Validation of the AGDISP model for predicting airborne atrazine spray drift: A South African ground application case study

Sifiso A. Nsibande[1], James M. Dabrowski[2], Etienne van der Walt[3], Annette Venter[3], and Patricia B.C. Forbes*[1]

[1] Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Lynnwood Road, Pretoria 0002, South Africa

[2] CSIR, Natural Resources and Environment, PO Box 395, Pretoria 0001, South Africa

[3] Agricultural Research Council, Plant Protection Research Institute, Private Bag X134,Queenswood 0121, South Africa

Abstract

Air dispersion software models for evaluating pesticide spray drift during application have been developed that can potentially serve as a cheaper convenient alternative to field monitoring campaigns. Such models require validation against field monitoring data in order for them to be employed with confidence, especially when they are used to implement regulatory measures or to evaluate potential human exposure levels. In this case study, off-target pesticide drift was monitored during ground application of a pesticide mixture to a sorghum field in South Africa. Atrazine was used as a drift tracer. High volume air sampling onto polyurethane foam (PUF) was conducted at six downwind locations and at four heights at each sampling point. Additional data, including meteorological information, required to simulate the spray drift with the AGDISP® air dispersion model was collected. The PUF plugs were extracted by a plunger method utilising a hexane:acetone mixture with analysis by GC-NPD (94.5% recovery, 3.3% RSD, and LOD 8.7 pg). Atrazine concentrations ranged from 4.55 ng L^{-1} adjacent to the field to 186 pg L^{-1} at 400 m downwind. These results compared favourably with modeled output data, resulting in the validation of the model up to 400 m from the application site for the first time.

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*Corresponding author: Patricia B.C. Forbes
Tel: +27 12 420 5426
Email: patricia.forbes@up.ac.za

Sensitivity studies showed the importance of droplet size distribution on spray drift, which highlighted the need for good nozzle maintenance. Results of this case study indicate that the model may provide meaningful input into environmental and human health risk assessment studies in South Africa and other developing countries.

Keywords: Atrazine; spray drift; air dispersion modeling; PUF; pesticides; AGDISP.

Highlights:

- Active ingredient used as a tracer for spray drift monitoring and model validation
- Good correlation was found between modeled and experimental pesticide spray drift levels
- AGDISP model was validated for airborne pesticide spray drift up to 400 m from the application site
- Droplet size distribution significantly affected airborne spray drift

1 Introduction

Pesticides can enter the atmosphere through wind effects or evaporation processes and can therefore exist in the atmosphere either in the particulate or gaseous phase in addition to the liquid form (Sanusi *et al.*, 1999). Spray drift is an important and direct pathway through which pesticides enter the atmosphere and is defined as movement (drift) of airborne spray droplets beyond the target area during or immediately after spray application (Carlsen *et al.*, 2006). Off-target deposition of these droplets or particulates may cause serious contamination of surrounding natural resources, including surface water systems. Although most pesticides are designed to have low persistence in the environment, many, including triazines, are sufficiently stable to undergo atmospheric transport at a regional or global scale (van Dijk & Guicherit, 1999). Apart from drift due to turbulent air masses during application, pesticide residues may become concentrated in atmospheric inversions or stable air masses, or be transported over long distances Unsworth *et al.*, 1999). This phenomenon makes pesticide spray drift an important environmental concern.

Studies have indicated that spray drift is one of the important routes for pesticide contamination of natural surface waters and other off-target habitats (Dabrowski & Schulz, 2003). Pesticide contamination can compromise water quality and have negative effects on aquatic life, and in addition many studies have shown that some pesticides may have endocrine disrupting effects (Kojima *et al.*, 2004). Pesticide mixtures in water can also interact synergistically thereby causing enhanced toxicity to aquatic life (Norgaard & Cedergreen, 2010). Since pesticide spray drift is a significant route for contamination, it is important to monitor the atmospheric dispersion of pesticides during application.

There are a number of factors that affect pesticide spray drift that have been well studied including: (i) the application technique used (Foqué *et al.*, 2014), (ii) the canopy type and height (Hoffmann *et al.*, 2007), (iii) meteorological conditions (Miller *et al.*, 2011) and (iv) the physiochemical properties of the spray material being applied (Fritz *et al.*, 2010; Hilz & Vermeer, 2013).

Since monitoring of airborne spray drift during application can be expensive, time consuming, labour intensive and sometimes inaccurate, the use of predictive computational models may provide a practical alternative. Models may, however, generate different results from real field data due to factors which may be difficult to account for mathematically and computationally. For example, discrepancies may be due temporal and spatial variations in the environmental conditions (Gil & Sinfort, 2005) which are difficult to model. It is therefore important to test and validate these models using actual measurements before they can be used with confidence in risk assessment studies to provide a reasonable estimation of spray drift.

The AGricultural DISPersal model (AGDISP) was originally developed for estimating airborne concentrations and off-target deposition of pesticide spray drift arising from aerial applications (Bilanin *et al.*, 1989) and a number of studies have successfully validated the performance of the model in this regard (Bird *et al.*, 2002; Fritz *et al.*, 2010; Hoffmann, 2006; Teske *et al.*, 2002). More recently, a feature for simulating spray drift from ground application of pesticides with boom sprayers was incorporated into the model (Teske *et al.*, 2009). Studies conducted to validate this feature of the model have primarily been based on wind tunnel experiments and/or the use of fluorescent compounds (Connell *et al.*, 2012; Fritz *et al.*, 2011; Teske *et al.*, 2009) or added metal salts (Woodward *et al.*, 2008; Zabkiewicz *et al.*, 2009) as drift tracers. Although these methods have advantages of quick and easy analysis, they may not provide a true representation of the spray drift of the actual active ingredient due to physico-chemical differences, which may affect parameters such as evaporation and deposition rates. Degradation of fluorescent tracers upon exposure to sunlight may also result in uncertainties (Yates *et al.*, 1976). The active ingredient, malathion, has been used to monitor spray drift up to 5 m downwind, where the results were compared to empirical formulae (Yarpuz-Bozdogan and Bozdogan, 2009).

The objective of this work was to compare modeled and monitored data with respect to airborne concentration of atrazine arising from spray drift. This widely used chlorinated triazine herbicide is used to control both pre- and post-emergent broadleaf weeds. Muir *et al.* (2004) showed by means of both empirical and modeling approaches that atrazine is capable of regional atmospheric transport, thus making it an important pesticide to study. A recent South African pesticide prioritisation study by Dabrowski *et al.* (2014) featured atrazine as the highest ranked pesticide. Owing in part to its wide use in maize production, this herbicide has frequently been detected in South African freshwater systems (Dabrowski *et al.*, 2013; Du Preez *et al.*, 2005; Pick *et al.*, 1992). A study by Ravier *et al.* (2005) had previously used atrazine to monitor atmospheric spray drift up to 134 m downwind. The use of atrazine as a spray drift tracer in this case study was also motivated by its ease of analysis by gas chromatography with nitrogen phosphorus detection (GC-NPD), without a derivatization step, as this can incur analyte losses and analytical uncertainties. Using the active ingredient prevents uncertainties inherent in using a drift tracer to simulate pesticide drift, as differences in chemical properties of the compounds concerned could impact on the results. This case study forms part of a larger integrated project examining the risks of current agricultural pesticide use to human and animal health (WRC, 2011). AGDISP was selected in this instance as inhalation of airborne concentrations of pesticides by communities living adjacent to agricultural areas was considered to be an important route of exposure.

2 Materials and Methods

2.1 Study area

Spray drift monitoring was conducted during application of a herbicide mix containing atrazine to a sorghum field in Standerton, South Africa. The crop was 0.9 m high and was grown in a 7.6 ha field surrounded by farm houses and grazing land. The farm cultivates approximately 1000 ha of sorghum. A Nikon LASER range finder (model 1200S) was used to position the downwind samplers in a setup which was based on that of Caldwell (2006). The sampling line was approximately parallel to the wind direction (Fig. S-1 in the Supplementary Data), as a good estimate of the wind direction was obtained during sampler setup by observation and short term measurements. The pesticide solution was applied using a John Deere 4720 'Hi-Boy' ground sprayer equipped with 56 Turbo TwinJet® TTJ60 nozzles, (Tip No. 5) (TeeJet® Technologies) which were uniformly distributed at 0.5 m intervals along a 32 m boom. The pesticide was released from the sprayer at 0.4 m above the crop.

2.2 Sampling

Airborne spray drift was collected using high volume air samplers equipped with polyurethane foam (PUF) cartridges, as studies by Gish *et al.* (1995) have shown the successful use of PUF for sampling atrazine in the atmosphere. Cartridges consisting of two pre-cleaned PUF plugs in series (each 6 cm diameter, 4 cm long) were housed in aluminium holders. The PUF cartridges were supported by means of a mast and were positioned at four vertical heights (0.5, 1.0, 1.5 and 2.0 m). The four cartridges were each connected to a generator powered vacuum pump through a manifold (Fig. S-2 in the Supplementary Data). The flow rate through each PUF cartridge was measured with a Planton GAP air flow meter and was over 220 L min^{-1} in each case (average flow rate of 348 L min^{-1}). Continuous air sampling was conducted simultaneously for 60 min over all distances and for all 24 sampling cartridges, which included 10 min of pesticide application. After sampling, each PUF cartridge was wrapped in aluminium foil and stored in a refrigerator below 0 °C prior to analysis.

2.3 Sample extraction and analysis

A plunger based solvent extraction technique (van der Walt, 2000) was used to extract the PUF samples, where each PUF plug was extracted five times with 25 mL acetone:hexane (1:3) mixture (High Purity Pesticide Grade, Burdick & Jackson) by repeatedly squeezing it with a stainless steel plunger ten times. Each extract was filtered through filter paper (Grade 480, Lasec South Africa) and extracts from the same cartridge were then combined and concentrated to <1 mL using a rotary evaporator at 40 °C. Extracts were then reconstituted to 5 mL with hexane. Samples taken closer to the sprayed field were diluted as necessary.

The atrazine concentration in the extracts was determined using an Agilent 6870N gas chromatograph equipped with a nitrogen phosphorous detector (GC-NPD) (Agilent Technologies). 1 µL of sample was injected in splitless mode and the carrier gas was nitrogen (Air Products) at a flow rate of 1.0 mL min^{-1}. A DB-5MS fused silica column (30 m, 0.25 mm ID, 0.25 µm film thickness, J&W Scientific) was used. The temperature programme started at 60 °C (held for 1 min), then was raised at 25 °C min^{-1} to 210 °C (held for 4 min), and was finally taken to 250 °C at 30 °C min^{-1}. The detector temperature was 310 °C and the detector gas flow rates were 4 mL min^{-1} (hydrogen) and 60 mL min^{-1} (air) and the makeup gas (nitrogen) was 22 mL min^{-1}.

2.4 Quality assurance

An atrazine standard (PESTANAL, 98.8% purity, Sigma-Aldrich) was used for external calibration of the instrument and for surrogate spikes. A good linear fit was found for the calibration standards (R^2 = 0.9956). The limit of detection (LOD) was 8.66 pg and the limit of quantification (LOQ) was 25.99 pg. The method showed good repeatability (3.3 % RSD, n=6) and the mean recovery of PUF cartridges spiked at three different concentrations was 94.5 % (3.0 % RSD). Blank solvent was periodically injected between sample runs to ensure no analyte carryover occurred. Sensitivity was constantly checked throughout the analysis by injecting calibration standards. Field blanks were also analysed to correct for any atrazine residues that might have been in the atmosphere before spraying.

2.5 Computer Modeling

The AGricultural DISPersal (AGDISP) v8.27 software programme was used to model the spray drift, as it was suitable for our ground boom sprayer application scenario and was readily available. It employs both Lagragian and Gaussian-type equations to calculate the droplet trajectories as they are released from the nozzles and spray drift predications up to a few hundred km from the source are possible. The reader is referred to (Teske *et al.*, 2009; Teske *et al.*, 2003) for a detailed discussion of the mathematics and algorithms utilised by the model, which has been employed by the United States Environmental Protection Agency and the Australian Government. The predictions of pesticide downwind drift generated by the model are dependent on a number of parameters including equipment conditions, nozzles and the drop size distribution (DSD), spray material properties, surface features (topography), and ambient meteorology. This information was thus collected during the sampling campaign (Table S-1 in the Supplementary Data) according to the methods described in the following sections.

2.5.1 Model input parameters

2.5.1.1 Meteorology

Meteorological data was continuously monitored throughout the application and sampling period using an RM Young set of instruments mounted on a mast which was positioned ~25 m downwind. Data was measured every second and logged as 1 min averages of wind speed and direction (RM Young model 0513 Wind Monitor-RE, Young Co.). Temperature and relative humidity were measured with an RM Young Multi-plate radiation shield (model 41003), while solar radiation was monitored with an RM Young pyranometer (model PY51486). All the meteorological data was logged by means of a datalogger (model CR215, Campbell Scientific) and later downloaded to a computer with LogaNet software (version 7.0). The data was then averaged over the 60 min sampling period corresponding to the 10 min pesticide application time and 50 min post-application sampling time, similar to previous spray drift studies (Fritz *et al.*, 2011). A wind rose was generated with WRPLOT View™ (Version 7.0.0).

2.5.1.2 Droplet Size Distribution

In the absence of a laser diffraction spectrophotometer, the magnesium oxide method initially described by May (1950) was used to determine the droplet size distribution produced by the sprayer.

Magnesium oxide coated slides were clamped on rods 1 m above the ground and placed along the edge of the sorghum field to capture spray droplets during application. Images of the impressions made by the droplets were taken using a Zeiss Stemi SR microscope equipped with a Schott KL 1500-Z light source and AxioVision (version 3.0.6.38) software at 20× magnification. Image analysis was performed using Droplet Retrograde software (2004 version) to determine the droplet size distribution (DSD). From the three slides that were analysed, three sets of DSDs were generated (Table S-2 in the Supplementary Data) and were used as a "User-defined" input to the AGDISP model.

2.5.1.3 Additional Input data

Default values for the parameters not listed were not changed in the model. Since the spray material was predominantly water, the evaporation rate of water (84.76 $\mu m^2\ {}^{\circ}C^{-1}\ s^{-1}$) was used as an estimate of the evaporation rate of the atrazine spray solution (Riley *et al.*, 1995). This is supported by studies which showed that agrichemicals in water-based carriers will behave similarly to water in terms of evaporation (Hewitt *et al.*, 2002b).

2.5.2 Sensitivity Analysis

The model sensitivity to various input parameters was determined by varying one parameter while keeping the others constant. The parameters that were investigated are shown in Table S-3 in the Supplementary Data. The meteorological parameters were varied according to maximum, minimum and average values that were obtained during the sampling period while the other parameters were varied to accommodate possible variations in these values.

3 Results and Discussion

3.1 Monitoring Results

The GC-NPD method showed good resolution of the atrazine peak (at 8.26 min) from the other closely eluting triazines, especially terbuthylazine and the atrazine peaks were well above the detection limits for all samples.

Fig. 1 shows the air concentrations of atrazine determined from the PUF samples relative to the downwind distance from the edge of the field and at different vertical sampling heights, which were calculated based air sampling flow rates (Table S-4 in the Supplementary Data). The percentage recoveries were not used in calculating these results, as is a common practice with environmental monitoring studies where recoveries are good (Thompson *et al.*, 1999).

The experimental PUF results (Fig. 1) show a decrease in atrazine air concentrations with downwind distance – a trend that was observed for all four sampling heights. Closer to the field (10 and 25 m) there was greater variation in atrazine concentration with vertical height compared to samples from further downwind. This could be because the effect of the moving tractor is much more significant near field compared to far-field distances. Also, as the spray cloud drifts away, it disperses and mixes with the atmosphere to form an expanded plume of almost homogenous concentration. It can be noted that near-field (10 and 25 m downwind) the atrazine levels were slightly lower at 0.5 m compared to 1 m above the ground. This could be because the material was released around 1.4 m above ground level and therefore the majority of the droplets had still not settled closer to the ground. The lowest concentration of atrazine (0.138 pg L^{-1}) was detected at 400 m downwind at 2 m vertical height.

Uncertainties in the monitoring of airborne pesticide drift in this study would largely have arisen during the sampling step, as the analytical uncertainty was determined to be relatively small in terms of

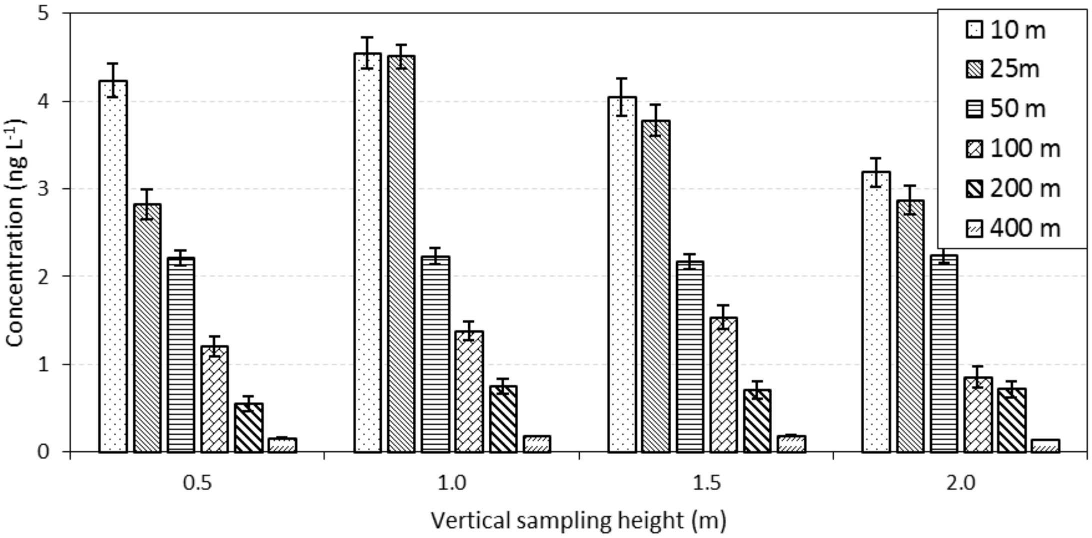

Figure 1 Airborne atrazine concentrations (± standard deviation) determined from the PUF samples at different distances downwind of the application site and at different vertical sampling heights above ground.

repeatability, extraction efficiency and calibration linearity, and field blanks were not contaminated (Section 2.4). It should be noted that the use of air samplers to assess airborne drift flux is challenging, as air may be drawn through the sampler from a wider area than their immediate location by active pumping. Uncertainties may also arise due to changes in the wind direction during sampling. A backup PUF plug was employed in the samplers to minimise breakthrough losses of atrazine and samples were stored at low temperatures to prevent losses.

Single ANOVA treatment of the data revealed no significant difference in concentrations of samples that were taken at different heights ($p > 0.05$). However, visual comparison shows that samples taken at 2 m height have slightly lower concentrations compared to the other heights. This could be attributed to both deposition and settling of the pesticide to the ground as well as diffusion processes.

3.2 Comparison of model versus experimental results

A comparison of modeled versus experimental airborne concentrations of atrazine at the different vertical heights is shown in Fig.2. Comparison of airborne pesticide concentrations at 0.5 m vertical sampling height was not possible, as the model only generated results at vertical heights greater than the canopy height of 0.9 m. The model results showed the expected general decrease in concentration with downwind distance, which was also observed for the experimental results. However, the model results showed a marked decrease in concentration with vertical height from 1 m to 2 m while the experimental results showed only a slight decrease. This is could be a consequence of the actual versus predicted rates of volatilization and dispersion of the spray plume. Linear regression results showed that for all the sampling heights there was a good correlation between experimental and model generated results ($R^2 > 0.79$), which indicates the potential use of this model in predicting pesticide spray drift arising from ground applications in developing countries.

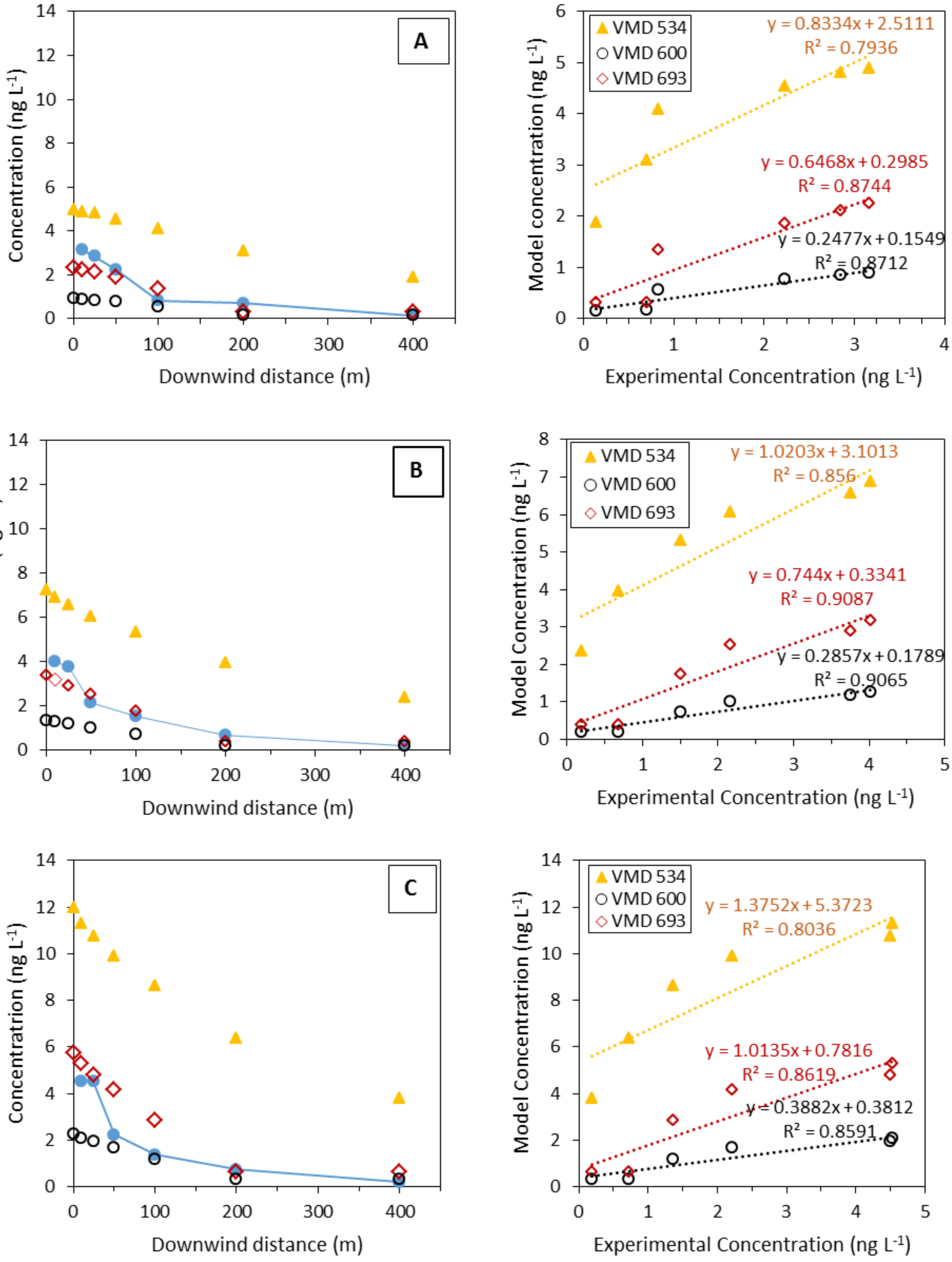

Figure 2 Left: Comparison of model versus experimental ● results at three different vertical heights (a) 2.0 m (b) 1.5 m (c) 1.0 m. Three model runs were made using different droplet size distributions ○VMD600 (207.957 µm diameter) ◇VMD693 (166.484 µm diameter) and ▲VMD534 (145.253 µm diameter).

The correlation between experimental and model results was found to be very dependent on the average droplet size (Fig. 2). It is acknowledged that modern equipment based on laser diffraction spectrophotometry is preferable for accurate droplet size determinations in spray drift studies, however these resources are usually not available in developing countries, as in this case study. MgO coated slides were therefore employed, which require an extensive amount of time to analyse manually. This limits the number of slides which can practically be processed, therefore in this study three different droplet size distributions were obtained from the analysis of three different MgO slides. The best correlation between experimental and modeled results was observed when the droplet size distribution with an average size of 166.484 µm was used. When simulations were done with smaller droplet sizes (145.253 µm), the model over-predicted the concentration by up to 3 times near-field but predicted the concentration further downwind slightly better. Using 207.957 µm diameter droplets gave a reasonable correlation to the experimental results although the model under predicted concentrations closer to the field. These results show the importance and sensitivity of the model output to the droplet size where slight changes can have a significant impact on the model output. It is also evident that acceptable results can be obtained even with the uncertainties inherent with using the MgO slide method for droplet size determinations, including spray collection efficiencies, evaporation losses and limited droplet sample size, which indicates the potential of using this method in developing countries where more modern approaches to droplet size determination are not available.

3.3 Model sensitivity

Among the parameters that were investigated, the model was found to be most sensitive to the droplet size distribution (Fig. 3), with a very high variability with variation in droplet size especially closer to the application site. For lighter droplets the model predicted a higher concentration, suggesting that

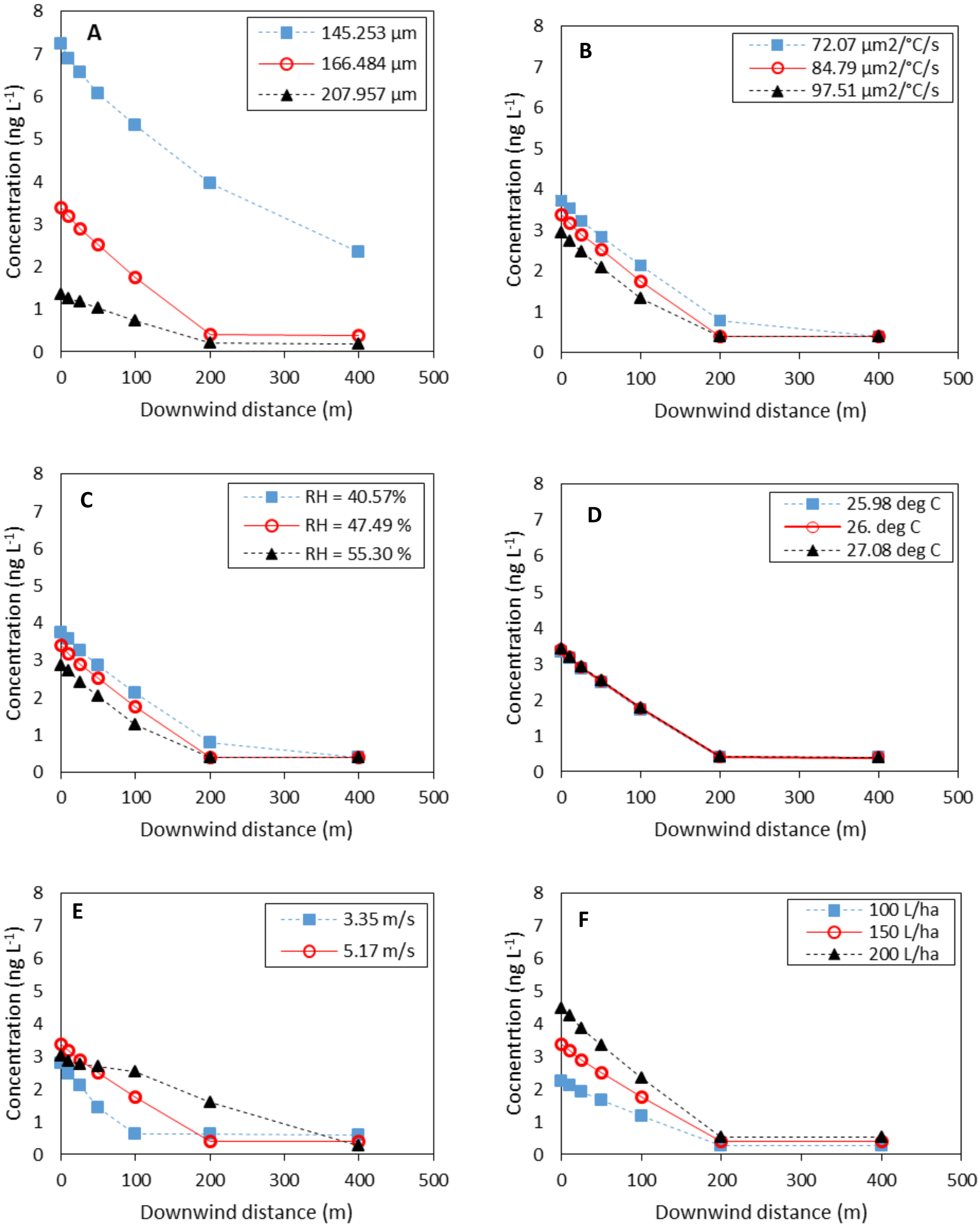

Figure 3 Sensitivity of the airborne concentrations of atrazine predicted at 1.5 m height by the AGDISP model to the variation in six different input parameters (a) Droplet size (b) Evaporation rate (c) Relative humidity (d) Temperature (e) Wind speed (f) Application rate

they are more likely to remain airborne, whilst larger droplets settle to the ground more readily. The results also showed that varying the evaporation rate (~±10 %) did not have much of an impact on the predicted concentrations hence assuming that the spray mix had an evaporation rate similar to that of water should not have had much of an impact on the predicted results. Among the meteorological parameters tested (where the minimum and maximum values measured were compared to the averages used), the model was found to be more sensitive to changes in wind speed than the other parameters, with higher wind speed resulting in higher levels of spray drift, as expected.

An ANOVA test revealed that there was indeed more variation in concentrations when changing the droplet size distribution ($p < 0.05$) than with any of the other parameters tested and that among the meteorological parameters, the model was more sensitive to wind speed. These results agree with previous studies where droplet size was reported to be the most significant parameter affecting spray drift (Miller *et al.*, 2011) and that wind speed was reported to be the most significant meteorological parameter (Phillips & Miller, 1999). Another AGDISP model sensitivity study by Huang *et al.* (2010) concluded, however, that wind speed is more significant than the droplet size. This could be because their simulation was for aerial application whilst our study was for ground based application. In addition the range in variables tested differed: in our case we chose possible variations during our specific sampling campaign, whilst Huang *et al.* considered extremes. Consequently for droplet size their range was from very fine to very coarse, while ours ranged from 145 to 208 μm, and the maximum and minimum wind speeds were 0.45 to 6.71 m s^{-1} (Huang *et al.*, 2010) versus 3.35 to 7.27 m s^{-1} (this study). This shows that the most significant variable may be different for different pesticide application scenarios.

It should also be noted that the AGDISP model does not take localized turbulence (such as that due to nearby buildings) into account, which may impact on the results obtained. The results of any pesticide modeling study should be used with caution, and it is important to note that an over prediction is preferable to provide cautionary levels rather than an under prediction which would underestimate potential human health and environmental effects as a consequence of pesticide spray drift.

4 Conclusions

In this case study, the active pesticide ingredient, namely atrazine, was successfully used to monitor downwind spray drift during pesticide application. This was due in part to the stability of atrazine in the atmosphere, with a half-life of approximately one day (De Rossi, 2010), as well as to its compatibility with the sampling and analytical method that was developed and employed. It is a common practice in pesticide spray drift studies to collect both airborne and deposition samples, as was done in this study (deposition results are reported elsewhere). Airborne samples are important in assessing inhalation exposure, whilst deposition samples give an indication of possible contamination of nearby fresh water bodies, for example. The different but complementary information thus provided is useful in risk assessment studies and in better understanding the evolution of the spray cloud as it drifts away from the application site.

For airborne spray drift monitoring, the PUF adsorbents proved to be suitable samplers for atrazine. Although the extraction method used a fair amount of solvents, it gave very good recoveries. The GC-NPD method was both selective and sensitive, which allowed for the determination of atrazine down to 0.138 pg L^{-1} at 400 m downwind. Satisfactory agreement was found between the modeled and experimental results, particularly when using the larger droplet size distribution. We suggest, therefore, that the model can provide a good estimate of airborne spray drift concentrations provided one has reliable input parameters that are representative of the actual application conditions. Previous validation studies have shown variation in airborne pesticide spray drift of approximately two orders of magnitude between field and AGDISP modeled results (Woodward *et al.*, 2008). In comparison, this case study has shown promising correlations between experimental results and those predicted by the model. This improvement could be because the actual active pesticide ingredient was monitored instead of a tracer compound, and that the data set was reliable in terms of high volume airborne pesticide monitoring results, meteorology and droplet spectra.

Sensitivity studies showed that the model is strongly dependent on the droplet size, where smaller droplets are more likely to remain airborne and drift further downwind whilst larger droplets easily deposit to the ground and are less likely to drift downwind (Fritz *et al.*, 2010). The fact that droplet size was shown to be the major variable affecting off-target spray drift is supported by the results of previous studies (Hewitt *et al.*, 2002a). Depending on the DSD input, the model may either overestimate or underestimate the atrazine concentration. The accurate determination of the DSD is therefore important. In addition, the effect of the ingredients in the pesticide mix on the evaporation rate thereof requires further investigation. Future model validation studies should also include different molecular classes of pesticides to confirm the model validation for use as a predictor of general pesticide spray drift.

In this case study, the AGDISP pesticide air dispersion model was validated for the first time for use in South Africa. In contrast to many other international validation studies conducted on this model, we used high volume air sampling of the active ingredient for model validation and validated the model at relatively long downwind distances. The simple, cost-effective MgO slide method was successfully used for droplet size determination, which is of relevance to developing countries without access to modern laser-based measuring equipment. Results of this ground application case study indicate that the model may provide meaningful input into environmental and human health risk assessment studies in South

Africa and other developing countries. This is particularly relevant considering that limited financial and technical resources generally limit rigorous monitoring studies as performed in this study.

5 Acknowledgements

This research originated from a project initiated, managed and funded by the Water Research Commission (WRC project No. K5/1956: Investigation of the contamination of water resources by agricultural chemicals and the impact on environmental health). The Agricultural Research Council - Plant Protection Research Institute (ARC-PPRI) is acknowledged for assistance with sampling, meteorology, droplet determinations and analytical equipment. Lastly we thank the farm owners in Standerton for allowing us to use their farm for this study and Justinus Shadung and Ernst Bekker for their assistance with sampling.

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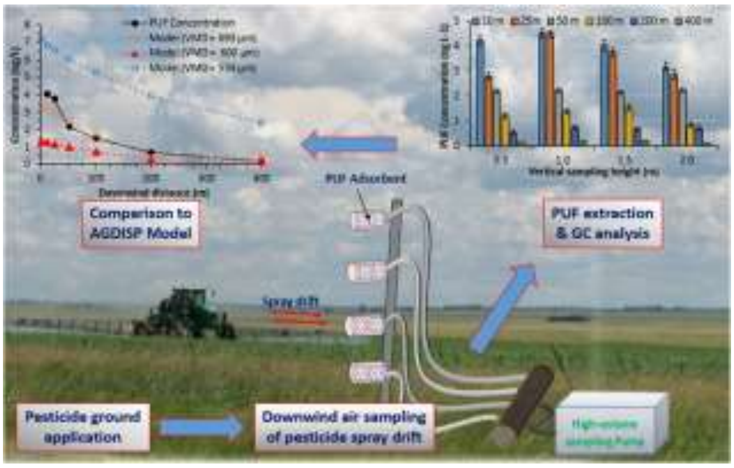
Graphical abstract



Supplementary data

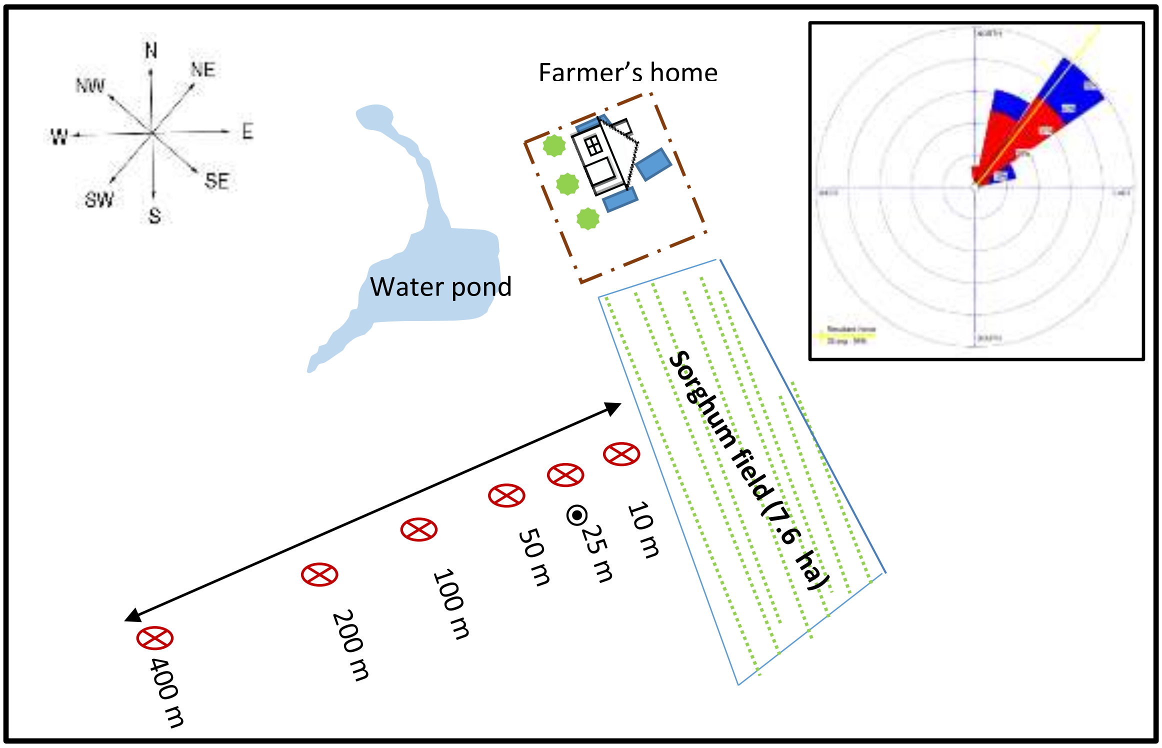


Figure S-1 Schematic diagram showing the sorghum field and downwind sampling points ⊗ in Standerton, South Africa. A portable weather station⦿ was positioned in the field to measure meteorological data. The inserted wind rose shows the average wind direction during the 1 hr sampling period (adapted from a Google Earth image of the area).

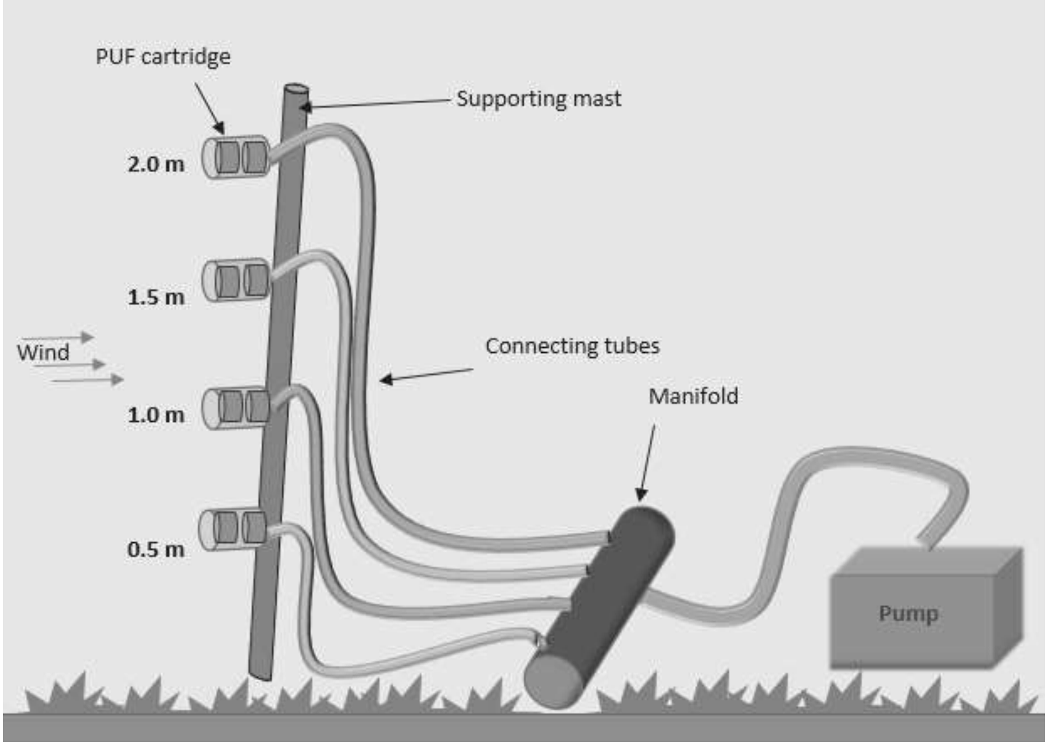


Figure S-2 PUF active samplers used to sample air at over 300 L min^{-1}. PUF cartridges were mounted vertically on a mast at four different heights (0.5, 1.0, 1.5, and 2.0 m) and were connected to a vacuum pump through a manifold.

Table S-1: Input parameters for AGDISP used for modeling atrazine spray drift

Parameter	Input	Parameter	Input
Application method	Ground sprayer	Wind speed (m s^{-1})	5.17
Boom pressure (bar)	4.8	Wind direction (°)	-90
Nozzle type	Flat fan	Temperature (°C)	26.57
Number of nozzles	56	Relative humidity (%)	47.49
Nozzle inter distances (cm)	50	Spray material evaporates	Yes
DSD	User-defined	Spray volume rate (L ha^{-1})	150
Release height (m)	1.4	Active fraction	0.0113
Spray lines	8	Active fraction of tank mix	0.0113
Swath width (m)	32	Evaporation rate (µm^{2} °C^{-1} s^{-1})	84.76
Swath displacement (m)	0	Canopy height (m)	0.9

Table S-2 Three sets of experimentally determined droplet size distributions (DSD) used as user defined inputs to the AGDISP model

	$Dv_{0.5}$ = 693.28			$Dv_{0.5}$ = 600.64			$Dv_{0.5}$ = 534.24		
#	**Diameter (µm)**	**Fraction**	**Cumulative Volume Fraction**	**Diameter (µm)**	**Fraction**	**Cumulative Volume Fraction**	**Diameter (µm)**	**Fraction**	**Cumulative Volume Fraction**
1	48.74	0.0010	0.0010	42.05	0.0005	0.0005	41.19	0.0006	0.0006
2	108.59	0.0168	0.0178	88.52	0.0032	0.0037	85.94	0.0159	0.0165
3	168.44	0.0381	0.0559	134.99	0.0078	0.0115	130.69	0.024	0.0405
4	228.29	0.0195	0.0754	181.46	0.0016	0.0275	175.43	0.0302	0.0707
5	288.14	0.0336	0.1090	227.93	0.0403	0.0678	220.18	0.0092	0.0799
6	348.00	0.0593	0.1683	274.44	0.0603	0.1281	264.93	0.008	0.0879
7	407.85	0.0477	0.2160	320.87	0.0563	0.1844	309.68	0.0128	0.1007
8	467.70	0.0480	0.2640	367.34	0.1206	0.305	354.43	0.0575	0.1582
9	527.55	0	0.2640	413.82	0	0.305	399.18	0.0548	0.213
10	587.40	0.0475	0.3115	460.29	0.0949	0.3999	443.93	0.0377	0.2507
11	647.25	0.0636	0.3751	506.76	0.095	0.4949	488.68	0.0503	0.301
12	707.11	0.1657	0.5408	553.23	0	0.4949	533.43	0.1961	0.4971
13	766.96	0	0.5408	599.7	0	0.4949	578.18	0.1665	0.6636
14	826.81	0.1325	0.6733	646.17	0.2626	0.7575	622.93	0.2082	0.8718
15	886.66	0.3268	1	692.64	0.2425	1	667.67	0.1282	1

Table S-3: AGDISP sensitivity test matrix showing the range of various input values investigated

Parameter	**Input values**		
	Minimum/ Trial 1	**Average/ Trial 2**	**Maximum/ Trial 3**
Temperature (°C)	25.98	26.58	27.08
Relative humidity (%)	40.57	47.49	55.30
Wind speed (m s^{-1})	3.35	5.17	7.27
Evaporation Rate (μm^2 $°C^{-1}$ s^{-1})	74.79	84.79	94.79
Droplet size distribution - VMD (µm)	534.34	600.64	693.27
Application rate (L ha^{-1})	100	150	200

Where MVD is the mean volume diameter

Table S-4 PUF atrazine results from GC-NPD analysis

Downwind distance (m)	Vertical height (m)	Flow rate (L min^{-1})	Sampled air (L)	Concentration in sampled air (ng L^{-1})
10	0.5	375	22500	4.21
	1.0	410	24600	4.53
	1.5	350	21000	4.02
	2.0	440	26400	3.16
25	0.5	350	21000	2.80
	1.0	425	25500	4.50
	1.5	330	19800	3.76
	2.0	350	21000	2.85
50	0.5	350	21000	2.20
	1.0	320	19200	2.22
	1.5	330	19800	2.16
	2.0	350	21000	2.23
100	0.5	250	15000	1.18
	1.0	260	15600	1.36
	1.5	220	13200	1.51
	2.0	250	15000	0.826
200	0.5	350	21000	0.534
	1.0	350	21000	0.727
	1.5	300	18000	0.680
	2.0	315	18900	0.698
400	0.5	350	21000	0.157
	1.0	350	21000	0.183
	1.5	350	21000	0.188
	2.0	300	18000	0.139