material that volatilized during the actual spraying process, and not from the wetted fields. These model calculations show no contribution to the air samplers from the volatilizing spray after 9:30 a.m., during the period when the peak gas phase samples were observed. During the afternoon period there was only one spray event. Wind directions clearly ruled out that transport of the vaporizing spray droplets could have contributed to the peak afternoon measurements. We conclude that volatilizing spray particles were not the main source of measured mass in the air-sampler data in this case study.

(b) Even though the samplers are supposed to measure only gases they could be capturing some spray particles which contribute to the AI mass being measured, i.e. there could be potential over-sampling of mass due to inflow of particles. We concluded that particle loading should not be a major contributing factor for two reasons:

First, the aspiration efficiency vs. particle size for the samplers used was calculated as a function of flow rate, wind velocity, sampler inlet diameter and sampler orientation. A lognormal particle size

distribution with median diameter of 300 μm and GSD 2.5 was used with the calculated aspiration efficiency to measure the mass fraction of particles that may have been incorrectly sampled by the air samplers. This size distribution was selected by Tsai et al. (2004) to model particulate transport based on numerical fitting of deposition samplers in the study area. They used a least-squares optimization technique to minimize the differences between the measured data and model predictions, over a range of median diameters (10–500 μm) and a range of GSDs from 1 to 5.5. For the sampler characteristics and ambient conditions that represent the data collection for that day, only approximately 5% of the mass of particles could be aspirated into the air samplers (see Appendix A). This is not a significant contribution from particles.

Secondly, the winds during the afternoon were from the North Westerly direction, blowing from the field sprayed in the afternoon in the direction away from the samplers and the community (Fig. 1). The higher air concentration values seen during this time were therefore not from direct transport of sprayed particles or due to immediate evaporation of falling particles during the release, but rather came from wetted surfaces upwind of the sampler locations during the post-spray period.

We conclude from these observations that the 'contamination' of the measured gaseous concentrations of methamidophos by particles is not likely to be very significant, thus implying that the most significant contribution to the air concentration data is in fact from emissions arising from volatilization of the wetted surface of the fields.

(c) The emission factor for volatilization from the VEFM is too low. The discrepancy between measured and calculated data may arise from the strength of the emission factor, which directly influences the mass of AI volatilizing from the wetted fields.

5.1. Comparison of VEFM with other methods

Two other methods were used to calculate the fluxes to compare with the VEFM. One method was using the Knudsen equation (Tinsley, 1979). This equation describes molecular effusion from pure material and includes only intermolecular interactions (as reflected by VP) in the material

$$Q = \beta P \left(\sqrt{\frac{M}{2\pi RT}} \right) \text{g cm}^{-2} \text{ s}^{-1},$$

$\beta = 1.98 \times 10^{-5}$. Beta is a factor that corrects for fact that chemical is escaping into air and not a vacuum. This value was found as an average of 18 compounds (Tinsley, 1979).

The second method used was the correlation method described by Woodrow et al. (1997). Their work examined the correlations between physicochemical properties of various pesticides to published volatilization rates. They found a good correlation between volatilized flux and the VP of various compounds using the relationship (ln Flux (μg m^{-2} h^{-1}) = 11.779 + 0.85543 * ln (VP)).

Hourly flux in μg m^{-2} h^{-1} was calculated for methamidophos using the VEFM EPA model, the Knudsen equation and the correlation method (Table 2). The calculations are very sensitive to temperature and VP. The EPA model bases its calculations on a 30-day average. Since the 24-h average temperature in July was about 23°C at the field site, the comparisons were made at 23°C.

The emission factor from the VEF model is lower by a factor of about 20 compared with the Woodrow et al. calculation and a factor of 15 from the Knudsen equation estimates. This result is in general agreement with the finding that the VEFM also had underpredicted the volatilized fluxes (as compared to the measurements) immediately after the spray. However the Woodrow et al. calculation and the Knudsen equation both assume that only intermolecular interactions in the applied material, as reflected in the pesticide's VP, determine volatility. The flux calculated in these methods is not a function of application rate. The flux calculated in the VEFM method is a function of application rate as well as VP.

It is important to note that the use of the VEFM in our case study is not without limitations. Firstly, the VEFM estimates emissions due to volatilization over a 30-day period. The air-sampler data was only collected during and immediately (several hours) after the spray. The 30-day estimate was used to calculate emissions for the time-period over which the data was collected. Since the volatilization rate is highest immediately after spray

Table 2
Results of flux calculations from the three methods

	VEFM (EPA) (for a 1 lb acre^{-1} application rate)	Woodrow et al.	Knudsen equation
Volatilization flux μg m^{-2} h^{-1} at 23°C	~80	~1500	~1200

and declines after, the extrapolation that we did may not be the most representative. In future studies, it would be very useful to collect emissions data over an extended period of time (post-spray) and calculate the time-dependent dissipation rates from the data. Secondly, it is worth mentioning that the VEFM is best used for VPs in the range 10^{-3} to 10^{-6} Torr (EPA, 1994), which is the range of VPs most commonly found at ambient temperatures. The temperatures at the field site were high—as high as $40°C$—but the VP of methamidophos at $40°C$ is calculated to be 4×10^{-3} Torr, which is still within the range of VPs that the model is intended to represent.

It is likely that the emission factor calculated by the VEF model published by the EPA is low when used directly after a spray event. Follow up studies will need to be carried out to determine that quantitatively as well as to create a more accurate time-varying volatilization emission factor, i.e. one that represents that the highest volatilization occurs in the hours immediately after the spray event.

5.2. Effects of dissipation rates

The other parameter which affects the mass volatilizing into the atmosphere is the half-life of the AI. The half-life is a measure of the mobility of the AI and its chemical breakdown in the atmosphere. A short half-life implies high environmental mobility, which leaves less of the AI available for volatilizing from the surface. Acceptable ranges of half-life for methamidophos range from 1 to 4 days (US EPA, 1989). A half-life of 3 days was used for this set of calculations. However, recent studies show that the uptake of methamidophos by plants can be very high (Prieto et al., 2002). This implies that a half-life shorter than 3 days may be appropriate.

Careful examination of the measured data (Table 1) shows high air concentrations immediately after the spray and a rapid fall in those values several hours later. The VEFM emission source term is calculated from a decay factor derived from the 30-day loss estimate. Using a constant dissipation rate through the 30-day period does not accurately reflect the short-term losses after spraying. The AI is diluted in water and the evaporation rate is highest in the first several hours after the spray—approximately from 6 a.m. to 6 p.m. on the day of the spray.

6. Conclusions

Organophosphates (OPs) are of major concern to human health since they are widely used as pesticides and are known to have toxic effects. Specifically, the potentially adverse effects on children's health as a result of exposure to OPs are a subject of extensive research (Eskenazi et al., 1999), and as cited in a National Research Council (1993), childrens' OP exposures are of special concern because "exposures to neurotoxic compounds at levels believed to be safe for adults could result in permanent loss of brain function if it occurred during the prenatal and early childhood period of brain development".

This study compares measurements of methamidophos made after a spray event to predictions from an emissions model coupled with a transport model. Volatilization appears to provide a significant source of the AI into the atmosphere for the conditions encountered in this study. The VEFM, which estimates pesticide emissions from sprayed fields over a 30-day period based on the VP of the compound, was used to calculate the emission of volatilized AI material after the spray. The emissions were then used as source input to the FDM to model the transport of the volatilized material. The air concentrations of methamidophos were highest in the afternoon when the temperatures were highest reflecting the increased VP. In the period immediately after spraying, the VEFM underestimates the release of volatile gases from the wetted surfaces, while on the following day the VEFM slightly overestimates the volatilization. Incorrect particle sampling and volatilization of the particles during the spray event were examined as possible explanations for the discrepancy between measurements and calculations but these explanations have largely been ruled out.

The VEFM calculates a 30-day average emission. However, volatilization from the fields is not likely to be a linear process. As seen by our data, the more intense volatilization occurs immediately after the spraying. The next day the measurements showed significantly lower mass concentrations of the AI from volatilization. Supporting this conclusion is the finding that other methods for estimating fluxes indicate a stronger volatilization factor than that calculated by the VEFM. Studies in the database of reports that the VEFM was derived from also indicate in many instances that the strongest volatilization occurs in the few hours after spray (Willis et al., 1980; Glotfelty et al., 1984).

Our results demonstrate that post-spray volatilization could be a potentially high percentage of inhalation exposure at times when people do not anticipate that there will be a risk of exposure, i.e. after the spray is done. This has implications in agricultural communities, where children are allowed to play outside immediately after spraying while under the assumption that probabilities of exposure are minimal once the spraying is over. Young children may be especially vulnerable to pesticides since their organ systems are immature and developing. They may also have a lesser ability to detoxify the chemicals (Benke and Murphy, 1975; Lu et al., 1965; Mortensen et al., 1996). Studies have also

associated parental exposure to pesticides or pesticide use in the home with childhood brain tumors, leukemias, lymphomas, testicular cancers and other cancers (Buckley et al., 1989; Blair et al., 1992; Leiss and Savitz, 1995; Kristensen et al., 1996). Guillette et al. (1998) showed that low-level chronic exposure of children to pesticides can lead to adverse health consequences. It is therefore important to accurately quantify children's exposure risk from all possible sources.

An important extension to this study would be to collect data immediately following a spray event and up to several days to see how rapidly the fall off of emission occurs. It would also be very interesting and useful to see how this model works with other pesticides and fungicides. Since the volatilization estimates are a function of the VP of the compound, we expect that it would be simple to extrapolate this model to other pesticide applications. For instance, we plan to measure and model volatilization of applied chlorothalonil, in our next field-study phase. Chlorothalonil is of particular interest since it is under EPA scrutiny, is the most applied fungicide on vegetables in the state of Texas (according to the USDA) and also has a higher VP than methamidophos (10^{-3} mmHg at $20°C$).

In conclusion, the results suggest that the VEFM method if improved shows promise in its ability to provide input to the FDM to estimate transport. The FDM models transport well. However more data is needed to account for short-term losses that can alter emissions immediately following spraying. More information on the foliar residue data immediately after the spray would help characterize the dissipation rate better.

Acknowledgements

Appendix A

Calculations of E_a (aspiration efficiency curves) for ambient velocities of 1–5 m s^{-1} were made based on Grinshpun et al., 1994). The inlet sampling efficiency (ISE) is the ratio of the particle mass concentration passing into the sampler inlet to the actual ambient mass concentration in the atmosphere. For a particular particle size this ratio depends on ambient and sampling conditions such as wind velocity, the sampler inlet geometry, sampling flow rate and orientation. Following Grinshpun et al. (1994) we assumed iso-axial sampling in the horizontal plane and calculated the aspiration efficiency for varying particle sizes with theta, the angle between the axis of the inlet and the wind direction $= 0°$; and phi—the angle between inlet direction and gravity $= 90°$.

Appendix B

$$\ln p = \frac{RT}{\Delta Hvap} + C,$$

which can be simplified to:

$$\frac{p_1}{p_2} = \exp(k(T_1 - T_2)).$$

Using p_1 at $20°C = 1.725 \times 10^{-5}$ mmHg and p_2 at $30°C = 3 \times 10^{-4}$ mmHg; $k = 0.285018997$ for methamidophos.

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